Formation of Binuclear Metal Complexes with Multidentate Schiff-base Oxime Ligand: Synthesis and Spectral Investigation

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Abstract

The new polydentate Schiff-base oxime (1E,1`E)-2hydroxy-3-((E)-(2-((E)-2-hydrxy3-((E)-(hydroxyimino)methyl)-5-methylbenzyldeneamino)ethylimino)methyl)-5-methylbenzaldehyde oxime H_4L and its binuclear metal complexes with Mn(II), Fe(II), Co(II) and Cu(II) are reported. The reaction of 2,6 diformyl–4–methyl phenol with hydroxyl amine hydrochloride in mole ratios of 1:1 gave the precursor (E)-2-hydroxy-3-((hydroxyimino)methyl)-5-methylbenzaldehyde. Condensation reaction of precursor with ethylenediamine in mole ratios of 2:1 gave the new N_4O_2 Schiff-base oxime ligand H_4L. Upon complex formation, the ligand behaves as a tribasic hexadantate species. The mode of bonding and overall geometry of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed tetrahedral geometries for Mn(II), Fe(II), Co(II) complexes and square planar geometry about Cu(II) complex of general formulae $[M_2(HL)](Cl)(H_2O)$. Molecular structure of the for Mn(II), Fe(II), Co(II) complexes has been optimised by CS Chem 3D Ultra Molecular Modeling and Analysis Program and supported four coordinate geometry.

Keywords: Schiff-base ligand; (1E,1`E)-2hydroxy-3-((E)-(2-((E)-2-hydrxy3-((E)(hydroxyimino)methyl)-5-methylbenzyldeneamino)ethylimino)methyl)-5-methylbenzaldehyde oxime; Binuclear complexes; Structural study.

Introduction

The development of Schiff-base species based on transition metal compounds and polydentate ligands has been the subject of extensive research due to their potential applications in materials science [1, 2] and environmental chemistry and medicine. Schiff-base compounds play a vital role in coordination chemistry, due to their ability to react with a range of metal ions forming stable complexes which have applications in different fields. One interesting application in the field of coordination chemistry has been to investigate the use of Schiff-base ligands to develop phenoxo-bridged binuclear complexes with homometallic and/or heterometallic centres. This includes design molecules containing paramagnetic metal centres are able to self-assemble through metal-ligand interactions rendering supramolecular assemblies with interesting structural and magnetic properties. [3-7]. Schiff-base metal complexes also have applications in biomedical [8, 9], biomimetic and catalytic systems [10, 11]. Oxime chemistry is one vital research field for inorganic and bioinorganic chemist. The role of oximes and their metal complexes, in particular cobalt-oximes, in the biological systems make them one interested branch in the coordination and organometallic chemistry. Significant publications dealt with the development of coordination chemistry are related to the preparation and charachterisation of oximes and their metal complexes. These include the investigation of new synthetic methods and coordination modes of oxime species upon complexation [12]. It is well known that oxime and oximato species can bind a metal in different coordination modes. Gupta et al. [13] reported a simple and general route to the synthesis of organo-cobaloximes with mixed dioxime ligands of the general formula, [RCo(L)(dpgH)py] (where: L= dmgH and ChgH; R= Me–Decane: DmgH= dimethyl glyoxime; ChgH= 1,2–cyclohexanedioneglyoxime). The mode of bonding was investigated through physico-chemical and spectroscopic methods. X–ray crystal structures confirmed the preparation of six-coordinate cobal-oxime complexes. It is well documented that oxime compounds and their complexes with transition metals have many applications in medicine, biology, industry, and catalysis [14]. Recently, we reported the formation of polymeric chain assemblies of some phenoxo-bridged binuclear transition metal ions with the mutidentate Schiff-base (E)-6,6`-((1E,1`E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-ylidene))bis(4-methyl-2-((E)(pyridine-2-ylmethylimino)methyl) phenol). The ligand has been specifically designed in which the involvement of the pyridyl moieties played effective role in ensuring the formation of ladder-type structures [15]. As part of our continuing efforts to explore the use of multidentate Schiff-base ligands for the synthesis of new complexes, we describe here the synthesis and spectral investigation of some phenoxo-bridged binuclear transition metal ions with the new multidentate oxime- Schiff-base ligad namely (1E,1`E)-2hydroxy-3-((E)-(2-((E)-2-hydrxy3-((E)-(hydroxyimino)methyl)-5-methylbenzyldeneamino)ethylimino)methyl)-5- methylbenzaldehyde oxime H_4L.

Experimental

Materials and methods

All reagents were obtained commercially (Aldrich) and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use. 2,6-Diformyl-4-methyl-phenol was prepared by a method published in [16].

Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr or CsI discs using a Shimadzu 8300 FTIR spectrophotometer from 4000-250 cm^{-1}. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Electronic spectra were measured from 200-900 for 10^{-3} M solutions in DMF at 25°C using a Shimadzu 160 spectrophotometer. Mass spectra obtained by positive Electron Impact (EI) recorded on a VG autospec micromass spectrometer. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Jonson Mattey Catalytic System Division).

Synthesis

Preparation of the precursor (E)-2-hydroxy-3-((hydroxyimino)methyl)-5-methylbenzaldehyde To a mixture of 2,6–diformyl–4–methyl phenol (5.0 g, 30.0 mmol) dissolved in ethanol (5 mL) was added a mixture of hydroxylamine hydrochloride (2.12 g, 30.0 mmol) in H_2O (15mL). The mixture was stirred, and then cooled to (–5°C). An aqueous solution of sodium hydroxide (20 %) was added slowly, and the temperature was kept below (0 °C) with vigorous stirring for 2 h. The mixture was diluted with water (50 mL), and unreacted materials were removed by filtration. Glacial acetic acid was added to the filtrate to adjust it to a neutral pH. The solid was collected by filtration, washed with benzene and air dried, to give (3.25 g, 60%) of the title compound, m.p. = 142°C. IR data (cm^{-1}): 3238 ν(O–H)oxime, 3310 ν(O–H)phenol, 1637 ν(C=O), 1604 ν(C=N), 1265 ν(C–O), 1060 ν(N–O).

Preparation of the Schiff-base H_4L

A solution of ethylenediamine (0.5g, 8.0 mmol) in methanol (10 mL) was added slowly to a mixture of the precursor (3.0 g, 16 mmol) dissolved in methanol (20 mL). The reaction mixture was allowed to reflux for 2 h, and then stirred at room temperature for a further 1 h. A light brown solid was collected by filtration, recrystallised from a mixture of hot methanol/ H_2O (1:1) and dried under vacuum to give the ligand as a light–brown solid. Yield (3.75 g, 59%), m.p = 165°C. IR data (cm^{-1}): 3310 ν(O–H)phenolic; 3238 ν(O–H)oxime; 1629, 1637 ν(C=N)imine; 1575, 1565 ν(C=N)oxime; 1373 ν(Phenoxide); 1039, 1020 ν(N-O); 1373 ν(phenoxide) and 2374 $\nu(H–O^{\cdots}H)$. The positive EI mass spectrum of H_4L showed the following fragments; 338 (5 %) $[M–(CH=N–OH)]^+$, 231 (3 %) $[M–(CH=N–OH–C_6H_2–Me–OH)]^+$, 214 (64 %) $[M–\{CH=N–OH–C_6H_2–Me–(OH)_2\}]^+$, 186 (12 %) $[M–\{CH=N–OH–C_6H_2–Me–(OH)_2–N=CH\}]^+$, 132 (3 %) $[M–\{CH=N–OH–C_6H_2–Me–(OH)_2–N–CH–(CH_2)_2–N=CH\}]^+$, 89 (5 %) $[M–\{CH=N–OH–C_6H_2–Me–(OH)_2–N=CH–(CH_2)_2–N=CH–CH=N–OH\}]^+$.

General synthesis of the complexes

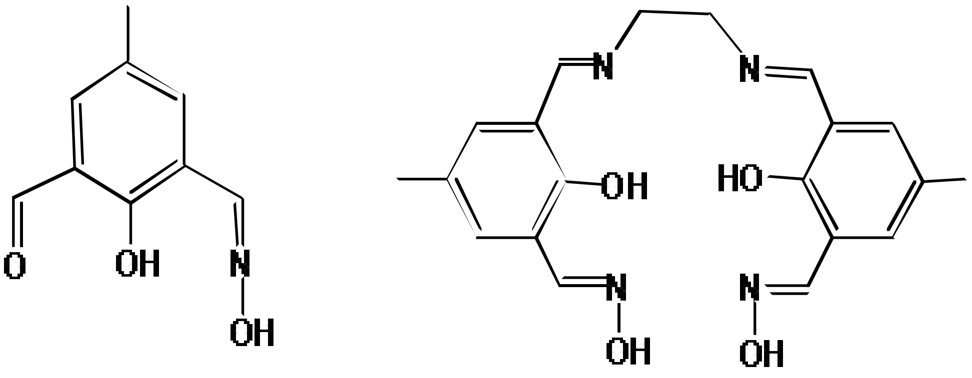
A solution of the Schiff-base (1 mmol) and potassium hydroxide (2.1 mmol) in methanol (25 mL) was stirred for 15 min. A methanolic solution (15 mL) of the metal chloride salt (2 mmol) was then added dropwise. The resulting mixture was refluxed under N_2 for 2 h, resulting in the formation of a solid mass which was washed several times with methanol (10 mL), and then ether (15 mL). Elemental analysis data, colours and yields for the complexes are given in (Table 1).

Molecular modelling

3D molecular modelling of the proposed structure of the complexes was performed using CS Chem 3D Ultra Molecular Modelling and Analysis Program [17]. It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It is well known program and has the ability to handle transition metal complexes [18]. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries.

Results and Discussion

The precursor (E)-2-hydroxy-3-((hydroxyimino)methyl)-5-methylbenzaldehyde (Scheme 1 A) was obtained by condensation reaction using one equivalents of 2,6-diformyl-4-methyl-phenol and one equivalent of hydroxyl amine hydrochloride. The IR spectrum of the precursor showed characteristic bands due to the ν(O-H) oxime and ν(O-H) phenol, ν(C=O), ν(C=N), ν(N-O), and ν(C=C) functional groups. The reaction of (E)-2-hydroxy-3-((hydroxyimino)methyl)-5-methylbenzaldehyde with ethylenediamine in mole ratios of 2:1, respectively afforded the new Schiff-base oxime (1E,1`E)-2hydroxy-3-((E)-(2-((E)-2-hydrxy3-((E)-(hydroxyimino)methyl)-5-methylbenzy-ldeneamino)ethylimino)methyl)-5-methylbenzaldehyde oxime H_4L in moderate yield (Scheme 1B).



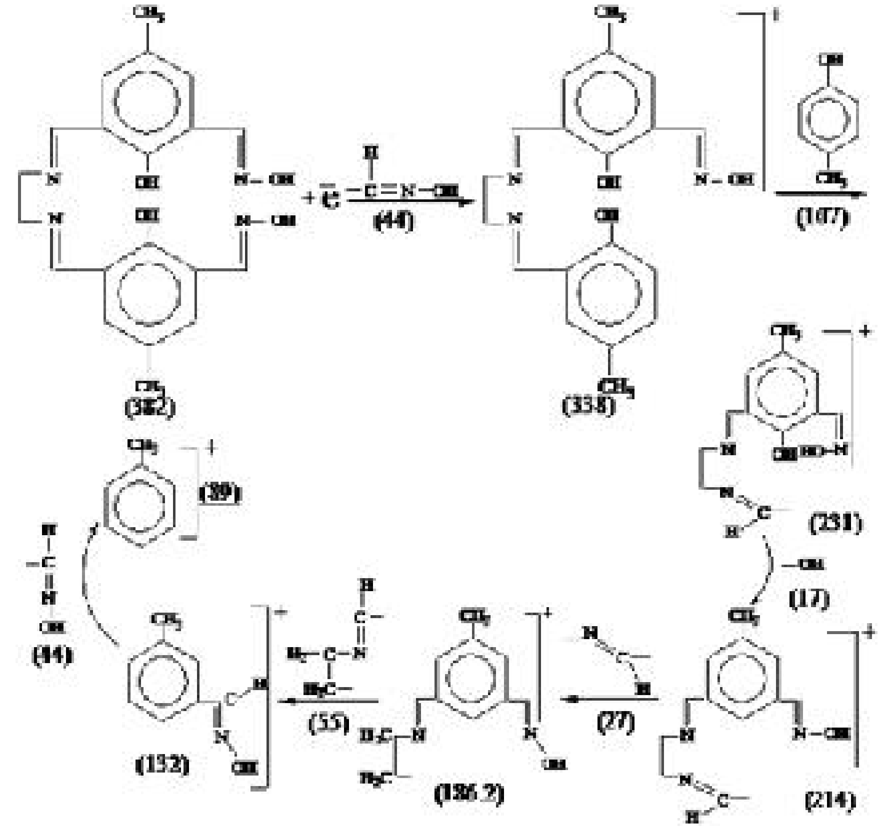
A

B

Scheme 1: Chemical structures of precursor and Schiff-base oxime ligand

The Schiff-base oxime was characterised by elemental analysis (Table 1), IR (Table 2), UV–Vis (Table 3) spectroscopy and mass spectrometry. The IR spectrum of the free Schiff-base shows characteristic bands at 1629; 1576; 1039, 1020 and 3238 cm^{-1} due to the ν(C=N) imine, ν(C=N) oxime, ν(N-O) and ν(O-H) of the oxime functional groups, respectively. The spectrum showed also abroad band at 3310 cm^{-1} assigned to the ν(O–H) stretching of the phenol group. The weak bands appeared around 2374 and 1762 cm^{-1} are due to the ν(H–O¨H) stretching and δ(H–O¨H) bending indicating the presence of the hydrogen bonding in the molecule. The UV-Vis spectrum of H_4L

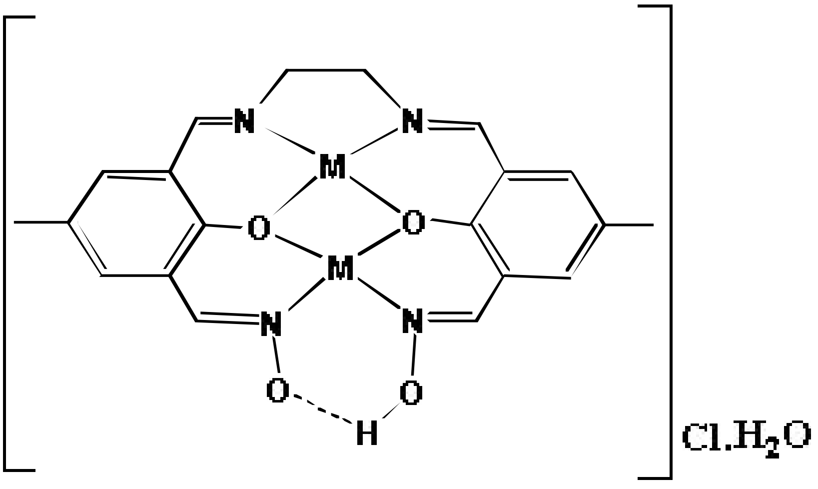
exhibits an intense absorption peak at 285 nm, assigned to $\pi \rightarrow \pi^*$. The peak at 350 nm assigned to $n \rightarrow \pi^*$ transition. The mass spectrum does no show the parent ion fragment (M). This may be due to the harsh condition (EI technique) used to obtain the spectrum. The mass spectrum was consistent with the proposed structural formula. Figure 1 shows the EI spectrum of the ligand, while the fragmentation pattern of the ligand displayed in scheme 2.



Scheme 2: Mass fragmentation pattern of the Schiff base oxime ligand

The bridged phenoxy binuclear complexes of the ligand with Mn^{II}, Fe^{II}, Co^{II} and Cu^{II} were synthesised by heating 1 mmole of the ligand with 2 mmole of the metal chloride in methanol using potassium hydroxide as a base. The use of a base in these reactions was found to be essential since otherwise only an intractable mixture was recovered. However, in methanolic potassium hydroxide, deprotonation of the ligand occurs facilitating the formation of the complexes $[M^{II}_2(HL)](Cl).H_2O$ (M = Mn(II), Fe(II), Co(II) and Cu(II)) (Scheme 3). The complexes are air-stable solids, soluble in DMF but not in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra.

The analytical data (Table 1) agree well with the suggested formulae. Conductivity measurements of Mn(II), Fe(II), Co(II), Cu(II), Cd(II) and Hg(II) complexes lie in the 54.6-77.9 $cm^2\Omega^{-1}mol^{-1}$ range, indicating their 1:1 electrolytic behavior (Table 1) [19].



M = Mn(II), Fe(II), Co(II), Cu(II)

Scheme 3: Proposed structures of binuclear Schiff-base oxime ligand

The important infrared bands for the complexes together with their assignments are listed in Table 2. The IR spectra of the complexes exhibited H_2L bands with the appropriate shifts due to complex formation (Table 2). The absence of a peak around 3310 cm^{-1} in all the complexes

indicate the absence of phenolic ν(OH) due to deprotonation followed by complexation [20]. The ν(C=N)imine and ν(C=N)oxime stretching bands at 1637 and 1575 cm^{-1}, respectively in the free Schiff-base is shifted to lower frequency and observed around 1610-1629 cm^{-1} and 1496-1560 for the complexes. The bands are assigned to a ν(C=N) stretch of reduced bond order. This can be attributed to delocalisation of metal electron density (t_{2g}) to the π-system of the ligand [21, 22], indicating coordination of nitrogen of the C=N moieties to the metal atoms [23]. Further, bands in the region of 1527–1558 cm^{-1} in all the complexes suggest phenoxide bridging with the metal atoms [15, 24]. The strong ν(N–O) stretching bands at 1039 and 1020 cm^{-1} in the free ligand are shifted to higher frequencies and appeared at 1085-1184 and 1033-1160 cm^{-1} for the complexes. The increase in the N–O bond order can be attributed to the distribution of the π-electron of the oxime moiety upon complex formation

[25]. It seems that the two N–O bands are non–equivalent. These results are in accord with those reported by Al–Jeboori et al. [26]. At lower frequency the complexes exhibited bands around 410–450 and 536–581 cm^{-1} which could be assigned to ν(M–N) and ν(M–O) vibration modes, respectively [15, 21]. Due to the larger dipole moment change for M–O compared to M–N, the ν(M–O) usually appears at higher frequency than the ν(M–N) band [27]. Additional bands at 2516–2560 and 1650–1750) cm^{-1} were assigned to ν(H–O¨H) and δ(H–O¨H), respectively. The broad band observed around 34800-3527 cm^{-1} assigned to (H_2O) lattice molecule [28]. The electronic spectra and magnetic moment data of the dimeric complexes are summarised in (Table 3). The electronic spectra of the complexes Mn(II), Fe(II), Co(II) and Cu(II) exhibit a high intensity peak around 299-355 nm related to the intra-ligand field transition. The electronic spectrum of the Mn(II) complex showed additional peaks at 315 and 396 nm assigned to the charge transfer (CT) and d–d transitions, respectively in a distorted tetrahedral geometry [29, 30]. The observed magnetic moment of this complex is typical for a terahedral structure. The electronic spectrum of the Fe(II) complex is consistent with tetrahedral assignment [29, 31]. The magnetic moment of this complex is typical for tetrahedral structure. The spectrum of the Co(II) complex exhibited two bands characteristic of tetrahedral Co(II) complexes [29-32]. The magnetic moment was consistent with the tetrahedral environment around Co(II). The magnetic moment value (Table 3) observed for the Cu(II) complex agrees well with the proposed square planar geometry. The electronic spectrum of the Cu(II) complex shows a broad band which can be attributed to $^2B_1g \rightarrow {}^2B_2g$ transition, corresponding to square planar geometry [29, 33]. The magnetic moment values for the binuclear complexes at RT are lower than the predicted values. This may arise from metal–metal interactions through the phenolic oxygen atoms and/or extensive electron delocalisation, which may be related to the formation of dimeric structures [34, 35].

Dmolecular modelling and analysis of bonding modes

Molecular mechanics attempts to reproduce molecular geometries, energies and other features by adjusting bond length, bond angles and torsion angles to equilibrium values that are dependent on the hybridization of an atom and its bonding scheme. In order to obtain estimates of structural details of these complexes and in view the four-coordination of all the complexes, we have optimized the molecular structure of $[Co^{II}_2(HL)](Cl)(H_2O)$ as a representative compound (Figure 2). The details of bond lengths and bond angles per the 3D molecular structure are given in Tables 4. Energy minimization was repeated several times to find the global minimum [36]. The energy minimization value for tetrahedral and without restricting the structure for the Co-complex is almost same i.e, 560.8472 Kcal /mol. The molecular modelling for the modulated Co(II)-complex (figure 2 and Table 4) shows the bond lengths bond angles around copper atom which indicate the distorted tetrahedral geometry around Co(II) ion [37], and thus the proposed structure of the Co(II)-complex as well as of the others, are acceptable.

Conclusion

In this paper, we have explored the synthesis and coordination chemistry of some binuclear complexes derived from the multidentate Schiff-base oxime ligand H_4L. The ligand behaves as a tribasic octadentate species upon complexation with the involvement of the nitrogen atoms of the oxime groups in coordination for all complexes. The low magnetic moment values of these complexes are in accord with the formation of phenoxy-bridged binuclear metal complexes.

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Table(1): Colours, yields, elemental analyses, and molar conductance values.

Compound	Colour	Yield (%)	m.p °C	Found (Calcd.) (%)					Λ_M(cm$^2\Omega^{-1}$mol^{-1})
				M	C	H	N	Cl	
H_4L	Light brown	59	165	-	62.9 (62.8)	6.3 (5.6)	14.2 (14.6)	-	-
$[Mn^{II}_2(HL)](Cl)(H_2O)$	Brown	70	190	19.4 (19.7)	45.7 (45.3)	3.9 (4.2)	9.9 (10.1)	6.8 (6.4)	54.6
$[Fe^{II}_2(HL)](Cl)(H_2O)$	Dark red	65	210	19.5 (20.0)	45.5 (45.2)	3.8 (4.2)	9.9 (10.0)	6.1 (6.4)	77.9
$[Co^{II}_2(HL)](Cl)(H_2O)$	Blue	68	180	21.2 (20.9)	45.1 (44.7)	4.2 (4.1)	9.6 (9.9)	6.6 (6.3)	70.8
$[Cu^{II}_2(HL)](Cl)(H_2O)$	Green	66	215	22.3 (22.1)	43.7 (44.0)	3.7 (4.0)	10.1 (9.8)	5.8 (6.2)	69.7

Table (2): IR frequencies (cm^{-1}) of the compounds.

Compound	ν(C=N)iminic	ν(C=N)oxime	ν(Phenoxide)	ν(N-O)	ν(H–O⋯H)	ν(M-O)	ν(M- N)
H_4L	1637, 1929	1575, 1565	1373	1039, 1020	2374	-	-
$[Mn^{II}_2(HL)](Cl).H_2O$	1620	1560	1538	1085, 1033	2518	536	450
$[Fe^{II}_2(HL)](Cl).H_2O$	1618	1550	1545	1087, 1047	2516	541	410
$[Co_2(HL)](Cl).H_2O$	1610	1504	1527	1114, 1083	2518	584	425
$[Cu_2(L)(H_2O)_2]Cl_2$	1629	1569	1558	1184, 1160	2560	585	435

Table(3): Magnetic moment and u.v-vis spectral data in DMF solutions.

Compound	μ_{eff} (BM) (per atom)	Band position (λnm)	Extinction coefficient ε_{max}($dm^3 mol^{-1} cm^{-1}$)	Assignments
H_4L		285	930	$\pi \rightarrow \pi^*$
		350	420	$n \rightarrow \pi^*$
$[Co^{II}_2(HL)](Cl).H_2O$	3.88	299	1600	Ligand field
		607	185	${}^4T_1g^{(F)} \rightarrow {}^4T_1g^{(P)}$
		678	281	${}^4T_1g^{(F)} \rightarrow {}^4A_2g^{(F)}$
$[Mn^{II}_2(HL)](Cl).H_2O$	4.9	297	780	Ligand field
		366	1100	CT
		414	101	${}^6A_1g \rightarrow {}^4T_1g$
$[Fe^{II}_2(HL)](Cl).H_2O$	5.2	355	644	Ligand field
		375	388	CT
		418	200	${}^5E_2^{(D)} \rightarrow {}^5T_2^{(D)}$
$[Cu^{II}_2(HL)](Cl).H_2O$	1.46	299	1500	Ligand fied
		383	478	CT
		650	250	${}^2B_1g \rightarrow {}^2A_1g$

Table(4): Proposed bond lengths and bond angles of $[Co_2(HL)](Cl)(H_2O)$.

Type of bond	Bond lengths(Å)	Type of bond	Bond angles(°)
Co_1–N_1	1.844	N_1–Co_1–N_2	81.0196
Co_1–N_2	1.849	N_4–Co_2–N_3	79.7111
Co_2–N_3	1.855	O_2–Co_1–O_1	58.6714
Co_2–N_4	1.857	O_1–Co_2–O_2	58.5915
Co_1–O_1	1.872	N_1–Co–O_1	83.7982
Co_1–O_2	1.877	N_1–Co_1–O_2	128.0165
Co_2–O_1	1.860	N_2–Co_1–O_1	112.1927
Co_2–O_2	1.893	N_2–Co1–O_2	81.8360
N_3–O_3	1.381	N_3–Co2–O_2	110.1736
N_4–O_4	1.333	N_4–Co2–O_2	79.6107
C=N_1	1.872	N_4–Co2–O_1	128.2319
H_2C=N_1	1.510	N_3–Co_2–O_1	87.0565
H_2C=N_2	1.502	Co_1–O_2–Co_2	98.8544
C=N_3	1.274	Co_1–O_1–Co_2	100.2434
C=N_4	1.278		
C–O_1	1.547		
C–O_2	1.529		
O–H	0.894		
O⋯H	1.199		

(Å) = Angstrom (°) = Degree

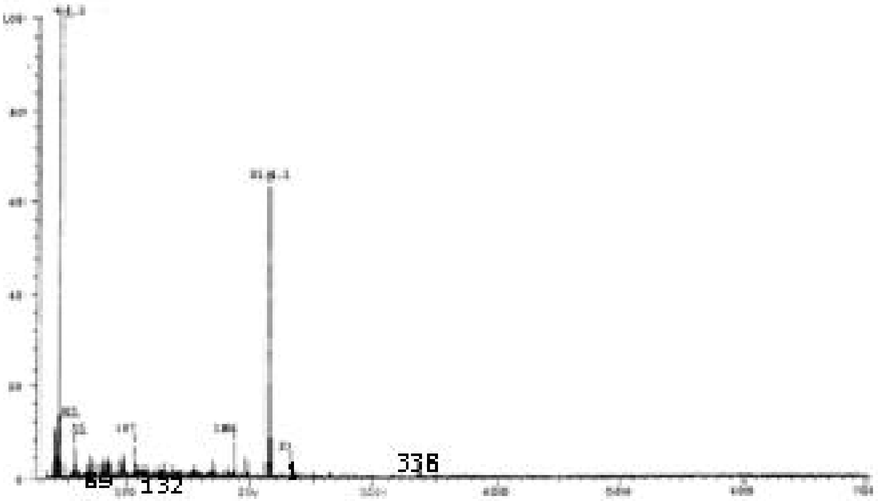

Fig.(1): (EI) mass spectrum of the Schiff-base oxime ligand

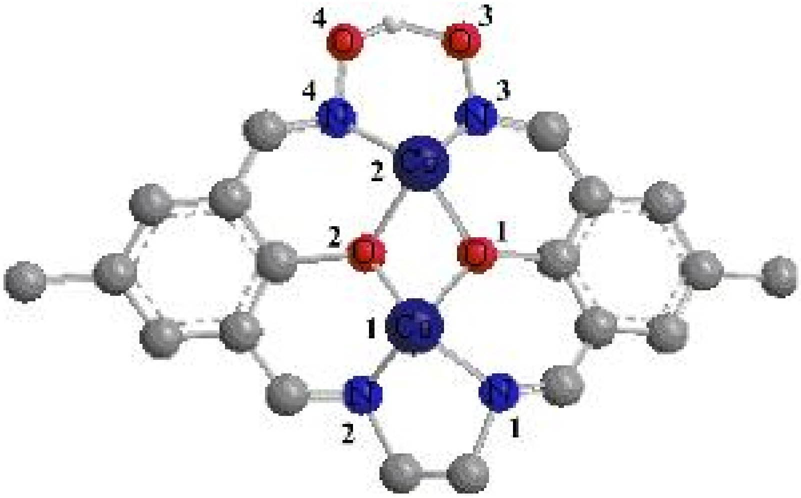

Fig.(2): 3D molecular modelling of complex $[Co^{II}_2(HL)]^+$

تكوين معقدات ثنائية النواة لليكاند قواعد شف اوكزيمية متعددة السن
تحضير مع دراسات تشخيصية:

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قبل البحث في :12 تشرين الثاني 2008

الخلاصة

تضمن البحث تحضير ليكاند قاعدة شف اوكزيمية متعددة السن [ثنائي (2- هايدروكسي-3- فورمايل أوكسيم-5- ميثل بينزيالدأمايد)- نتروجين- اثيلين(H_4L) ومعقداتها ثنائية النواة مع (الكوبلت$^{(II)}$، المنغنيز$^{(II)}$، الحديد$^{(II)}$، النحاس$^{(II)}$) . تم تحضيرالليكاند بمفاعلة 2,6 diformyl–4–methyl phenol مع hydroxyl amine hydrochloride . وبالنسبة المولية1:1 ليعطي المشتق (E)-2-hydroxy-3-((hydroxyimino)methyl)-5-methylbenzaldehyde

في الخطوة الاخيرة تم مفاعلة المشتق مع الاثلين داي امين وبالنسبة المولية2:1 ليعطي اليكاند الاوكسيمي نوع (H_4L N_4O_2)عند تكوين المعقد يكون اليكاند ثلاثي القاعدية سداسي المنح(السن).طبيعة التأصر واشكال المعقدات تم تعينها بالطرق الطيفيةوالفيزياوية.اعطت هذه الدراسات التناسق الرباعي السطوح لمعقدات (الكوبلت$^{(II)}$، المنغنيز$^{(II)}$، الحديد$^{(II)}$)وشكل المربع المستوي حول ايون النحاس وبالصيغة العامة التالية:

$[M_2(HL)](Cl)(H_2O)$.

تم توضيح الشكل الجزيئي للمعقدات باستخدام برنامج CS Chem 3D والذي اوضح التناسق الرباعي للمعقدات.

الكلمات المفتاحية :قواعد شف ،ليكاند،اوكزيم ،معقدات ثنائية النواة تحضير مع دراسات تشخيصية