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Synthesis and Characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) Complexes with [(N-(N-benzilidin aminoethyl) Iodomethylene Dithiocarbamate]

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ABSTRACT

A new series of transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II), with Schiff base (L) (N-(N-benzilidine aminoethyl) iodomethylene dithiocarbamate) is derived from (2- aminoethyldithiocarbamato -iodomethane) and benzoyl, by (1:2) metal to ligand molar ratio. The complexes were characterized by metal analysis, magnetic susceptibility, molar conductance and IR, UV-Vis, spectral studies. The data showed that these complexes have the composition of [ML_2Cl_2] type. The UV-Vis spectral and magnetic susceptibility of the complexes suggest an octahedral geometry around each central metal ion.

Keywords: Schiff base, complexes, transitions metals.

تحضير وتشخيص معقدات المنغنيز والكوبلت والنيكل والنحاس والخارصين والزئبق الثنائي مع قاعدة شيف (N) -N – بنزلدين امينو ايثايل-ايودوميثان ثنائي ثايو كاربامیت

الملخص

يتضمن البحث تحضير معقدات جديدة للمنغنيز (II) والكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) والزئبق (II) مع ليكاند [N) -N – بنزلدين امينو ايثايل – ايودوميثان)] ثنائي ثايو كاربامیت بنسب مولية (1: 2) فلز: ليكاند لتكوين معقدات جديدة ذوات الصيغة العامة [ML_2Cl_2]. تم تشخيص المعقدات المحضرة بواسطة قياسات التوصيلية الكهربائية المولارية واطياف الاشعة تحت الحمراء وفوق البنفسجية المرئية والقياسات المغناطيسية والامتصاص الذري بينت قياسات التوصيلية الكهربائية المولارية ان المعقدات غير موصلة في حين بينت الاطياف الاليكترونية والعزوم المغناطيسية بان المعقدات تمتلك بنية ثمانية السطوح.

INTRODUCTION

The Schiff bases and their metal complexes have more importance recently (Mobinlkhaledi *et al.*, 2010 ; Saritha *et al.*, 2006) because of their variety of applications in many fields: biological, inorganic and analytical chemistry (Omprakash *et al.*, 2010; Singh *et al.*, 2007). They have been found to possess the pharmacological activities such as antimalarial (Li *et al.*, 2003), anticancer (Villar *et al.*, 2004) antibacterial (Venugopal *et al.*, 2008), antifungal (Pandey *et al.*, 2003), antitubercular (Kathikeyan *et al.*, 2006) and antimicrobial (Wadher *et al.*, 2009). Schiff base ligands are able to coordinate with different metal ions and to stabilize them in various oxidation states (Chandra and Gupta, 2005; Fabbrizzi, 2010; Fry, 1997). The Schiff base complexes have been used in catalytic reactions (Mobinlkhaledi *et al.*, 2010). Furthermore, Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N, O and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules (Singh *et al.*, 2007). The aim of the present study was to prepare and characterize a new Schiff base ligand [N-(N-benzilidine aminoethyl) iodomethylene dithiocarbamato] derived from 2-aminoethyldithiocarbamatoiodo methane with benzoyl, and their complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II), (Fig.1).

EXPERIMENTAL

Material and Measurements

All chemicals were of reagent grade and used as supplied without further purification. Infrared absorption spectra were recorded on FTIR spectrophotometer Tensor 27, Brucker 2003 in the 400-4000cm^{-1} range using KBr discs. Electronic spectra were recorded by using a Shimadzu UV-Vis-Spectrophotometer UV-1650 for 10^{-3} M solution of the compounds in dimethylformamide (DMF) at 25 °C with 1 cm quartz cell. Conductivity measurements were made on 10^{-3} M solutions of the complexes in DMF at 25 °C using conductivity measuring apparatus model PCM$_3$, Jenway. The metal contents of the complexes were determined using Shimadzu AA670 Atomic Absorption Spectrophotometer, after digestion with concentrated nitric acid. The magnetic susceptibility measurements were made at 25 °C by the Faraday method on the solid in a pyrex tube using Bruker BM6 instrument.

Preparation of 2-aminoethyldithiocarbamato iodo methane

The ligand was prepared by the addition of (0.1mol, 6.68ml) of ethylenediamine dropwise to a mixture of carbon disulfide (0.1mol, 6.06ml) and diiodomethane (0.1 mol, 8.056ml) in ethanol (15 cm^3). The mixture was stirred for about 1h, keeping the temperature at 0 °C. The white solid product so obtained was filtered of, washed with ethanol and dried in vacuum (Desai *et al.*, 2006).

Preparation of the ligand [N-(N-benzilidine aminoethyl)iodomethylane) dithiocarbamate].

Schiff base ligand was prepared as follows: (0.01 mol, 2.74g) of 2-aminoethyldithiocarbameto iodomethane dissolved in ethanol 20 cm^3 was mixed with (0.01 mol, 2.10g) of Benzil. The resulting mixture was refluxed with boiling for 2h under constant stirring. The precipitate was then removed from the reaction mixture by filteration, washed with ethanol and dried in vacuum. (Prakash *et al.*, 2011).

Preparation of complexes:

All the complexes were prepared by mixing 1:2 metal salt to Schiff base ligand ratio as follows: A hot ethanolic solution 20 cm^3 of $MnCl_2.4H_2O$ (0.01 mol, 1.97g), $CoCl_2.6H_2O$ (0.01 mol, 2.37g), Ni $Cl_2.6H_2O$ (0.01 mol, 2.37g), $CuCl_2.2H_2O$ (0.01mol, 1.75g), $ZnCl_2$ (0.01 mol,1.36g), $HgCl_2$ (0.01mol, 2.71g) was mixed with hot ethanolic solution 15 cm^3 of Schiff base ligand (L) (0.02 mol, 9.35g) the mixture was refluxed for about 1h. The precipitated complexes were filtered off, washed with ethanol followed by diethylether and dried in vacuum.

Table 1: Analytical and some physical properties of the ligand and its complexes

Compound	Color	m.p (^{o} C)	ΛM (DMF) (Ω^{-1}. mol^{-1}. cm^2)	% Yield	Found (Calculated) (%)M
L(C_{18} H_{17} S_2N_2OI)	White	177	---	73	---
[$Mn(L)_2Cl_2$]	Pale - pink	197	20	57	5.77 (5.17)
[$Co(L)_2Cl_2$]	Violet	233	3	67	5.97 (5.53)
[$Ni(L)_2Cl_2$]	Green	255	26	60	5.07 (5.51)
[$Cu(L)_2Cl_2$]	Blue	276	16	70	6.06 (5.93)
[$Zn(L)_2Cl_2$]	White	190	10	60	5.73 (6.09)
[$Hg(L)_2Cl_2$]	White	187	17	57	16.07 (16.61)

RESULTS AND DISCUSSION

The analytical data for the ligand and complexes together with some physical properties are summarized in Table (1). The data from complexes correspond well with the general formula [ML_2Cl_2], where M = Mn(II), Ni(II), Co(II), Cu(II), Zn(II), and Hg(II), L = ($C_{18}H_{17}S_2N_2OI$). The magnetic susceptibility of the complexes at room temperature was consistent with octahedral geometry around the central metal ion. All the complexes are solid and stable at 25 °C. The complexes are insoluble in common organic solvents but they are relatively soluble in DMF and DMSO. The molar conductance values indicate the non-electrolyte nature of the complexes in DMF (Geary, 1971), Table (1).

IR Spectra:

The infrared spectra of the ligand are recorded in the 400-4000 cm^{-1} region and compared with the spectra of the complexes. The characteristic of the ligand and complexes bands are listed in Table (2). The ligand spectrum showed absorption bands at 1679,1618, 1027 and 869 cm^{-1} that are assigned to υ(C=O), υ(C=N), (C=S) and (C-S), respectively (Nakamoto, 1970).

The band corresponding to υ (C=N) vibration group is shifted to lower values in the spectra of the complexes indicating that the nitrogen atom shared in coordination with metal ion in these complexes (Shaker *et al.*, 2010). The υ (C=O) absorption is also shifted to a lower frequency indicating that the ligand is coordinated with the metal ion through the oxygen of the carbonyl group (Chandra and Gupta, 2005). The υ (C= S), υ (C-S) vibration groups are not shifted to lower frequencies in the complexes indicating that there is no coordination to the metal ions. The other band in the ligand spectrum at 3415 cm^{-1} is due to the NH group remained unaltered in the complexes indicating that there is no coordination through the NH group. The other band at (542)cm^{-1} due to (C–I) group remained unaltered in the complexes indicating that there is no coordination through the (C– I) group (Nakamoto,1970). Moreover, all complexes show new bands at (460-511) and (415-425) cm^{-1} assigned to (M-O) and (M-N) stretching vibrations respectively indicating that the ligand is coordinated through the azomethine nitrogen and carbonyl oxygen (Shaker, 2010).

Table 2: Characterization infrared bands (cm^{-1}) of the free ligand and its complexes

Compound	**ν(C=O)**	**ν(C=N)**	**ν(C=S)**	**ν(C-S)**	**ν(M-O)**	**ν(M-N)**
(L)($C_{18}H_{17}S_2N_2OI$)	1679s	1618s	1027s	869s	-	-
[Mn$(L)_2Cl_2$]	1643s	1597s	1024 s	875s	486w	415s
[Co (L) $_2Cl_2$]	1659s	1594 s	1021 s	875m	466s	421s
[Ni(L) $_2Cl_2$]	1658s	1572s	1020s	873s	478s	420s
[Cu(L) $_2Cl_2$]	1659s	1592s	1022s	876m	460w	415w
[Zn(L) $_2Cl_2$]	1659s	1594s	1021m	875w	488s	424m
[Hg(L) $_2Cl_2$]	1660s	1595s	1023s	875s	511w	425s

w=weak, m=medium, s=strong

Electronic spectra:

The electronic spectra of the ligand showed an absorption bands in (29576 -32467 cm^{-1}) Table (3), which can be assigned to $\pi \longrightarrow \pi^*$ of the aromatic rings and to $n \longrightarrow \pi^*$ transition in the C=O, C=N and C=S chromophoric groups respectively. These transitions were found in the spectra of the complexes but shifted to lower frequencies indicating coordination of the ligand to the metal ion. (Mukta and Singh, 2006).

The electronic spectra of Mn(II) complex had only ligand bands in addition to many very weak absorptions characteristic of d^5 electronic configuration for octahedral high spin complex, d-d transitions due to spin and laporte- forbidden. The very weak bands arise from promotion of an electron to give various excited states containing only three unpaired electrons which may be assigned to the transitions : $^{6}A_{1}g \longrightarrow {}^{4}T_{1}$ (G), $^{6}A_{1}g \longrightarrow {}^{4}Eg$(G), $^{6}A_{1}g \longrightarrow {}^{4}A_{1}g$ (G) , $^{6}A_{1}g \longrightarrow {}^{4}Eg$(D), and $^{6}A_{1}g \longrightarrow {}^{4}T_{1}g$ (p) , exhibit a very small intensity and are conceald by the intraligand transitions. The absorption band at (25371, 30675) cm^{-1} can be attributed to the charge transfer of ligand to metal. (Chandra and Gupta, 2005).

Cobalt (II) complex gave two bands at 11211, 20921 and 26455cm^{-1} which were attributed to transitions $^{4}T_{1}g(F) \longrightarrow {}^{4}A_{2}g$ (F) υ_{2} , $^{4}T_{2}g(F) \longrightarrow {}^{4}T_{1}g(P)$ υ_{3} respectively and other bands at (29070) cm^{-1} region which could be attributed to charge transfer transition. These bands are consistent with the octahedral geometry of the complex (Agarwal *et al.*, 2006; Cotton *et al.*,1999).

The Ni(II) complex exhibits three absorption bands 10893,15015 and 22321 cm^{-1} which may be attributed to the $^{3}A_{2}g(F) \longrightarrow {}^{3}T_{2}g(F)(\upsilon_{1})$, $^{3}A_{2}g(F) \longrightarrow {}^{3}T_{1}g(F)(\upsilon_{2})$ and $^{3}A_{2}g(F) \longrightarrow {}^{3}T_{1}g(P)$ (υ_{3}), respectively indicating octahedral geometry. (Prasad and Agarwal, 2008 ; Cotton *et al.*,1999).

Cu(II) complex also showed the presence of one broad band at (14577) cm^{-1}, which can be attributed to the transitions $^{2}B_{2}g \longrightarrow {}^{2}A_{2}g$, $^{2}B_{1}g \longrightarrow {}^{2}B_{2}g$ and $^{2}B_{1}g \longrightarrow {}^{2}Eg$ characteristic for Cu(II) ions in an octahedral environment. (Mahapatra *et al.*, 2010; Monika *et al.*, 2011)

Two transitions of the ligand are found also in the spectra of the Zn(II) and Hg(II) complexes, but they shifted towards lower frequencies, confirming the coordination of the ligand to the Zn(II) and Hg(II) ions. (Dunn, 1960 ; Alexia *et al.*, 2007).

Magnetic properties:

The magnetic moment for Mn (II) complex at 25°C temperature was 6.01 B.M, corresponding to five unpaired electrons, the characterization based and metal analyses, suggesting an octahedral geometry (Kulkarni *et al.*, 2009).

For Co(II) complex the magnetic moment was 4.70 BM, this high value is due to the orbital contribution in high spin octahedral geometry (Ajaykumar *et al* ., 2009).

The magnetic moment of Ni(II) complex was (2.87) B.M this value is within the range (2.8-3.4 BM), found for paramagnetic complex of Ni(II) with octahedral geometry (Nicholls, 1973; Jha and Mukharjee, 2007). The Cu(II) complex which had the magnetic moment (1.97) BM was in agreement with octahedral environment (Dianu *et al.*, 2010; Lever,1984).

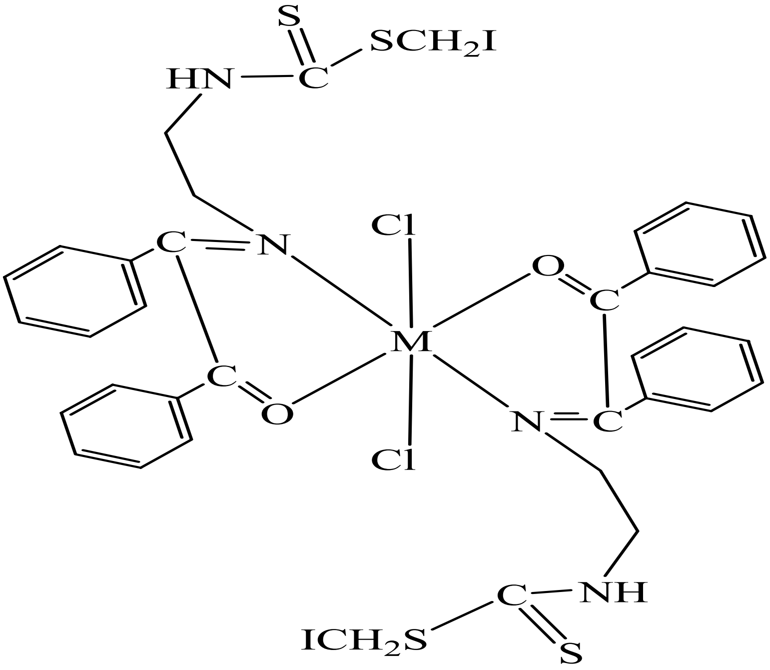
The Zn(II), and Hg(II) complexes were diamagnetic as expected for d^{10} system. Based on these data, an octahedral geometry has been assigned to the Zn(II) and Hg(II) complexes (Dunn, 1960 ; Alexia *et al.*, 2007) (Fig.1).

Table 3: The electronic spectra and magnetic moment of the ligand and its complexes

Compound	Absorption region (cm^{-1})	Possible assignment	μ_{eff} B.M
(L)($C_{18}H_{17}S_2N_2OI$)	32467 29576	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	------
[Mn(L)$_2$Cl$_2$]	(25371, 30675)	C.T*	6.01
[Co (L) $_2$Cl$_2$]	11011 20042-26415	$^4T_1g(F) \rightarrow {}^4A_2g(F)$ $^4T_1g(F) \rightarrow {}^4T_2g(F)$	4.70
[Ni(L) $_2$Cl$_2$]	10893 15015 22321	$^3A_2g(F) \rightarrow {}^3T_2g(F)$ $^3A_2g(F) \rightarrow {}^3T_1g(F)$ $^3A_2g(F) \rightarrow {}^3T_1g(P)$	2.87
[Cu(L) $_2$Cl$_2$]	14577	$^2Bg \rightarrow {}^2Eg$	1.97
[Zn(L) $_2$Cl$_2$]	(24200, 31447)	C.T*	**Diam
[Hg(L) $_2$Cl$_2$]	(24876, 31447)	C.T*	**Diam

C.T* =* Charge transfer transition
* * Diam = Diamagnetic

According to the different results, the ligand behaves as bidentate and coordinate with the metal ions through nitrogen atom of azomethine and oxygen of carbonyl with two chloride ions form octahedral complexes as shown in (Fig.1).



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II)

Fig.1: Suggested structure for the complexes

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