sw uobaghdad edu iqSynthesis and Characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) Complexes with Symmetrical Schiff base

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Abstract:

New binuclear Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) Complexes of N_2S_2 tetradentate or N_4S_2 hexadentate symmetric Schiff base were prepared by the condensation of butane-1,4-diylbis(2-amino ethylcarbamodithioate) with 3-acetyl pyridine. The complexes having the general formula $[M_2LCl_4]$ (where L=butane-1,4-diyl bis (2-(z)-1-(pyridine-3-ylethylidene amino))ethyl carbamodithioate, M= Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II)), were prepared by the reaction of the mentioned metal salts and the ligand. The resulting binuclear complexes were characterized by molar conductance, magnetic susceptibility ,infrared and electronic spectral measurements. This study indicated that Mn(II), Ni(II) and Cu(II) complexes have octahedral geometry, while Co(II) Zn(II) and Hg(II) complexes are proposed to be tetrahedral structure .

Key words: Schiff base, transition metal complexes, dinuclear complexes.

Introduction:

Polydentate ligands having different geometry can coordinate to two or more metal ions [1]. Metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity and sensitivity towards the central metal atom[2]. Schiff bases have been used as chelating ligands in the field of coordination chemistry and their metal complexes of N and S have attracted considerable attention because of their physicochemical properties and pronounced biological activities. The N and S atoms play important role in coordination of metals at the active sites of numerous metallobiomoles[3]. Schiff base have wide applications in food industry, dye industry ,analytical chemistry , catalysis, antifungal, anticancer and herbicidal activites[4-6]. In the present investigation we report the preparation and characterization of N S-donor Schiff base butane-1,4-diyl bis(2-(z)-1-(pyridine-3-ylethylidene amino)) ethyl carbamodithioate and its complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) metal ions. The ligand and its complexes were characterized by physicochemical and spectral studies.

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Materials and Methods:

All the chemicals and solvents were of analytical grade reagents and used without further parification. Elemental analysis are carried out by using spectroscopic method on and reasonable results were obtained as given in (Table-1).

Infrared spectral analysis were recorded using fourier transform IR spectrophotometer Tensor 27, Brucker 2003 in the 400-4000 cm^{-1} range using KBr discs. Electrical conductivity measurements were carried out using conductivity measuring apparatus model PCM$_3$ Jenway at 25 ºC in 10^{-3} M solution of the compounds in DMF. The electronic spectra measurements were recorded on a Shimadzu UV-Vis. Spectrophotometer UV-1650 for 10^{-3} M solution of the compounds in DMF at 25 ºC using 1 cm quartz cell. The magnetic susceptibility measurements of complexes in the solid state were determined by the Faraday method at 25 ºC in a pyrex tube using Brucker BM6 instrument.

Preparation of ammonium -2-aminoethyldithiocarbamate [7]:

(0-1 mole, 6.68ml) of ethylenediamine was added drop wise to a mixture of (0.01 mole, 6.02ml) carbondisulfide and (0. 1 mol, 3.18ml) ammonium hydroxide in 20 cm^3 ethanol. The solution was stirred at 0ºC for about 1h. The white solid precipitate so obtained was filtered and isolated washed with coold ethanol and dried in vacuum.

Preparation of butane-1,4-diylbis(2-aminoethylcarbamodithioate[3]:

(0.02 mole, 3.06g) of ammonium-2-aminoethydithiocarbamate in the 15 cm^3 ethanol and chilled, to this a solution of (0.01 mol, 0.56g) potassium hydroxide in aqueous ethanol was mixed with constant stirring. An ice cold (0.01 mol,1.47ml) 1,4-dichlorobutane added to the mixed solution, keeping the temperature of the reaction mixture at 0ºC for 2hrs. After stirring the solution was allowed to room temperature and then filtered. The filtrate product was reduced to half its volume by evaporation. A yellow solid product separated out which was filtered, washed with small portion of ether and dried in vacuum .

Preparation of Schiff base ligand (L) [3]:

Schiff base ligand was prepared as follows: (0.01 mol, 3.26g) of butane-1,4-diylbis(2-aminoethylcarbamodithioate) dissolved in ethanol 50 cm^3 was mixed with (0.02 mol, 2.61ml) of 3-acetylpyridine. The resulting mixture was refluxed with boiling for 2hrs under constant stirring. The precipitate was then removed from the reaction mixture by filteration, washed with ethanol and dried in vacuum.

Preparation of complexes:

All the complexes were prepared by mixing 2:1 metal to ligand ratio as follows: A solution of (0.02 mol) Mn $Cl_2.4H_2O$ (3.94g), Co $Cl_2.6H_2O$ (4.74 g) ,Ni $Cl_2.6H_2O$ (4.74g) ,$CuCl_2.2H_2O$ (3.50g) ,$ZnCl_2$ (2.72g) , $HgCl_2$ (5.42g) in 20

cm^3 ethanol have been added to the solution 15 cm^3 of Schiff base ligand (L) (0.01 mol, 5.32g) with heating until a clear solution has been resulted.The resulting mixture was refluxed for one hour. Followed by evaporation to half its vacuum then called. The product was separated by filteration, washed with ether and dried in vacuum.

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

Compound	**Color**	**m.p (^oC)**	**ΛM (DMF) ($\Omega^{-1}.mol^{-1}.cm^2$)**	**% Yield**	**M% Found (calculated)**
L ($C_{24}H_{32}S_4N_5$)	Red	97	---	60	---
$[Mn_2(L)Cl_4]$	Pink	133	10	56	14.02 (13.60)
$[Con_2(L)Cl_4]$	Deep violet	127	17	70	14.88 (14.33)
$[Ni_2(L)Cl_4]$	Green	160	23	77	14.84 (14.33)
$[Cu_2(L)Cl_4]$	Violet	181	25	60	15.86 (15.76)
$[Zn_2(L)Cl_4]$	Pink	146	20	55	16.25 (16.77)
$[Hg_2(L)Cl_4]$	pink	117	10	55	37.31 (36.70)

Results and discussion:

The formation of the complexes may be represented by the following reaction:

$$2\ MCl_2.\ nH_2O\ +\ (C_{24}H_{32}S_4N_6) \longrightarrow [M_2(C_{24}H_{32}S_4N_6)Cl_4] + nH_2O$$

Where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), or Hg(II)
n = 0,2,4, or 6.

From the analytical data (Table 1), it was found that 2:1 metal to ligand molar ratios were obtained for complexes. All complexes are coloured solids , stable to air at room temperature and have good keeping qualities. They are insoluble in most organic solvents but they are soluble in dimethyl formamide (DMF) and dimethylsulphoxide (DMSO). Elemental analysis revealed that the complexes have the compositions $[M_2(L)Cl_4]$.

The molar conductivities Λ_M of the complexes in 10^{-3} M DMF are determined, the values shown in (Table-1) approached those expected for nonelectrolytes[8,9]. The active site of the ligand and its coordination to the metal ion were inferred by careful comparsion of the infrared spectra of the free ligand and their complexes. The infrared spectra of the ligand (Table-2) shows a bond in the region 1659 cm^{-1} as due to υC=N of the azomethine group[10,11], which shifts towards lower frequency region by about 22-39 cm^{-1} in case of the all complexes, suggesting coordination through N atom of the azomethine group[12,13]. The infrared spectra of dithiocarbamate group showed bond at 1014 cm^{-1} assigned to υC=S group shifted towards a lower frequency on coordination [3,12,13]. Another band which appeared at 1563 and 656 cm^{-1} due to υ(C=N)py stretching and bending in the free ligand are shifted to the lower field in the prepared complexes. This observation suggested coordination through pyridine nitrogen atom for complexes (1,3 and 4)[14]. Furthermore, the IR spectra of all complexes showed another band observed at about 3415 cm^{-1} due to the υNH group remained unaltered in the complexes indicating that there is no coordinaton through the NH group.

For the chloro complexes the υ(M-S), υ M-Cl band could not be observed because it is located below the limits of the infrared spectrophotometer. For all complexes new bands were found located at 472-538 cm^{-1} assigned to M-N stretching vibrations [3,12,13,18].

The infrared spectra of the complexes 1,3 and 4 showed bands at 635-652cm^{-1} due to υ(C=N)py [15]. The presence of these bands supported the formation of the complexes under investigation (Table-2).

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

Compound	υ (C=N)	υ (C=S)	υ (M=Py)	υ (C=N Py)	υ (M-N)
L ($C_{24}H_{32}S_4N_5$)	1659	1014	----	1563	----
[Mn_2(L)Cl_4]	1635	986	642	1532	483
[Con_2(L)Cl_4]	1635	978	----	---	480
[Ni_2(L)Cl_4]	1624	977	652	1539	480
[Cu_2(L)Cl_4]	1620	919	635	1540	472
[Zn_2(L)Cl_4]	1637	998	----	1562	489
[Hg_2(L)Cl_4]	1634	977	----	1561	538

The electronic spectra of the Schiff base ligand and its complexes were recorded at 25 ºC in DMF as the solvent (Table-3). The ligand is characterized by two absorption bands in the UV. region. A high intensity band appeared at 33770 cm^{-1} is attributed to π π^* transition of pyridine ring and a second band with lower intensity appeared at 29500 cm^{-1} is attributed to

n$\longrightarrow$ π^* transition of azomethine group[2,16,17].

The electronic spectra of manganese (II) complex the d-d trsansitions, doubly forbidden from the term $^{6}A_{1}g$ towards, the quartet terms $^{4}T_{1}g(G)$, $^{4}T_{2}g(G)$, $^{4}A_{1}g$, $^{4}Eg(G)$ exhibit a very small intensity and are conceald by the intraligand transitions. The absorption band at 25381-29412 cm^{-1} can be attributed to the charge transfer of ligand to metal[17,18].

The complex shows magnetic moment in the range 6.00 BM. Basing on this discussion a high spin octahedral arrangement may be proposed around Mn(II) ion(18). The Co(II) complex showed less intense band in the region 14577 cm^{-1} which correspond to the $^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(P)$ υ_{3} transition. This band is specific to the Co(II) ion in tetrahedral stereochemistry, a geometry also confirmed by the magnetic moment of the complex which is of 4.6 BM.[19,20]. The other two bands due $^{4}A_{2}(F) \longrightarrow {}^{4}T_{2}(F)$ υ_{1} and $^{4}A_{2}(F)$ $^{4}T_{1}(F)$ υ_{2} transitions were absence because they fall bellow the limits of our instrument. In the spectrum of the Ni(II) complex three bands of absorption at (14451, 15723 and 24631 cm^{-1}) are assignable to the transitions $^{3}A_{1}g(F)$ $^{3}T_{2}g(F\ )$ υ_{1} , $^{3}A_{2}g(F)$ $^{3}T_{1}g(F)$ υ_{2} and $^{3}A_{2}g(F)$ $^{3}T_{1}g(P)$ υ_{3}respectively These transition are characteristic of Ni(II) ion in octahedral coordination and this geometry is also supported by the value of the magnetic moment of 2.77 BM[20,21].

In case of Cu(II) complex, a brood asymmetric band was observed at 10870 cm^{-1} and assigned to the three combined transitions $^{2}B_{1}g \longrightarrow {}^{2}A_{1}g$, $^{2}B_{1}g$ $^{2}B_{2}g$ $^{2}B_{1}g$ ^{2}Eg . On the basis of electronic spectra distorted octahedral geometry around Cu(II) ion is suggested. The magnetic moment determination experimentally is of 2.0 BM and it supports an octahedral structure[18,22].

The 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. They were found to be diamagnetic as expected for d^{10} system[23,24]. Based on these data, a tetrahedral geometry has been assigned to the Zn(II) and Hg(II) complexes. Table-2 and Table-3.

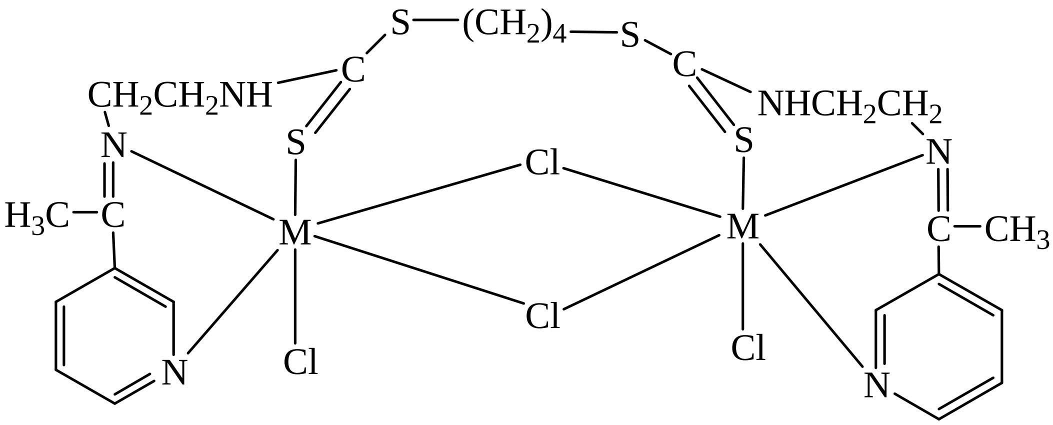
Table(3): The electronic spectra and magnetic moment of the ligand and its complexes.

Compound	Absorption region (cm^{-1})	Possible assignment	μeff B.M
L ($C_{24}H_{32}S_4N_6$)	*33770* *29500*	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	------
[$Mn_2(L)Cl_4$]	(25381, 29412)	C.T*	6.00
[$Co_2(L)Cl_4$]	14577	$^2A_2(F) \rightarrow {}^4T_1$ (P)	4.60
[$Ni_2(L)Cl_4$]	14451 15723 24631	$^3A_1g(F) \rightarrow {}^3T_2g(F)$ $^3A_1g(F) \rightarrow {}^3T_1g(F)$ $^3A_1g(F) \rightarrow {}^3T_1g(F)$	2.77
[$Cu_2(L)Cl_4$]	10877	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	2.00
[$Zn_2(L)Cl_4$]	(26178 ,32895)	C.T*	**Diam
[$Hg_2(L^3)Cl_4$]	(27624 , 29412)	C.T*	**Diam

C.T* =* Charge transition

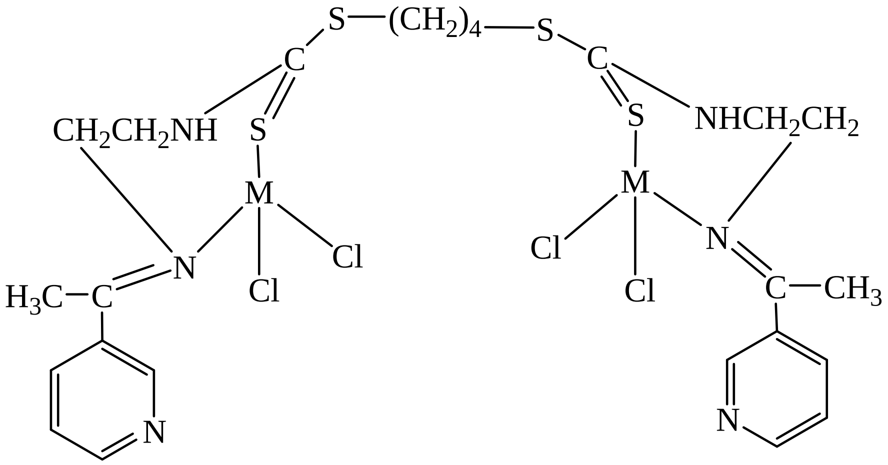
* * Diam = Diamanetic

From the above discussion of various physicochemical and spectral studies, we conclude that the Schiff base ligand (L) in all complexes coordinated as a tetra or hexacoordination chelating ligand. The ligand is used as stabilizer for dinuclear metal complexes and accordind to the measurements and theoretical calculations the Mn(II), Ni(II) and Cu(II) complexes have octahedral geometries, while Co(II) , Zn(II) and Hg(II) complexes have tetrahedral geometry around central metal ion, Fig.1 and Fig.2.



M = Mn(II), Ni(II) or Cu(II)

Fig.(1): Suggested structure of the octahedral homobinuclear complexes.



M = Co(II), Zni(II) or Hg(II)
Fig.(2) Suggested structure of the tetrahedral complexes.

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تحضير وتشخيص معقدات Mn(II) و Co(II) و Ni(II) و Cu(II) و Zn(II) و Hg(II) مع قواعد شيف المتماثلة.

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الخلاصة:

تضمن البحث تحضير معقدات ثنائية النوى الجديدة للمنغنيز (II) والكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) والزئبق (II) مع ليكاند قاعدة شيف المتماثلة الذي يكون رباعي التناسق عن طريق الذرات المانحة N_2S_2 او سداسي التناسق عن طريق الذرات المانحة N_4S_2 والمحضرة من تكثيف بيوتان -4,1-ثنائي يل بس (2-امينو اثيل كارباموثنائي ثايويت) مع 3-استيل بريدين. ان الصيغ الكيميائية لهذه المعقدات هي $[M_2LCl_4]$ (عندما L= بيوتان-4,1-ثنائي يل بس (2-(z)-1-(بريدين-3-يل اثيليدين امينو)) اثيل كارباموثنائي ثايوويت M = (Mn(II)، Co(II)، Ni(II)، Cu(II)، Zn(II)، Hg(II))). تم تشخيص المعقدات ثنائية النوى الناتجة بطريقة قياس التوصيلية المولارية والخواص المغناطيسية واطياف الاشعة تحت الحمراء والاطياف الالكترونية. اظهرت هذه الدراسات بان معقدات المنغنيز والنيكل والنحاس الثنائية الموجبة تمتلك التناسق السداسي ولها بنية ثماني السطوح واما معقدات الكوبلت والخارصين والزئبق الثنائية الموجبة فكانت رباعية التناسق ذات بنية رباعي السطوح الاكثر احتمالا.