

Synthesis and Spectroscopic Characterization of Some Bismuth (III) Schiff Base Complexes

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Abstract:

The synthesis and spectroscopic (UV-visible, IR, ^1H NMR spectra) characterization of a series of Schiff bases derived from the interaction of ethane-1, 2-diamine or benzene-1, 2-diamine and 4-methyl-benzaldehyde, 4-chloro-benzaldehyde, 2-hydroxy-1-naphthaldehyde or 4-bromo-benzaldehyde with and their bismuth (III) complexes are presented. Most of the Schiff bases behave as bi-dentate ligands (NN) and mono basic fashion. The electronic spectra of the bismuth (III) complexes showed one well defined band in the region of $23.784\text{--}26.210 \times 10^3 \text{ cm}^{-1}$ due to LMCT in Oh symmetry. The cyclic voltammetry (CV) of some of the bismuth (III) complexes was assigned in terms of donor-acceptor interaction of the substituent in the phenyl ring of the carbonyl compound. The electron-donating substituents stabilized bismuth (III) complexes. The mechanism and the electrochemical parameters of the electro active species of bismuth (III) are strongly dependent on the substituent.

Keywords: Bismuth (III) Complexes Schiff bases, Spectroscopic, Redox behavior

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1-Introduction:

Last decades have seen an upsurge of interest in the applications of spectroscopic and electro analytical techniques to study the oxidation and reduction reaction of many types of chelating agents and their metal chelate [1, 2]. Schiff bases, hydrazones and their metal chelates represent an important class in coordination chemistry and pigment industry [3]. These compounds also possess excellent bacteriostatic properties in vitro against microorganisms and facilitate the iron mobilization from ^{59}Fe labeled reticulocytes. The

chelates also have a remarkable anticancer affect in tumor growth and antileukemic activity [4].

Schiff bases act as multidentate ligands with transition metal ions forming colored chelates [5]. Some of these complexes have been used as selective and sensitive reagents for accurate determination of some metal ions in aqueous media. The ligands may be coordinated to the metal ion through the nitrogen atoms either alone or in combination with some other electro active oxygen atoms [5, 6]. Biological activities may relate to the redox properties of the complexes [7]. The redox properties include oxidation and reduction of the central metal ion various oxidation and reduction of the ligands and the processes may also involves both the central atom and the ligand [7-11].

It is well known that bismuth (III) complexes have medicinal application in the treatment of a variety of gastrointestinal disorders for examples gastric and duodenal ulcers, dyspepsia and colitis [12 - 13] and have a direct antibacterial effect on the chronic gastritis and peptic ulcer [14]. Bismuth (III) form stable different sulfur reagents containing sulfur e.g. metallothionein, MT forms a stable complex of general formula $[[Bi_7MT]]$. Bismuth (III) complexes of most Schiff bases e.g. with thiosemicarbazide derivatives are characterized by high stability [15]. The electrochemical behavior of bismuth (III) complexes with a series of thiosemicarbazide and its derivatives thiosemicarbazones has been investigated in the last few years [15]. Hitherto no data involving the redox characteristics of bismuth (III) complexes of Schiff bases involving 1, 2-diamine or benzene-1, 2-diamine are reported. Thus, the present manuscript reports the synthesis and geometry of the prepared bismuth (III) complexes. The redox properties and mechanism of the electrode couples of some of the prepared bismuth (III) complexes were critically discussed. The Schiff bases involving *o,o*-phenylenediamine and compounds provide good opportunity for investigating the azomethine nitrogen coordination.

2. Experimental:

2.1. Reagents and materials:

All the chemicals used are of BDH grade and were used as supplied. The reagents 4-methyl-benzaldehyde, MB; 4-chloro-benzaldehyde, CB and 2-hydroxy-1-naphthaldehyde, HN; ethane-1, 2-diamine, ED and benzene-1, 2-diamine, BD were obtained from BDH (Poole, England). The oxynitrate of bismuth (III) i.e. $\text{BiONO}_3 \cdot 2\text{H}_2\text{O}$ was obtained from Aldrich, France and was dissolved in few drops of nitric acid (3.0 mol L^{-1}). Bismuth (III) was determined with employing inductive-coupled plasma atomic emission spectrometry. The supporting electrolyte tetrabutylammonium tetrafluoroborate ($\text{TBA}^+\text{BF}_4^-$) was used in cyclic voltammetry employing N, N – dimethylformamide solvent.

2.2. Physical measurements

Infrared (IR) spectra ($200\text{-}4000 \text{ cm}^{-1}$) as KBr discs were measured on a Matson 500 FT-IR spectrometer at room temperature. ^1H NMR in DMSO-d_6 and electronic spectra in CH_2Cl_2 ($\sim 5 \times 10^{-4} \text{ mol L}^{-1}$) were recorded on a Varian Gemini VM-200 and a Unicam UV₂₋₁₀₀ UV-visible spectrometers, respectively. The cyclic voltammetric measurements were performed on a Metrohm 746 VA trace analyzer and 747 VA stand. A three-compartment borosilicate (Metrohm) voltammetric electrochemical cell (10 ml) configuration system incorporating Pt working electrode (surface area of 0.38 mm^2), double-junction Ag/AgCl, (3M KCl) and platinum wire (BAS model MW-1032) as a reference and counter electrodes, respectively. The electrochemical data were then recorded at room temperature and the peak current heights were measured using the "tangent fit method". CEM microwave system (Mars model, 907500, USA) and digital pH-meter (model MP220, Metter Toledo) were used for sample digestion and pH measurements with absolute accuracy limits ± 0.1 at the pH measurements being defined by NIST buffers, respectively. Teflon digestion vessel (HP 500) was used for the digestion of the food stuffs in the microwave system. An inductively coupled plasma atomic emission spectrometry (ICP-AES) from Perkin-Elmer (USA) model Optima 4100 DV was used for the determination of bismuth (III) determination after microwave digestion.

2.3. Preparation of the Schiff bases:

A series of Schiff bases namely N,N-bis 4- methyl-benzaldehyde ethylene diamine, MBED; N,N-bis 4- chloro-benzaldehyde ethylene diamine, CBED; N,N-bis 2- hydroxy 1- naphthaldehyde ethylene diamine, HNED; N,N-bis 4- methyl-benzaldehyde *o,o* - phenylenediamine diamine, MBPD; N,N-bis 4- chloro-benzaldehyde *o,o* - phenylene - diamine diamine, CBPD and N,N-bis 2- hydroxy 1- naphthaldehyde *o,o* - phenylene- diamine diamine,HNPD were prepared as follows: The aldehyde compound (8 mmole) 4-methyl-benzaldehyde, 4-chloro-benzaldehyde or 2-hydroxy-1-naphthaldehyde in hot ethanol (25 mL) was mixed with hot solution containing 1, 2- diamino ethane or 1, 2- diamino benzene (4.0 mmole) in ethanol (10 mL) in the presence of few drops of glacial acetic acid. The resultant solution mixtures were refluxed under constant stirring for 6 h, and the resultant yellow colored precipitates were separated out, filtered off, washed thoroughly with hot ethanol to remove any nonspecifically material and finally re crystallized from hot ethanol as pale yellow crystals, dried under vacuum at 50 °C and stored on a desiccator'. The formulae are in good agreement with the stoichiometries concluded from their micro analytical data and confirmed from their IR spectra.

2.4. Synthesis of the Schiff base metal complexes:

The complexes were prepared by heating under reflux a 1:2 molar mixture of the Schiff base (4.0 mmole) and $\text{BiONO}_3 \cdot 2\text{H}_2\text{O}$ (2.0 mmole) in hot ethanol (25 mL). The reaction mixtures on a water bath for 2-3 h. Brownish black, brownish green and brownish green precipitates were formed immediately. The precipitates formed were then separated out, filtered off, washed with ethanol, ether and finally dried under vacuum at 60-70 °C. The yield was in the range 75-80 %.

3. Results and discussion:

Interaction of transition metal ions with Schiff bases containing *o, o*- phenylenediamine moiety are of greet importance in view of the role of M-N and / or M-O bond in the initiation of some chemical reactions and catalytic activity of the resultant metal complexes e.g. the catalytic activity of ruthenium (II) or (III) complexes towards

oxidation of carbonyl compounds and / or other unsaturated compounds e.g. olefins [16-21]. The prepared Schiff bases are yellow colored, stable and have moderate melting points owing to their inherent stability. The abbreviations, color and analytical data of the Schiff bases are summarized in Table 1. Most of the Schiff bases are pale yellow or yellow and have melting point below 160 °C. The proposed chemical structures of the prepared Schiff bases are in good agreement with the stoichiometries concluded from the analytical data. On the other hand, the isolated complexes are insoluble in water and common organic solvents and highly soluble in DMF or DMSO. The complexes are stable in air and are yellow or brown in color. The analytical data and color of the prepared bismuth (III) complexes are listed in Table 2.

3.1. Spectral studies:

In the IR spectra of the free Schiff bases, the ν C=N vibration band was observed in the range 1610-1635 cm^{-1} [22]. The ν OH vibration of the free hydroxyl group on the Schiff bases HNED and HNPD was noticed at 3415 and 3435 cm^{-1} , respectively. A large number of vibration bands with variable changes in their positions are noticed and most of them generated by aromatic and aliphatic substituents were noticed.

The significant IR frequencies of the bismuth (III) complexes in the range 200- 4000 cm^{-1} with their probable assignments are summarized in Table 3. A careful comparison of the IR spectra of the ligands and their bismuth (III) complexes have shown that, the ν C=N band of the free ligands (1610-1635 cm^{-1}) is shifted to lower wave numbers in the range 1594-1600 cm^{-1} on complex formation (Table 3) with bismuth (III) ions, indicating participation of the azomethine nitrogen of the Schiff bases to bismuth (III) ions. In the complexes $[\text{Bi}(\text{HNED})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, the phenolic oxygen of the two ligands HNED and HNPD participate on the coordination as indicated from the shift of ν (OH) band by 15-20 cm^{-1} to lower frequency. The observed band at 505-535 cm^{-1} in the complexes is assignable to ν (Bi-O). In the IR spectra of the complexes $[\text{Bi}(\text{HNED})_3]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_3]\text{NO}_3$, the observed bathochromic shift of ν (OH) from 3415 and 3435 cm^{-1} to 3470 to 3490 cm^{-1} corresponding to the dissociation of its hydrogen bonding with C=N during the complex formation.

The Schiff bases MBED, CBED, MBPD and CBPD are bonded to bismuth (III) as bidentate via their two azomethine nitrogen's (ν C=N), while the other two Schiff bases HNED and HNPD are coordinated to bismuth (III) as dibasic tetradentate ligands via their two azomethine nitrogen's and the two deprotonated oxygen's of the hydroxyl group form producing the two complexes $[\text{Bi}(\text{HNED})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, respectively. The coordination of the azomethine nitrogen (ν C=N) to the bismuth (III) ions was also confirmed by the appearance of new ν M-N mode in the range 455-475 cm^{-1} for all complexes. The presence of coordinated water molecules in the complexes $[\text{Bi}(\text{HNED})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$ by the presence of extra bands at 544-657 and 790-865 cm^{-1} and are safely assigned to wagging and rocking vibrations of the water molecules [23], respectively. The nitrate bands are observed at 1675-1697, 1425-1470 and 1043-1129 cm^{-1} due to ν_s , ν_s^- and ν_{as} , respectively, confirming that the nitrate ion is ionic and present in the outer sphere of the complex [24]. Thus, the most probable structures of the two complexes $[\text{Bi}(\text{HNED})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$ is given in Fig.1

3.2. Electronic spectra:

The electronic spectra of the prepared Schiff bases and their bismuth (III) complexes were carried out in DMF solution at ambient temperature. The most significant electronic absorption bands are summarized in Table 4. The positions of the absorption bands were not significantly different, showing that no electronic or geometric change of the species in dissolution in DMF and the composition of the chromophores of the compounds 1, 2, 4 and 5 are similar. The Schiff bases have $\pi \rightarrow \pi^*$ band in the range at 37,170-43,120 cm^{-1} and the transition $n \rightarrow \pi^*$ band at 30,940-32,740 cm^{-1} . In the complexes, little changes in the energies of the absorption bands were noticed. On the other hand, a band in the range 29,500 – 26,180 cm^{-1} was observed on the Schiff bases HNED and HNPD and their complexes and is safely assigned to $n \rightarrow \pi^*$. The observed band in the spectra of the complexes in the region 26.190 – 23.980 cm^{-1} is most likely assigned to LMCT confirm the coordination of the ligands to bismuth (III) ions through nitrogen for the complexes 1,2,4 and 5 and through N and O of the ligands.

3.3. Electrochemical studies:

The cyclic voltammetric behavior of some selected bismuth (III) complexes of the formulae $[\text{Bi}(\text{MBPD})_3](\text{NO}_3)_3$, $[\text{Bi}(\text{HNED})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, and in $\text{DMF-TBA}^+\text{BF}_4^-$ at Pt working electrode *versus* in the potential range from +1.2 to -1.6 V *versus* Ag/AgCl were recorded. A representative CV of the complex $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$ is shown in Fig.2. The CV's of the 2-hydroxyl-1-naphthaldehyde Schiff base bismuth (III) complex showed similar trend and displayed two irreversible electrode couples. The $E_{p,c}$ of the first electrode was noticed in the potential range -1.17 to -0.96 V and was coupled with an ill defined peak, $E_{p,a}$ in the range -0.62 to -0.44 V with $\Delta E_p > 0.28$ V. The complex $[\text{Bi}(\text{MBPD})_3](\text{NO}_3)_3$ showed a single reversible one electron reduction couple with $E_{p,c} = -0.36$ V coupled with an anodic wave at $E_{p,a} = -0.30$ V with $\Delta E_p \cong 0.06$ V. The single irreversible one - electron nature of the observed electrode couples of the complexes has been assigned to the couple $\text{Bi}^{\text{III}}/\text{Bi}^{\text{IV}}$. This assignment was established by comparing the current heights of the peaks observed with similar complexes of bismuth (III). The assignment was confirmed by performing the controlled potential electrolysis under a purified nitrogen atmosphere at a Pt net electrode under the same experimental conditions. The potential was controlled at the potential for both first reduction and oxidation i.e. on the limiting current plateau of the redox wave of the complex $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, taken as a typical example of the series of the studied cobalt (II) complexes.

The ratio of the cathodic to anodic peak currents i.e. $i_{p,c}/i_{p,a}$ versus the square root of the sweep rate (v) i.e. $v^{1/2}$ for the couple $\text{Bi}^{\text{III}}/\text{Bi}^{\text{IV}}$ was almost constant. On the other hand, the plot of $i_{p,c}$ and $i_{p,a}$ versus the square root of the sweep rate is given in Fig.3. This behavior is a typical for a chemical reaction coupled between two charge-transfer processes i.e. an "ECE" mechanism in which an irreversible first order chemical reaction is interposed between the two charge-transfer processes and is most likely indicative of some kinetic complications of the electrochemical process involved. Another electrode couple with anodic direction in the range 0.2-0.34 V coupled with cathodic peak potential in the range -0.4-0.5 V, versus Ag/AgCl reference electrode.

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Table 1. Abbreviations, color and analytical data of the prepared Schiff bases

Schiff Base Abbreviations	Color	Analytical data		
		Found (Calcd.), %		
		C	H	N
MBED	Pale yellow	80.24 (81.8)	6.94 (7.52)	9.8 (10.63)
CBED	Pale yellow	63.8 (62.95)	4.2 (4.59)	8.7 (9.18)
HNED	Deep yellow	78.26 (80.12)	5.08 (5.43)	7.63 (7.3)
MBPD	yellow	85.91 (84.61)	5.95 (6.44)	8.34 (8.97)
CBPD	Deep yellow	68.9 (67.98)	3.65 (3.96)	7.42 (7.93)
HNPD	Deep yellow	81.8 (80.76)	4.5 (4.8)	6.3 (6.73)

Table 2. Abbreviations, color and analytical data of the prepared bismuth (III) complexes

Complex	Color	Analytical data			
		Found (Calcd.), %			
		C	H	N	Bi
1 [Bi(MBED) ₃] (NO ₃) ₃	Pale yellow	55.21 (54.59)	4.64 (5.05)	9.73 (10.61)	16.95 (17.7)
2 [Bi(CBED) ₃] (NO ₃) ₃	Pale yellow	42.87 (43.96)	3.34 (3.2)	9.11 (9.61)	16.34 (15.95)
3 [Bi(NHED)(H ₂ O) ₂] NO ₃	Deep yellow	41.45 (42.73)	3.05 (3.41)	5.94 (6.23)	30.10 (31.10)
4 [Bi(MBPD) ₃] (NO ₃) ₃	Yellow	58.92 (59.52)	4.21 (4.53)	8.91 (9.46)	15.12 (15.70)
5 [Bi(CBED) ₃] (NO ₃) ₃	Deep yellow	49.92 (49.51)	3.13 (2.88)	6.95 (7.42)	15.32 (14.37)
6 [Bi(NHPD)(H ₂ O) ₂] NO ₃	Deep yellow	47.23 (46.53)	3.29 (3.19)	5.54 (5.81)	29.13 (28.92)

Table 3. Infrared spectral data (cm^{-1}) of the prepared bismuth (III) Schiff base complexes

Complex	ν OH	ν C=N	ν M-O	ν M-N	ν NO ₃
[Bi(MBED) ₃] (NO ₃)		1615		447	1675, 1450, 1043
[Bi(CBED) ₃] (NO ₃)		1610		439	1697, 1425, 1120
[Bi(NHED)(H ₂ O) ₂] NO ₃	3472 s	1605	545	466	1685, 1444, 1110
[Bi(MBPD) ₃] (NO ₃) ₃		1600		467	1689, 1460, 1115
Bi(CBED) ₃] (NO ₃) ₃		1603		465	1679, 1437, 1129
[Bi(NHPD)(H ₂ O) ₂] NO ₃	3510	1580	495	447	1684, 1445, 1117

Table 4. Electronic spectral data (cm^{-1}) of the prepared Schiff base bismuth (III) complexes and their log molar absorptivities

Complex	Intra ligand band, cm^{-1}	Charge transfer band, cm^{-1}
[Bi(MBED) ₃] (NO ₃)	29,432; 37,785; 41, 874	25436, 25,987
[Bi(CBED) ₃] (NO ₃)	29,879; 32,769; 42,324	24,768, 25,234
[Bi(NHED)(H ₂ O) ₂] NO ₃	36,765; 41,547; 43,653	25,564; 27,235
[Bi(MBPD) ₃] (NO ₃) ₃	33,654; 37,563; 39,621	23,768
Bi(CBED) ₃ (NO ₃) ₃	29,634; 32,786; 39,563	-----
[Bi(NHPD)(H ₂ O) ₂] NO ₃	30,342; 37, 245; 42,342	24,465; 24,988

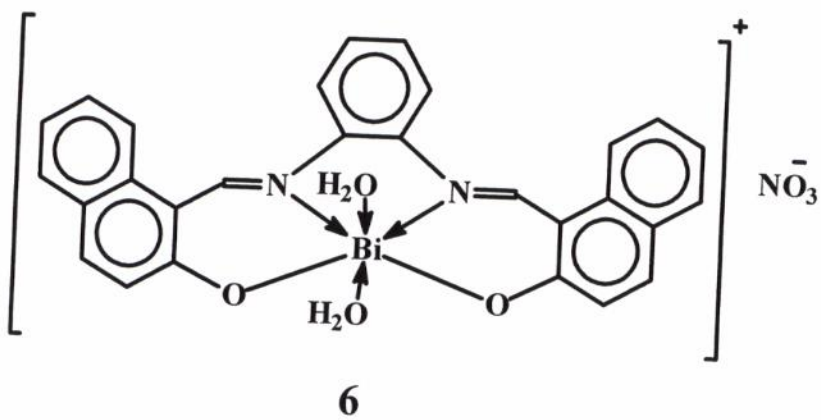
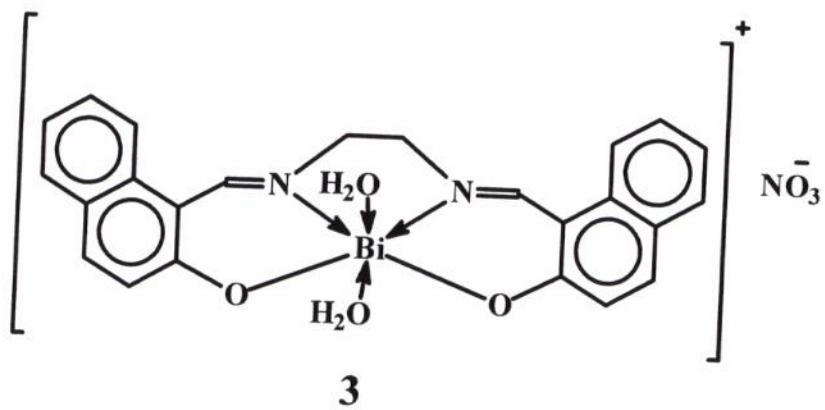
Figure captions:

Fig. 1. The proposed chemical structure of the complexes $[\text{Bi}(\text{HNED})(\text{H}_2\text{O})_2]\text{NO}_3$, **3** and $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, **6**.

Fig.2. Cyclic voltammogram of the bismuth (III) complex $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$, in DMF-TBA⁺BF₄⁻ at 100 mVs⁻¹ vs. Ag/AgCl electrode.

Fig.3. Influence of the square root of the scan rate on $i_{p,c}$ or $i_{p,a}$ of the couple Bi^{III}/Bi^{IV} of the bismuth (III) complex $[\text{Bi}(\text{HNPD})_2(\text{H}_2\text{O})_2]\text{NO}_3$.

Fig.1



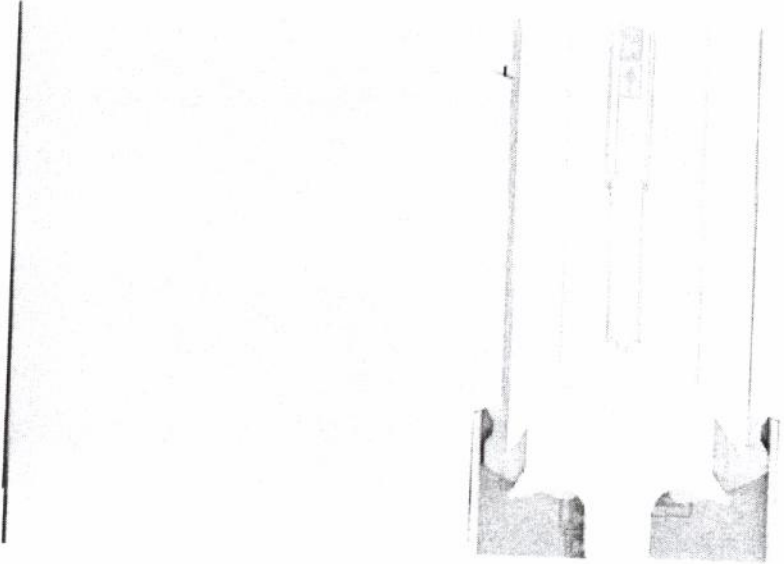
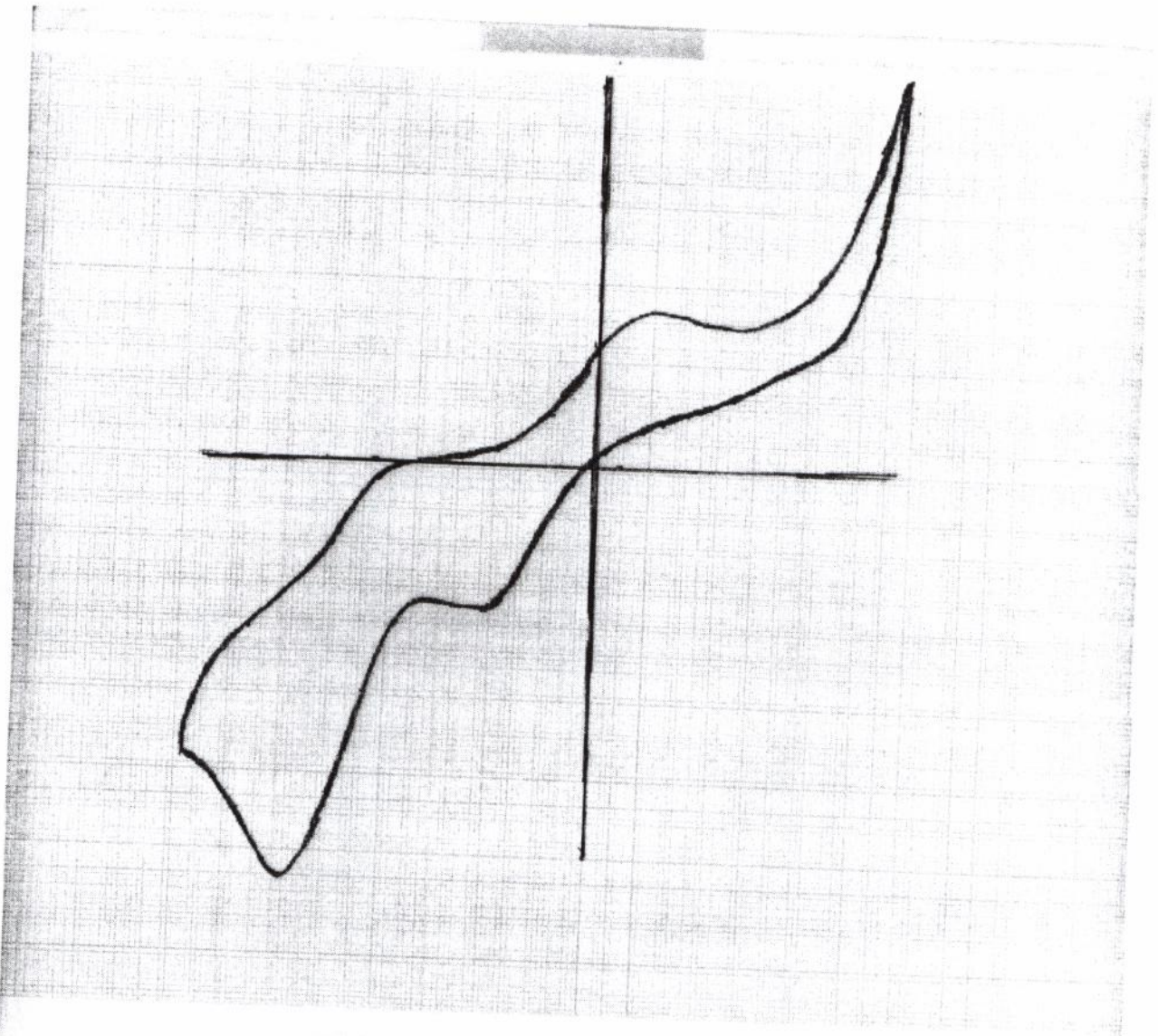


Fig.3.

