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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS AND STUDY OF ELECTRICALLY
CONDUCTIVE POLYMERS BASED ON
AROMATIC DIAMINES**

Speciality: 2307.01 – Physico-chemistry

Field of science: Chemistry

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The work was performed at the laboratory "Molecular magnets and conductors" of the Institute of Catalysis and Inorganic Chemistry named after academician M. Naghiyev of the Ministry of Science and Education.

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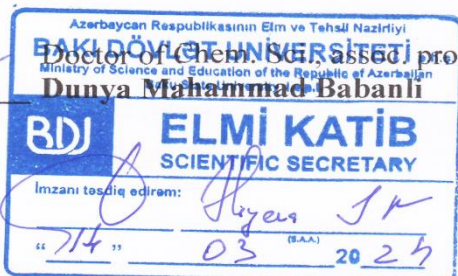
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GENERAL DESCRIPTION OF WORK

The relevance of the topic and its practicality. The rapidly and globally increasing demand for energy is not only the conversion of electrical energy, but also leads to the creation of problems related to its storage. Pumped hydroelectric power plants, various types of systems including cable and electrochemical energy storage systems are available depending on the required capacity and power value. In particular, batteries, fuel cells, and supercapacitors are the focus of current research because of their key role in "mobile energy" and because of the rapid development of active radio frequency identification (ARI) tags, smart cards on integrated circuits, mobile sensor systems, and smart clothing. The use of conductive polymers in this type of devices is a very relevant and important issue nowadays¹.

Conductive polymers have attracted great interest in recent years because of their unusual properties. Although they have a short history, these polymers are used in many applications. After the unexpected discovery in the late seventies of the electrical conductivity of polyacetylene, for which the Nobel Prize in Chemistry was subsequently awarded in 2000, the field of conductive polymers began to develop further. The biggest advantage of conductive polymers is their processability. Conductive polymers are plastic and can therefore combine the mechanical properties of plastics (flexibility, strength, elasticity, etc.) with high electrical conductivity².

Recently, polymers based on aromatic diamines were found to be more multifunctional than polyaniline (PANI) and polypyrrole (PPy) due to the presence of a single free amino group in the repeating link of the polymer chains. Poly(p-phenylenediamines) (PpFDs) are electroactive polymers belonging to the family of aromatic diamines. Their structure is closely related to polyani-

¹ Hameer, S. A review of large-scale electrical energy storage / S.Hameer, J.L. van Niekerk // *International Journal of Energy Research*, - 2015. 39(9), - p. 1179–1195.

² Bresser, D., Passerini, S. *Handbook of Battery Materials*. Second Edition / D.Bresser, S.Passerini // *Energy Technology*, - 2013. 1(10), - p. 617–618.

line, which stimulates their application in electronic devices such as supercapacitors and batteries.

For this reason, in accordance with the topic of the presented thesis, it is relevant to study the structure and properties of electrically conducting polymers based on o- and p-phenylenediamine and benzidine and complex compounds formed by them with ions of some transition metals.

Object and subject of research. The object of our research is electrically conductive compounds based on aromatic diamines (ortho- and para-phenylenediamine and benzidine) and complexes with some transition elements such as Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and Ag(I). The subject of the research is the study of the synthesized polymers and their transition-order metal complexes and determination of their applications.

Aims and objectives of the research. The main purpose of the work is to develop methods for the synthesis of electrically conductive compounds based on phenylenediamines and benzidine and their complex compounds with Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and Ag(I) metal ions, and to determine their physicochemical parameters.

The following tasks are envisaged to achieve the objective:

- development of methods for the synthesis of electrically conducting compounds based on ortho- and para-phenylenediamine and benzidine and their complex compounds with Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and Ag(I) metal ions;
- study of electrical conductivity of polymers synthesized on the basis of ortho- and para-phenylenediamines;
- study of structure and properties of synthesized polymers and their metal complex compounds by modern methods of physicochemical analysis;
- Study of fluorescence properties of polyimine complex compound Zn(II) synthesized on the basis of p-phenylenediamine and glyoxal;
- investigation of fluorescence properties of complex compound of Zn(II) with N,N'-bis-(2-hydroxybenzyl)benzidine;
- investigation of the electrochemical properties of

N,N,N',N'-tetraacetobenzidine lithium salt and metal complexes.

Research Methods. The validity of the results obtained in the thesis was investigated using modern physicochemical methods of investigation - IR, UV, EPR, DTC. The fluorescence intensity of the samples was measured using a Hitachi F-7000 fluorescence spectrophotometer, electrical conductivity was measured using a Keithley 6517A electrometer, electrochemical properties were measured using a Gamry Reference 600 potentiostat/galvanostat, surface morphology was measured using a JCM-5000 JEOL NeoScope Benchtop scanning electron microscope, and thermodynamic parameters were measured using the Coulters-Redfern method.

The main points presented for defense:

- new electrically conductive compounds based on o- and p-phenylenediamines and methods of synthesizing their complexes with metal ions Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and Ag(I) have been developed, their structure and properties have been studied using modern research methods;

- the electrical conductivity of polymers synthesized on the basis of o- and p-phenylenediamines was investigated;

- thermodynamically active indices of polymers synthesized on the basis of ortho- and para-phenylenediamine were calculated using the Coulters-Redfern equation from the results of thermogravimetric analysis;

- a new chelating polyimine based on p-phenylenediamine and glyoxal and its metal complexes were synthesized, their structure and properties were studied, fluorescent properties of Zn(II) complex were studied;

- the fluorescence properties of the Zn(II) complex of N,N'-bis-(2-hydroxybenzyl)benzidine have been studied;

- stability of cation-radicals formed by N,N'-bis-(2-hydroxybenzyl) benzidine and its transition metal complexes was studied by UV-spectroscopy;

- The electrochemical properties of the lithium salt of N, N, N', N'-tetraacetobenzidine and complex compounds have been studied.

Scientific novelty of the study:

- An optimal method for the synthesis of new redox-active polymers based on o- and p-phenylenediamines has been developed, and metal complexes of these polymers have been synthesized.

- the electrical conductivity of polymers synthesized based on o- and p-phenylenediamine increased to 10^{-6} - 10^{-5} $\text{Ohm}^{-1}\text{cm}^{-1}$, respectively, with increasing amount of graphite. At the same time, the addition of graphite also increases the σ -value. In all samples, the decrease in conductivity at high temperature is due to the accumulation of filler or nanofiller in the presence of external factors, such as temperature, affecting the electron mobility in the materials.

- The fluorescence intensity of the Zn(II) complex of a new chelate polyimine synthesized on the basis of p-phenylenediamine and glyoxal is directly proportional to the volume ratio of water. It was found that the Zn(II) complex exhibits maximum intensity at a wavelength of 551 nm at a water volume fraction of 80%.

- When analyzing the fluorescence spectrum of Zn(II) N,N'-bis(2-hydroxybenzyl) benzidine complex, it was observed that the maximum intensity at the wavelength of 550 nm at 60% volume ratio of water. The reason for the high fluorescence intensity is that the electronic excitation of HOMO/LUMO occurs at lower energies.

- Comparison of the electronic spectra of Wurst-type cation radicals formed by N,N'-bis-(2-hydroxybenzyl)-benzidine and its metal complexes shows that the complex compounds form more stable cation radicals than the free ligand. Thus, while the stability of the cation radicals formed by the free ligand is quenched within 6 minutes, the stability of the cation radicals formed by the complexes remains stable for 30 minutes.

- Analysis of the electrochemical properties of the lithium salt of N,N,N',N'-tetraacetobenzidine by rotational and diffusion-controlled indicates that two reduction (R1 -0.81 V and R2 -1.50 V vs. SCE) and two oxidation (O1 vs. SCE 1.03 V and O2 -0.07 V) process occurs. By analyzing the complex compounds of

N,N,N',N'-tetraacetobenzidine, it is found that the cobalt complex at 0.722 V is attributed to the Co(II)/Co(I) pair, while the nickel complex at 0.742 V Ni(II)/Ni(I) shows an irreversible peak associated with this pair. By electrolysis of Cu(II) complex, it is found that copper is stabilized at +1 oxidation degree.

Theoretical and practical value of the study. The relationship between the structure and functional properties of the synthesized compounds has been established. Purposefully synthesized substances in the future can be used as electrode materials in organic polymer batteries. In particular, polyimine polymer complex Zn(II) based on p-phenylenediamine and glyoxal and N,N'-bis-(2-hydroxybenzyl) benzidine complex Zn(II) synthesized by us exhibit high fluorescence activity. This makes it possible to apply them in organic light-emitting devices (OLEDs).

Author's personal involvement. The main leading role belongs to the author when posing the question before the thesis topic, forming the main ideas in the course of the work, research directions, conducting experiments, explaining and generalizing the obtained results.

Published research papers: On the main provisions of the thesis topic 13 scientific papers have been published, including 5 articles (2 are single articles), the rest are theses. 3 articles were abstracted in the international indexing system "Scopus" and published in local and foreign journals recommended by the Higher Attestation Commission under the President of the Republic of Azerbaijan.

The main scientific and practical innovation of the thesis work was reflected in the listed journals: "Baku University News, Natural Sciences Series, 2017", "Journal of General Chemistry, 2018", "Azerbaijan Chemical Journal 2019", "Chemical Problems 2020", "Azerbaijan Chemical Journal 2022".

Approbation of the work. Innovations and results of the thesis work were reported and discussed at annual conferences and seminars, official and scientific symposia:

- International conference "Nagiyev Readings" dedicated to the 110th anniversary of academician Murtuza Nagiyev. Baku-

2018.

- "All-Russian cluster of conferences on inorganic chemistry, InorgChem 2018", Astrakhan-2018.

- International scientific conference "Actual problems of modern natural and economic sciences" dedicated to the 95th anniversary of the birth of national leader Heydar Aliyev. May 04-05, Ganja-2018.

- VI Republican Scientific Conference "CHEMISTRY OF COORDINATING CONNECTIONS" dedicated to the 80th anniversary of the Department of Analytical Chemistry. December 16-17, Baku-2015.

- "X Republican Scientific Conference of doctoral students, undergraduates and young researchers "Actual problems of chemistry" dedicated to the 93rd anniversary of the birth of national leader Heydar Aliyev". May 04-05, Baku-2016.

- Republican Scientific Conference dedicated to the 80th anniversary of the M.Nagiyev Institute of Catalysis and Inorganic Chemistry. November 15-16, 2016.

- International Scientific Conference "Chemistry of Coordination Compounds: Actual Problems of Analytical Chemistry" dedicated to the 85th anniversary of Academician Rafiga Aliyeva. November 16-17, Baku-2017.

- «Second International Scientific Conference of Young Scientists and Specialists Multidisciplinary approaches in solving modern problems of fundamental and applied sciences. Dedicated to the 75th anniversary of Azerbaijan National Academy of Sciences» Baku-2020.

Scope and structure of the paper. The dissertation consists of an introduction, 3 chapters, a conclusion, 281 literature references, 6 tables, 71 figures and 12 charts. The total volume of the dissertation is 169795 characters (excluding figures, tables, graphs, appendices and bibliography).

In the introductory (12491 character) part the relevance, purpose, scientific novelty and practical significance of the work are indicated. In the first chapter (64789 character) , called literature review, a comparative analysis of recent literature materials

on the synthesis, some chemical transformations and application of polymers synthesized on the basis of aromatic diamines and some of their transition metal complexes is given. The second chapter (29110 character) reflects the experimental part of the research work and information about the physicochemical methods used. In the third chapter (47181 character), the methods developed for the synthesis of polymeric compounds synthesized on the basis of o- and p-phenylenediamines, benzidine and their complexes of transition metals Co(II), Ni(II), Cu(II), Zn(II) and Mn(II) are discussed. The composition and structure of the newly synthesized compounds were determined in detail by IR, UV-visible, EPR spectroscopy and DTQ analysis.

MAIN CONTENT OF WORK

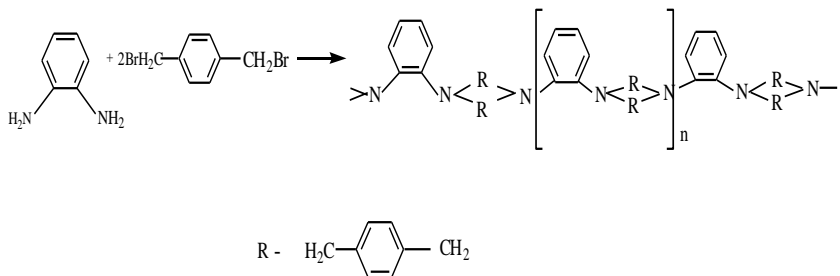
1. Synthesis and properties of poly-o-phenylenediamine (PoPD).

Polyaryldiamines, partly poly-ortho- and poly-para-phenylenediamines, have unique redox properties and are used in electrocatalysis and as sensor and protective coatings. The number of scientific works devoted to the study of electrophysical properties of this type of polymers with high electrical conductivity is increasing day by day. For this reason, the synthesis of new redox-active polymers containing phenylenediamine groups is of considerable interest. Thus, we have synthesized a new redox-active polymer by condensation of ortho-phenylenediamine with paraxylene dibromide. This polymer has the ability to form polycationic Wurst radicals.

Condensation of o-phenylenediamine was carried out in various solvents - benzene, chloroform, methanol, ethanol, etc. Thus, the analysis of IR spectra showed that the free amino groups in the reaction product are not completely substituted. The best result was observed when dioxane was used as a solvent [7 p. 800, 801].

Ideally, a polymer synthesis leading to complete substitu-

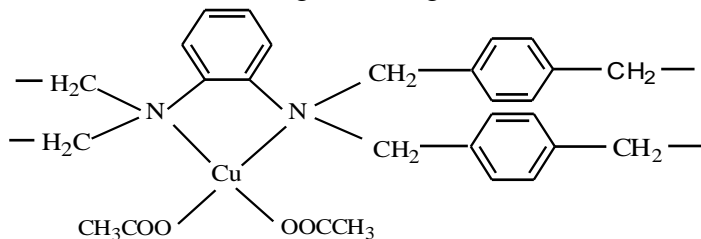
tion of hydrogen atoms in the o-phenylene moiety was envisioned (Scheme 1.1):



Scheme 1.1. Mechanism of synthesis of poly-o-phenylenediamine.

When the reaction was carried out in dioxane solution in the presence of triethylamine it was observed that some amino groups were not substituted. This was followed by the presence of absorption bands of amino groups at 1615 cm^{-1} and 3350 cm^{-1} in the IR spectra. Therefore, the polymer synthesis was carried out under more stringent conditions: in a water-dioxane solution in the presence of alkali in a closed ampoule at 150°C .

The presence of two nitrogen atoms in the o-position of the benzene ring allows the formation of stable complex compounds with metal ions. Complex compounds are prepared by the metal ions Ag(I), Co(II), Ni(II) and Cu(II) with our synthesized polymeric ligand (Scheme 1.2). All polymer complexes were synthesized by heating (100°C) the salts of the corresponding metals with poly-o-phenylenediamine in a molar ratio of 1:1 in aqueous medium and constant stirring on a magnetic stirrer:



Scheme 1.2. Probable structure of the polymeric complex of Cu(II) with poly-o-phenylenediamine.

1.1 Spectral analysis of poly-o-phenylenediamine and its complex compounds.

The IR spectrum of poly-o-phenylenediamine shows absorption bands at 2861 cm^{-1} and 1470 cm^{-1} . Which can be explained by valence and strain vibrations of methylene groups. The valence vibrations of the $\nu(\text{C-N})$ bond are observed at 1115 cm^{-1} and 1080 cm^{-1} . The absorption observed at 1600 cm^{-1} can be explained by the vibrational motion of the aromatic ring.

When poly-o-phenylenediamine is heated in air in the temperature range of $100\text{-}300^\circ\text{C}$, its color changes from light gray to black, and significant changes are observed in the infrared spectra. The intensity of the absorption bands of methylene groups gradually decreases and completely disappears at 300°C . At this time, a weak band at 2220 cm^{-1} appears, which can be explained by the absorption of $\nu(-\text{CH}=\text{C}-)$ groups of the quinindimethine fragment bound by a double bond [7 p. 803].

In the IR spectra of the complex compounds, in addition to poly-o-phenylenediamine bands, anionic groups are present: carboxylate group $\nu(\text{COO}^-)$ at 1590 cm^{-1} and 1310 cm^{-1} (for cobalt(II), nickel(II)), copper(II) complexes) and absorption bands of nitrate group at 1560 cm^{-1} (for silver(I) complex).

The electronic spectra of poly-o-p-phenylenediamine can be clearly seen from the bands observed for tetrabenzyl-p-p-phenylenediamine in the electronic absorption spectrum of the sample obtained by extraction of poly-o-p-phenylenediamine with ethyl alcohol, implying that the polymer structure has a tetrasubstituted o-phenylenediamine moiety (Figure 1.1.1).

In the electronic spectra of monomeric transition metal complex compounds, charge transition bands at $23500\text{-}22500\text{ cm}^{-1}$ and d-d transitions in the ultraviolet and visible regions of the spectrum are observed in all cases. The frequency of these transitions depends on the nature of the metal ion. For example, a weak absorption band at 34500 cm^{-1} , 33000 cm^{-1} and 18500 cm^{-1} is observed for Cu(II) complex. This can prove that the metal ion has a distorted and flat square coating:

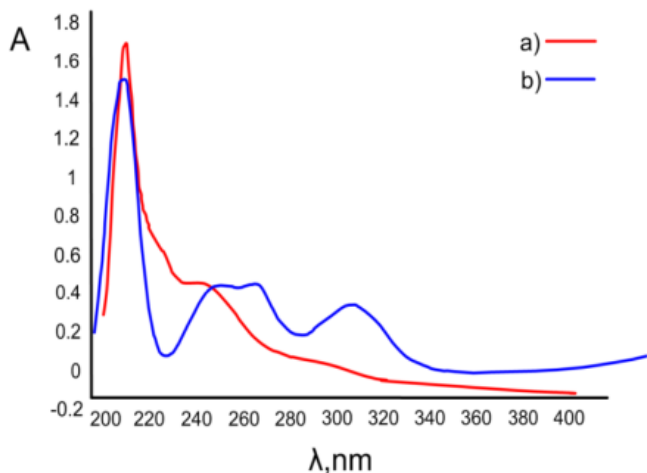
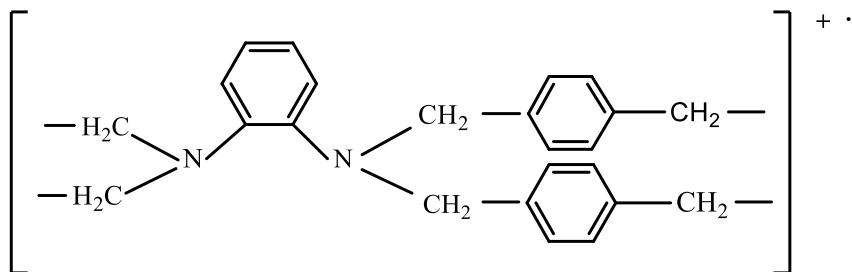


Figure 1.1.1 Electronic absorption spectra of the polymer (a) and tetrasubstituted o-phenylenediamine (b).

1.2. EPR analysis of poly-o-phenylenediamine. By EPR method it was found that the initial polymer contains cation-radicals formed as a result of oxidation by a small amount of air oxygen (Scheme 1.2.1.):



Scheme 1.2.1. Cation-radical of poly-o-phenylenediamine.

When the polymer sample is exposed to elemental bromine, the color of the polymer turns red due to an increase in the number of cation radicals. The EPR spectrum of the polymer consists of a singlet with a line width of 7G between points of maximum slope and a g-factor of 2.009.

1.3. Thermogravimetric analysis of metal complexes of polyorthophenylenediamine.

Thermal decomposition of polymer complexes synthesized on the basis of polyorthophenylenediamine was studied in the temperature range of 20-500°C at a heating rate of 20 deg/min. Figure 1.3.1 shows the thermal decomposition spectrum of the Ni(II) complex. The results of thermogravimetric analysis show that the decomposition of the polymer complex occurs in several stages. At the initial stage (60-170°C) there is a weight loss of 1.8% due to the moisture contained in the substance. The second stage proceeds in the temperature range of 200-340°C. At this time a mass loss of ~20% is observed due to the separation of carboxylate groups. In the following stages, this is accompanied by loss of oligomers and complete polymer degradation. It should be noted that the coordinated polymer exhibits higher stability than the uncoordinated polymer. Thus, the uncoordinated polymer is completely destroyed at 350°C.

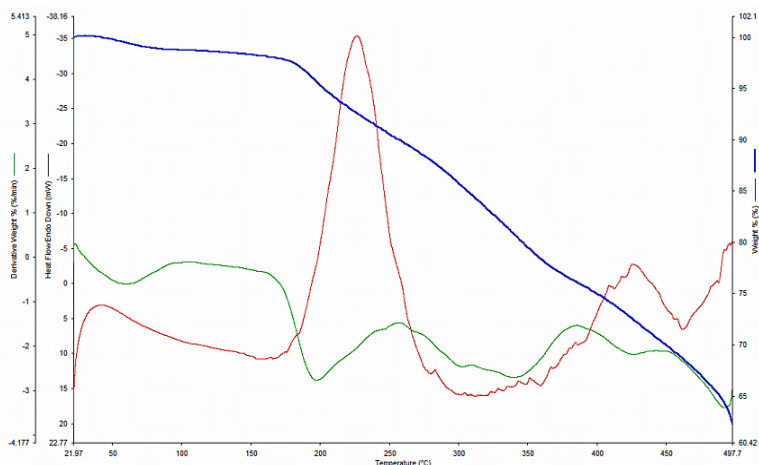


Figure 1.3.1. Thermogravimetric analysis spectrum of the polymeric Ni(II) complex with polyorthophenylenediamine.

Thermodynamically active parameters of complex decomposition processes (activation energy (E^*), enthalpy (ΔH^*) and

Gibbs free energy change (ΔG^*) were found using the Coutes-Redfern equation:

$$\log \left[\frac{\log \{W_f/W_f - W\}}{T^2} \right] = \log \left[\frac{AR}{\theta E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303RT} \quad (1.3.1)$$

Here W_f is the mass loss at the end of the process, W is the mass loss up to temperature T , R is the universal gas constant (8.314 C/mol·K), E^* is the activation energy (kC·mol⁻¹), θ is the heating rate (1-(2RT/ E^*)) $\cong 1$, A - is the Arrhenius coefficient. The activation entropy (ΔS^*), activation enthalpy (ΔH^*) and activation free energy (ΔG^*) were found based on the following equations:

$$\Delta S^* = 2.303 \left[\log \left(\frac{Ah}{kT} \right) \right] R \quad (1.3.2)$$

$$\Delta H^* = E^* - RT \quad (1.3.3.)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (1.3.4)$$

The data are summarized in Table 1.3.1:

Table 1.3.1.
Thermodynamic parameters of thermal decomposition of metal complexes of polyorthophenylenediamine (PoPD).

Compo und	Decomposition temperature, °C	E^* , kC·mol ⁻¹	A , S ⁻¹	ΔS^* , kC·mol ⁻¹	ΔH^* , kC·mol ⁻¹	ΔG^* , kC·mol ⁻¹
PoPD-Cu(II)	60-170	34.71	$1.19 \cdot 10^5$	-106	73.26	72.54
	200-340	48.36	$4.01 \cdot 10^7$	-132	61.19	95.98
	350-500	93.21	$4.48 \cdot 10^{10}$	-221	98.34	48.46
PoPD-Ni(II)	70-180	55.27	$2.06 \cdot 10^6$	-112	42.74	41.39
	200-330	73.42	$5.96 \cdot 10^7$	-103	73.38	78.65
	340-500	86.14	$3.58 \cdot 10^{10}$	-55.47	28.39	90.86
PoPD-Co(II)	50-190	81.72	$4.22 \cdot 10^{10}$	-35.62	72.96	87.26
	200-350	144.1	$8.65 \cdot 10^{14}$	-108.7	194.2	155.8
	350-500	224.2	$6.78 \cdot 10^{12}$	-184.4	261.8	201.4
PoPD-Ag(I)	80-170	118.3	$7.02 \cdot 10^{16}$	-45.62	135.1	166.4
	200-340	318.3	$6.77 \cdot 10^{12}$	-51.02	228.2	204.9
	350-500	124.8	$5.04 \cdot 10^{11}$	-96.27	341.5	304.9

As can be seen from the table, the decomposition activation energies range from 34.71 to 318.3 kC mol⁻¹. The activation entropy has negative values in all complexes.

1.4. Electrical conductivity of poly-o-phenylenediamine.

The electrical conductivity of poly-o-phenylenediamine was investigated by pressing mixtures of POFD and graphite in mass ratios of 3:1 and 4:1 in the form of tablets with a diameter of 1 cm and thickness of 1 mm on a hydraulic press. Conductivity was measured by the four-probe method and recorded using a Keithley type 6517 A electrometer. The spent tablets are placed between two copper electrodes and connected to the two leads of the Keithley electrometer.

As can be seen from Figure 1.4.1a, the voltage and current dependence of PoFD and graphite samples taken at different mass ratios is a straight line obeying Ohm's law. The conductivity of PoFD and graphite samples taken at both mass ratios was calculated using the following equation:

$$\sigma = \frac{th}{AR} \quad (1)$$

Here σ - is the electrical conductivity, th - is the thickness, A - is the area of the electrolyzer, and R - is the resistance:

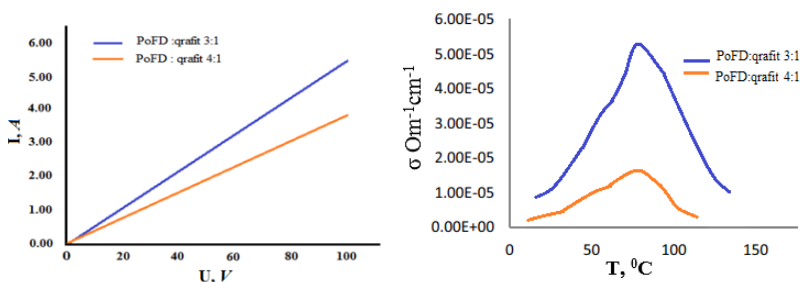


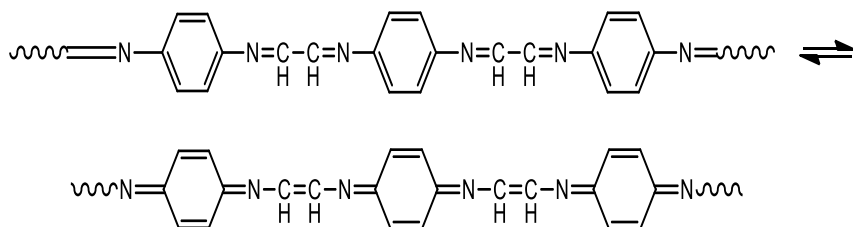
Figure 1.4.1. a) current-voltage dependence and b) temperature dependence of specific conductivity.

The results are shown in Figure 1.4.1b. It was found that with increasing amount of graphite, the electrical conductivity increases up to 10^{-6} - 10^{-5} $\text{Om}^{-1}\text{cm}^{-1}$ respectively. All samples show a decrease in conductivity at high temperature, which is attributed to the accumulation of filler or nanofiller in the presence of external factors, such as temperature, affecting the electron mobility in the materials.

2. Synthesis and properties of a new chelate polyimine based on p-phenylenediamine and glyoxal.

A new polyimine soluble in dimethylformamide and dimethyl sulfoxide was synthesized by condensation of glyoxal and p-phenylenediamine [3 p. 445, 2 p. 360]. It was found that this polyimine has chelating properties and is able to firmly bind transition metal ions. For this reason, its complexes of Mn(II), Ni(II), Cu(II), and Zn(II) were synthesized and their structure and properties were studied.

The synthesized polyimine can exist in two tautomeric forms (benzoyl and quinoid) (Scheme 2.1):



Scheme 2.1. Tautomeric forms of polyimine synthesized on the basis of p-phenylenediamine and glyoxal.

2.1 Spectral analysis of polyimine and its complex compounds.

The IR spectrum of polyimine demonstrates the aromatic structure of the benzene ring. Indeed, the IR spectrum at 1604 cm^{-1} , 829 cm^{-1} and 936 cm^{-1} shows absorption bands associated with valence vibrations $\nu(\text{C-C})$ and p-substitution in the benzene ring [3 p. 446]. In addition to these bands, an absorption band at 1667 cm^{-1} is observed in the spectrum of polyimine. This is the absorption band of the vibrations of the azomethine group $\nu(\text{C=N})$.

Three absorption bands with wavelengths of 210 nm, 255 nm and 300 nm are observed in the electronic spectrum of polyimine in the ultraviolet region and these bands are the absorption band of the aromatic ring (Figure 2.1.1a). The band observed in the visible region at a wavelength of 432 nm can be attributed to the $n \rightarrow \pi$ -transition of the azomethine group $C=N$ attached to the benzene ring:

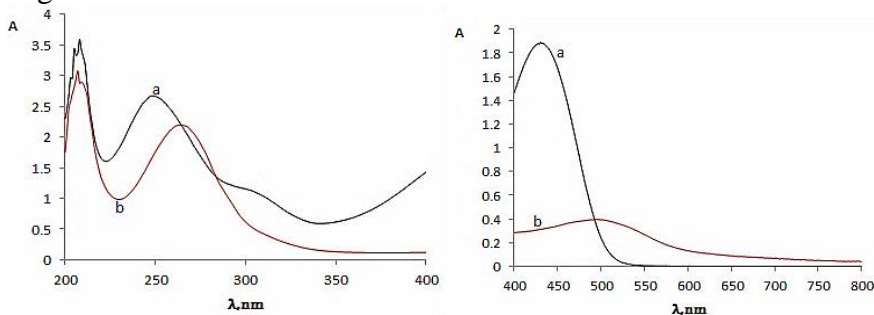


Figure 2.1.1. Electronic absorption spectra of a) polyimine based on p-phenylenediamine and glyoxal, b) Cu(II)-complex of polyimine.

Metal-containing polymers are prepared by interaction of polyimine with salts of Cu(II), Ni(II), Co(II) and Mn(II). Electronic absorption spectra as well as EPR spectra indicate the formation of metal-polymer complexes. In the electronic absorption spectra of the polymeric complexes, in addition to the absorption bands belonging to the polymeric ligand, there are also absorption bands associated with the d-d transition (Fig. 2.1.1b). For example, the polymeric complex of Cu(II) with polyimine exhibits two absorption bands in the visible region at wavelengths of 500 and 620 nm, which are not observed in the original polymeric ligand.

The synthesized Zn(II) polyimine complex has fluorescent properties, is long term stable in air, readily soluble in dimethylformamide and dimethyl sulfoxide, insoluble in water and other polar solvents. Therefore, to measure the fluorescence properties of Zn(II) complex, a solvent was prepared by mixing dimethylformamide and water in different volume ratios (10% to 90%). Then a part of the

initial solution of Zn(II) complex in dimethylformamide was added dropwise to the prepared solvent mixture. Then their fluorescence spectra and maximum emission intensity were measured.

The fluorescence emission of the Zn(II) complex varies depending on the volume ratio of dimethylformamide and water. At the volume fraction of water up to 40%, the intensity of the fluorescence spectra is practically negligible. However, at higher ratios of volume water content, this intensity gradually increases and the maximum intensity (at a wavelength of 551 nm) is observed at a volume ratio of 80% (Figure 2.1.2):

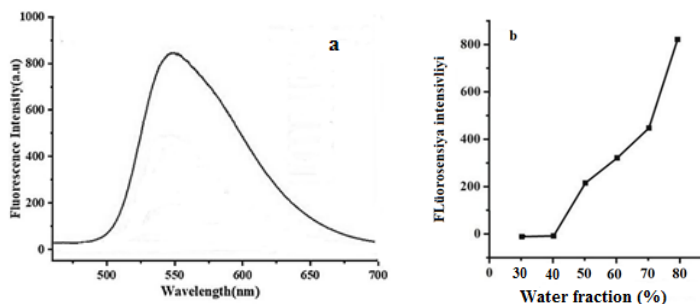


Figure 2.1.2. a) Fluorescence spectrum of Zn(II) complex at water volume fraction of 80%, b) fluorescence intensity of Zn(II) complex as a function of the amount of water fraction.

Under the UV lamp, the color of the Zn(II) complex changes from colorless to yellow (Figure 2.1.3). The higher the water volume fraction, the worse the solubility of the Zn(II) complex and the higher the fluorescence intensity:



Figure 2.1.3: Images of Zn(II) complex in different volume ratios of water (10-90%) under UV lamp.

2.2. EPR spectrum of polyimine metallocomplexes. The EPR spectrum of Cu(II) complex with synthesized polyimine (Fig. 2.2.1a) has two values of g-factor: $g_{\parallel} = 2.07$, $g_{\perp} = 2.25$. The extreme interaction constant with Cu^{63,65} nucleus is 155 Gs. The presented results confirm that the complex has axial symmetry and is probably surrounded by a metal ion in the form of an "elongated" octahedron.

An unusual EPR spectrum is observed for the Mn(II) complex (Fig. 2.2.1 b). This spectrum has a central singlet with g-factor $g = 2.00$ and line with $\Delta H = 20$ Gs, as well as two different hyperfine splittings in the Mn nucleus with constants of 69 Gs and 110 Gs:

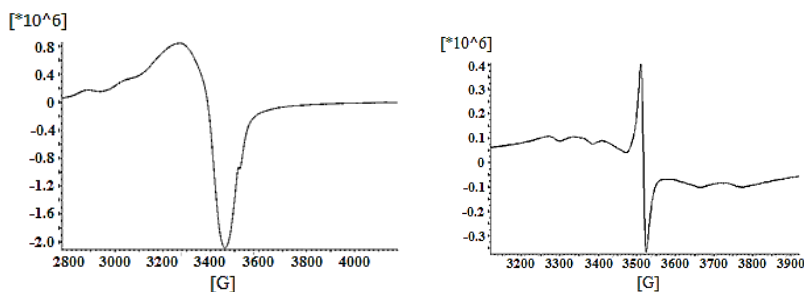


Figure 2.2.1. EPR spectra of Cu(II) (a) and Mn(II) (b) polymer complexes.

3. Synthesis of N,N'-bis-(2-hydroxybenzyl)benzidine and its metal complexes.

Multifunctional Schiff bases have a versatile series of ligands. Which combine with transition metal ions to form complexes with properties suitable for theoretical studies or practical use. In this connection, the field of studies of complexes with multidentate schiff bases formed by aromatic diamines and carbonyl compounds has developed considerably. At the same time, when analyzing the literature data, no complex compounds with hydrogenated Schiff bases were found among these compounds. Thus, we have synthesized N,N'-bis-(2-hydroxybenzyl)benzidine (H₂L') and its transition metal complexes and studied their structure and properties.

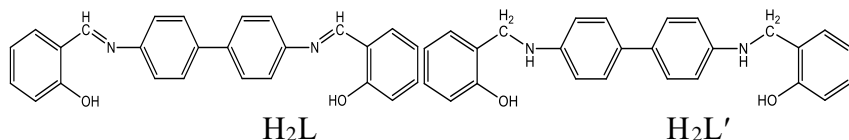


Figure 3.1. Structure of Schiff base ligand (H₂L) and hydrogenated Schiff base (H₂L').

Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with N,N'-bis(2-hydroxybenzyl)benzidine were synthesized in a 1:1 molar ratio [4 p. 94]. The complexes are insoluble in solvents such as water, ethanol, methanol, acetone, chloroform, benzene, diethyl ether. They are soluble only in DMF and DMSO.

The IR spectrum of LH₂ of Schiff base shows absorption bands of azomethine group $\nu(\text{C}=\text{N})$ at 1620 cm^{-1} . However, these bands are not observed in the infrared spectrum of the H₂L' hydrogenated ligand. Two absorption bands of the secondary N-H groups of the hydrogenated Schiff base H₂L' are observed: the first narrow intense at 3260 cm^{-1} and the second at 1605 cm^{-1} deformed absorption bands. In addition, there is an absorption band of the valence vibrations of the $\nu(\text{C}-\text{N})$ group at 1240 cm^{-1} .

In the IR spectrum of the Cu(II) complex with H₂L ligand, the absorption band of the $\nu(\text{C}=\text{N})$ group shifts to the lower wavelength region and is observed at 1600 cm^{-1} . This band is weaker in the parent ligand. The weak band observed at 3440 cm^{-1} can be attributed to hygroscopic water. The absorption band of the hydroxyl group of phenol is not observed. Considering these results, we can say that the nitrogen atom of the azomethine group and the oxygen of the phenol group participate in the coordination.

According to the results of elemental and thermal analysis, it was found that the molar ratio of metal ion:ligand is 1:1, and the composition of the [Cu₂L₂] complex corresponds to this ratio. Co(II) and Ni(II) complexes with hydrogenated Schiff base ligand have similar structure.

The IR spectrum of the Ni(II) complex with N,N'-bis-(2-hydroxybenzyl)benzidine loses the absorption band observed at

3275 cm^{-1} in the free ligand. The bands at 3157 cm^{-1} and 3400 cm^{-1} indicate the entry of the amino group into the coordination of $\nu(-\text{NH})$ with the Ni(II) ion.

The infrared spectrum of the Cu(II) complex with the ligand L'H₂ shows a broadened band at 3150 cm^{-1} in the valence vibration region of the $\nu(-\text{NH})$ group. Which can be attributed to the coordinated group $\nu(-\text{NH})$. The intense narrow band observed at 3465 cm^{-1} can be attributed to the hydroxyl group of the coordinated water molecule.

The electronic absorption spectrum of the ligand L'H₂ shows two absorption bands in the ultraviolet region at 210 nm and 295 nm. In the electronic spectrum of the [Cu₂L'(CH₃COO)₂(H₂O)₂] complex, very weak bands at 260 nm and 320 nm, and in the visible region at 440 nm and 460 nm (bending) and at 600 nm are present along with ligand-specific absorption bands. The reflection spectrum of the complex [Cu₂L'(CH₃COO)₂(H₂O)₂] consists of broad and low-intensity bands centered at 15873-16420 cm^{-1} and 17543-22026 cm^{-1} . The magnetic moment of this complex is 1.8 B.m.

The reflectance spectrum of the [Co₂L'₂] complex gives a high-energy ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition for the tetrahedral transition at a wavelength of 14900 cm^{-1} . In addition, the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ transition as well as the rather low-energy ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition at wavelengths 16649 cm^{-1} and 19600 cm^{-1} , respectively, are observed. The magnetic moment of the [Co₂L'₂] complex is $\mu_{\text{eff}} = 4.8$ B.M. This shows that the Co(II) ion in this compound is in a high spin state and has a tetrahedral geometric structure. In the electronic spectrum of the [Co₂L'₂] complex, a band at 280 nm parallel to the bands belonging to the ligand is also observed. In contrast to Cu(II) and Co(II) complexes, the [Zn₂L'₂] complex is diamagnetic, which unambiguously confirms its planar symmetry. The electronic spectrum of the nickel complex is similar to that of the cobalt complex (Fig. 3.2):

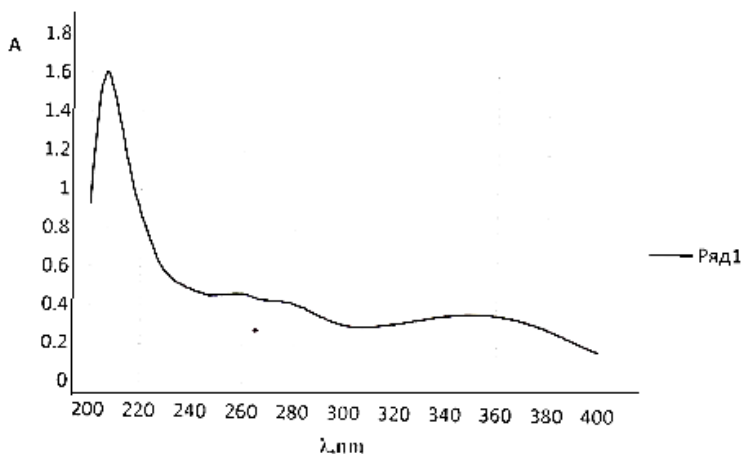


Figure 3.2. Electronic spectrum of the Ni₂L₂' complex.

The Zn(II) N,N'-bis-(2-hydroxybenzyl)benzidine complex is fluorescent, soluble in DMFA and DMSO, but insoluble in water and other polar solvents. Therefore, to measure the fluorescence properties of Zn(II) complex, a solvent was prepared by mixing dimethylformamide and water in different volume ratios (10% to 90%). Then a part of the initial solution of Zn(II) complex in dimethylformamide was added dropwise to the prepared solvent mixture. Then their fluorescence spectra and maximum emission intensity were measured.

The fluorescence emission of the Zn(II) complex varies depending on the volume ratio of dimethylformamide and water. At the volume fraction of water up to 50%, the intensity of the fluorescence spectra is practically negligible. However, this intensity increases dramatically with water volume fraction up to 50%, and the maximum intensity at 550 nm wavelength is observed at a volume fraction of 60% (Fig. 3.3). Then there is a gradual decrease in the volume fraction of water to 70% and a sharp decrease to 80%:

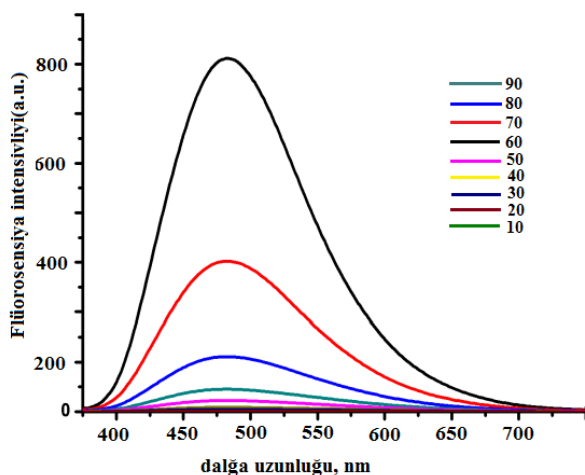


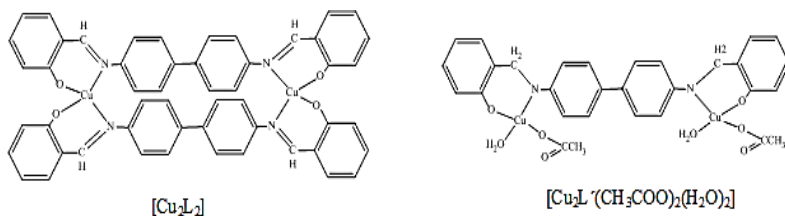
Figure 3.3. Fluorescence spectra of the Zn(II) complex N,N'-bis(2-hydroxybenzyl)benzidine in 10-90% aqueous dimethylformamide.

Sufficiently high fluorescence intensity is related to the structure of the synthesized ligand. The synthesized ligand consists of an aromatic ring structure bound to salicylic aldehyde. Typically, combining such structures with multiple aromatic rings increases the density and allows electronic excitation of HOMO/LUMO at lower energies.

The EPR spectrum of copper complex $[\text{Cu}_2\text{L}_2]$ in the polycrystalline state is axial and has two g -factor values: $g_{\parallel} = 2.34$ and $g_{\perp} = 2.06$. Also, anisotropic superfine splitting with anisotropy constant $A_{\parallel} = 0.185 \text{ cm}^{-1}$ is observed in the $\text{Cu}^{63,65}$ nucleus (nucleus spin $3/2$).

The complex $[\text{Cu}_2\text{L}'(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ also has a spectrum characterized by axial symmetry, and the g -factors are $g_{\parallel} = 2.51$ and $g_{\perp} = 2.10$. The EPR spectra of Cu_2L_2 and $[\text{Cu}_2\text{L}'(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ complexes have an axial character, and other results (elemental analysis, thermogravimetric analysis, etc.) suggest the flat-square symmetry of the complexes.

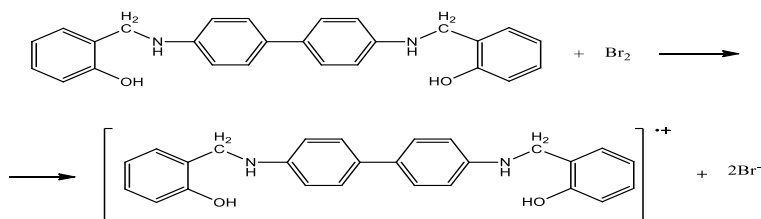
The obtained results suggest the following structure of the copper complex with Schiff base LH_2 and its hydrogenated analog $\text{L}'\text{H}_2$ (Scheme 3.1):



Scheme 3.1. Structure of Cu(II) complexes with ligands LH₂ and L'H₂.

Diaminobenzidine derivatives are considered analogs of p-phenylenediamine and therefore should be redox active like p-phenylenediamine. Transition metal complexes of diaminobenzidine derivatives, especially hydrogenated Schiff bases, have the ability to form cation radicals when treated with one-electron oxidizing agents as initiating ligands. It is of great interest to compare the stability of the resulting cation radicals of the ligand and its complexes.

Under the action of bromine solution in acetic acid, Wurst-type cation radicals are formed by the following reaction (Scheme 3.2):



Scheme 3.2. Scheme of formation of N,N'-bis-(2-hydroxybenzyl)-benzidine cation radical.

Comparing the N,N'-disubstituted cation-radical of p-phenylenediamine and benzidine cation-radical, we see that the benzidine cation-radical is less stable. Thus, the formation and extinction of cation-radicals can be observed using electron spectroscopy. The absorption bands of the cation-radical are observed at wavelengths of 470 nm, 840 nm, and 970 nm. Comparison of the electronic spectra of the cation radicals of the L'H₂ complex and the [Cu₂L'(CH₃COO)₂(H₂O)₂] complex shows that the quenching of the

4.1. Spectral analysis of N,N,N',N'-tetraacetobenzidine. If we look at the IR spectrum of TAB, we can see that the spectrum does show the aromatic structure of the benzene ring. The IR spectrum shows absorption bands at 1610 cm^{-1} , 878 cm^{-1} and 944 cm^{-1} associated with valence vibrations of $\nu(\text{C-C})$ and p-substitution in the benzene ring. Along with these bands, an absorption band at 1575 cm^{-1} and 1299 cm^{-1} is observed. Which can be attributed to the absorption band of $\nu(\text{C=O})$ vibrations of the carboxyl group. The valence vibrations of the $\nu(\text{C-N})$ bond are observed at 1115 cm^{-1} and 1080 cm^{-1} .

In the IR spectra of TAB metal complexes, new absorption bands at 478 cm^{-1} and 405 cm^{-1} are observed along with the bands characteristic of the ligand. These bands can be attributed to the absorption bands of $\nu(\text{M-O})$.

The magnetic moment of the Cu(II) binuclear complex of TAB is $\mu_{\text{eff}} = 2.46\text{ B.M.}$ Indeed, for each Cu^{2+} ion $\mu_{\text{eff}} = 1.8\text{ B.M.}$ If we take this into account, the calculated magnetic moment for the copper binuclear complex is $\mu = \sqrt{2}\mu_{\text{Cu}^{2+}}^2 = 2.53\text{ B.M.}$ This value is very close to the experimentally determined value of the magnetic moment. Accordingly, the electron-exchange interaction between Cu^{2+} ions in the binuclear copper complex is very small.

Absorption bands at $\lambda_{\text{max}}=205\text{ nm}$, 230 nm , 290 nm and 405 nm are observed in the electronic spectra of solutions of TAB complex compounds in ethyl alcohol (Fig. 4.1.1):

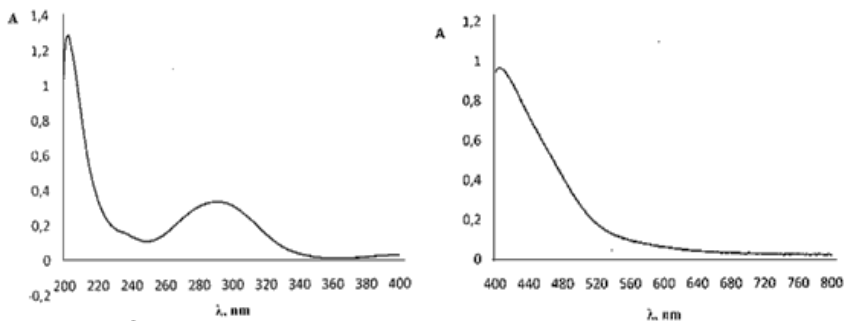


Figure 4.1.1. Electronic spectrum of the Cu(II)-complex of N,N,N',N'-tetraacetobenzidine.

By comparing the electronic spectra of the TAB complex compounds with the electronic spectrum of TAB ($\lambda_{\text{max}} = 200 \text{ nm}, 265 \text{ nm}$), the absorption bands at 230 nm, 290 nm and 405 nm can be attributed to the electronic transitions of metal ions:

The EPR spectrum of Cu(II) TAB complex has an axial character with $g_{\parallel}=2.25$ and $g_{\perp}=2.11$. This also corresponds to the configuration of the D_{4h} complex.

4.2 Thermogravimetric analysis of $N_2N_2N'_2N'$ -tetraacetobenzidine.

Thermogravimetric analysis of the complex $\text{Cu}_2\text{TAB}\cdot n\text{H}_2\text{O}$ was carried out in the temperature range of 20-900°C (Fig. 4.2.1):

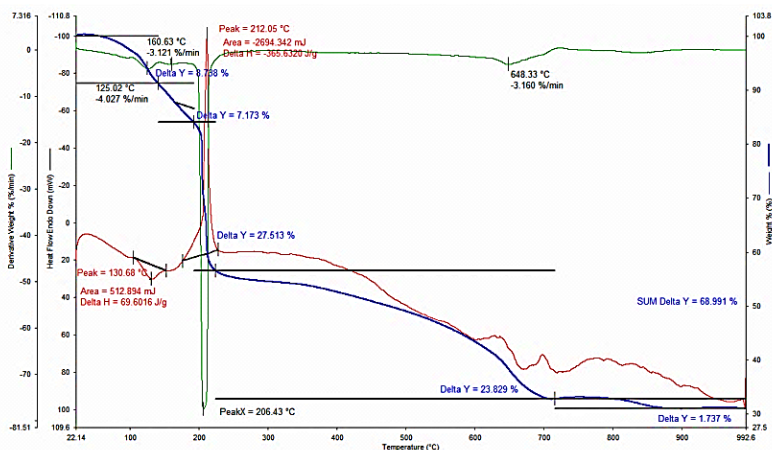


Figure 4.2.1. Thermal decomposition spectrum of the Cu(II) biuclear complex $N_2N_2N'_2N'$ -tetraacetobenzidine.

The decomposition process proceeded in the temperature range of 95-990°C and was expressed in four stages. In the first two stages, the process was observed to lose 16.01% of the total mass of coordinated and uncoordinated water molecules. The next two steps led to the decomposition of the organic part of the ligand in the temperature range 212-900°C with the formation of a precipitate in the form of metal oxide and the completion of the process. The total weight loss is 68.99%. Based on the percentage

(24%) of copper oxide in the sample, the amount of copper oxide remaining as precipitate corresponds to 29.86%. The first step involved the separation of 6.24% of uncoordinated water molecules (6.9% theoretically calculated) and 6.12% of coordinated water molecules between 125-212°C (6.7% theoretically calculated).

4.3 Electrochemical properties of the lithium salt of N,N,N',N'-tetraacetobenzidine.

The redox reaction of the lithium salt of TAB was carried out using a voltammetric device on a platinum electrode in vacuum in the electrolyte system dimethylformamide/tetrabutylammonium perchlorate (DMF/TBAP). From this, electrochemical data such as distribution, redox couple determination and half-wave peak potentials ($E_{1/2}$), anodic to cathodic peak current ratio (I_{pa}/I_{pc}), potential peak separation (ΔE_p) were obtained. For redox couples, the ratios of anodic and cathodic current peaks are close to unity, and ΔE_p exhibits rotational property in the range of 60-80 mV at a scan rate of 0.100 V/s (an internal ferrocene standard was obtained at ΔE_p 0.080 V and a scan rate of 0.100 V/s.). Lithium salts of polymeric compounds based on aromatic diamines, in addition to ligand-based electron transfer reactions, also exhibit similar electrochemical properties to metal reduction and oxidation processes (Table 4.3.1):

Table 4.3.1
Electrochemical data for the lithium salt of TAB in DMF/TBAP.

Compound	Parameters	Ox. of the ligand	Li ⁺ /Li ⁰	Red. of the ligand
	^a $E_{1/2}$ (V)	-0.07	1.04	-1.52
	^b ΔE_p ^c I_{pa}/I_{pc}	0.098	82	0.049
	$I_p V S. v^{1/2}$	1.01	0.71	1.08

^a: $E_{1/2} = (E_{pa} + E_{pc})/2$ at a frequency of 0.100 Vs⁻¹.

^b: $\Delta E_p = E_{pa} - E_{pc}$ at a frequency of 0.100 Vs⁻¹.

^c: rate of change of potential 0.100 Vs⁻¹ for I_{pa}/I_{pc} reduction, I_{pc}/I_{pa} oxidation processes.

It was found that the redox couple current peaks of lithium salt TAB are usually directly proportional to the square root of the rate of change of potential, indicating its diffusion-controlled nature. The cyclic rectangular voltammetric voltammetry patterns of the lithium salt of N,N,N',N'-tetraacetobenzidine in an electrolyte system with the coordination polar solvent DMF/TBAP are shown in Figure 4.3.1:

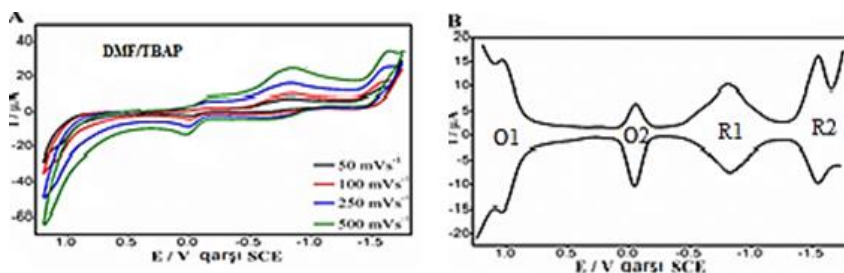


Figure 4.3.1. (A) CV of the lithium salt of N,N,N',N'-tetraacetobenzidine in DMF/TBAP solvent on Pt probed at different rates, (B) SWV-I N,N,N',N'-tetraacetobenzidine lithium salt, SWV parameters: number of pulses = 100mV; Step number: 5mV; Frequency: 25Hz.

Li-salt TAB exhibits reversible and diffusion-controlled two reduction processes (R1 -0.81 V and R2 -1.50 V compared to SCE) and two oxidation processes (O1 1.03 V vs. 'O2 -0.07 V compared to SCE). Figure 4.3 initially assumes that the O1 oxidation and R1 reduction processes are metal-based and the O2 and R2 processes are ligand-based. Also from variant (B) of Figure 4.3.1, the reversibility of chemical and electrochemical processes in the form of forward and reverse processes through the SWV is clearly visible.

4.4 Electrochemical properties of metal complexes of N,N,N',N'-tetraacetobenzidine.

The electrochemical properties of Co(II), Ni(II), and Cu(II) complexes of N,N,N',N'-tetraacetobenzidine were investigated in DMFA solution at a rate of potential change of 0.1 V/s. The results are summarized in Table 4.4.1. The cobalt complex shows an irreversible peak at 0.722 V belonging to the Co(II)/Co(I) pair. The nickel complex also shows an irreversible peak at 0.742 V associated with the Ni(II)/Ni(I) pair:

Table 4.4.1
Electrochemical data of metal complexes of N,N,N',N'-tetraacetobenzidine (TAB) in DMFA.

Substance	Pairs	E_{pc} (V)	E_{pa} (V)	I_{pc} (μ A)	I_{pa} (μ A)
TABCo	Co(II)/Co(I)	-0.722	-	15.1	-
TABNi	Ni(II)/Ni(I)	-	0.742	-	3.2
TABCu	Cu(II)/Cu(I)	-0.614	-0.501	12.7	9.3

The cyclic voltammetry of Cu(II) complex (Fig. 4.4.1) was recorded in DMFA solution at 300 K in the potential range from +0.2 to -1.2 V and potential change rate of 0.1 V/s:

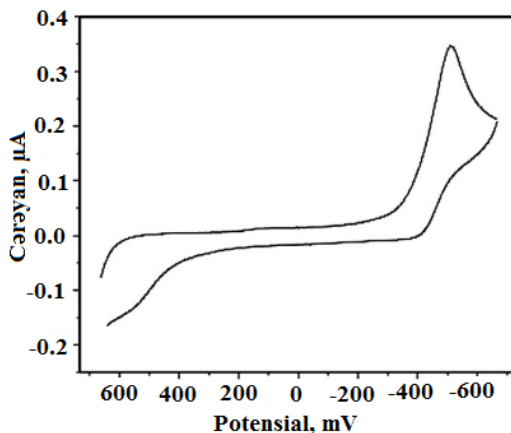


Figure 4.4.1. Cyclic voltammetry of Cu(II) complex N,N,N',N'-tetraacetobenzidine.

This indicates a well-defined redox process corresponding to the quasi-rotating Cu(II)/Cu(I) pair. The anodic peak at $E_{pa} = 0.501$ V with respect to Ag/AgCl and the associated cathodic peak at $E_{pc} = 0.614$ V correspond to the Cu(II)/Cu(I) pair. The Cu(II) complex exhibits quasi-rotational behavior with non-equivalent current strength and separation ($\Delta E_p = 113$ mV) of cathodic and anodic peaks. It was found that during electrolysis of Cu(II) complex, copper is stabilized in the oxidation degree +1. It was observed that the ligand stabilizes cobalt, nickel and copper to Co(I), Ni(I) and Cu(I) oxidation states upon electrolysis of the complexes.

RESULTS

1. Optimal methods of synthesis of new redox-active materials based on ortho- and para-phenylenediamines, their complex compounds with Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and Ag(I) ions have been developed, their structure and properties have been extensively studied using modern research methods;

2. The addition of graphite to polymers synthesised on the basis of ortho- and para-phenylenediamines has been found to increase the specific electrical conductivity of the polymers;

3. The temperature dependence of the specific electrical conductivity of polymers based on ortho- and para-phenylenediamines was found to be characterised by a maximum;

4. The fluorescence properties of the Zn(II) complex of a new chelating polyimine, based on para-phenylenediamine and glyoxal, have been studied in different volume ratios of dimethylformamide and water and found to have a maximum fluorescence intensity at a wavelength of 551 nm at a volume ratio of 80% water;

5. The fluorescence properties of N,N'-bis(2-hydroxybenzyl)benzidine Zn(II) complex were studied in different volume ratios of dimethylformamide and water and it was found that at a volume ratio of 60% water it has a maximum fluorescence in-

tensity at a wavelength of 550 nm;

6. The results of electron spectroscopy show that the Wurst-type cation radicals formed by N,N'-bis-(2-hydroxybenzyl)benzidine are more stable than the cation radicals formed by metal complexes. Thus, the cation radicals formed by the ligand remain stable for 30 minutes, while the cation radicals formed by the complexes remain stable for 6 minutes.

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