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Preparation and Study the Structural Properties and Magnetic Susceptibility of a Liquid Crystal

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Abstract

Two ligands have been synthesized from benzidine and hydrazine derivatives. These ligands have been mixed with metal ions such as Cu^{II} and Ni^{II} to synthesis liquid crystalline complexes. By using polarizing optical microscopy (POM) techniques, it is found that these prepared compounds have liquid crystalline behavior and characterization by physical and chemical techniques such as spectroscopic (UV-Visible, FT-IR, X-ray powder diffraction (XRD)), magnetic susceptibility, and molar conductivity. The aim of the study show enantiotropy nematic phase (marble and schleiren textures through heating and cooling respectively) for all compounds, the prepared complexes are paramagnetic, and study their structural, and magnetic susceptibility.

Keywords: liquid crystalline materials, complexes, POM, XRD, Mesogenic organic magnets.

الخلاصة

تم تحضير ليجاندين من مشتقات البنزدين والهيدرازين مع معقداتهما من ايونات النحاس (Cu) و النيكل (Ni) الثنائية التكافؤ والتي تمتلك الصفات البلورية السائلة طبقا للفحوصات البصرية المشخصة بالمجهر ذي الضوء المستقطب (POM). تم دراسة الخصائص الكيميائية والفيزيائية للمواد المحضرة من خلال استخدام التقنيات الآتية: مطيافية الأشعة فوق بنفسجية–المرئية (UV-VIS), مطيافية الأشعة تحت الحمراء(FT-IR)، حيود الاشعة السينية (XRD)، الحساسية المغناطيسية, والتوصيلية المولارية. ان هدف الدراسة هو تحضير مواد بلورية سائلة من الطور النيماتي (تظهر التراكيب النسيجية عند التسخين و التبريد) تشمل ليجاندين مع معقداتهما الفلزية, و المعقدات المحضرة جميعا ذات صفة بارا مغناطيسية. و دراسة خصائصها التركيبية والمغناطيسية.

الكلمات الدلالية: بلورات سائلة, معقدات بلورية سائلة، حيود الأشعة السينية, مجهر ذي الضوء المستقطب, مغانط عضوية ميزوجينية.

1. Introduction

Liquid crystals phase is an intermediate phase. It has mechanical, optical, and structural properties between those of the crystal solid and the corresponding isotropic liquid [Satyendra, 2001]. Materials that exhibit such unusual phases are often called mesogens and the various phases in which they could exist are termed mesophases [Iam-Choon, 2007]. The Austrian botanist Friederich Reinitzer discovered the liquid crystals in (1888) [Virgil and Dimitris, 1992]. He described observations, published that year (Reinitzer, 1888), that esters of cholesterol appeared to have two melting points between which the liquid showed iridescent colors and birefringence [Donald *et al*., 2006].

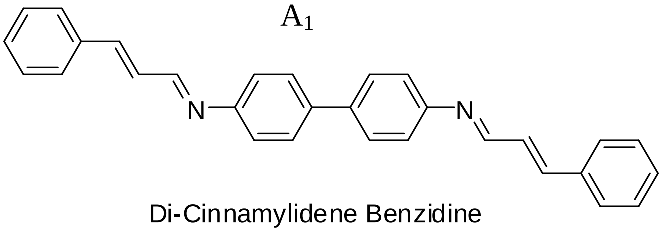
Materials that exhibit liquid crystal mesophases typically have molecular structures that can be classified as spherical, rod-like, disc-like, or even any regular geometrical shape, with combinations of the two producing phasmidic liquid crystals [John W.*et al*., 2009], depending on the physical chemical parameters responsible for the phase transitions to thermotropic and lyotropic [Antonio M., and Silvio R., 2005]. Thermotropic liquid crystal phases are formed by pure mesogens in a certain temperature range and hence the prefix (thermo) referring to phase transitions in which heat is generated or consumed [Ian, 2007]. While lyotropic liquid crystal, the transition is induced by the influence of solvents [Tai-Shung C., 2001] under appropriate conditions of concentration and temperature [Kirill and Sabine, 2011]. With development of liquid crystal science and technology, more mesogens have been prepared and studied [Si *et al.*, 2010].

In the last decades, the introduction of a metal ion leads to a new class of liquid crystals metallomesogens. The metal complexes which contain organic mesogens as ligands may retain these properties. Also, the introduction of a metal ion in an organic compound which does not exhibit liquid crystal properties lead to a new complex with liquid crystal properties [Liliana *et al.*, 2005].

The magnetic materials can be divided into temporary materials soft or hard solid materials according to the amount of magnetic permeability or its ability to retain magnetic fields. As for the phenomenon of materials magnetization as a result of falling under the influence of an external magnetic field, it is attributed to the change that is happening in the movement of electrons in the atoms of the material and that leads to the movement of the magnetic moments, and magnetic moment directions given by the magnetic behavior under the influence of a magnetic field moving [Abdul-Aziz, 2004].

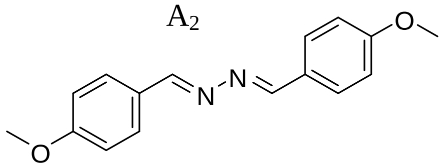
In this paper, two ligands have been synthesized which are [Di-Cinnamylidene Benzidine] with symbol (A_1), and [Bis-4-Methoxy-benzylidene-Hydrazine] with symbol (A_2), and their complexes with (Cu^{II}, Ni^{II}) take symbols (M_1A_1, M_2A_1, M_1A_2, M_2A_2) respectively. These compounds are characterized by POM, UV-VIS, FT-IR, XRD, magnetic susceptibility, and molar conductivity. The specific ultimate goal is to synthesisze materials are belong to fourth state of substance (liquid crystals (LC)) as LC ligands and its LC complexes with transitional metals. This topic is of great interest as some organic materials can be utilized for multidisciplinary functions such as mesogenic organic semiconductors and magnets.

A_1



Di-Cinnamylidene Benzidine

A_2



Bis-4-Methoxy-benzylidene- Hydrazine

2. Theoretical Part

The assignment of the mesophases is based on different experimental techniques. Phase transitions are usually detected not only by calorimetry but also by polarizing optical microscopy. Textural features obtained by polarizing microscopy give first hints about the mesophase type. The most important method for the structural characterization is X-ray diffraction measurements [Ayyalusamy R., 2007]. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. XRD is an easy tool to determine the size and the shape of the unit cell for any compound [Theivasanthi and Alagar, 2010]. Crystalline size (average grain size) has been estimated using Debye-Scherrer formula:

$G_s = 0.94\, \lambda / \beta \cos\theta$ ……………………………………..…….. (1)

Where (λ) is wave length of X-Ray (0.15405 nm), (β) is FWHM (full width at half maximum), (θ) is the diffraction angle and (G_s) is particle diameter size.

The magnetic susceptibility is anisotropic, and so magnetic fields can be used to control the alignment of liquid crystal samples. Magnetic susceptibility is the physical quantity describing material properties in the external magnetic field[Marcon and Ostanina K., 2012], is defined as ratio between magnetization (M) of the material in the magnetic field and the field intensity (H) [Naomi C. *et al.*, 2011].

$\chi = M / H$ ………………………………………………………. (2)

$\chi_g = [\ \ell C\ (R-R_o)\ ] / [m\times10^9]$ …………………………….….…. (3)

$\chi_m = \chi_g .\ M.Wt.$ ……………………………………………....… (4)

$\chi_A\ = \chi_m + D$ ……………………………………………………. (5)

$\mu_{eff} = 2.828\ (\chi_A \times T)^{1/2}$ $(B.M.)$ ……………………………….. (6)

Where:

(C) constant (0.5); (ℓ) sample height (1 cm); (R) reading from the digital display of the sample plus tube; (R_o) reading from the digital display of the tube; m: sample Weight.; (χ_m) molar susceptibility; (χ_g) mass susceptibility; (M.Wt.) molecular Weight; (χ_A) atomic susceptibility; (T) absolute temperature; (D) Factor of diamagnetic correction; (μ_{eff}) effective magnetic moment; (B.M.) (Bohr Magnetons), which is a unit of magnetic moment and equal to (eh/4πmc) = 9.27×10^{-21} erg/gauss.

3. Experimental Part:

3.1. Physical Measurements:

Liquid crystalline properties were investigated by Polarizing Optical Microscopy (POM) using a Leitz Laborlux 12 pols attached to a Linkam with hot stage and digital camera. Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for (1×10^{-3}) M solutions in absolute ethanol at 25°C using a Shimadzu 1800 spectrophotometer matched quartz cell. FT-IR data were acquired on Shimadzu-FTIR spectrophotometer in the frequency range of (4000-400) cm^{-1} with samples embedded in (KBr) discs. Magnetic susceptibility of complexes was measured by using device model (M.S.B) Auto .Structural characterization of compounds and their metal complexes are well documented by X-ray diffraction patterns.

Conductivity measurements were made with dimethyl formamide (DMF) using a (DDS-307W) digital conductivity meter at room temperature. Melting points (m.p.) were obtained on a Stuart SMP-30 capillary melting point apparatus.

3.2. Procedures of Synthesis:

3.2.1. Synthesis of Di-Cinnamylidene Benzidine (A_1):

Di-cinnamylidene benzidine was prepared by mixing (1.84 g; 0.01 mol) of benzidine dissolved in (10 mL) of absolute ethanol with (2.64 g; 0.02 mol) of cinnamaldehyde in (10 mL) of absolute ethanol, then added to the prepared mixture three drops of glacial acetic acid. Reaction mixture was refluxed for (2) hours, resulted yellow solid product. The crystal product filtered and washed with absolute ethanol repeatedly and re-crystallization was done by absolute ethanol [Malathy *et al.*, 2014].

3.2.2. Synthesis of Bis-4-Methoxy-Benzylidene- Hydrazine (A_2):

Bis-4-Methoxy-Benzylidene-Hydrazine was prepared by mixing (1.04 g; 0.01 mol) of hydrazine diluted in (10 mL) of absolute ethanol with (2.72 g; 0.02 mol) of *p*-methoxy benzaldehyde in (10 mL) of absolute ethanol, then added to the prepared mixture three drops of glacial acetic acid. Reaction mixture was refluxed for (2) hours, resulted shining yellow solid product. The crystal product filtered and washed with absolute ethanol repeatedly and re-crystallization was done by absolute ethanol [Malathy*et al.*, 2014].

3.2.3. General Synthesis of Complexes:

(0.001 mol) of both Ni^{II} and Cu^{II} of chlorinated salts dissolved in (10 mL) of absolute ethanol was mixed with (0.001 mol) of (A_1, and A_2), where the ratio of reactants (1:1). Reaction mixture was refluxed for (1) hour, produced mixture was filtered and washed with absolute ethanol repeatedly and re-crystallization was done by absolute ethanol. As in following Table, where: X is coordinated molecules of water [Mustafa *et al.*, 2014].

Table (1) Molar conductance and m.p. of ligands and its complexes.

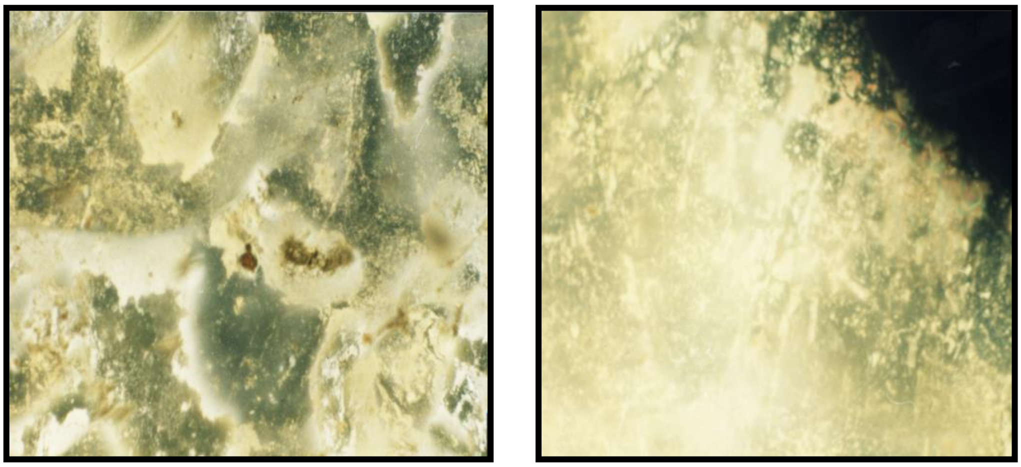
No.	**Compounds formula**	**Compounds symbol**	**Compounds color**	**m.p. °C**	**$\Lambda \times 10^{-3}$ $\Omega^{-1}mol^{-1}cm^2$**
1	$C_{30}H_{24}N_2$	A_1	Yellow	270.3	—
2	$C_{16}H_{16}N_2O_2$	A_2	Yellow shining	165	—
3	$[Cu(C_{30}H_{24}N_2)]\ Cl_2.X$	M_1A_1	Dark green	264	102.3
4	$[Ni(C_{30}H_{24}N_2)]\ Cl_2.\ X$	M_2A_1	Dark yellow	275	250
5	$[Cu(C_{16}H_{16}N_2O_2)]\ Cl_2.\ X$	M_1A_2	Yellow	169.1	185.8
6	$[Ni(C_{16}H_{16}N_2O_2)]\ Cl_2.\ X$	M_2A_2	Light green	296	235

4. Results and Discussion

4.1. Mesomorphic Properties:

The compounds are examined by using (POM), showed by heating nematic phase taking marble form, while by cooling from isotropic liquid exhibit schleiren texture by separation of distinct droplets growing to form a large colored flooring when continued cooling, this is distinguishes nematic phase. Figure (1) shows a photograph showing nematic phase of (A_1) compound at heating and cooling.

Reason of exhibited nematic phase in heating and cooling attributable in (A_1) ligand and their complexes to presence of four aromatic rings in the molecular structure, and in (A_2) ligand and their complexes to presence of nitrogen atoms linked directly in the case of resonant in center of the molecule, aromatic rings and nitrogen atoms give a suitable length of the molecule and high hardness, in addition to the breadth of sequencers electronic on the long axis of the molecule, which leads to increased polarity molecule resulting from terminal attractive forces[Alaa K., 2005].



Heating

Cooling

Figure (1) Nematic phase of ligand (A_1).

4. 2. UV-VIS Spectroscopic:

The UV-Vis spectra of ligands showed two bands at (370) nm assigned to (σ→σ*) and (π→π*) and (420-560) nm assigned to (n→π*). While the UV-Visible spectra for the prepared complexes showed one broadband between (410-470) nm [Mostafa M. *et al.*, 2012].

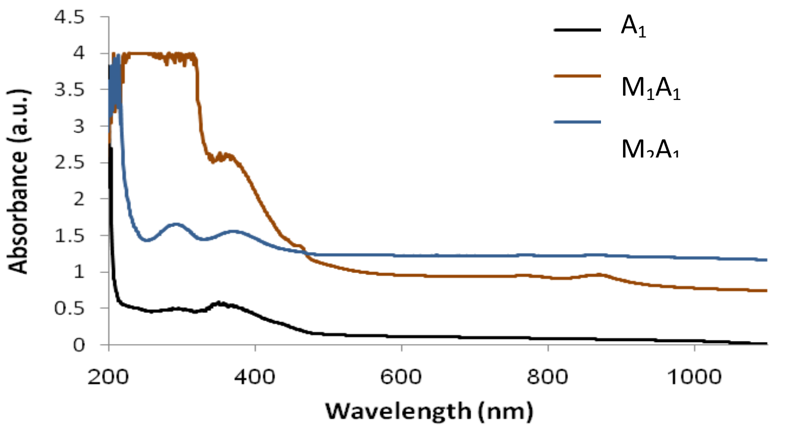


Figure (2) UV-Visible spectra of ligand (A_1) and its complexes.

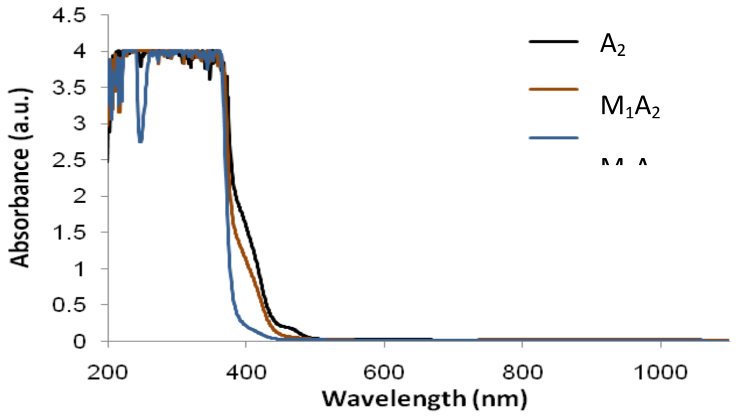


Figure (3) UV-Visible spectra of ligand (A_2) and its complexes.

4.3. FT-IR Analysis:

Main characteristic FT-IR absorption bands of ligans and complexes are presented in table (2). The IR data of the complexes are compared with respective of the free ligand in order to identify the coordination modes upon the chelation process. FT-IR of ligands (A_1, and A_2) have vabiration band (1630, and 1664) cm^{-1} for (C═C) aromatic, and (1605, and 1600) cm^{-1} for azomethine groups (CH═N) this group is active [Ibrahim B. *et al*.,2014], while these bands shift lower wave numbers upon complexation with the metal ions. The new bands appearing in the region (464-522) cm^{-1} probably due to the formation of (M-N). Figure (4) exhibits band absorption of (A_1)

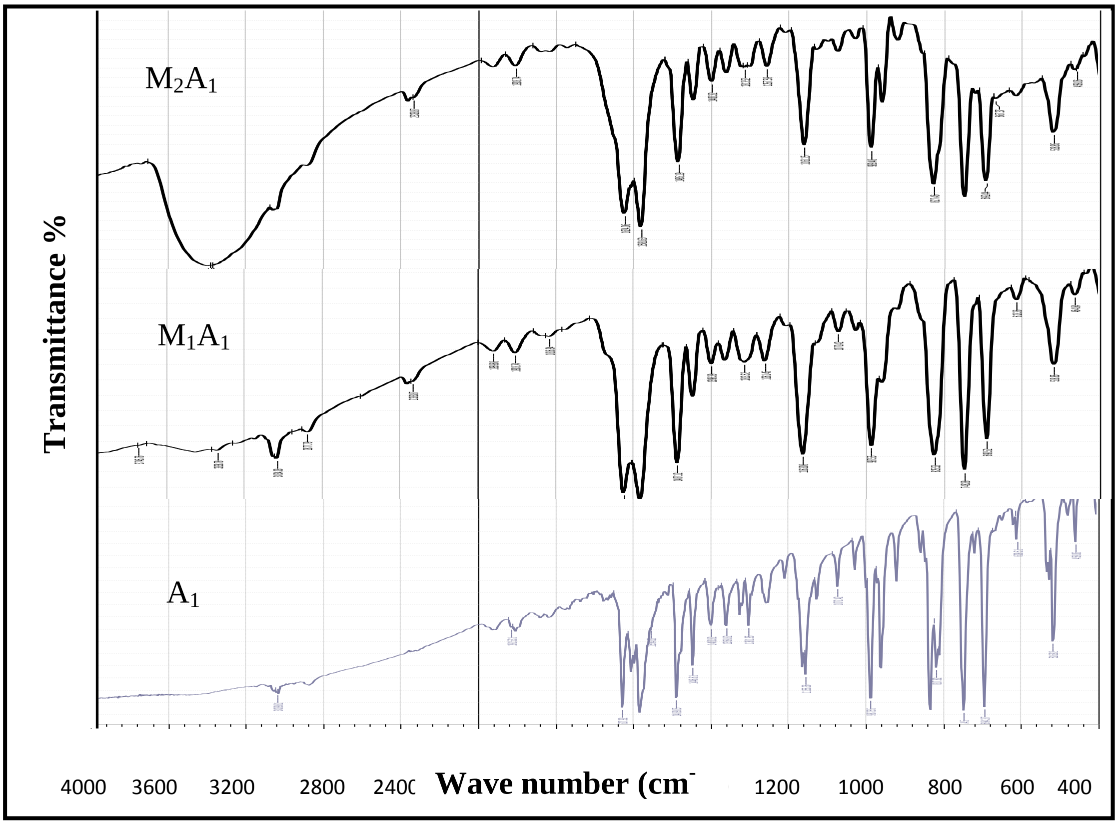


Figure (4) FT-IR spectra of ligand (A_1) and its complexes.

Table (2) FT-IR characteristic bands frequencies (cm^{-1}) of the ligands and its complexes.

No.	Compounds symbol	Stretch of (aromatic) C=C	Stretch of (C=N)	Stretch of (M–N)
1	A_1	1630	1605	—
2	A_2	1664	1600	—
3	M_1A_1	1620	1580	464
4	M_2A_1	1624	1581	469
5	M_1A_2	1655	1588	522
6	M_2A_2	1650	1575	522

4.4. Molar Conductance Measurements:

The molar conductivity measurements in DMF solutions of the complexes (M_1A_1, M_2A_1, M_1A_2, and M_2A_2) lay in the range (102.3–250) (Ω^{-1} mol^{-1} cm^2), which indicating their electrolytic behavior, this result was clearly indicated that complexation of their ligands were happened by ratio (1:1), and chloride ions were responsible for charge transfer by their swimming outside coordination sphere in the solution, as show in Table (1) [Sulekh and Poonam, 2014].

4.5. Structural Properties:

Liquid crystal compounds and their complexes are examined by (XRD) to identifying the crystalline composition. The tests find that ligands (A_1, and A_2) have polycrystalline structure, complexes (M_1A_1, M_2A_1, and M_2A_2) have monoclinic structure, and complex (M_1A_2) have orthorhombic structure. From this study, crystalline size (average grain size) has been estimated using equation (1), the grain size values are between (10-79) nm. Figure (5) shows XRD spectrum of (A_1) compound.

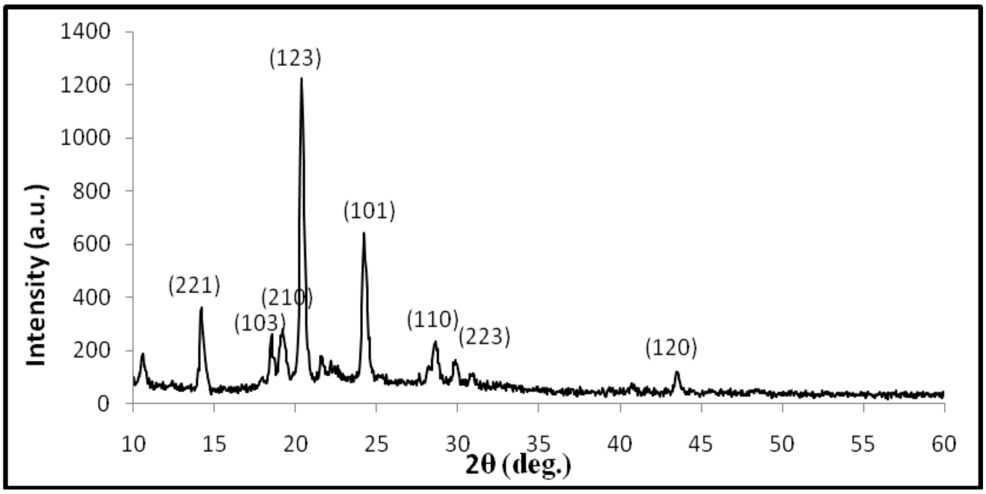


Figure (5) XRD spectrum of ligand (A_1).

4.6. Magnetic Properties:

The magnetic moment data of all the complexes were measured at room temperature in the solid state. Magnetic moment values were used to propose the structure of the complexes. Magnetic moment of complexes calculated by using equation (6). The μ_{eff} values of complexes (M_1A_1, M_2A_1, M_1A_2, and M_2A_2) are (1.91, 2.65,1.76, and 2.3) B.M., which suggested that the Cu(II) and Ni(II) complexes exhibits a square planar geometry, this result supported the appearance of LC property [Malathy *et al.*, 2014]. Measurements of magnetic susceptibility of complexes referred to property of paramagnetic susceptibility.

5. Conclusions

Based on various physiochemical and structural investigations, we conclude that the ligands and its complexes with Cu^{II}, and Ni^{II} exhibit nematic phase at heating and cooling, UV-VIS spectra of two ligands show two bands at (370) nm, and (420-560) nm, while the complexes show one broadband between (410-470) nm. FT-IR spectra show shift bands to lower wave numbers indicating that complexation with the metal ions is happen. XRD spectra show that all compounds have polycrystalline, monoclinic, and orthorhombic structure, magnetic susceptibility indicat that complexes have paramagnetic property. Molar conductance shows electrolytic behavior of complexes in the range of organic semiconductors.

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