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**ABSTRACT**

of the dissertation for the degree of Doctor of Science

**MIXED LIGAND COMPLEXES OF SOME *d*- AND *f*-  
TRANSITION ELEMENTS WITH 2,6-DITHIOLPHENOL, ITS  
DERIVATIVES AND HYDROPHOBIC AMINES AND  
APPLICATION OF THEM IN EXTRACTION OF HEAVY  
METALS AND A IN PHOTOMETRIC ANALYSIS**

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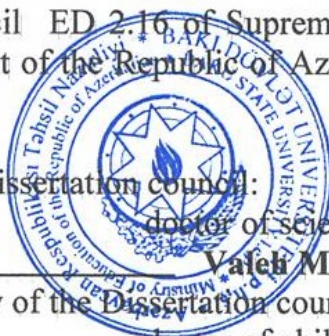
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## General description of work

**Relevance and elaboration of the topic.** One of the main causes of genetic abnormalities in living organisms is the increasing influence of technogenic and anthropogenic factors on the environment, which in some cases leads to irreversible changes in the composition of the biosphere. This requires continuous monitoring of technogenic pollutants and the migration of toxic substances in the environment and creates the need for operational and reliable control of the content of heavy metals with toxic properties.

The urgent task of analytical chemistry is the development of methods for monitoring the quality and safety of food products, which not only increase the expressness of analysis, but also significantly improve their metrological characteristics. Modern analytical chemistry of noble and rare metals has a fairly powerful arsenal of chemical, physico-chemical and physical determination methods, which often have low sensitivity and selectivity, require the use of expensive equipment, as well as the use of toxic organic extractants. Among the above methods, spectrophotometry using organic reagents. This method provides high sensitivity, accuracy, selectivity and expressiveness of the analysis, covers a wide range of determined concentrations and compares favorably with universality, economy, and the availability of hardware design. The simplicity of the experiment and the sufficient accuracy of the determination results make the spectrophotometric method one of the most sought-after and economically viable methods in analytical chemistry. One of the urgent tasks of spectrophotometry remains the search for new reagents that increase the selectivity of the determination of metals in a wide range of concentrations and in various oxidation states.

Organic reagents with a high complex-forming ability in relation to many metal ions are constantly in the focus of researchers. They have the property of sharply changing color during complexation and are used in spectrophotometric methods of analysis.

Despite the large number of studies on photometric analysis, many of its directions have not yet been sufficiently developed. The use of reactions of the formation of mixed ligand complexes (MLC) is one of these areas. With the formation of outer-sphere complexes

or the introduction of hydrophobic amines into the inner sphere, not only the spectrophotometric, but also the thermodynamic characteristics of the complexes change. In turn, Cu, Hg, Ti, V, Nb, Ta, Mo, W, Mn, U, Fe, Co, and Ni are increasingly used in the chemical, electronic, textile, and other sectors of the national economy. For the rapid determination and concentration of a large number of elements, in the analysis of high-purity materials for the content of impurities, extraction plays an important role in analytical chemistry. It provides high concentration efficiency, speed and availability of analysis. Organic solvent extraction is widely used to eliminate the interfering influence of extraneous ions and to increase the sensitivity of photometric reactions. Increasing the selectivity and contrast of reactions, as well as improving extraction and other properties, is often carried out using MLC. The use of hydrophobic amines in the formation of MLC gives a positive analytical effect: the strength of the complex increases, its solubility in water decreases and the negative charge of the homogeneous ligand complex (HLC) is compensated. The low solubility of these compounds in water, good in organic solvents, allows their use in extraction-photometric analysis. To increase the sensitivity and selectivity of photometric determinations of metals, MLC is used, due to the possibility of various combinations of reagents.

Recently, mixed ligand complexes with a mixed coordination sphere have been of increasing interest, which is related to their features and specific properties that the HLC do not possess or exhibit very rarely. In this regard, MLC are widely used in analytical chemistry and chemical technology.

Despite the existence of a large assortment of photometric reagents for the determination of elements, work continues on the search and study of new photometric reagents having various functional groups. From this point of view, reagents are very promising, having in the molecules a hydroxyl and two sulfhydryl groups-2,6-dithiolphenol and its derivatives. These reagents are sulfur-containing analogues of mononuclear polyphenols, where two oxygen atoms are replaced by sulfur atoms. Such reagents acquire new properties - the spectrum of their action with metal ions changes and

their sensitivity to them increases, complexes with metals absorb light into wider in the range of wavelengths, however, the selectivity decreases. The presence of two different-valued donor atoms - sulfur and oxygen-contributes to the formation of stable complexes owls with metal ions. As a result of this systematic study of 2,6-dithiolphenol and its derivatives, the identification of their analitical effects opportunities, the study of their interaction with metals and the development of new effective methods based on them is one of the urgent tasks analytical chemistry.

The dissertation was carried out at the Department of Analytical and Organic Chemistry of the Azerbaijan State Pedagogical University (reg.№ 0309Az 1515).

**The purpose and objectives of the study.** The aim of the work was to find new effective and affordable photometric reagents for Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II), the synthesis and identification of dithiolphenols (DP), the study of the physico-chemical, extraction and analytical properties of the synthesized compounds, study of mixed-ligand complexes with DP in the presence of hydrophobic amines (Am), development of selective extraction-spectrophotometric methods for the determination of these elements in various complex natural and industrial materials.

To achieve this goal, the following tasks were solved:

- synthesis of nitrogen and sulfur-containing organic reagents and the study of their physico-chemical, extraction and analytical properties;

- study of the conditions for the formation and extraction MLC of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) with DP and Am.

- determination of the composition of the MLC and the study of the mechanism of complexformation;

- determination of physico-chemical and analytical characteristics of the MLC;

- establishment of the structure of individually allocated MLC methods of IR and electronic spectroscopy, as well as using x-ray and thermogravimetric analyzes;

- study of the effect of the nature of hydrophobic amines on the formation of MLC;
- study of the role of the ligand-ligand interaction in the formation of MLC;
- determination of the valence state of some elements by the EPR method;
- establishment of possible correlation dependencies between the acidic properties of complexing reagents and the analytical characteristics of the MLC;
- study of the influence of extraneous ions and masking substances on the formation of MLC;
- development of effective methods for extraction-spectrophotometric determination of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II), characterized by improved metrological properties and their application to various objects.

**Research methods.** In identifying the synthesized complexing reagents, as well as studying the composition and properties of complex compounds, a number of chemical and physicochemical methods were used (spectrophosphometry, IR and NMR spectroscopy, thermogravimetry, etc.).

**The main provisions for the defense.** The main provisions to be defended:

1. Identification of DP by IR and NMR spectroscopy, and the study of their physico-chemical characteristics;
2. Establishing the form of existence of DP in solution depending on pH;
3. A study of the physicochemical and analytical properties of multi-ligand complexes Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) with DP and Am;
4. Determination of the oxidation state of vanadium, molybdenum, tungsten, iron and cobalt in MLC;
5. The study of ligand-ligand interaction;

6. Determination of the composition, structure and properties of the compounds obtained by elemental analysis, IR spectroscopy, magnetochemistry, x-ray diffraction and thermal analysis;

7. Photometric determination of elements similar in chemical properties (Nb and Ta; Mo and W; Co and Ni);

8. Development of new effective, express, highly selective, characterized by improved metrological properties of methods of extraction spectrophotometric determination of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) with DP and Am;

9. Application of the developed methods to the analysis of complex natural and industrial materials.

**The scientific novelty of the work.** For the first time, new photometric reagents, dithiolphenols, have been proposed for the extraction, selective separation, and determination of certain *d*- and *f*-elements.

The main quantitative characteristics of dithiolphenols - distribution and ionization constants, solubility, stability in various media were obtained for the first time. The synthesized compounds were identified by NMR and IR spectroscopy.

For the first time, the MLC of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) with 2,6-dithiolphenol (DTP) and its derivatives (2,6-dithiol-4-methylphenol (DTMP), 2,6-dithiol-4-ethylphenol (DTEP), 2,6-dithiol-4-propylphenol (DTPP) and 2,6-dithiol-4-*tert*-butylphenol (DTPP)) in the presence of hydrophobic amines (Am). As hydrophobic amines, aromatic (aniline (An), *N*-methylaniline (mAn), *N,N*-dimethylaniline (dAn), *p*-chloroaniline (*p*-Cl-An), *p*-bromaniline (*p*-Br-An), diphenylguanidine (DPG), triphenylguanidine (TPG), benzylamine (BA), tribenzylamine (TBA), *o*-, *m*- and *p*-phenylenediamines (*o*-, *m*- and *p*-PDA), heterocyclic (phenanthroline (Phen), batophenanthroline (BPhen), dipyridyl (Dip), pyridine (Py), *o*-, *m*-, *p*-aminopyridines (*o*-, *m*- and *p*-AmPy)) and hydroxyl-containing amines (aminophenols - 2-(*N,N*-dimethylaminomethyl)-4-methylphenol (AP<sub>1</sub>), 2-(*N,N*-dimethylaminomethyl)-4-chlorophenol (AP<sub>2</sub>), 2-(*N,N*-dimethylaminomethyl)-4-bromophenol (AP<sub>3</sub>), 2,6-bis(*N,N*-dimethy-

laminomethyl)-4-methylphenol (AP<sub>4</sub>), 2,6-bis(N,N-dimethylaminomethyl)-4-chlorophenol (AP<sub>5</sub>), 2,6-bis (N,N-dimethylaminomethyl)-4-bromophenol (AP<sub>6</sub>), 2-(N,N-diethylaminomethyl)-4-methylphenol (AP<sub>7</sub>), 2-(N,N-dimethylaminomethyl)-4-ethylphenol (AP<sub>8</sub>) 4-chloro-2-(N,N-dimethylaminomethyl)-6-thiophenylmethylphenol (AP<sub>9</sub>), 2-(N,N-di-ethylaminomethyl)-4-bromophenol (AP<sub>10</sub>), 2-(N,N-diethylaminome-thyl)-4-ethylphenol (AP<sub>11</sub>), 2-(N,N-diethylaminomethyl)-4-*tert*-butylphenol (AP<sub>12</sub>)), as well as pyrazolone-5 derivatives (anti-pyrine (Ant), diantipyrylmethane (DAM), diantipyrylpropylmethane (DAPM), diantipirilheksilmetan (DAHM) and diantipirilfenilmetan (DAPM)).

It was shown that, unlike HLC, MLC of copper, mercury, titanium, vanadium, niobium, tantalum, molybdenum, tungsten, uranium, manganese, iron, cobalt and nickel, they are extracted with low-polar solvents, and their formation reactions are highly selective and sensitive.

Various physicochemical methods determined the composition and showed the formation of MLC of Hg(II), Ti(IV), Nb(V), Ta(V), W(V), U(VI) ions with DP and Am form only outer-sphere MLC, and Cu(II), V(II,IV), Mo(V), Mn(II), Fe(II), Co(II), and Ni(II) form both outer-sphere MLC and MLC with a mixed coordination sphere.

New selective, sensitive and rapid methods of extraction-spectrophotometric determination, extraction separation and separation of metals from many associated elements are proposed. The developed methods are applied to the determination of metals in various natural and industrial objects. Methods have been developed for separating elements with similar chemical properties (molybdenum and tungsten; niobium and tantalum; cobalt and nickel).

**The theoretical and practical significance of the work.** The high complexing ability of dithiolphenols made it possible to develop new selective methods for the extraction and spectrophotometric determination of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V)), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II). The methods for determining these elements in the form of MLC with DP and its derivatives in the presence of hydrophobic amines are characterized by high sensitivity and selectivity.



The practical implementation of the research results was reflected in the development of new express and reliable extraction spectrophotometric methods for the determination of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II). The availability of reagents and the analytical advantages of the developed methods made it possible to determine these metals in soils, alloys, steels of various grades, water, biological materials, pharmaceutical samples, alunite, oil and products of its processing.

The results of IR spectroscopic, derivatographic, radiographic, and EPR studies of complex compounds can serve as reference material when reading a special course of lectures on coordination chemistry.

**Publications.** On the topic of the dissertation, 86 works were published, including 50 articles in journals and 36 materials and abstracts of reports at scientific conferences.

**Approbation.** The main results of the thesis are presented at the II All-Russian Conference (with international participation) "Analytics of Russia" dedicated to the anniversary of academician Yu.A. Zolotova (Krasnodar, 2007), republican scientific conference "Organic Reagents in Analytical Chemistry" dedicated to the 95th and 100th anniversary of A.A. Verdizade (Baku, 2009, 2014), IV International Conference "Extraction of Organic Compounds. EOS-2010" (Voronezh, 2010), VIII Baku International Mammadal Conference on Petrochemicals (Baku, 2012), V Republican Scientific Conference "Chemistry of Coordination Compounds" (Baku, 2012), Republican Scientific Conference dedicated to the 100th anniversary Academician M.Nagiyev (Baku, 2013), III All-Russian (with international participation) and the V International Scientific Conferences "Advances in synthesis and complexing" (Moscow, 2014 and 2019), XI-XVI International Conferences "Spectroscopy of Coordination Compounds" (Tuapse, 2014-2019), at the VI Republican Scientific Conference "Chemistry of coordination compounds" dedicated to the 80th anniversary of the Department of Analytical Chemistry of BSU (BSU, Baku, 2015), IV All-Russian Conference on Organic Chemistry (IOKh RAS, 2015), international Congress

“Kost-2015” on the chemistry of heterocyclic compounds, dedicated to the 100th anniversary of A.N.Costa (Moscow State University, Moscow, 2015), OrgChem-2016 Conference Cluster of Organic Chemistry (St. Petersburg), International Conference “Chemical Sciences & Applications” (2016, Alex. Egypt. ICCSA 2016), Nineteenth All-Russian Conference of Young scientists - chemists (Nizhny Novgorod, 2016), VI All-Russian Conference (with international participation) "Modern problems of chemical science and pharmacy", dedicated to the 50th anniversary of ChSU named after I.N.Ulyanova (Cheboksary, 2017), the international conference “Chemistry of Coordination Compounds: Actual Problems of Analytical Chemistry” dedicated to the 85th anniversary of Academician R.A. Alieva.

**The volume and structure of the dissertation.** The total volume of the thesis is 394 pages (373003 characters), consists of an introduction, 8 chapters (including a literature review), conclusions, a list of references for 542 titles of domestic and foreign authors, contains 119 tables and 76 figures.

In the introduction, the relevance of the topic is justified, the purpose and objectives of the work are formed, the main position is stated that is protected by the author.

In the literature review, photometric, extraction-photometric and other methods for the determination of certain *d*- and *f*-elements, Cu(II), Ti(IV), Hg(II), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), U(VI), Fe(II), Co(II), Ni(II) and Mn(II). The difficulties of determining some *d*- and *f*-elements in natural objects, industrial designs and food products are shown; ways to increase the sensitivity and selectivity of photometric determination methods.

In the second chapter (26256 characters) some physico-chemical characteristics of complexing reagents are given. The third chapter (41971 characters) is devoted to the study of MLC of Cu(II), Ti(IV) and Hg(II) with DP and Am. The fourth chapter (37725 characters) presents the optimal conditions for the formation, analytical and chemical properties of MLC V(II,IV), Nb(V) and Ta(V) with DP and Am. The fifth chapter (27943 signs) is devoted to the study of the optimal conditions for the formation, analytical and chemical properties of MLC Mo(V), W(V), U(VI) and Mn(II) with DP and

Am. The sixth chapter (28823 signs) presents the analytical and chemical properties of the MLC of Fe(II), Co(II) and Ni(II) with DP and Am. The seventh chapter is devoted (51687 characters) to the development of extraction-photometric methods for the determination of some *d*- and *f*-transition elements. The eighth chapter is devoted (54863 characters) to the analytical application of the developed extraction-photometric methods for the determination of some *d*- and *f*-transition elements.

**Personal contribution of the author.** The personal contribution of the applicant consisted in the general setting of tasks, systematization of literature data, preparation and conduct of all experimental stages of research, processing, interpretation and presentation of the obtained experimental data, preparation of materials for publication and presentation of the results at conferences. All research described in the dissertation was carried out personally by the author or in collaboration with colleagues.

### Summary of work

DP were synthesized by a known method and identified by elemental analysis, NMR and IR spectroscopy. In the IR spectra of the DP, a wide intense band in the region of 3600–3200  $\text{cm}^{-1}$  with a maximum of about 3550  $\text{cm}^{-1}$  corresponds to  $\nu_{\text{OH}}$ . The indicated region is characterized by intermolecular bonds with the formation of dimeric and polymer molecules, as well as intramolecular hydrogen bond. The middle band in the region of 2600–2550  $\text{cm}^{-1}$ , which is associated with  $\nu_{\text{SH}}$ , perturbed by an intramolecular hydrogen bond.

The solubility of DP in water is 3.5–4.0 g/l. Alkyl groups as substituents decrease the solubility of the ligand and complex in an aqueous medium, but increase their solubility in solvents mixed with water, and therefore they can be extracted with such mixtures. With increasing pH of the aqueous phase, the solubility of DP increases.

The pK of acid dissociation of sulfhydryl and hydroxyl groups was determined by potentiometric titration. The dependence of the ionization constants DP on the ionic strength of the solution is linear at  $\mu = 0-1$  and is expressed by the equations:

$$\text{DTP} \quad \text{pK}_1 = 6.55 - 0.78\sqrt{\mu}; \quad \text{pK}_2 = 8.46 - 0.65\sqrt{\mu}, \quad \text{pK}_3 = 10.96 - 0.62\sqrt{\mu};$$

DTMP  $pK_1=7.11-0.56\sqrt{\mu}$ ;  $pK_2=8.89 - 0.43\sqrt{\mu}$ ,  $pK_3 = 11.32 - 0.44\sqrt{\mu}$ ;  
DTEP  $pK_1=7.05-0.65\sqrt{\mu}$ ;  $pK_2=8.82 - 0.54\sqrt{\mu}$ ,  $pK_3 = 11.27 - 0.49\sqrt{\mu}$ ;  
DTPP  $pK_1=6.93-0.59\sqrt{\mu}$ ;  $pK_2= 8.73 - 0.39\sqrt{\mu}$ ,  $pK_3 = 11.25 - 0.43\sqrt{\mu}$ ;  
DTBP  $pK_1=7.21-0.678\sqrt{\mu}$ ;  $pK_2=8.98-0.62\sqrt{\mu}$ ,  $pK_3 = 11.47 - 0.59\sqrt{\mu}$ .

The dissociation constants of dithiolphenols increase with increasing ionic strength. The DP molecule and its alkyl derivatives have three acidic groups capable of dissociation. Despite the lower electronegativity of the sulfur atom than of oxygen, it is expected that the hydrogen ion of the -SH group will be split off primarily under the influence of the solvent. This is apparently explained by the higher stability of thiolate ions due to the better delocalization of the negative charge in comparison with alkoxide ions.

Alkyl-substituted dithiolphenols are slightly weaker acids in comparison with DTP. Acidic properties of DP decreases in the series DTP-DTPP-DTEP-DTMP-DTBP. The substituents -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, and others have only a positive inductive effect and practically do not change the appearance of the spectrum.

**Investigation of MLC of Cu(II), Ti(IV) and Hg(II) with DP and Am.** By spectrophotometric methods, we studied the MLC of Cu(II), Hg(II) and Ti(IV) with dithiolphenols (DTP, DTMP, DTP, DTPP and DTPB) and hydrophobic amines. Of the hydrophobic Am, An, mAn, dAn, *p*-Cl-An, *p*-Br-An, DPG, *o*-, *m*- and *p*-AmPy, Phen, BPhen, Dip, BA, Py, TPG, DAM, DAPM, DAPhM, AP<sub>1</sub>-AP<sub>6</sub>, AP<sub>10</sub> and AP<sub>12</sub>. The acidity of the aqueous phase was created with 1M KOH and NaOH solutions, as well as with an acetate buffer solution (pH 1.8-8.0). The pH value of the aqueous phase after extraction was taken as equilibrium pH. At the beginning, with an increase in acidity, the extraction of these elements increases, and with a further increase, it gradually decreases, which is obviously associated with a decrease in the concentration of ionized forms of DP. At high pH values, the complexation process is complicated by the hydrolysis of a metal ion. The interaction of Cu(II) with DP and Am and their extraction into the organic phase, regardless of the nature of the mineral acids, occurs in the range of pH 1.5-9.4 ( $pH_{opt}$  4.3-8.5). At pH 9.4, the complexes are practically not extracted, which is apparently associated with a decrease in the degree of protonization of Am. On

the other hand, the concentration of non-extractable complexes  $[\text{Cu}(\text{DP})_2]^{4-}$  and  $[\text{Cu}(\text{DP})_3]^{7-}$  in the aqueous solution increases, since the dissociation of DP in the second -SH group ( $\text{pK}_2 = 8.25-8.78$ ) continues to increase. With an increase in the pH of the solution to 4.8 or higher, extraction of Hg(II) complexes is practically not observed, which is apparently associated with the hydrolysis of mercury(II) ions ( $\text{pH}_{\text{opt}} 2.0-4.5$ ). For the formation and extraction of MLC of Ti(IV)  $\text{pH}_{\text{opt}} 3.1-5.9$ . The presence of one maximum optical density within the indicated pH range confirms the assumption that one complex compound is formed. The MLC of Cu(II), Hg(II) and Ti(IV) with DP and AP are formed at higher pH values than complexes with DP and other amines. Apparently, this is due to the fact that AP have stronger bases.

If a solvent with a high dielectric constant is used for the extraction, complexes containing the solvent can be obtained. Solvents of the Hal-C-H type are suitable for the extraction of MLC  $[\text{MX}_n]^{m-}$  - amine, which are the best solvents for these compounds. The most effective in terms of the maximum degree of extraction of Cu(II), Hg(II) and Ti(IV) in the form of MLC and the rapid achievement of equilibrium was chloroform. Upon a single extraction with chloroform, 98.2-99.5% Cu(II), 98.3-99.4% Hg(II), and 97.5-98.9% Ti(IV), respectively, are extracted as MLC.

The maximum analytical signal during the complexation of Cu (II) with DP and Am is observed at 470-650 nm. DP absorb as much as possible at 272-280 nm. During complexation, a bathochromic shift of the light absorption maximum by 195–205 nm is observed. The light absorption of MLC of Cu(II) with DP in the presence of An, mAn, dAn, Py, Phen, BPhen, and Dip is very different from HLC, which indicates the formation of a MLC with a mixed coordination sphere. Chloroform extracts of mixed ligand complexes Hg(II) -DP-Am have light absorption maxima at 458-475 nm ( $\Delta\lambda = 188-195$  nm). The maximum analytical signal during the complexation of Ti (IV) with DP and Am is observed at 428–480 nm. The bathochromic shift is 150-200 nm. In the case of DAM and its analogues, MLC are formed with a maximum of light absorption at 472-480 nm.

The optimal condition for the formation and extraction of compounds is  $(0.72-1.08) \times 10^{-3}$  mol / L DP concentration. For maximum binding of anionic complexes in the MLC,  $(0.56-1.08) \times 10^{-3}$  mol/ L - Am is required. The results of studying the  $V_{ag}/V_o$  ratio for the extraction of Cu(II), Hg(II), and Ti(IV) as MLC showed that, regardless of the basicity and nature of the amines, the optimal  $V_{ag}/V_o$  is 5/5-80/5. This fact makes it possible to use MLC of ions Cu (II), Hg (II), Ti (IV) with DP and Am for extraction concentration. The MLC complexes of Cu(II) and Ti(IV) with DP and Am are stable in aqueous and organic solvents and do not decompose for three days, and after extraction for more than a month. MLC of mercury(II) do not decompose within 48 hours, and after extraction more than a month.

The stoichiometry of the studied MLC was established by the methods of equilibrium shift, straight line, and relative yield. Cu(II) interacts with DP and Am in a ratio of 1:2:2 (in the case of AP<sub>4</sub>, AP<sub>5</sub> and AP<sub>6</sub> =1:2:1). In the presence of An, mAn and dAn, is formed MLC, with the ratio Cu(II):DP:Am=1:2:4. In the case of heterocyclic diamines, all three components (Cu(II), DP, and Am) are part of the MLC in the ratio 1: 1:1. In the interaction of Hg(II) with DP and Am, complexes are formed with the composition of Hg(II): DP: Am = 1:2:2. In the composition of titanium MLC, one mole of metal accounts for two moles of DP and Am (in the case of AP<sub>4</sub>, AP<sub>5</sub> and AP<sub>6</sub> -1:2:1). In the case of DAM and its analogues, an MLC with the composition of Ti(IV) is formed: DP: Am = 1:1:1.

To elucidate the bond mechanism in the MLC, the IR-spectra of the isolated complexes Cu(II)-DTMP-An (I), Cu(II)-DTEP-Phen (II), Hg(II)-DTEP-An (III), Ti(IV) -DTBP-DPG (IV) and Ti(IV) -DTBP-DAM (V). An intense absorption band appears in the IR spectra of complexes in the 960-950 cm<sup>-1</sup> region, which is due to the stretching vibration of the metal - ligand bond. The decrease in the intensity of the pronounced band at 2580 cm<sup>-1</sup> observed in the DTMP spectrum and the appearance in the IR spectra of complexes of two absorption bands, one of which is shifted toward lower frequencies, suggests that one of the -SH groups is involved in the formation of a bond with metal. The disappearance of the absorption band in the region of 3600-3200 cm<sup>-1</sup> with a maximum at 3460 cm<sup>-1</sup>

indicates the absence of free-OH groups. The absorption band in the IR spectrum of complex I at  $2360\text{ cm}^{-1}$  indicates the presence of protonated An, and the absorption band at  $1365\text{ cm}^{-1}$  indicates the presence of coordinated An. In the IR spectrum of complex II, a pronounced absorption band at  $1370\text{ cm}^{-1}$  indicates the presence of a coordinated phen. Thus, in the interaction of Cu(II) with DP in the presence of An and Phen, MLC with a mixed coordination sphere are formed. The detection of absorption bands at  $2270\text{ cm}^{-1}$  in the IR spectra of complex III indicates the presence of protonated An. An intense absorption band appears in the IR spectrum of complex IV in the region of  $810\text{--}780\text{ cm}^{-1}$ , which is caused by the stretching vibration of the  $\text{Ti}(\text{OH})_2^{2+}$  group. In the IR spectrum of complex V, the absorption band of the  $-1660\text{ cm}^{-1}$  carbonyl group disappears.

An x-ray analysis method was used to study a single crystal of a complex of copper with DTMP and Phen. According to x-ray diffraction data, the complex is monomeric, the central atom is coordinated by 5 donor atoms. The donor environment of copper in the studied complex is formed by 2 nitrogen atoms, 2 oxygen atoms and a sulfur atom ( $\text{CuN}_2\text{O}_2\text{S}$ ). The coordination polyhedron of the central copper atom is a distorted square pyramid. The basal plane (equatorial plane) is formed by the nitrogen atom Phen, the phenolic oxygen atom, the ligand sulfur atom (DTMP) and the oxygen atom of the water molecule. The second nitrogen atom, N2 (Phen), is in the apical position. Thus, the copper ions in the complex are pentacoordinated, the coordination polyhedron of copper is a square pyramid. The top of the pyramid is the second nitrogen atom, Phen.

Thermogravimetric studies of the complexes Cu-DTMP-Phen and Cu-DTEP-Phen showed that their thermal decomposition occurs in three stages. The dehydration of the complexes is evidenced by the dehydration temperature ( $110\text{ - }130\text{ }^\circ\text{C}$ ) on the DTA curves by the endothermic effect (weight loss - 4.035-4.160%). After complete dehydration, anhydrous complexes of the composition  $\text{Cu}(\text{DP})(\text{Phen})$  are formed. In the temperature range  $425\text{--}500\text{ }^\circ\text{C}$ , the maximum mass loss rate is observed, which is associated with the removal of Phen (weight loss 40.36-41.66%). Further weight loss of the substance

(39.35-41.25%) is due to the combustion of DTMP at 500-540 °C. The final product of the thermolysis of the complexes is CuO.

During the thermolysis of the Ti (IV) -DTMP-DPG complex, significant weight loss begins at temperatures above 300 ° C, which indicates a fairly high thermal stability of the test sample. Thermal decomposition of the complex proceeds in three stages. At 60-80 ° C, water evaporates (weight loss 4.07%). Apparently, in the crystalline hydrates of the complexes, two water molecules are outer-sphere, as evidenced by the low temperature of dehydration. In the temperature range 320-510 °C, the weight loss is 48.2%, which is most likely due to the destruction of bonds in the coordination compound and the removal of DPG bound into the complex and its combustion products, accompanied by an exothermic effect. The last stage of decomposition in the temperature range 520-590 ° C is due to intense exothermic effects (weight loss 38.46% - DTMP decomposes). The end product of the complex thermolysis is TiO<sub>2</sub>.

It was found that the complexing form of copper(II), mercury(II), and titanium(IV) is Cu<sup>2+</sup>, Hg<sup>2+</sup>, and Ti(OH)<sub>2</sub><sup>2+</sup>, respectively. In this case, the number of protons displaced by it from one DTMP molecule turned out to be equal to 1.

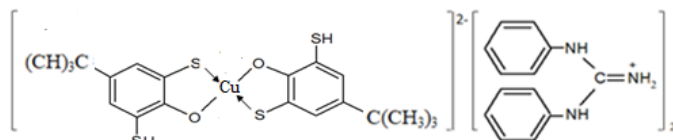
The nature of the second ligand can change the nature of the bond between the metal and the chelating ligand. Cu(II) with dsp<sup>2</sup> hybrid orbitals form flat square complexes. The addition of an additional ligand is not typical for such complexes. However, planar square Cu(II) complexes with one unpaired electron are able to attach additional ligands. Additionally attached ligands are located at a more distant distance from the central atom, unlike others. In this case, octahedral complexes (4 + 2) are formed. In some cases, one additional ligand can attach Cu<sup>2+</sup> ions (coordination number Cu<sup>2+</sup> - 5 (4 + 1)). The composition of the MLC can be represented by the formula [Cu(HR)<sub>2</sub>](AmH)<sub>2</sub>. In the presence of heterocyclic diamines, an MLC of the composition [Cu(DP)Am] is formed. The formation of a positive feedback π-bond increases the effective charge on the central ion and the addition of the second ligand to the complexed metal becomes energetically more advantageous than the addition of the ligand to the hydrated central ion. The MLC of Cu(II), Hg(II), and



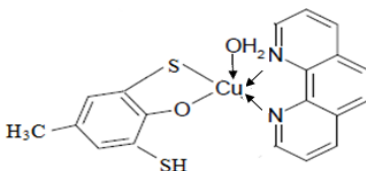
Ti(IV) with DP and Am in the organic phase do not polymerize and are in monomeric form ( $\gamma = 1.05-1.12$ ).

For 98.3-99.2% stripping, it is necessary to shake the organic phase with an equal volume of 0.5 M HCl and perhydrol solutions in a 1:1 ratio. When using 0.5 M  $\text{NH}_4\text{OH}$ , the degree of stripping reaches 99%. Mixed coordination sphere collapsing at  $\text{pH} > 9$ , a mixture (10:1) of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  solutions with  $\text{pH} 9.0$  was used for copper reextraction.

Cu-DTP-An, Cu-DTP-mAn, Cu-DTMP-An, Cu-DTMP-mAn, Ti-DTBP-DPG, Ti-DTBP-TFG and Ti-DTBP-An are isolated in an individual state and analyzed for content metal, S, C, and N. Elemental analysis confirms the composition of the complexes found by spectrophotometric methods. Considering the ratio of reacting components, the ionic form of Cu(II), the state of the complexes formed in the organic phase, the number of displaced hydrogen atoms, IR spectroscopic and thermogravimetric studies, as well as literature data, the composition of the extracted complexes can be represented as the formula:

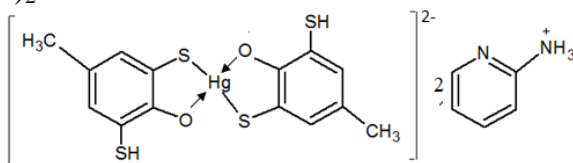


The composition of the MLC with DP and heterocyclic diamines on the example of  $\text{Cu}(\text{Phen})(\text{DTMP})$  can be represented as follows:

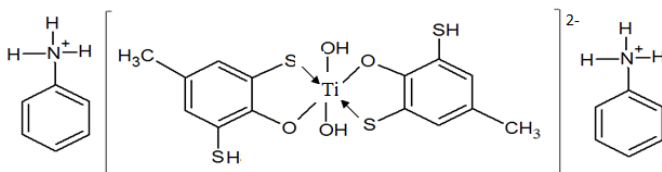


The addition of a neutral ligand to a chelate increases the degree of metal extraction into the organic phase. In the formation of complexes with  $\pi$  feedback, a significant role is played by the solvent. A decrease in the polarity of the solvent enhances the transfer of electron density over the ( $\text{M} \rightarrow \text{R}$ ) bond. The composition of the

extracted Hg(II) complexes can be represented by the formula:  $[\text{Hg}(\text{HR})_2](\text{AmH})_2$ .

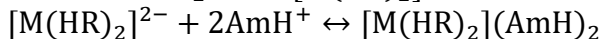
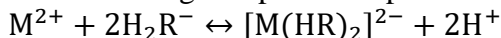


Thus, Hg(II) with DP and amines forms ionic associates or MLC with the outer sphere. It is assumed that the  $\text{Hg}^{2+}$  cations in the complexes are linked by a coordination bond with oxygen of the –OH group and a valence bond with sulfur from the SH group. Ti(IV) with DP and Am forms ionic associates or MLC with the outer sphere. The composition of the MLC on the example of Ti(IV)-DTMP-An can be represented as



MLC of titanium(IV) with other DP and Am have a similar structure. Only in the presence of DAM and its analogues is an MLC with a mixed coordination sphere formed.  $\epsilon$  to the MLC levels of copper, mercury, and titanium are  $(2.92\text{-}4.92)\times 10^4$ ,  $(2.68\text{-}3.88)\times 10^4$ , and  $(2.12\text{-}3.54)\times 10^4$ , respectively. The two-phase stability constants of the complexes Cu(II), Hg(II), and Ti(IV) are determined by the curve intersection method.

It is assumed that during complexation processes occur:



Where  $\text{M}-\text{Cu}^{2+}$ ,  $\text{Ti}(\text{OH})_2^{2+}$  and  $\text{Hg}^{2+}$

In the table 1 shows the main spectrophotometric characteristics of MLC of the Cu(II), Hg(II) and Ti(IV).

A decrease in the acidic properties ( $\Delta\text{pK}_1$ ) of the reagent leads to a shift in the pH ( $\Delta\text{pH}_{50}$ ) of complexation to a weaker acid region. With a decrease in the acidic properties of the reagents, the strength of the complex compounds formed by them with the studied metal

ions increases linearly. With an increase in the molar mass of the substituent, pK increases (Fig. 1).

**Table 1**

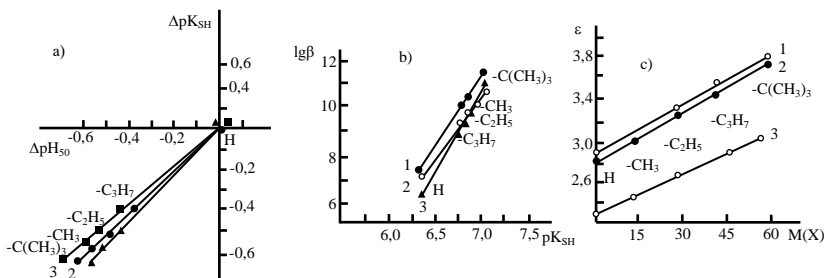
Formation conditions and some physico-chemical and optical characteristics of the MLC of Cu(II), Hg(II) and Ti(IV) with DP and Am

Compound	pH <sub>opt</sub>	λ, nm	Δλ, nm	ε×10 <sup>-4</sup>	lgβ	lgK <sub>p</sub>	lgK <sub>эк</sub>
[Cu(DTMP)(BPhen)]	6.6-8.1	635	361	4.37	11.94	6.79	10.32
[Cu(DTMP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	5.2-6.3	475	201	3.85	10.53	7.64	12.17
[Cu(DTMP) <sub>2</sub> ](AP <sub>4</sub> H <sub>2</sub> )	5.5-6.9	480	206	3.75	9.84	5.85	10,24
[Cu(DTMP) <sub>2</sub> ](AP <sub>6</sub> H <sub>2</sub> )	5.7-6.8	470	196	3.88	9.58	5.72	10.29
[Cu(DTEP) <sub>2</sub> ](An) <sub>2</sub> ](AnH) <sub>2</sub>	4.5-5.5	538	262	3,33	11.92	6,71	10,85
[Cu(DTEP)(BPhen)]	6.4-7.7	640	364	4.82	10.96	6.81	10.47
[Cu(DTBP)(Phen)]	6.9-8.2	644	364	3.91	11.95	6.75	11,04
[Cu(DTBP)(Phen)]	7.1-8.5	650	370	4.92	12.26	6.84	11.18
[Cu(DTBP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	5.9-7.0	485	205	3.95	10.95	7.79	12.82
[Cu(DTBP) <sub>2</sub> ](AP <sub>4</sub> H <sub>2</sub> )	5.9-7.3	485	205	3.85	10,18	5.90	10.09
[Cu(DTBP) <sub>2</sub> ](AP <sub>6</sub> H <sub>2</sub> )	6.2-7.4	480	200	3.96	9.95	5.77	10.12
[Hg(DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.9-3.9	462	192	3.05	6.98	5.09	9.53
[Hg(DTP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.0-4.0	465	195	3.20	7.05	5.28	9.61
[Hg(DTMP) <sub>2</sub> ](AnH) <sub>2</sub>	3.1-4.1	460	186	3,05	10,10	6,06	12,55
[Hg(DTMP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.2-4.2	464	190	3,20	10,21	6,19	12,69
[Hg(DTEP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.3-4.1	465	189	3.24	9.75	5.95	12.20
[Hg(DTEP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.4-4.2	470	194	3.50	9.80	6.12	12.28
[Hg(DTPP) <sub>2</sub> ](o-AmPyH) <sub>2</sub>	3.6-4.4	465	187	3.40	9.34	5.25	11.79
[Hg(DTPP) <sub>2</sub> ](m-AmPyH) <sub>2</sub>	3.3-4.3	468	190	3.28	9.28	5.16	11.76
[Hg(DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.4-4.4	470	190	3.80	10.64	6.32	13.34
[Hg(DTBP) <sub>2</sub> ](o-AmPyH) <sub>2</sub>	3.4-4.5	470	190	3.38	10.85	6.18	13.60
[Ti(OH) <sub>2</sub> (DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.2-4.3	430	160	2.38	6.32	5.63	8.44
[Ti(OH) <sub>2</sub> (DTMP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.3-4.9	432	158	2.41	10.36	5.65	12.59
[Ti(OH) <sub>2</sub> (DTMP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	3.7-5.2	430	156	2.62	9.53	6.35	11.76
[Ti(OH) <sub>2</sub> (DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.7-5.3	435	161	2.74	9.45	6.25	11.68
[Ti(OH) <sub>2</sub> (DTEP) <sub>2</sub> ](AnH) <sub>2</sub>	3.3-4.5	438	162	2.50	9.75	5.38	11.85
[Ti(OH) <sub>2</sub> (DTEP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.4-4.6	446	170	2.65	9.95	5.49	11.97
[Ti(OH) <sub>2</sub> (DTEP) <sub>2</sub> ](AP <sub>4</sub> H <sub>2</sub> )	3.6-5.1	435	159	2.55	8.52	5.12	10.65
[Ti(OH) <sub>2</sub> (DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.5-5.2	440	160	3.15	10.63	5.79	13.16
[Ti(OH) <sub>2</sub> (DTBP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.2-5.5	460	180	3.32	10.27	6.25	12.25
[Ti(OH) <sub>2</sub> (DTBP) <sub>2</sub> ](AP <sub>10</sub> H) <sub>2</sub>	3.2-5.7	480	200	3.54	10.28	5.23	11.55
[Ti(OH) <sub>2</sub> (DTBP) <sub>2</sub> ](AP <sub>12</sub> H) <sub>2</sub>	3.2-5.6	465	185	3.42	10.15	5.27	11.48

**Study of the optimal conditions for formation, analytical and chemical properties of the MLC of V(II,IV), Nb(V) and Ta(V).** When V(V) interacts with DP, it is reduced to V(IV). Spectrophotometric data and EPR spectra allow us to imagine the interaction

mechanism in the systems under study. V(V) initially restored DP to V(IV), the latter then enters into a complexation reaction with DP and Am. V(V) has no unpaired electrons and is diamagnetic, while V(IV) has one *d*-electron and has electron paramagnetic absorption. In accordance with the value of the nuclear spin  $J = 7/2$ , the EPR spectra of the V(IV) complexes consist of eight lines of the hyperfine structure caused by the interaction of the magnetic moment of the unpaired electron with the magnetic moment of the  $^{51}\text{V}$  nucleus ( $g = 1.961$ ,  $A(^{51}\text{V}) = 110.5$  Hz). When interacting with DP, the oxidation state of V(II) does not change.

Spectrophotometric methods were used to study V(II,IV), Nb(V) and Ta(V) with DP (DTP, DTPM, DTP, DTPP and DTPP) and Am. Of the hydrophobic amines, An, MAN, dAN, *o*-thol, *m*-thol, *p*-thol, *o*-AmRu, DPG, TPG, Ant, DAM, DAPM, DAGM, DAPM, Phen, BPhen, Dip, Ba, TBA, AP<sub>1</sub>-AP<sub>5</sub>, AP<sub>7</sub>-AP<sub>9</sub>, and AP<sub>12</sub>. For the extraction of the complexes, CHCl<sub>3</sub>, CCl<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>3</sub>, C<sub>4</sub>H<sub>9</sub>OH, C<sub>6</sub>H<sub>5</sub>Cl, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, methyl isobutyl ketone, as well as organic solvents and their mixtures were used. In the case of polar halogenated derivatives of aliphatic and aromatic hydrocarbons, the extraction increases markedly. The best extractants were CHCl<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, and C<sub>6</sub>H<sub>5</sub>Cl.



**Fig. 1.** Correlation between ( $\Delta pK_{SH}$ ) and  $\Delta pH_{50}$  (a),  $\lg\beta$  and  $pK_{SH}$  (b), the molar mass of the substituent ( $M(X)$ ) and the molar absorption coefficient (c) for the Cu(II)-DP-An complexes (1), Hg(II)-DP-An (2) and Ti(IV)-DP-An (3)

A single extraction with chloroform extracts 97.5-98.9% V(II,IV), Nb(V) and Ta(V) in the form of MLC. Due to the fact that

DP are rather strong acids than polyphenols and exist in solution in the forms  $H_3R$ ,  $H_2R^-$ ,  $HR^{2-}$  and  $R^{3-}$ , the interaction of Cu(II), Hg(II), and Ti (IV) with DP during depends a lot on the acidity of the environment. The optimal range of acidity, in which the optical density of the complexes V(II) with DP and Am is maximum and constant, is at  $pH_{opt}$  2.4-7.2. For the formation and extraction of MLC of V(IV), pH 3.2-7.8 is optimal. When Nb(V) and Ta(V) interact with DP in the presence of Am, the analytical signal reaches its maximum value at pH 2.9-5.6 and pH 2.5-6.0 for Nb(V) and Ta(V), respectively. The acid-base properties of hydrophobic amines to a lesser extent affect the formation and extraction of complexes. In the series dAn - MAn-*p*-Cl-An-*p*-Br-An, the pH of the reaction decreases. With an increase in  $pK_{NH^+}$ , the optimal pH of complexation and extraction shifts to a weaker acid region. With an increase in pH 8, the extraction of MLC of V(II,IV), Nb(V) and Ta(V) is practically not observed. This, apparently, is associated with a decrease in the degree of protonization of Am and an increase in the concentration of free molecules of aromatic Am.

The maximum light absorption of complexes V(II,IV) is observed at  $\lambda = 582-650$  nm. The maximum absorption of the Nb(V) and Ta(V) complexes is observed at 430-460 nm. Colored chloroform extracts of dithiolphenolate-amine (metal-free) complexes absorb maximally at 325-335 nm. The optimum  $V_{ag} / V_o$  is the ratio 5/5-80/5. The optical density of the MLC remains unchanged for 2 days, and after extraction for more than a month. The color of the solution of the vanadium complex with DP and DAM develops after five minutes of shaking the mixture of all components for 30 minutes. Over the specified time, light absorption increases by 20%. MLC of Nb(V) and Ta(V) are stable in aqueous and organic solvents and do not decompose within 72 hours, and after extraction, 15 days. The optimal condition for the formation and extraction of compounds V(II,IV), Nb(V), and Ta(V) is the concentration of  $(0.88-1.20) \times 10^{-3}$  mol / L DP and  $(0.60-0.88) \times 10^{-3}$  mol / L Am.

Upon transition from HLC to MLC, the sensitivity of the reaction increases, i.e., the molar absorption coefficients of the complex increase, and thus, lower V(IV) contents can be determined. Appa-

rently, a new modified reagent is formed in this case, the combined ligand with other molecular orbitals, which then interacts with the metal ion. Depending on the nature and degree of oxidation of the central ion, the ligands form a coordination bond with one functional atom, in while the other functional atom remains free and can take part in the formation of the ligand-ligand handicap communication.  $\pi$ -acceptor ligands, reduce the energy of the metal orbital and increase its effective charge, thereby facilitating the formation of bonds with other ligands. In most cases, MLC is more stable than HLC, which is due to the mutual influence of heterogeneous ligands in the coordination sphere of the complexing agent. In the resulting complexes, the ratio M : DP : Am = 1:2:2 (in the case of AP<sub>4</sub>, AP<sub>5</sub> and AP<sub>6</sub> - M : DP : Am = 1: 2: 2). In the case of *o*-AmPy, Phen, BPhen and Dip, V(II) MLC is formed with a component ratio of 1:1:2. The complexes of V(IV) with DP in the presence of DAM and its derivatives, as well as heterocyclic Am, have the composition VO: DP: Am = 1:1:1, and in the presence of Ant - VO:DP:Am =1:1:2.

The disappearance of the pronounced band at 2580 cm<sup>-1</sup> observed in the IR spectrum of DTMP and the appearance of two absorption bands in the spectra of the complexes V(II)-DTMP-An, Nb(V)-DTEP-An and Ta(V)-DTEP-An, one of which is shifted toward lower frequencies, suggests that one of the SH-groups is involved in the formation of the complex. The disappearance of the absorption band at 3460–3440 cm<sup>-1</sup> indicates that the -OH group is involved in the formation of a bond with the central atom. The detection of absorption bands at 2385–2375 cm<sup>-1</sup> indicates the presence of protonated An. In the IR spectra of the V(IV)-DTMP-Phen complex, the absorption band at 1385 cm<sup>-1</sup> indicates the presence of coordinated Phen. The intense absorption band at 980 cm<sup>-1</sup> is due to the stretching vibration of the VO<sup>2+</sup> group.

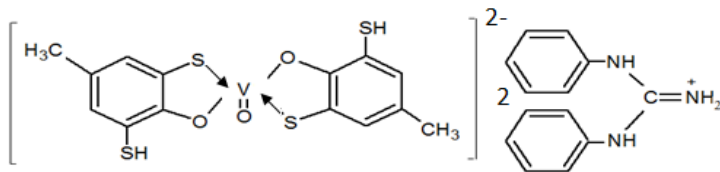
In the process of complexation with DAM, the reaction center is the oxygen of the carbonyl group containing an unshared pair of electrons, as evidenced by the disappearance of the absorption band of the C = O bond, which was observed in the spectrum of free DAM at 1670 cm<sup>-1</sup> and the appearance of a new band instead of it at 1580 cm<sup>-1</sup> due to the interaction of the reagent with the metal cation as an

electron acceptor with the formation of an interstitial complex. An intense absorption band appears in the IR spectra of the Nb(V) - DTEP-An and Ta(V)-DTEP-An complexes in the region of 870–920  $\text{cm}^{-1}$  due to the stretching vibration of the M-OH bond. IR spectroscopic studies show that in the interaction of V(II,IV), Nb(V) and Ta(V) with DP and Am, outer-sphere MLC complexes or ionic associates are formed. In the presence of heterocyclic Am, DAM, and its analogues, an MLC with a mixed coordination sphere is formed. In the formation of complexes V(II) and V(IV), the complexing ion is  $\text{V}^{2+}$  and  $\text{VO}^{2+}$ , respectively. In the case of MLC of Nb(V) and Ta(V), an integer value  $n = 1$  is obtained for the ions  $\text{M}(\text{OH})_3^{2+}$ . The number of hydrogen ions displaced from a single DP molecule is 1. The MLC in the organic phase are not polymerized and are in monomeric form ( $\gamma = 1.05\text{-}1.19$ ).

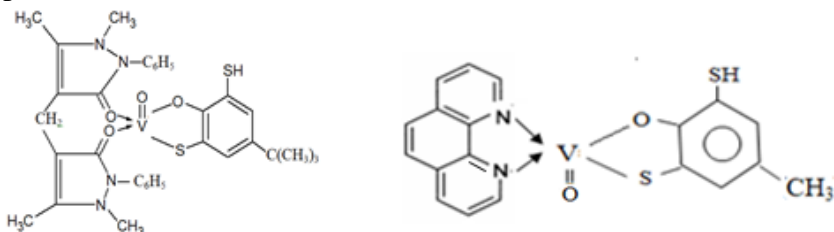
The complex VO-DTMP-Phen was investigated by  $^1\text{H}$  NMR spectroscopy. The singlet observed in the spectrum of the DTMF ligand at 5.48 ppm bound to the phenol group -OH disappears. This clearly indicates that the -OH group is involved in complexation. The intensity of the signal observed at 3.28 ppm bound to the thiol group -SH decreases by half and shifts somewhat to a weaker field (3.41 ppm). This confirms that one thiol group is involved in the complexation.

Thermogravimetric study of the V(IV)-DTEP-Phen complex shows that the rapid decomposition of the complex begins at 360-460  $^\circ\text{C}$ , where the mass loss is 49.1% (calculated 49.7%), which corresponds to the removal of phenanthroline. At 510-650  $^\circ\text{C}$ , a weight loss of 39.1% occurs (calculated 39.8%). DTEP stands out. The final product of thermolysis of the complex is  $\text{V}_2\text{O}_5$ .

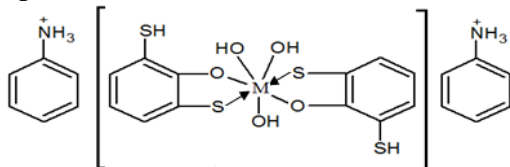
For reextraction of V(IV), Nb(V) and Ta(V), aqueous solutions of 0.5 M  $\text{NH}_4\text{OH}$  were mainly used (degree of reextraction - 98.0-99.1%). When using acids HCl and  $\text{H}_2\text{SO}_4$  with a concentration of 1M, the degree of reextraction is 97.3-98.1. Given the ratio of components in the complexes formed, the number of protons displaced during the reaction, the ionic form of V(IV) and reagents, we can imagine the following most probable structure of the MLC, using the example of V(IV)-DTMP-DPG:



The composition of the MLC with a mixed coordination sphere by the example of VO(DAM)(DTBP) and VO(Phen)(DTBP) can be represented as:



The coordination of the second ligand with the central atom in the MLC leads to the appearance of new absorption bands associated with charge transfer. The MLC absorption band is located in the longer wavelength part of the spectrum as compared with the HLC absorption band. Given the ratio of components in the complexes formed, the number of protons displaced ( $2n = 2$ ) and the ionic form of niobium and tantalum  $M(\text{OH})_3^{2+}$ , we can imagine the likely structure of the complex:



The molar absorption coefficients are  $(2.1-3.9) \times 10^4$ ,  $(2.1-3.9) \times 10^4$ , and  $(1.88-3.41) \times 10^4$ , respectively, for the complexes V(II,IV), Nb(V), and Ta(V). The introduction of alkyl substituents in the p-position of the -OH group increases the stability of chelates; it has a slight effect on sensitivity. Phen, BPhen, and Dip are typical chelating agents that form strong coordination-saturated complexes with metal cations Cu, Co, Ni, Hg, Mn, Fe. The accumulation of aromatic rings in the system occurs, therefore, there is more likelihood for the delocalization of electron density in the conjugation chain.



And this, in turn, leads to a bathochromic shift of the absorption bands and an increase in the stability of complex compounds. Depending on the nature of the complexing reagents, the stability of the complexes decreases in the series DTBP > DTMP > DTEP > DTTP > DTP. The spectrophotometric characteristics of the MLC systems V(II,IV), Nb(V) and Ta(V) are presented in table 2 and 3. A decrease in the acidic properties ( $\Delta pK_1$ ) of the reagent leads to a shift in the pH ( $\Delta pH_{50}$ ) of complexation to a weaker acid region (Fig. 2).

The obtained correlation dependences have the form:

for vanadium complexes:

$$\Delta pH_{50} = 0.658 \times \Delta pK_1 - 0.095 \quad \text{or} \quad \Delta pK_1 = \frac{\Delta pH_{50} + 0.095}{0.658}$$

for niobium complexes:

$$\Delta pH_{50} = 0.675 \times \Delta pK_1 - 0.125 \quad \text{or} \quad \Delta pK_1 = \frac{\Delta pH_{50} + 0.125}{0.675}$$

for tantalum complexes:

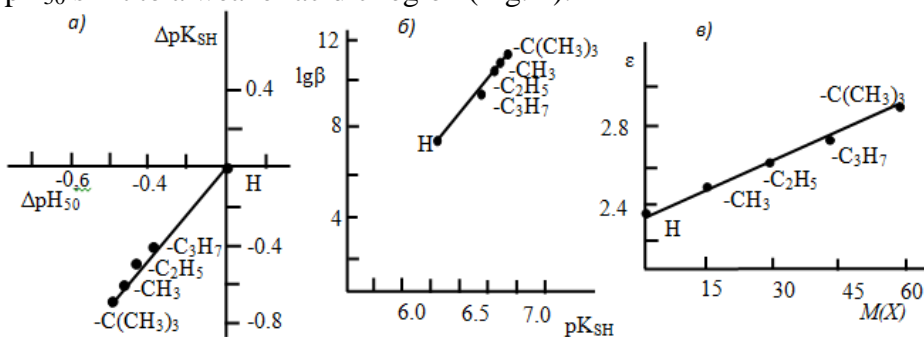
$$\Delta pH_{50} = 0.803 \times \Delta pK_1 - 0.08 \quad \text{or} \quad \Delta pK_1 = \frac{\Delta pH_{50} + 0.08}{0.803}$$

**Table 2**

Some chemical-analytical properties of MLC of vanadium(II,IV) with 2,6-dithiolphenol, its alkyl derivatives and hydrophobic amines

Compound	pH		$\lambda$ , nm	$\Delta\lambda$ , nm	$\varepsilon \cdot 10^{-4}$	$\lg K_p$	$\lg \beta$	$\lg K_{\text{жк}}$
	form	opt						
[V(DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.0-7.5	4.8-5.8	582	308	2.86	6.67	6.75	9.44
[V(DTMP) <sub>2</sub> ](AP <sub>4</sub> H) <sub>2</sub>	3.0-6.9	4.4-5.3	586	312	2.73	5.89	6.21	8.82
[V(DTBP)(BPhen) <sub>2</sub> ]	2.5-7.5	4.5-7.2	650	370	2.66	5.58	7.95	10.85
[V(DTBP) <sub>2</sub> ](AnH) <sub>2</sub>	2.2-5.6	2.8-4.4	625	345	2.94	5.53	7.02	10.01
[VO(DTP) <sub>2</sub> ]( <i>p</i> -tolH) <sub>2</sub>	2.3-6.5	3.9-4.9	620	350	3.05	5.96	7.71	10.19
[VO(DTP)](AnH) <sub>2</sub>	1.8-5.8	3.3-4.2	628	358	2.39	5.21	7.45	9.86
[VO(DTMP) <sub>2</sub> ](AP <sub>4</sub> H) <sub>2</sub>	3.0-7.5	4.3-5.2	630	356	4.15	5.39	9.23	12.13
[VO(DTMP) <sub>2</sub> ](AP <sub>10</sub> H) <sub>2</sub>	3.0-7.6	3.8-4.9	620	346	3.79	5.65	8.67	11.21
[VO(DTEP) <sub>2</sub> ](AnH) <sub>2</sub>	2.0-6.0	3.2-4.4	638	362	2.64	5.75	10.44	12.46
[VO(DTEP)(BPhen)]	4.8-8.4	7.0-7.5	615	339	3.84	5.62	10.73	13.42
[VO(DTEP)( <i>o</i> -AmPy)]	3.8-7.5	5.0-6.6	620	344	3.05	5.35	10.04	12.59
[VO(DTTP) <sub>2</sub> ](AnH) <sub>2</sub>	1.9-5.7	3.3-4.3	630	352	2.75	5.88	9.70	12.15
[VO(DTTP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.1-6.0	3.5-4.5	634	356	2.85	5.94	9.65	12.29
[VO(DTBP) <sub>2</sub> ](BAH) <sub>2</sub>	2.0-8.0	3.5-5.0	590	310	3.21	5.98	11.45	13.56
[VO(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.0-6.6	3.6-4.8	645	365	2.74	6.23	11.42	13.43
[VO(DTBP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.2-6.5	3.5-4.7	642	362	2.98	6.12	11.25	13.95
[VO(DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	2.2-6.6	3.6-4.8	645	365	2.95	6.15	11.20	13.98
[VO(DTBP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.0-7.5	4.5-5.9	615	345	4.30	6.12	11.36	14.55

With the introduction of electron-donating substituents in the structures, that is, with a decrease in the acid properties of the phage reagent, the strength of the complexes increases, and the  $\text{pH}_{\text{opt}}$  and  $\text{pH}_{50}$  shift to a weaker acidic region (Fig. 2).



**Fig.2.** Correlations between  $\Delta\text{pK}_{\text{SH}}$  and  $\Delta\text{pH}_{50}$  (a),  $\lg\beta$  and ( $\text{pK}_{\text{SH}}$ ) (b) the molar mass of the substituent ( $M(X)$ ) and the molar absorption coefficient (c) for complexes V(IV)-DP-An

**Investigation of the MLC of Mo(V), W(V), U(VI) and Mn(II) with DP and Am.** When interacting with the DP, Mo(VI) and W(VI) are reduced to M(V), and in both cases the same compound M(V) is formed. An ESR study proved that M(VI) is initially reduced by dithiolphenols to M(V), the latter then undergoes a complexation reaction.

Physicochemical methods were used to study MLC of Mo(V) with DP (DTP, DTMF, DTP, DTPP, DTPP) and Am. Of the hydrophobic amines, *p*-Cl-An, An, mAn, dAn, *o*-thol, *m*-thol, *p*-thol, *o*-, *m*- and *p*-PDA, BA, AmRu, DFG, AP<sub>1</sub>, AP<sub>4</sub> and AP<sub>8</sub> were used. We studied MLC of W(V) with DTP, DTMP, DTEP, DTPP, and DTBP in the presence of hydrophobic amines (*p*-AmPy, An, mAn, DPF, AP<sub>1</sub>, AP<sub>2</sub>, and AP<sub>3</sub>). Physico-chemical analysis methods were used to study MLC of U(VI) with DP (DTP, DTMP, DTEP, DTPP, DTBP) and hydrophobic amines. Of the hydrophobic amines, An, mAn, dAn, Phen, Dip, DPG, TPG, BA, AP<sub>1</sub> and AP<sub>3</sub> were used. The MLC of Mn(II) with DP (DTP, DTMP, DTEP and DTPP) and Am (Phen, BPhen, Dip and AP<sub>1</sub>-AP<sub>6</sub>) were studied.

The complete transition of M(V) MLC from DP and Am to the organic phase corresponds to pH 2.8-6.5 and 2.9-7.1 for Mo(V) and

W(V), respectively. The optimal region of the formation and extraction of MLC of U(VI) and Mn(II) are at pH 3.6-7.0 and 5.3-7.5, respectively. The best solvent for Mo(V), W(V), and U(VI) was CHCl<sub>3</sub>. Practical complete recovery (97.2-99.8%) is achieved by a single extraction (in the case of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and CCl<sub>4</sub> 96.2-97.3% is recovered).

**Table 3**

Some chemical-analytical properties of the radionuclide of Nb(V) and Ta(V) with 2,6-dithiolphenol, its alkyl derivatives and hydrophobic amines

Compound	pH		$\lambda$ , nm	$\varepsilon \cdot 10^{-4}$	lgK <sub>e</sub>	lg $\beta$	lgK <sub>ex</sub>
	form.	opt					
[Nb(OH) <sub>3</sub> (DTP)](dAnH) <sub>2</sub>	1.7-5.5	3.3-4.3	440	2.4	5.55	7.25	9.46
[Nb(OH) <sub>3</sub> (DTP)](AP <sub>3</sub> H) <sub>2</sub>	2.0-7.0	3.8-5.0	440	2.9	5.82	8.40	10.67
[Nb(OH) <sub>3</sub> (DTMP)](mAnH) <sub>2</sub>	1.7-5.7	3.3-4.6	445	2.6	5.75	10.82	13.08
[Nb(OH) <sub>3</sub> (DTMP)](dAnH) <sub>2</sub>	2.0-5.8	3.5-4.7	448	2.7	5.83	10.93	13.22
[Nb(OH) <sub>3</sub> (DTMP)](AP <sub>3</sub> H) <sub>2</sub>	2.2-7.4	3.6-5.4	445	3.8	5.88	10.95	10.33
[Nb(OH) <sub>3</sub> (DTEP)](dAnH) <sub>2</sub>	1.9-5.8	3.3-4.5	450	2.9	5.92	10.50	12.81
[Nb(OH) <sub>3</sub> (DTEP)](AP <sub>3</sub> H) <sub>2</sub>	2.1-7.2	3.6-5.0	448	3.9	5.95	10.50	12.73
[Nb(OH) <sub>3</sub> (DTPP)](AnH) <sub>2</sub>	1.5-5.2	3.1-4.0	445	3.0	5.65	9.26	11.08
[Nb(OH) <sub>3</sub> (DTPP)](mAnH) <sub>2</sub>	1.6-5.4	3.3-4.2	448	3.2	5.72	9.41	11.26
[Nb(OH) <sub>3</sub> (DTBP)](dAnH) <sub>2</sub>	2.2-6.0	3.6-4.9	450	3.6	5.92	11.22	13.64
[Nb(OH) <sub>3</sub> (DTBP)]( <i>o</i> -AmPyH) <sub>2</sub>	2.4-6.8	4.0-5.1	460	3.5	5.87	11.25	13.59
[Ta(OH) <sub>3</sub> (DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	1.6-5.0	2.7-3.8	435	2.21	5.22	6.52	8.71
[Ta(OH) <sub>3</sub> (DTP) <sub>2</sub> ](dAnH) <sub>2</sub>	1.7-5.2	3.0-4.0	438	2.25	5.35	6.78	9.07
[Ta(OH) <sub>3</sub> (DTMP) <sub>2</sub> ](dAnH) <sub>2</sub>	2.0-6.3	3.5-4.7	440	2.33	5.83	9.73	12.04
[Ta(OH) <sub>3</sub> (DTMP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.8-7.3	4.3-5.3	445	3.12	5.82	8.40	10.96
[Ta(OH) <sub>3</sub> (DTEP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.4-6.7	3.0-4.4	450	2.35	5.65	9.26	11.66
[Ta(OH) <sub>3</sub> (DTEP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.6-7.2	4.1-5.6	448	3.29	5.86	7.95	10.32
[Ta(OH) <sub>3</sub> (DTEP) <sub>2</sub> ](DypH) <sub>2</sub>	1.8-6.0	3.3-4.5	450	2.43	5.92	7.50	9.95
[Ta(OH) <sub>3</sub> (DTPP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.3-6.5	2.8-3.9	454	2.64	5.55	8.60	11.05
[Ta(OH) <sub>3</sub> (DTPP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.3-7.0	4.9-6.0	460	3.41	5.65	7.46	9.75
[Ta(OH) <sub>3</sub> (DTBP) <sub>2</sub> ](mAnH) <sub>2</sub>	1.9-6.5	3.5-4.8	455	2.76	5.82	9.93	12.35
[Ta(OH) <sub>3</sub> (DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	2.0-6.8	3.6-4.9	455	2.97	5.86	10.15	12.57
[Ta(OH) <sub>3</sub> (DTBP) <sub>2</sub> ]( <i>o</i> -AmPyH) <sub>2</sub>	2.0-7.0	4.0-5.1	460	2.84	5.87	9.79	12.13

The maximum analytical signal during the complexation of Mo(V) and W(V) with DP and Am is observed at 520-546 nm and 465-490 nm, respectively. The bathochromic shift is 200-266 nm. The maximum analytical signal during the complexation of U(VI) with DP and Am is observed at 430-478 nm ( $\Delta\lambda=150-298$  nm). The Mn(II)-DP-Am is absorbed as much as possible at  $\lambda = 420-480$  nm. The optimal condition for the formation and extraction of compounds Mo(V), W(V), U(VI) and Mn(II) is the concentration of  $(0.60-1.12) \times 10^{-3}$  mol / L DP and  $(0.64-0.96) \times 10^{-3}$  mol / L Am. MLC are

stable in aqueous and organic solvents and do not decompose within three days, and after extraction, more than a month. The maximum optical density is achieved within 5-10 minutes after the addition of reagents. In independence from the nature of Am, the color of the complexes develops in the same way. Changing the temperature within 10-70 ° C does not affect the color of the complexes.

Regardless of the basicity of amines and their nature, the optimal  $V_{ag} / V_o$  is 5/5-80/5. This fact allows us to use the MLC of these elements for their extraction concentration.

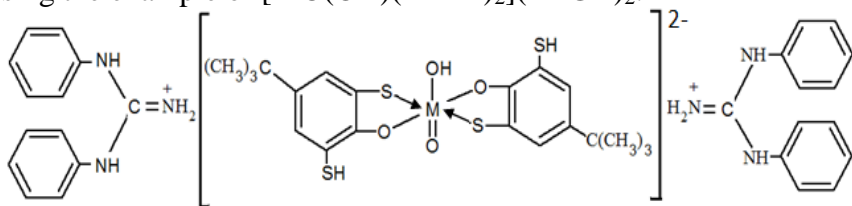
The ratio of reacting components in the MLC M : DP: Am = 1: 2: 2 (in the case of AP<sub>4</sub>, AP<sub>5</sub> and AP<sub>6</sub> - 1:2:1). These AP are part of the complex in a double protonated form. In the presence of Dip and Phen, an MLC with a mixed coordination sphere is formed, with a composition of 1:1:1 for Mo(V) and 1:1:2 for Mn(II).

In the IR spectra of the complexes Mo-DTMP-An and W-DTMP-An, in addition to a narrow band in the region of 950-930  $\text{cm}^{-1}$ , corresponding to the M = O bond, a somewhat intense absorption band appears at 1090  $\text{cm}^{-1}$ , which indicates the presence of a group M-OH. In the IR spectrum of the U(VI) -DTMP-An complex in the region of 820-795  $\text{cm}^{-1}$ , an intense absorption band appears due to the stretching vibration of the  $\text{UO}_2^{2+}$  group. The disappearance of the pronounced band at 2580  $\text{cm}^{-1}$ , observed in the DTMP spectrum and the appearance of two absorption bands in the spectra of complexes, one of which is shifted toward lower frequencies, suggests that one of the -SH groups is involved in the formation of the complex. The disappearance of the absorption band in the region of 3600-3200  $\text{cm}^{-1}$  shows that the -OH group is involved in the formation of a bond with the complexing agent. The detection of absorption bands at 2380-2260  $\text{cm}^{-1}$  indicates the presence of protonated Am. The number of protons displaced by it from one DP molecule was determined by the Nazarenko method, based on the analysis of the dependences  $A=f(\text{pH})$ . In the formation of MLC of molybdenum and tungsten, the coordinating ion is  $\text{MO}(\text{OH})^{2+}$ . The complexing form of uranium and manganese is  $\text{UO}_2^{2+}$  and  $\text{Mn}^{2+}$ , respectively. Complexation occurs with the displacement of one proton from each

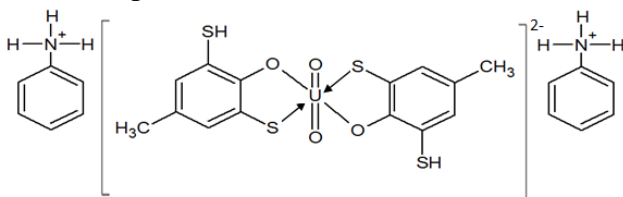
DP molecule. DP is strong enough reducing agents; therefore, the oxidation of Mn(II) is not possible.

The Mo(V)-DTMP-Dip complex was isolated in solid form and studied by x-ray diffraction. The study of a single crystal by x-ray diffraction analysis shows that the complex monomeric and central atom is coordinated by six donor atoms. The coordination environment of molybdenum is a distorted tetrahedron, which includes two dipyrindyl nitrogen atoms, one oxygen atom and one DTMP sulfur atom and two oxygen atoms of the  $\text{MoO}(\text{OH})^{2+}$  group, which is consistent with the data of vibrational and electron spectroscopy ( $\text{MoO}_3\text{SN}_2$ ). The crystal structure consists of discrete mononuclear molecules. The oxygen atom of the -OH group in the  $\text{MoOOH}^{2+}$  (O2) group and one of the dipipridyl nitrogen atoms (N1) are located in the promotional position. The oxygen atom (O1) and one sulfur atom (S1) of DTMP, the second oxygen atom (O3) in the  $\text{MoOOH}^{2+}$  group and the second nitrogen atom Dip (N2) are located in the equatorial position.

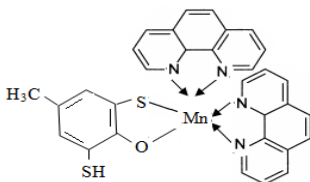
When using 0.3-0.4 M  $\text{NH}_4\text{OH}$  (or pH 7.2-8.0), the degree of reextraction of Mo(V) reaches 99%. Tungsten was reextracted from the organic phase with dilute acids  $\text{H}_3\text{PO}_4$  (1:3) or  $\text{H}_2\text{SO}_4$  (1:4). The experiments showed that for 98-99% reextraction, it is necessary to shake the organic phase with an equal volume of 0.2 M HCl and perhydrol solutions in a 1:1 ratio. The MLC of Mo(V), W(V), and Mn(II) with DP and Am were isolated in an individual state and analyzed for the content of metal, S, N and C. Considering the ratio of components in the complexes formed, the number of protons displaced, and the ionic shape of the metal and reagents, you can imagine the probable structure of the extracted complexes Mo(V), W(V) using the example of  $[\text{MO}(\text{OH})(\text{DTBP})_2](\text{DPGH})_2$ .



The mechanism formation of MLC can be represented as follows. When interacting with two molecules of DP, uranyl ions form doubly charged anionic complexes, which are extracted with two molecules of protonated Am. Based on the ratio of the components in the complexes formed, the number of protons displaced and the ionic form of the metal, one can imagine the probable structure of the complexes by the example of  $\text{UO}_2 - \text{DTMP} - \text{An}$ :



The structure of mixed-ligand manganese(II) complexes with a mixed coordination sphere can be represented by the example of  $\text{Mn}(\text{DTMP})(\text{Phen})_2$



The calculations showed that the MLC in the organic phase under the reaction conditions do not polymerize and are in monomeric form ( $\gamma=1.02-1.21$ ). Based on the data of spectrophotometric studies, molar absorption coefficients, two-phase stability constants, and also the equilibrium and extraction constants of MLC were found. The molar absorption coefficients are  $(4.32-5.41)\times 10^4$ ,  $(2.25-3.98)\times 10^4$ ,  $(2.68-3.82)\times 10^4$  and  $(2.45-3.72)\times 10^4$  for the MLC of Mo(V), W(V), U(VI) and Mn(II), respectively. Metal complexes with phen and bphen are usually more durable and intensely colored than complexes with dip. Extension of conjugation due to the inclusion of another aromatic ring in the case of Phen and BPhen creates energetically more favorable orbitals for the formation of back  $\pi$ -bond. Two-phase stability constants are determined by the curve intersection method.

Extraction photometric methods based on the introduction of heavy organic cations into the solution, which compensate for the negative charge of the anionic complex and reduce its hydrophilicity, can significantly increase the selectivity and often, due to concentration, somewhat increase the detection sensitivity elements.

In the table 4 and 5 show the chemical and analytical characteristics of the MLC of Mo(V), W(V), U(VI) and Mn(II) with DP and Am.

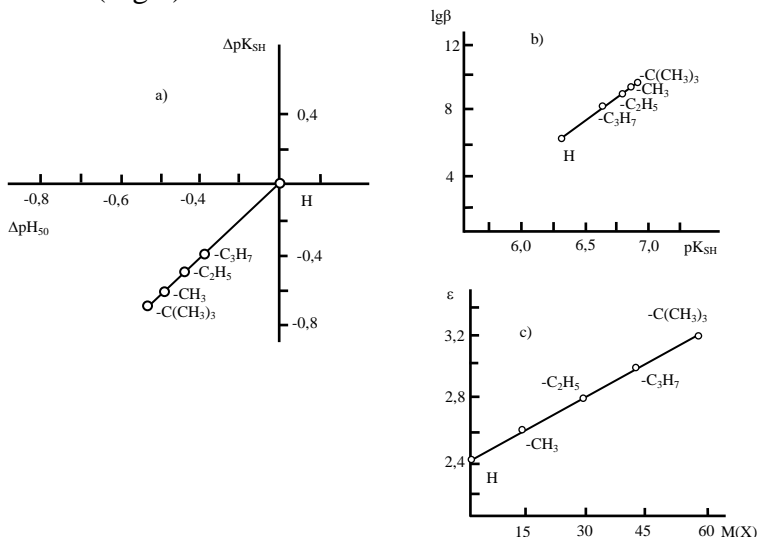
**Table 4**

The main chemical and analytical characteristics of the MLC of molybdenum and tungsten with DP and Am

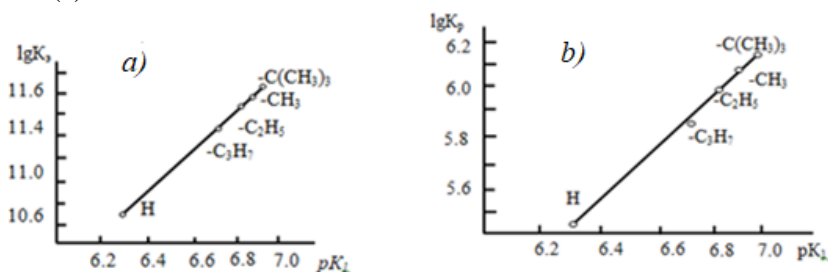
Compound	pH <sub>opt</sub>	R	λ, nm	ε×10 <sup>-4</sup>	lgβ	lgK <sub>e</sub>	lgK <sub>ex</sub>
[MoO(OH)(DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.2-4.7	97.6	530	4.86	6.83	6.5	9.04
[MoO(OH)(DTP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.4-4.9	97.7	534	5.03	6.89	6.8	9.15
[MoO(OH)(DTMP) <sub>2</sub> ](AnH) <sub>2</sub>	3.4-4.9	97.8	535	4.85	10.11	6.3	12.22
[MoO(OH)(DTMP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.6-5.0	98.2	542	5.25	10.25	7.1	12.36
[MoO(OH)(DTMP) <sub>2</sub> ](Phen)	5.0-6.5	98.7	523	5.22	14.9	6.2	15.36
[MoO(OH)(DTMP) <sub>2</sub> ](AP <sub>1</sub> H) <sub>2</sub>	4.6-5.8	98.7	525	5.28	10.35	6.5	12.84
[MoO(OH)(DTEP) <sub>2</sub> ](AnH) <sub>2</sub>	3.4-4.8	97.7	538	5.05	9.68	6.2	11.80
[MoO(OH)(DTPP) <sub>2</sub> ](AnH) <sub>2</sub>	3.3-4.7	97.6	540	5.10	8.92	6.1	10.90
[MoO(OH)(DTPP) <sub>2</sub> ](p-PDAH) <sub>2</sub>	4.4-5.9	98.3	530	5.24	7.81	6.0	10.57
[MoO(OH)(DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.8-5.3	98.7	540	5.36	10.62	7.2	13.01
[MoO(OH)(DTBP) <sub>2</sub> ](p-tolH) <sub>2</sub>	3.8-5.3	99.0	546	5.41	9.55	6.6	12.53
[MoO(OH)(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	4.3-6.5	99.2	520	4.75	10.52	6.5	13.20
[MoO(OH)(DTBP) <sub>2</sub> ](AP <sub>8</sub> H) <sub>2</sub>	4.2-5.6	99.8	515	4.96	10.70	6.0	13.68
[WO(OH)(DTP) <sub>2</sub> ](AnH) <sub>2</sub>	2.9-4,1	98.2	478	2.25	6.18	5.4	8.23
[WO(OH)(DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	3,2-4,2	98.3	483	2.41	6.24	5,5	8.34
[WO(OH)(DTMP) <sub>2</sub> ](mAnH) <sub>2</sub>	3,3-4,4	99.1	485	2,57	9.40	5.8	12.08
[WO(OH)(DTMP) <sub>2</sub> ](dAnH) <sub>2</sub>	3,5-4,5	99.2	490	2,68	9.42	5.9	12.15
[WO(OH)(DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3,9-5,1	99.6	480	2.92	9.89	6.7	12.75
[WO(OH)(DTEP) <sub>2</sub> ](AnH) <sub>2</sub>	3,1-4,2	98.7	482	2.56	8.95	5.5	11.04
[WO(OH)(DTEP) <sub>2</sub> ](DPGH) <sub>2</sub>	4,0-5,6	99.3	480	3.14	9.45	5.6	11.96
[WO(OH)(DTPP) <sub>2</sub> ](AnH) <sub>2</sub>	3,1-4,1	98.4	480	2.73	8.33	5.8	11.01
[WO(OH)(DTPP) <sub>2</sub> ](p-AmPyH) <sub>2</sub>	6.5-7,1	98.6	465	2.76	7.67	5.3	10.12
[WO(OH)(DTBP) <sub>2</sub> ](mAnH) <sub>2</sub>	3,5-4,6	99.2	480	2,95	9.75	6.1	12.45
[WO(OH)(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	4,5-6,0	99.4	485	3.38	8.48	6.6	12.46
[WO(OH)(DTBP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	4.4-5.3	99.7	490	3.98	10.6	6.8	13.11

A decrease in the acidic properties ( $\Delta pK_1$ ) of the reagent leads to a shift in the pH ( $\Delta pH_{50}$ ) of complexation to a weaker acid region. With an increase in the pK of reagents, the strength of the complex compounds formed by them increases linearly. With an increase in

the molar mass of the substituent, the molar absorption coefficient increases (Fig.3). A comparison of the equilibrium constants of  $\lg K_e$  and the extraction of the complexes of  $\lg K_{ex}$  uranium with  $pK_1$  reagents indicates the existence of a correlation dependence between these values (Fig.4).



**Fig. 3.** The correlation between  $\Delta pK_{SH}$  and  $\Delta pH_{50}$  (a),  $\lg\beta$  and  $pK_{SH}$  (b); the molar mass of the substituent ( $M(X)$ ) and the molar absorption coefficient (c).



**Fig. 4.** The correlation between  $\lg K_{ex}$  and  $pK_1$  (a);  $\lg K_e$  and  $pK_1$  (b) for complexes U(VI)-DP-An.

**Investigation of MLC Fe(II), Co(II) and Ni(II) with DP and Am.** The methods of spectrophotometry, IR spectroscopy, thermogravimetry, and chemical analysis were used to study MLC of



Fe(II). Of the DP used DTP, DTMP, DTEP and DTBP, and from hydrophobic amines - An, MAn, dAN, DPG, Phen, BPhen, Dip, AP<sub>1</sub>, AP<sub>2</sub>, AP<sub>3</sub> and AP<sub>8</sub>.

Spectrophotometric methods were used to study MLC of Co(II) and Ni(II) with DP in the presence of An, mAn, dAn, Gu, DPG, TPG, BA, *o*-PDA, *o*-AmPy, Phen, BPhen, Dip, AP<sub>1</sub>-AP<sub>8</sub>, AP<sub>10</sub> and AP<sub>12</sub>. The experiments showed that the MLC of Fe(II) and Fe(III) behave quite similarly during extraction: the absorption spectra and the pH range of the optimal extraction are almost the same.

**Table 5**

Chemical and analytical characteristics of complexes of uranium(VI) and manganese(II) with DP and Am

Compound	pH		R	$\lambda$ , nm	$\epsilon \times 10^{-4}$	lg $\beta$	lgK <sub>p</sub>	lgK <sub>эк</sub>
	form.	opt						
[UO <sub>2</sub> (DTP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.0-6.2	3.7-4.7	98.6	438	2.84	11.25	5.41	10.62
[UO <sub>2</sub> (DTP) <sub>2</sub> ](dAnH) <sub>2</sub>	2.2-6.4	3.9-4.9	98.7	440	2.95	11.38	5.53	10.68
[UO <sub>2</sub> (DTMP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.6-6.4	4.3-5.2	98.9	450	3.13	14.57	6.18	11.75
[UO <sub>2</sub> (DTMP) <sub>2</sub> ](DPGH) <sub>2</sub>	3.8-8.5	4.5-6.9	99.5	462	3.24	14.68	6.25	12.82
[UO <sub>2</sub> (DTMP) <sub>2</sub> ](AP <sub>1</sub> H) <sub>2</sub>	3.0-8.0	5.2-6.2	99.6	430	3.40	14.96	6.81	12.97
[UO <sub>2</sub> (DTEP) <sub>2</sub> ](dAnH) <sub>2</sub>	2.4-6.5	4.1-5.0	98.9	455	3.28	14.11	6.11	11.56
[UO <sub>2</sub> (DTEP) <sub>2</sub> ](DPGH) <sub>2</sub>	3.5-8.2	4.3-6.8	99.2	470	3.45	14.56	6.19	12.63
[UO <sub>2</sub> (DTEP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.5-7.5	5.2-6.6	99.4	438	3.82	14.75	6.73	12.53
[UO <sub>2</sub> (DTPP) <sub>2</sub> ](PhenH) <sub>2</sub>	1.5-6.8	3.6-5.9	98.1	463	3.36	15.10	5.42	11.20
[UO <sub>2</sub> (DTPP) <sub>2</sub> ](AmPyH) <sub>2</sub>	1.5-6.8	3.6-5.9	97.7	455	3.15	14.93	5.65	11.01
[UO <sub>2</sub> (DTBP) <sub>2</sub> ](mAnH) <sub>2</sub>	2.5-6.7	4.3-5.2	99.7	455	3.25	14.76	6.23	11.79
[UO <sub>2</sub> (DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.8-8.8	4.6-7.0	99.8	478	3.61	14.89	6.34	12.95
[UO <sub>2</sub> (DTBP) <sub>2</sub> ](BAH) <sub>2</sub>	2.7-6.7	4.2-6.8	99.7	455	3.58	14.85	6.30	11.90
[Mn(DTP)(BPhen) <sub>2</sub> ]	3.0-9.0	5.6-7.1	97.3	425	2.92	8.25	5.76	10.41
[Mn(DTP)(Dip) <sub>2</sub> ]	2.6-8.5	5.3-6.7	97.2	436	2.45	7.34	5.38	9.48
[Mn(DTP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	2.8-8.2	5.4-6.5	97.7	468	3.43	8.53	5.89	10.76
[Mn(DTP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	2.7-8.0	5.4-6.4	97.8	464	3.48	8.25	5.45	10.50
[Mn(DTMP) <sub>2</sub> ](AP <sub>1</sub> H) <sub>2</sub>	3.0-8.5	5.8-6.8	99.2	465	3.46	12.8	6.06	15.50
[Mn(DTMP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	2.8-8.4	5.6-6.7	99.3	462	3.53	12.8	6.18	15.55
[Mn(DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	2.8-8.3	5.6-6.6	99.2	460	3.57	12.7	6.25	15.40
[Mn(DTMP) <sub>2</sub> ](AP <sub>4</sub> H) <sub>2</sub>	3.2-8.6	6.0-7.3	98.8	470	3.34	10.6	5.32	13.12
[Mn(DTMP) <sub>2</sub> ](AP <sub>5</sub> H) <sub>2</sub>	3.0-8.5	5.8-7.1	98.9	465	3.42	10.5	5.39	13.06
[Mn(DTMP) <sub>2</sub> ](AP <sub>6</sub> H) <sub>2</sub>	2.8-8.5	5.7-7.0	98.7	462	3.50	10.3	5.37	12.78
[Mn(DTEP) <sub>2</sub> ](AP <sub>1</sub> H) <sub>2</sub>	2.9-8.2	5.7-6.7	98.5	472	3.55	12.3	6.12	14.72
[Mn(DTEP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	2.9-8.3	5.7-6.6	98.2	470	3.58	12.0	6.25	14.34
[Mn(DTEP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.0-8.0	5.7-6.5	98.3	465	3.62	12.8	6.28	15.16

The identity of the spectra makes it possible to conclude that Fe(III) is reduced by DP and in both cases the same compound Fe(II) is formed. The color intensity of the Fe(II) MLC is constant in the pH range 3.9-7.5. The yield of MLC of Co(II) and Ni(II) is maximum at pH 4.1-6.9. At pH 8, the MLC are practically not extracted, which is apparently associated with an increase in the concentration of non-extractable complexes  $[M(DP)_2]^{4-}$  and  $[M(DP)_3]^{7-}$ . Complexes with AP, DPG, and heterocyclic amines are formed in a weaker acid medium. DPG is in cationic form up to pH 10, which makes the range of its interaction wide. The presence of the second ligand led to a shift in the optimal acidity of complexation to a more acidic region, the  $pH_{opt}$  is wider than in the case of a two-component compound. Less basic amines form MLC with anionic dithiolphenolate complexes M(II) at lower pH values.

For the extraction of MLC, non-aqueous solvents were investigated: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, chlorobenzene, xylenes, isobutanol, n-butanol, isopentanol and their mixtures. The use of polar aprotic solvents, such as ethyl acetate and methyl isobutyl ketone, is impractical due to possible solvation processes, which can significantly complicate or change the complexation process. Upon a single extraction with chloroform, 98.3-99.8% Fe(II), Co(II) and Ni(II) are extracted as MLC. The basicity of Am does not significantly affect the conditions and extraction of the complexes. In the series DAM-DAPM-DAPM, the percentage of extraction increases. The introduction of hydrophobic radicals increases the solubility of the reagents in organic solvents. The maximum analytical signal during the complexation of Fe(II) with DP and Am is observed at 544-586 nm ( $\Delta\lambda = 245-255$  nm). In the presence of heterocyclic amines, a slight shift in the absorption maxima can be seen and, in some cases, their broadening. These changes indicate that in the presence of heterocyclic amines complex compounds are formed, in the inner sphere of which DP and Am enter. The maximum analytical signal during complexation of the Co(II) and Ni(II) MLCs is observed at 512-595 nm ( $\Delta\lambda = 245-255$  nm). In the case of Phen, BPhen, and Dip, the maxima in the absorption spectra are in the shorter wavelength region. The optimal

condition for the formation and extraction of compounds Fe(II), Co(II) and Ni(II) is the concentration of  $(0.72-0.96) \times 10^{-3}$  mol / L DP and  $(0.72-1.0) \times 10^{-3}$  mol / L Am. The optimal concentration of DP for the formation and extraction of MLC, depending on the basicity of hydrophobic amines, changes insignificantly.

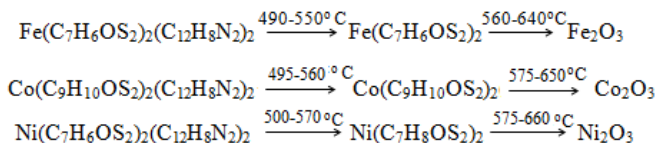
At an optimized pH value of the aqueous phase, the time to reach extraction equilibrium was determined at a ratio of the aqueous and organic phases of 4:1. The MLC of Fe(II), Co(II) and Ni(II) with DP and Am are stable in aqueous and organic solvents and do not decompose for 3-5 days, and after extraction for more than a month. The maximum optical density of the Co(II) and Ni(II) MLC with DP and Am is reached within 5-10 minutes. With weak heating (up to 30 ° C), the color develops instantly. The degree of extraction of Fe(II), Co(II) and Ni(II) in the form of MLC does not depend on the ratio of the volumes of aqueous and organic phases in a wide range (from 5:5 to 100:5), which allows simultaneous concentration and photometric determination specified items.

To determine the stoichiometric coefficients of the reaction of interaction of M(II) with DP and Am, various spectrophotometric methods were used: the equilibrium shift method, the Asmus straight line, and the relative yield. The composition of the MLC components are in the ratio M(II):DP:Am = 1:2:2. In the presence of DAM and its analogues, the ratio M(II):DP:Am = 1:1:1. In the case of heterocyclic diamines and o-PDA, M:DP:Am=1:1:2. DAM and its analogues are weak bicarbon bases in nature. They occupy two coordination places.

To study the nature of the bonds in the MLC, the IR spectra of Fe-DTBP-An, Fe-DTBP-Phen and Co(II)-DTMP-Dip complexes were measured and studied. The detection of absorption bands at  $2380 \text{ cm}^{-1}$  indicates the presence of protonated aniline. Detection of absorption bands at  $1390 \text{ cm}^{-1}$  indicates the presence of coordinated Phen.

The TG-DTG curves of the Fe(II)-DTP-Dip, Fe(II)-DTMP-Phen, Co(II)-DTMF-Phen and Ni(II)-DTMP-Phen complexes indicate that they are thermally stable up to 450 °C. The decomposition of the complexes occurs in two separate stages in the temperature ranges of 450-570 °C and 550-660 °C, respectively. The first stage

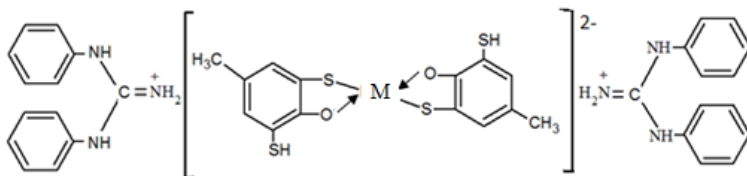
corresponds to the cleavage of Dip and Fen, and the second to the splitting of DP. The final product of the thermolysis of the complexes is  $M_2O_3$ . The process of allocation of 2,2'-dipyridyl is faster than phenanthroline. The thermal stability of the complexes in the solid phase changes in the same sequence as their thermodynamic stability in solutions. More resistant complexes are destroyed at higher temperatures.



To elucidate the mechanism of the complexation process, it is necessary to know the number of protons displaced from the FAG of the reagent, as well as to establish the form of the M(II) cation entering into interaction with the reagent. For this purpose, we applied the calculation-graphical method of Nazarenko. In the formation of MLC, the coordinating ion is  $M^{2+}$ . Complexation occurs with the displacement of one proton from one DP molecule. Under optimal conditions of extraction, DP in solution is in the form of  $H_2R^-$ , and most of the used amines are in the protonated form of  $AmH^+$ . For all studied systems, the value of  $\gamma$  is close to 1 ( $\gamma = 1.02-1.12$ ), i.e., the studied reagents form mononuclear complexes with M(II) ions.

In order to extract M(II) from the organic phase, solutions of acids and alkalis, as well as ammonia solution and hydrogen peroxide, were tested as reextractors. Mineral acid solutions mixed with  $H_2O_2$  have the best stripping properties. With an increase in the concentration of perhydrol in the solution, the reextraction of M(II) gradually increases. When using an ammonia solution, M(II) and DP quantitatively pass into the aqueous phase. The degree of reextraction is 96.8-98.4%. The MLC of Co(II) and Ni(II) with DP and Am were isolated in an individual state and analyzed for the content of metal, S, H, and C. The content of Fe(II), Co(II), and Ni(II) in the complexes was determined after their decomposition with aqua regia photometrically using salicylic acid, 1-nitroso-naphthol-2 and dimethylglyoxime, respectively.

Considering the molar ratio of the components in the complexes, the complexforming form of the central ion, the number of protons displaced, the monomer nature of the complexes in the organic phase, as well as the data of IR spectroscopic, thermogravimetric studies and chemical analysis, we can assume that the outer-sphere MLC complexes are formed:

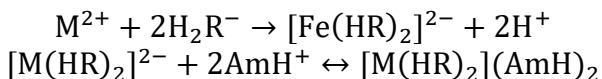


In the case of heterocyclic amines (Phen, BPhen, Dip and AmPy) and *o*-PDA, MLC with a mixed coordination sphere  $[M(\text{Am})_2(\text{DP})]$  is formed. Taking into account that the coordination number  $M(\text{II})$  is 6 and the ligand denticity is 2, the proposed structures of octahedral complexes can be represented by the following schemes:

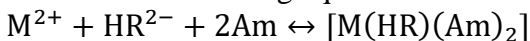


The introduction of electron-donating substituents in the DP molecule increases the relative stability of the MLC. The relative stability of the MLC increases with increasing differences in the properties of heterogeneous ligands.  $\pi$ -feedback ligands are optimally combined with oxygen-containing reagents. In the presence of Am, the molar absorption coefficient of the complex sharply increases, the absorption band shifts bathochromically, and the pH of the complexation shifts to a more acidic region. The molar absorption coefficients at  $\lambda_{\text{max}}$  are  $(3.05\text{-}4.4)\times 10^4$ ,  $(1.92\text{-}3.75)\times 10^4$ , and  $(1.82\text{-}3.85)\times 10^4$  for the Fe(II), Co(II), and Ni(II) complexes, respectively.

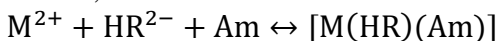
The stability of MLC with DP and heterocyclic amines is much higher than the stability of the corresponding HLC. The stability of the MLC with a shifted coordination sphere contributes to the formation of three five-membered cycles in the molecules of the complexes. With an increase in the basic properties of the third components, the stability constants of the complexes and the contrast of the complexation reaction increase. The reactions of MLC formation can be represented:



The reactions of formation of an MLC with a mixed coordination sphere (Phen, BPhen, Dip, o-PDA, o-AmPy, Py) can be represented in the form of the following equation:



In case of DAM, DAPM and DAPhM



In the table 6 the main spectrophotometric characteristics of the method for determining Fe(II), Co(II) and Ni(II) are presented. The study and comparison of the acid-base properties of the phage complex-forming reagents and the properties of the complexes made it possible to establish a quantitative correlation of the type  $\Delta pK_1$ - $\Delta pH_{50}$ ,  $pK_1$ - $lg\beta$ ,  $pH_{50}$ - $\sigma_n$ ,  $pK_1$ - $lgK_e$  and  $pK_1$ - $lgK_{ex}$ . The following correlations dependences were obtained for the MLC of Fe(II):

$$\Delta pK_1 = 1.118 (\Delta pH_{50})^{1.324} \quad (r=0.995) \quad \text{or} \quad \Delta pH_{50} = \left( \frac{\Delta pK_1}{1.118} \right)^{0.762}$$

$$pK_{SH} = 5.26 + 0.195 lg\beta \quad \text{or} \quad lg\beta = \frac{pK_{SH} - 5.26}{0.195}$$

$$pH_{50} = 3.34 + 4.13 \sigma_n \quad (r=0.98)$$

$$lgK_{\text{ex}} = \frac{pK_1 - 0.487}{0.593}$$

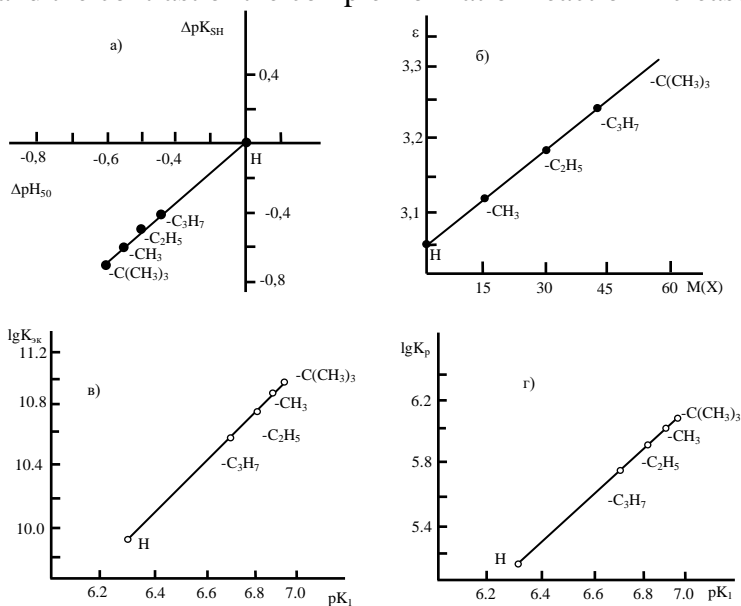
$$lgK_p = \left( \frac{pK_1}{1.86} \right)^{1.362}$$

With a decrease in the acidic properties of the phage reagent, the strength of the complexes increases, and the  $pH_{opt}$  and  $pH_{50}$  shift to a weaker acidic region. The degree of extraction of iron complexes correlates with  $pK_{NH^+}$ .  $R = 95.34 + 0.39 pK_{NH^+}$ . It has been establi-

shed that  $\epsilon c$  increases with an increase in the molar mass of the substituent (Fig. 5 and 6).

In the presence of Am, the molar absorption coefficient of the complex increases sharply, the absorption band shifts bathochromically, The complexation pH is shifted to a more acidic region.

The stability of the complexes allows the use of a number of masking substances, which increases the selectivity of the determination methods. Hydrophobic amines of various natures can change both the mechanism of complexation and the chemical-analytical characteristics of the complexes. With an increase in the main properties of the third components, the stability constants of the complexes and the contrast of the complexformation reaction increase.

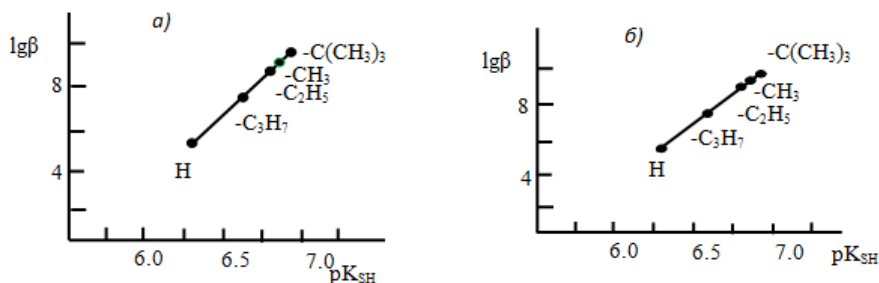


**Fig. 5.** The correlation between  $\Delta pK_{SH}$  and  $\Delta pH_{50}$  (a), the molar mass of the substitute ( $M(X)$ ) and the molar absorption coefficient (б),  $\lg K_{ex}$  and  $pK_1$  (в),  $\lg K_e$  and  $pK_1$  (г) for complexes Fe(II)-DP-An.

**Development of extraction-photometric methods for determining some *d*- and *f*-transition elements.** To determine the selectivity of the developed methods, the effect of foreign ions and mas-

king substances on complexation was studied. The interfering effect of foreign ions was eliminated using masking agents, changing the pH of the medium and using extraction. Under optimal complexation conditions, a grading plot was constructed, the range of concentration of metal ions obeying Beer's law, and the detection limit were determined. Based on the equations of the calibration graphs, the photometric detection limit and the limit of quantitative determination of the indicated elements in the form of MLC were calculated. Comparison of extraction-spectrophotometric determination methods with widely applicable methods shows the advantage of the proposed methods in reproducibility, sensitivity and also selectivity.

It was found that extraction spectrophotometric methods for determining Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) are highly selective, differ in accuracy, simplicity, expressivity and can be used in chemical analysis laboratories to determine them in various objects. The stability of the complexes allows the use of a number of masking substances, which increases the selectivity of the methods for determining these elements with DP and Am. Comparison of the analytical capabilities of the studied reagents and hydrophobic amines shows that the contrast and sensitivity of the reaction decreases in the series DTBP-DTPP-DTEP-DTMP-DTP.



**Fig. 6.** Correlation between  $\lg\beta$  and ( $pK_{SH}$ ) for the complexes Co(II)-DP-An (a) and Ni(II)-DP-An (b)



**Table 6**

Chemical and analytical characteristics of the MLC of iron(II), cobalt(II) and nickel(II)

Compound	pH <sub>обп.</sub>	pH <sub>опт.</sub>	$\lambda$ , nm	$\Delta\lambda$ , nm	$\epsilon \times 10^{-4}$	lg $\beta$	lgK <sub>e</sub>	lgK <sub>sx</sub>
[Fe(DTP)(BPhen) <sub>2</sub> ]	3.6-7.9	5.3-6.6	565	295	4.05	15.05	5.71	16.81
[Fe(DTMP) <sub>2</sub> ](mAnH) <sub>2</sub>	3.3-7.3	4.2-5.0	563	287	3.25	8.62	5.75	11.18
[Fe(DTMP)(Phen) <sub>2</sub> ]	3.8-8.2	5.9-7.2	565	291	3.42	18.46	5.71	19.36
[Fe(DTMP)(BPhen) <sub>2</sub> ]	3.6-8.1	5.8-7.0	574	300	4.22	18.45	5.86	19.53
[Fe(DTEP)(Phen) <sub>2</sub> ]	3.8-7.8	5.8-7.1	572	296	3.60	18.10	5.82	19.25
[Fe(DTEP)(BPhen) <sub>2</sub> ]	3.5-7.6	5.7-6.8	582	306	4.33	17.23	5.94	19.32
[Fe(DTEP)(Dip) <sub>2</sub> ]	3.4-7.4	5.6-6.6	568	292	3.26	16.79	5.73	19.17
[Fe(DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	3.7-7.6	4.6-5.4	575	295	3.57	9.04	6.11	11.54
[Fe(DTBP)(Phen) <sub>2</sub> ]	4.1-8.9	6.0-7.5	580	300	3.91	18.95	5.89	19.45
[Fe(DTBP)(BPhen) <sub>2</sub> ]	4.0-8.8	5.9-7.4	586	306	4.40	19.28	5.96	19.64
[Fe(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	2.3-7.0	4.6-5.7	545	265	3.45	8.78	6.03	11.45
[Co(DTP) <sub>2</sub> ](AP <sub>4</sub> H <sub>2</sub> )	2.5-8.0	4.5-5.7	528	258	2.88	7.12	5.68	9.94
[Co(DTP) <sub>2</sub> ](AP <sub>5</sub> H <sub>2</sub> )	2.6-8.0	4.6-5.8	530	260	2.97	6.95	5.68	10.24
[Co(DTMP) <sub>2</sub> ]( <i>o</i> -AmPy) <sub>2</sub> ]	3.3-8.5	5.9-7.3	518	244	2.76	14.35	5.08	16.12
[Co(DTMP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	3.0-8.2	4.8-5.9	535	261	3.35	10.34	5.76	12.35
[Co(DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	3.2-8.5	5.0-6.1	538	264	3.48	10.24	5.69	12.46
[Co(DTPP) <sub>2</sub> ](AnH) <sub>2</sub>	2.6-7.2	4.3-5.2	545	277	3.02	7.85	4.97	10.32
[Co(DTPP) <sub>2</sub> ]( <i>o</i> -AmPy) <sub>2</sub> ]	3.2-8.1	5.5-7.0	520	242	3.10	14.18	4.88	15.96
[Co(DTPP) <sub>2</sub> ](Phen) <sub>2</sub> ]	3.0-8.3	5.5-7.1	515	237	3.05	16.36	4.95	17.07
[Co(DTPP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	2.9-7.6	4.9-6.1	540	262	3.65	7.10	5.87	10.05
[Co(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	3.0-8.5	5.0-6.6	570	290	3.23	9.84	5.64	12.66
[Co(DTBP)(BPhen) <sub>2</sub> ]	3.0-8.6	5.6-7.9	520	240	3.75	19.6	5.38	18.34
[Ni(DTP) <sub>2</sub> ](BAH) <sub>2</sub>	3.0-9.5	4.7-6.4	512	242	2.96	6.50	4.89	8.63
[Ni(DTP) <sub>2</sub> ](DPGH) <sub>2</sub>	3.0-9.8	6.3-7.3	515	245	3.15	8.19	5.72	10.79
[Ni(DTMP) <sub>2</sub> ](AP <sub>2</sub> H) <sub>2</sub>	3.0-9.2	5.5-6.3	530	256	3.35	9.96	5.87	11.36
[Ni(DTMP) <sub>2</sub> ](AP <sub>3</sub> H) <sub>2</sub>	2.9-9.0	4.6-5.8	525	251	3.53	10.12	5.92	11.45
[Ni(DTMP) <sub>2</sub> ](BPhen) <sub>2</sub> ]	3.0-10.0	5.9-8.6	475	201	2.53	17.89	5.15	18.94
[Ni(DTEP) <sub>2</sub> ](AnH) <sub>2</sub>	3.0-7.8	4.5-5.7	530	254	3.33	8.62	4.75	8.07
[Ni(DTEP)(Phen) <sub>2</sub> ]	4.0-9.0	5.5-6.3	465	189	2.15	18.54	5.09	18.43
[Ni(DTBP) <sub>2</sub> ](DPGH) <sub>2</sub>	3.5-10.6	6.2-7.7	520	240	3.36	11.20	5.92	13.95
[Ni(DTBP) <sub>2</sub> ](dAnH) <sub>2</sub>	1.8-8.7	4.8-6.2	540	260	3.47	9.25	5.15	12.73
[Ni(DTBP) <sub>2</sub> ]( <i>o</i> -PDA) <sub>2</sub> ]	2.5-7.9	5.5-6.8	478	198	2.16	14.89	5.68	16.85

**Analytical application of the developed extraction-photometric methods for determining some *d*- and *f*-transition elements.** The proposed methods are characterized by satisfactory metrological characteristics, are not inferior at the lower limit of the determined contents to other photometric methods for the determination of Cu(II), Hg(II), Ti(IV), V(II,IV), Nb(V), Ta(V), Mo(V),

W(V), Mn(II), U(VI), Fe(II), Co(II) and Ni(II) and are distinguished by higher selectivity. This is possible due to the selectivity of the developed extraction-photometric methods. The proposed extraction spectrophotometric methods were used to determine copper(II) in steel of various grades, alloys, plants, food products, oil, apatite flour, pharmaceutical samples and natural waters; mercury - in soils, sea water, blood, wheat, cheese, beef liver, meat and fish; titanium - in steel of various grades, metallic aluminum, wastewater and sea waters, ferrotitanium, artificial mixtures and metallic niobium; vanadium - in soils, plants, steel of various grades, alloys, alunite, oil and products of its processing; niobium(V) and tantalum(V) - in steel of various grades; molybdenum and tungsten - steel of various grades, plants, soils and drinking water; uranium(VI) - in standard samples, soil, clay, sea water and in waters obtained by pumping oil; manganese(II) - in metallic nickel, tap water and plants; iron -in various natural and industrial materials (soils, meat, natural waters, blood, standard samples, fruits), Co(II) and Ni(II) - in steel of various grades, bronze, rocks, plants, bottom sediments and waste water (Table 7).

**Table7**

The results of the determination of metals in different objects ( $n=5, P=0.95$ )

Metal	Analyzed an object	Certified Amount metal, %	Methods	$S_r$	$\bar{X} \pm \frac{t_p S}{\sqrt{n}}$
1	2	3	4	5	6
Cu	Beans (mg / kg)		Rubeanic acid	0.045	6.08±0.29
			DTBP-AP <sub>2</sub>	0.026	5.82±0.16
	Rye (mg / kg)		Rubeanic acid	0.044	4.30±0.198
			DTP -BPhen	0.028	4.99±0.14
	Oil (%)		Rubeanic acid	0.034	(1.12±0.04)·10 <sup>-2</sup>
			DTMP -AP <sub>4</sub>	0.032	(1.15±0.04)·10 <sup>-2</sup>
	Alloy c16 <sup>6</sup>	0.219	DTBP -AP <sub>2</sub>	0.021	0.216±0.005
			DTBP -AP <sub>4</sub>	0.023	0.220±0.006
	Alloy c19 <sup>6</sup>	0.176	DTMP - AP <sub>2</sub>	0.025	0.175±0.0046
			DTMP - AP <sub>4</sub>	0.022	0.174±0.0040
	Alloy A195- 3	0.140	DTBP -PheH	0.029	0.140±0.0042
	Alloy A195- 4	0.110	DTBP -BPhen	0.043	0.110±0.0050
	Alloy A195- 5	0.040	DTBP -Dip	0.036	0.040±0.0015
	River water (river Kur) mg / L		DTBP -BPhen	0.051	0.32±0.013
Forest soil mg / kg		Rubeanic acid	0.030	18.89±0.59	
		DTEP -Phen	0.029	18.96±0.58	

continuation of table 7

1	2	3	4	5	6	
Ti	Steel C127 <sup>a</sup>	0.090	DTBP -mAn	0.019	0.091±0.0019	
	Alloy CII-1	0.470	DTEP -An	0.034	0.450±0.0016	
	Aluminum	0.029	DTBP -mAn	0.040	0.0244±0.0010	
	Wastewater (%)		DTBP -dAn	0.045	(3.33±0.15)·10 <sup>6</sup>	
	Sea water (%)		DTBP -dAn	0.030	(3.44±0.10)·10 <sup>6</sup>	
Hg	The soil (black soil) (mg / kg)		Dithizon	0.033	0.225±0.008	
			DTP -dAn	0.031	0.221±0.007	
	Sea water (mcg /mL)		DTEP -dAn	0.040	0.085±0.012	
			DTBP -dAn	0.049	0.094±0.015	
	Blood (mcg / kg )		DTP -dAn	0.049	6.85 ± 0.27	
			Dithizon	0.041	6.75±0.33	
	Beef liver (mcg / kg )		DTMP -mAn	0.041	57.8±0.25	
	Cheese (mcg / kg )		DTPP -An	0.032	75.0±1.37	
			DTBP -dAn	0.049	80.0±1.42	
	Fish (mcg / kg )		DTBP -dAn	0.041	89.2±1.43	
			Dithizon	0.049	90.0±1.25	
	V	Marine Soil		DTEP +BPen	0.034	(1.15±0.04)×10 <sup>-2</sup>
8-hydroxyquinoline				0.042	(1.12±0.05)×10 <sup>-2</sup>	
Potatoes (mg / kg )		8-hydroxyquinoline	0.051	6.14±0.32		
		DTPP -AP <sub>3</sub>	0.036	6.05±0.23		
Oil(%)		DTMP +AP <sub>1</sub>	0.028	(6.350±0.19)×10 <sup>-5</sup>		
		8-hydroxyquinoline	0.025	(6.30±0.65)×10 <sup>-5</sup>		
Masut (%)		DTEP -AP <sub>1</sub>	0.023	(2.48±0.061)×10 <sup>-3</sup>		
		8-hydroxyquinoline	0.018	(2.51±0.047)×10 <sup>-2</sup>		
Tar (%)		DTPP -AP <sub>3</sub>	0.042	(4.25±0.187)×10 <sup>-2</sup>		
		8-hydroxyquinoline	0.028	(4.25±0.125) ×10 <sup>-5</sup>		
CO-H-10		1.61	DTBP + AP <sub>8</sub>	0.024	1.58±0.0398	
C - 34 <sup>a</sup>		0.56	DTBP + DPG	0.042	0.57±0.0025	
Alunite (%)			DTPP -AP <sub>3</sub>	0.034	0.033±0.000120	
Nb	CBT-2	0.012	DTP -An	0.023	0.0124±0.00028	
	CO 231	0.37	DTP-mAn	0.029	0.38±0.011	
	CO 231 <sup>6</sup>	0.37	DTP-mAn	0.036	0.362±0.013	
Ta	CO 160 <sup>6</sup>	0.99	DTP-mAn	0.037	0.97±0.04	
	CBT-1	0.017	DTBP -dAn	0.019	0.0187±0.0027	
	CBT-3	0.029	DTP -dAn	0.043	0.0285±0.0024	
	CBT-6	0.147	DTPP -dAn	0.023	0.145±0.0019	

continuation of table 7

1	2	3	4	5	6
Mo	Barley (mg / kg)		DTBP-mAn	0.025	0.134±0.0038
	Peas (mg / kg)		DTMP-An	0.035	0.86±0.0346
	Rice (mg / kg)		DTMP-An	0.037	0.26±0.0101
	Marine soil (%)		DTMP-An	0.030	0.44±0.018
	69°	2.09	DTMP-AP <sub>1</sub>	0.043	2.114±0.063
	ЭИ-415	0.55	DTMP-AP <sub>1</sub>	0.035	0.535±0.021
W	White cabbage (mg / kg )		DTBP+dAn	0.042	0.142±0.0063
	Red cabbage (mg / kg )		DTBP+mAn	0.028	0.82±0.024
	Marine soil (%)		DTMP+dAn	0.021	0.47±0.011
			DTMP+mAn	0.030	0.43±0.014
	Steel 339	0.183	DTBP+mAn	0.050	0.182±0.009
			DTBP+dAn	0.040	0.181±0.008
U	Artificial mix	Uraninit 72%	DTEP-DPG	0.042	71.9±0.27
			DTEP-AP <sub>3</sub>	0.050	72.5±0.31
		Otenit 50%	DTEP-DPG	0.034	49.7±0.25
			DTEP-AP <sub>3</sub>	0.039	50.2±0.24
	Sea water (мг/л)		DTEP-AP <sub>3</sub>	0.034	6.14±0.22
Fe	Cherry (mg / kg )		DTEP-Phen	0.024	5.2±0.131
	White cherries (mg / kg )		DTEP-Dip	0.024	13.90±0.37
	dog-rose (mg / kg )		DTEP-BPhen	0.025	14.0±0.367
	Egg (mg / kg )		DTEP -Phen	0.023	68±1.64
	A95-4	0.025	DTMP-AP <sub>2</sub>	0.043	0.1289±0.0015
	ЛМЦ	0.5	DTMP-Dip	0.042	0.54±0.026
Mn	Beet (mg / kg )		DTEP+AP <sub>2</sub>	0.015	6.52±0.10
	Spinach (mg / kg )		DTPP+AP <sub>3</sub>	0.039	8.82±0.361
	Radish (mg / kg )		DTMP-AP <sub>4</sub>	0.031	1.6±0.048
	Garlic (mg / kg )		DTMP-AP <sub>4</sub>	0.043	7.95±0.358
	Drinking water (%)		DTMP-AP <sub>5</sub>	0.012	0.018±0.00030
	Soil (fertile) (mg/ kg )		DTPP-AP <sub>2</sub>	0.040	398±17
	Nickel (%)		DTMP-AP <sub>2</sub>	0.025	(9.78±0.25)×10 <sup>-2</sup>
Co	Steel M 441	0.012	DTBP-DPG	0.025	0.0125±0.00033
	Steel №156	0.56	DTMP-AP <sub>3</sub>	0.038	0.574±0.023
	Wastewater (mg/L)		DTMP-AP <sub>3</sub>	0.069	0.45±0.05
	The soil (black soil) (mg/ kg )		DTBP-DPG	0.035	15.68±0.57
Ni	8XΦ (C16 <sup>0</sup> )	0.258	DTEP+An	0.025	0.258±0.0074
			Dimethylglyoxime	0.028	0.259±0.0083
	Oats (mg / kg )		DTMP-Dip	0.041	0.42±0.018
			Dimethylglyoxime	0.046	0.46±0.014
	Soil (forest) (mg / kg)		DTEP- <i>o</i> -AmPy	0.038	31.20±1.40
Dimethylglyoxime			0.041	33.14±1.41	

To determine large amounts of vanadium, the differential spectrophotometric method in the form of the Mo(V) -DTBP-AP<sub>3</sub> complex has been developed with sufficient accuracy. Methods for the determination of V(II) in the presence of V(IV) have been developed. A method has been developed for the determination of molybdenum and tungsten in their joint presence. A differential spectrophotometric determination of Mo(V) with DTMP and AP<sub>3</sub> is proposed. Methods for the determination of Nb(V) in the presence of Ta(V), W(V) in the presence of Mo(V), Ni(II) in the presence of Co(II) have been developed.

## CONCLUSIONS

1. In order to search for effective analytical reagents for Cu(II), Ti(IV), Hg(II), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), U(VI), Mn(II), Fe(II), Co(II) and Ni(II), 2,6-dithiolphenol and its derivatives (2,6-dithiol-4-methylphenol, 2,6-dithiol-4-ethylphenol, 2,6-dithiol-4-propylphenol and 2,6-dithiol-4-*tert*-butylphenol). Reagents are synthesized by a known method and identified by NMR- and IR-spectroscopy.

2. Spectrophotometric methods were used to study the analytical and physicochemical properties of complexing agents. By potentiometric titration, the pK of acid dissociation of -SH and -OH groups were determined. To elucidate the complexation mechanism of some *d*- and *f*-elements with DP and Am, the molar fractions of molecular and ionized reagents are calculated depending on the pH of the medium: when the hydrogen atom in the *p*-position is replaced in the *p*-position by an alkyl radical with a positive inductive effect, the acid properties the resulting *p*-alkyldithiolphenols are reduced compared to 2,6-dithiolphenol. Acidic properties of complexing reagents decrease in the series DTP > DTPP > DTEP > DTMP > DTBP. The ionization constants of complexing organic reagents in solutions with different ionic strengths are calculated.

3. The optimal conditions for the formation and extraction of mixed-ligand complexes Cu(II), Ti(IV), Hg(II), Mn(II), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), U(VI), Fe(II), Co(II), Ni(II) with DTP and its derivatives (DTMP, DTEP, DTPP, DTBP) in the presence of

Am. The stoichiometric ratios are established, the constants of stability, equilibrium, extraction, as well as the molar absorption coefficients of the mixedligand complexes are calculated. During the formation of complexes, metal ions react with two molecules of complexing reagents, forming water-soluble anionic complexes. With the introduction of hydrophobic amines, outer-sphere MLC (ionic associates) or MLC with a mixed coordination sphere are formed.

4. Using the spectrophotometric method was studied the ion state of Cu(II), Ti(IV), Hg(II), Mn(II), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), U(VI), Fe(II), Co(II), Ni(II) in complex compounds with DTP and its derivatives (DTMP, DTEP, DTPP, DTBP) and the number of protons displaced by it from one molecule DTP and its derivatives (DTMP, DTEP, DTPP, DTBP). The role of the ligand-ligand interaction in the formation of MLC was studied. It has been established that with an increase in the stability of associates formed between DP and Am, the stability of the MLC increases, and the Gibbs free energy decreases.

5. The dependences between the acid-base properties of the -SH group of reagents ( $pK_{SH}$ ) and various parameters of the analytical reactions of metal ions ( $pK_{SH-lg\beta_{k,d}}$ ,  $pK_{SH-\Delta pH_{50}}$ ,  $\sigma_n-pK_{SH}$ ,  $pK_{SH-lgK_p}$ ,  $pK_{SH-lgK_{ex}}$ ) were found. The influence of the substituents is quantitatively characterized using the Hammett induction constant for p-substituents ( $\sigma_n$ ). A study of the effect of substituents (-CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> and -C(CH<sub>3</sub>)<sub>3</sub>) in the DP molecule on  $\epsilon_{max}$  showed that there is a linear relationship between the molar masses of the substituents and the molar MLC coefficients.

6. To clarify the nature of the bonds in the MLC under optimal conditions, the complexes were isolated in solid form and their IR spectra were recorded. The obtained spectra were compared with the IR spectra of the reagents.

- Some Mo, Cu, Co, Ni and Fe complexes were isolated in solid form and studied by thermal analysis. The Cu-DTMP-Phen and Mo-DTMP-Dip complexes were studied by x-ray diffraction.

- Cu(II), Ti(IV), Mn(II), V(II,IV), Fe(II), Co(II), Ni(II) and Mo(V) with DP and hydrophobic amines form outer sphere comp-

lexes or ionic associates, as well as MLC with a mixed coordination sphere;

–Hg(II), Nb(V), Ta(V), W(V) and U(VI) with DTP, its derivatives and hydrophobic amines form only outer-sphere mixed ligand complexes or ionic associates;

7. During complexation, the ions V(V), Mo(VI), W(VI) and Fe(III) are reduced by the influence of complexing reagents. The latter fact is confirmed by the identity of the spectrophotometric characteristics of the MLC of ions V(V) and V(IV), Mo(VI) and Mo(V), W(VI) and W(V), Fe(III) and Fe(II) with DP and Am, as well as using EPR studies.

8. A detailed study of the influence of foreign ions in a spectrophotometric study made it possible to identify the most selective ones, and on their basis to propose new simple, reliable extraction spectrophotometric methods for determining Cu(II), Ti(IV), Hg(II), Mn(II), V(II,IV), Nb(V), Ta(V), Mo(V), W(V), U(VI), Fe(II), Co(II) and Ni(II) in soils, alunite, plants, tap water, steels, pharmaceutical samples, oil and products of its processing, and also to develop methods for the separation of elements similar in properties (molybdenum and tungsten; niobium and tantalum; cobalt and nickel). The developed methods are highly selective, have low LOQ and LOD. The use of masking agents, the use of extraction and a change in pH made it possible to significantly increase the selectivity of spectrophotometric methods. Methods for the determination of V(II) in the presence of V(IV), Nb(V) in the presence of Ta(V), W(V) in the presence of Mo(V), Ni(II) in the presence of Co(II) have been developed.

9. Comparison of the determination methods developed by us with the existing ones, shows the advantage of the proposed ones in terms of sensitivity and reproducibility. Statistical processing of the analysis results shows that the developed methods ensure the accuracy and reliability of the results of spectrophotometric determination of elements in natural and industrial facilities.

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