Synthesis and Characterization of a New Tetradentate N-isopentylidine hydrazinedithiocarboxylic methyl ester Schiff Base Ligand for Three Homotrinuclear Metal Complexes

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Abstract

The new tetradentate N-isopentylidine hydrazinedithiocarboxylic methyl ester Schiff base ligand (L) was used as stabilizer ligand for the homotrinuclear complexes were prepared by condensation of ammonium hydrazinedithiocarboxylic methyl ester and 3-pentanone and to use them into in-situ reactions with metal chloride salts (M) in 3 : 2 molar ratio (Metal : Ligand) in ethanol solution to yield Schiff base homotrinuclear complexes of the general formula is $[M_3(L)_2Cl_2(H_2O)_2]$ where M refers to Co(II) (1), Ni(II) (2) and Cu(II) (3). The suggested structures of the complexes were characterized by using elemental analysis, molar conductivity, FT-IR and UV-Vis spectroscopy and magnetic susceptibility measurements as well as MM2 theoretical calculations of the complexes studied by using (CsChem3D Ultra program package) which is identical with the experimental results.

Key words: *Schiff base, ammonium hydrazinedithiocarboxylic methyl ester, 3-pentanone , Homotrinuclear complexes, Characterization.*

ملخص

تم في هذا البحث قاعدة شيف الجديدة رباعي السن n-ايزوبنتيلدين هيدرازين ثنائي ثايوكاربوكسيل ميثل استر (L) استعملت لاستقرار المعقدات الفلزية ثلاثية النوى المتجانسة التي حضرة بالتفاعل موضعيا و ذلك بتكاثف 3-بنتانون و هيدرازين ثنائي ثايوكاربوكسيل ميثل استر مع كلوريد الفلزات (M) و بنسبة مولية 2:3 (فلز : ليجاند) في محلول الايثانول لإنتاج معقدات قواعد شيف ثلاثية النوى والتي تحمل الصيغة العامة $[M_3(L)_2Cl_2(H_2O)_2]$ حيث تمثل M ايونات الكوبلت (II) او النيكل (II) او النحاس (II). التراكيب المقترحة لهذا الليجاند (L) و معقداتها تم تشخيصها عن طرق التحليل الدقيق للعناصر و التوصيلية المولارية الكهربائية و اطياف الاشعة تحت الحمراء و الاطياف الالكترونية و الحساسية المغناطيسية بالإضافة الى حساب MM2 لهذه المعقدات عن طريق برنامج (CsChem3D Ultra program package) حيث تم ربطها بالنتائج العملية

INTRODUCTION

Schiff base derivatives from dithiocarbamate have played and continue to play an important role in the development of coordination chemistry. Schiff bases and their metal complexes are becoming increasingly important in recent years due to their biological activity as antiviral[1], antibiotics [2] and anti-tumour agents [3] due to presence of their specific moiety and industrial applications as luminescencechemical probes sensors [4], catalysis [5] and antioxidants [6]. Also they are important due to their facile syntheses and multi-nuclear [7,8] a successful this strategy allowing for the control of the nuclearity consists in the ingenious use of compartmental ligands [9,10] which are organic molecules able to hold together two or more metal ions. Moreover, discrete homo and hetro-polynuclear complexes have contributed to understanding of the factors governing the sign and magnitude of exchange interaction between paramagnetic ions, either identical or different [11]. For example, Mirza A. H et al. have tested the ability of the 2-benzoylpyridine Schiff bases derived from S-methyl- and S-phenyldithiocarbazates ligands and their complexes to inhibit tumor cell growth against K562 leukaemia cell line [12]. The aim of the present research is the synthesis and characterzition study of new cobalt (II), nickel (II) and copper (II) coordination with new Schiff base ligand.

MATERIALS AND METHODS

General: Hydrazine hydrate, carbon disulphide, ammonium hydroxide, methyl iodide, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$, 3-pentanone and ethanol (96%) were of analytical reagent grade (BDH, Aldrich or Fluka). The ammonium hydrazinedithiocarboxylate, ammonium hydrazinedithiocarboxylate, hydrazinedithiocarboxylic methyl ester ligands and Schiff base complexes were analyzed for carbon, hydrogen and nitrogen using 1106 (Carlo Erba) microanalyser. Infrared absorption spectra were recorded on a Unicam SP-2000 spectrophotometer as CsI discs in the range

200-4000 cm^{-1}. The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker B.M. 6 instrument. The electronic spectra were recorded on a Shimadzu UV/Vis spectrophotometer (range 200-1100 nm), model 160 Koyoto (Japan) using acetonitrile as a solvent. Conductivity measurements were carried out on 10^{-3} M solutions of the complexes in acetonitrile at room temperature on a digital conductivity meter, model 4070 (Jenway). Theoretical computation was applied on the suggested structures of the prepared complexes using CsChem3D Ultra program package .

Preparation of the NH_4L ligand: Ammonium hydrazinedithiocarboxylate (NH_4L) is shown in the Figure 1, it was prepared by the reaction of hydrazine hydrate with Carbon disulphide in presence of ammonium hydroxide is shown in the equation 1 [13].

$$NH_2NH_2 + CS_2 \longrightarrow NH_2NH_2CS_2^{\ominus}H^{\oplus}$$

$$NH_2NCS_2^{\ominus}H^{\oplus} + NH2OH \longrightarrow NH_2NCS_2^{\ominus}NH_4^{\oplus} + H_2O$$

Equation 1: Preparation of the NH_4L ligand

Preparation of the HL ligand: Hydrazinedithiocarboxylic methyl ester (HL) is shown in the Figure 1, it was prepared by the methylation of the ammonium hydrazinedithiocarbamate 0.02 mol with methyl iodide 0.01 mol in aqueous solutions is shown in the equation 2 [13].

$$NH_2NCS_2^{\ominus}NH_4^{\oplus} + CH_3I \longrightarrow NH_2NCS_2CH_3 + NH_4I$$

Equation 2: Preparation of the HL ligand

Preparation of Schiff base complexes: Aqueous solution of 0.033 mol of the hydrated metal chloride ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$) was added to an ethanolic solution of the 0.022 mol of the hydrazinedithiocarboxylic methyl ester with 0.05 mol 3-pentanone. The mixture was refluxed for 15 min and then cooled to room temperature. The product was then washed with ethanol and dried over P_2O_5 in a desiccator vacuum for 24 h.

Theoretical calculations: The optimized geometry, steric energy and MM2 calculated of the prepared ligands and Schiff base complexes were done using CsChem3D Ultra program package [14].

RESULT AND DISCUSSION

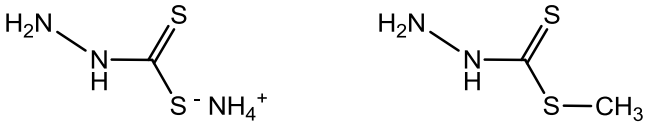
Syntheses and physical properties: The Schiff base complexes were obtained from a refluxing mixture of the ammonium hydrazinedithiocarboxylic methyl ester and 3-pentanone and to use them into in-situ reactions with metal chloride salts in 3 : 2 molar ratio (M : L). The following equation general reaction 3 represent formation of the Schiff base complexes. The complexes were characterized by using elemental analyses and magnetic susceptibility measurements are listed in the Table 1, the FT-IR data are listed in the Table 2 and the IR spectrum are shown in the Figures 4-7. The UV-Vis spectroscopy and molar conductivities of the complexes are listed in the Table 3 and the electronic spectrum are shown in the Figures 8-10. The selected bond lengths and bond angles calculated are listed in the Tables 3-5 and the optimized structures are shown in the Figures 11-13. They are quite stable in air and melt or decompose above 210 ^oC in the Table 1. They are insoluble in most organic solvent but soluble in DMSO and DMF. Based on the information gained from the above results, the suggested structure of the new N-isopentylidine hydrazinedithiocarboxylic methyl ester Schiff bas ligand (L) is shown in the Figure 2 and the suggested structures of the Schiff base complexes are shown in the Figure 3.

$$NH_2NHCS_2CH_3 + C_2H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_2H_5 + 3MCl_2.nH_2O$$

refluxed for 15 min on magnetic stirrer, at 25 ^oC

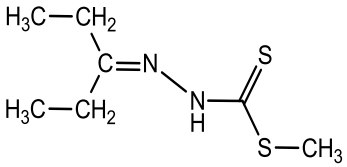
$$[M_3((C_2H_5)_2C{=}NNHCS_2CH_3)_2Cl_2(H_2O)_2] + 2CH_3COOH + 2NH_4CL$$

Equation 3: General reaction for the synthesis of the prepared complexes; M = Co(II) and Ni(II), n = 6 and M= Cu(II), n= 2



(NH_4L) (HL)

Figure 1: The structures of the NH_4L and HL ligands



(L)

Figure 2: The suggested structure of the Schiff base ligand (L)

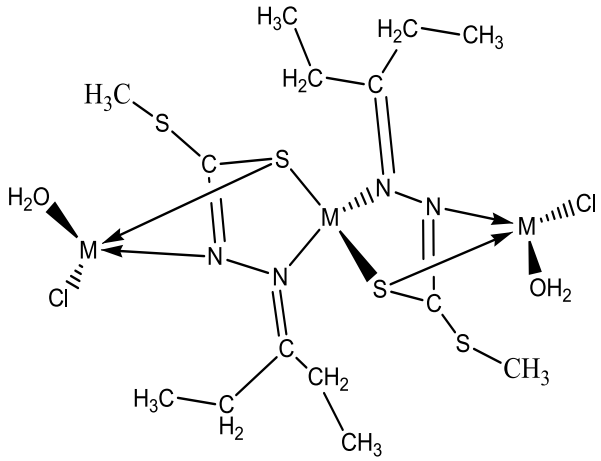


Figure 3: The suggested structures of the prepared complexes;
M = Co(II), Ni(II) and Cu(II)

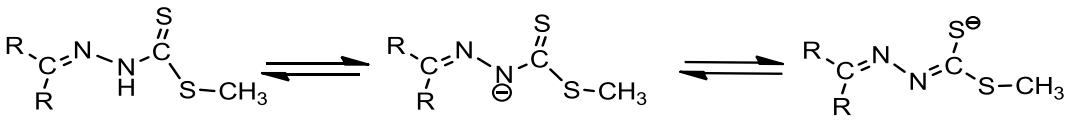
Molar conductivity measurements: The molar conductivities of 10^{-3} M solution the Schiff base complexes listed in the Table 3, the values observed in the range 11.5–14.5 $ohm^{-1}cm^2$ mol^{-1}, indicated that all complexes are non-electrolyte in DMSO solution [15].

Table 1: Physical properties of the ligands and Schiff base complexes

Seq.	Compound	Color	M.P (ºC)	Yield %	% Analysis, found (calcd)			μ_{eff} (B.M)
					C%	H%	N%	
	NH_4L	White	110*	70	9.34 (9.60)	5.90 (5.60)	33.35 (33.60)	-
	HL	Light green	90*	46	19.50 (19.70)	5.10 (4.90)	22.53 (22.95)	-
	L*	-	-	-	-	-	-	-
1	$[Co_3(L)_2Cl_2(H_2O)_2]$	Dark green	270	55	23.88 (24.10)	3.92 (3.73)	7.95 (8.03)	2.94
2	$[Ni_3(L)_2Cl_2(H_2O)_2]$	White green	210	68	23.96 (24.10)	3.88 (3.70)	7.96 (8.04)	3.80
3	$[Cu_3(L)_2Cl_2(H_2O)_2]$	Bright green	240	73	23.43 (23.70)	3.88 (3.70)	7.77 (7.90)	0.97

L* ligand has no results because it is formed during the preparation of the complexes.

IR-spectra and mode of bonding: The important IR frequencies of the methyl ester ligand (HL) and Schiff base complexes along with their relative assignments are presented in Table 2 and the IR spectrum are shown in the Figures 4-7. The IR spectrum of HL ligand is used in this study to compare it with Schiff base complexes due to the Schiff base free ligand can't be prepared it. The υ(C=S), υ(NH_2) and also υ(NH) bands are absence in the all complexes [16]. In the IR spectrum of the Schiff base complexes, a sharp bands observed in the range 1675-1678 cm^{-1} were assigned to the υ(C=N) band of the azomethine group, the shifted to lower frequency in all the complexes, indicating the coordination of the azomethine nitrogen to the metal ions centers [17,18]. Attempts to rearrange of the methyl ester ligand are successful due to the stabilization deprotonated in structure (II) in the Scheme 1 by strong conjugation of the C=N-N=C grouping of structure (III) will give strong thioureide band υ(C=N) in the range 1467-1495 cm^{-1}, this was shifted to lower frequency in all the complexes, indicating the thioureide band $\upsilon(C=N)_{NHCS}$ coordinate with the two terminal metal ions [17]. The ν(C=S) band is absent in complexes due to formed the υ(C-S-CH_3) band, in the range 875-900 cm^{-1} [17]. The spectra of υ(C─S) bands are appearance in the range 1000-1025 cm^{-1} in the complexes [17,18], the shifted to higher frequency, indicating the sulfur atom are coordinated with more than two metal ions and strongly supported that the complexes are homotrinuclear units [19]. The new bands υ(M-N), υ(M-S), υ(M-O) and υ(M-Cl) are appearance in the complexes in the range 400-420 cm^{-1} [19,16], 375-390 cm^{-1} [16,20-24], 560-580 cm^{-1} [25-27] and 250-275 cm^{-1} regions, respectively [28]. In the spectra of the complexes, indicating coordination of the methyl ester ligand through nitrogen and sulfur atoms and suggesting tetradentate attachment.



(I) (II) (III)

Scheme 1: Rearrange of the Schiff base methyl ester ligand

Table 2: Selected IR bands of methyl ester ligand and Schiff base complexes

Compounds / Assignments	HL	1	2	3
υ(C-S)	950 s	1025 m	1010 s	1000 m
υ(C=S)	890 s	-	-	-
υ(NH)	3075 w	-	-	-
$\upsilon(NH_2)_{as}$	3200 m	-	-	-
$\upsilon(NH_2)_{s}$	3270 m	-	-	-
$\delta(NH_2)$	1580 s	-	-	-
$\upsilon(C=N)_{NHCS}$	1450 m	1467 s	1481 s	1495 m
υ(C=N)azomethane	-	1675 m	1676 m	1678 m
$\upsilon(C\text{-}S\text{-}CH_3)$	850 w	875 s	900 m	875 m
υ(M-N)	-	415 m	420 w	400 s
υ(M-S)	-	390 m	380 m	375 m
υ(M-O)	-	580 m	560 w	560 m
υ(M-Cl)	-	250 s	275 s	275 s

For IR spectra, s = strong; m = medium; w = weak

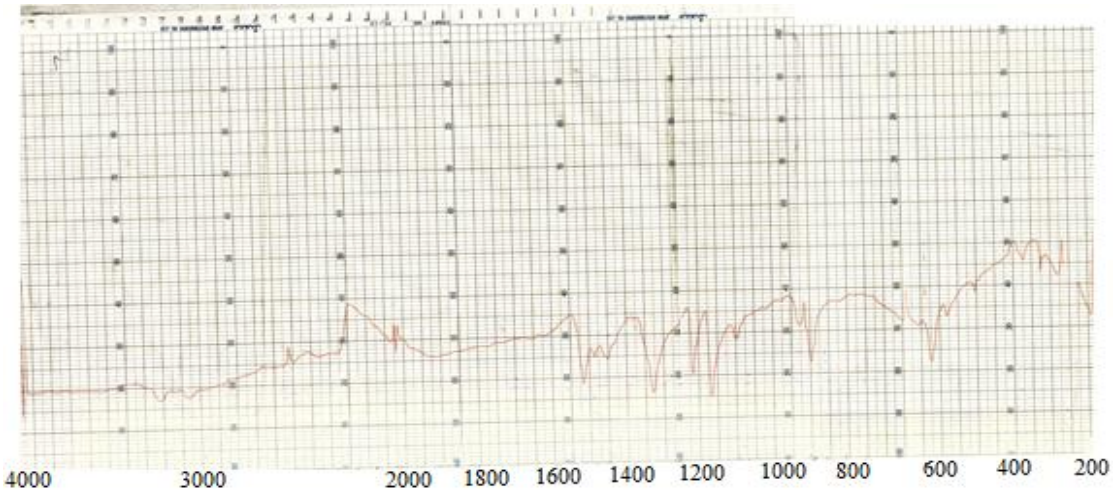


Figure 4: IR Spectrum for methyl ester ligand (HL)

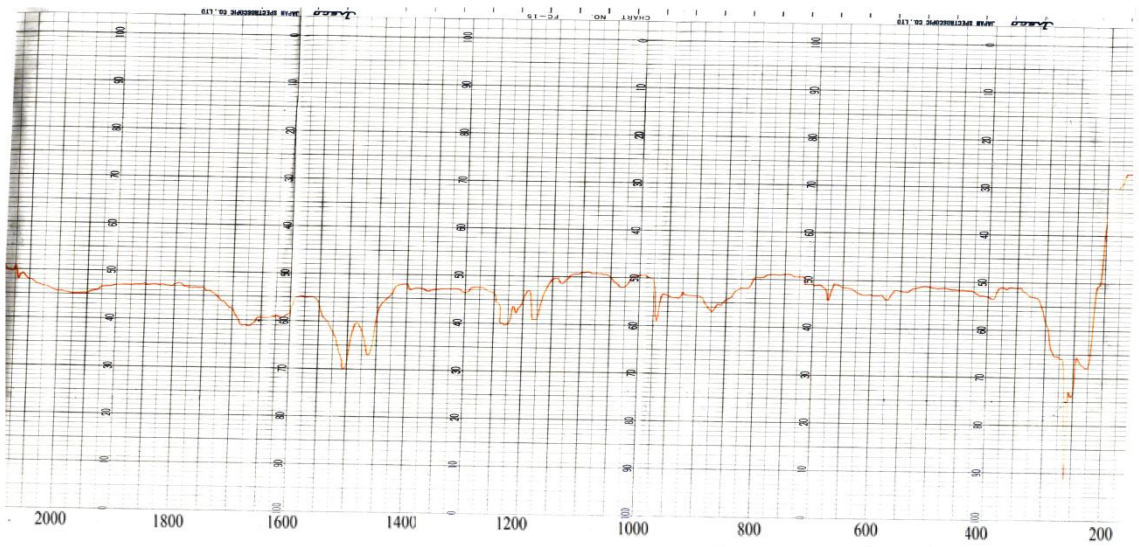


Figure 5: IR Spectrum for Schiff base cobalt complex 1

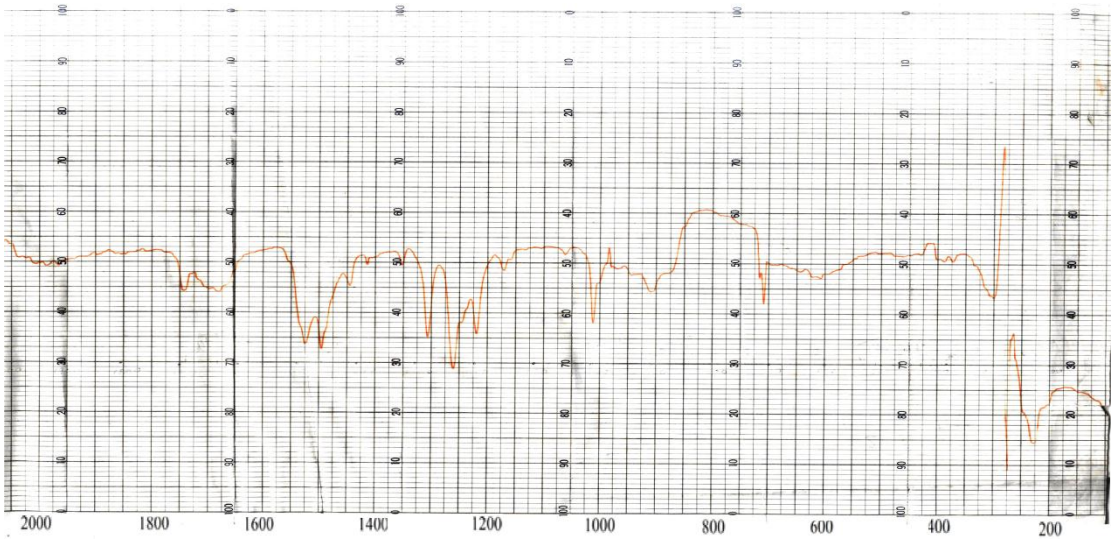


Figure 6: IR Spectrum for Schiff base nickel complex 2

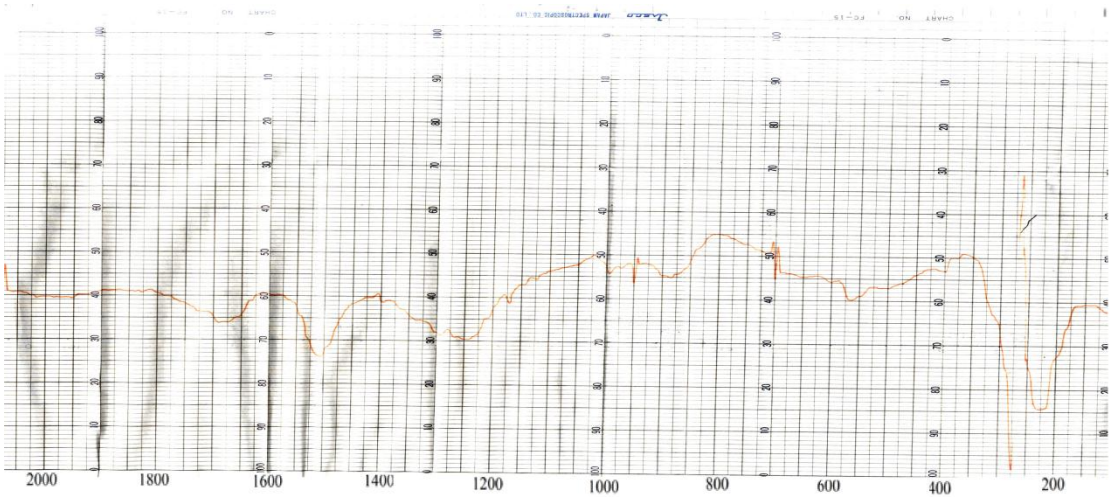


Figure 7: IR Spectrum for Schiff base copper complex 3

UV-Vis Spectra and magnetic susceptibility measurements: The electronic spectra of the Schiff base complexes were recorded in DMSO solution at room temperature were listed in Table 3. The magnetic properties of the cobalt (II) complex 1, exhibit μ_{eff} value of 2.94 B.M in the Table 1, which is the lower value is ascribed to antiferromagnetic interaction occurred between three cobalt ions, which is strongly supported that the complex is homotrinuclear units [23, 29-33]. The electronic spectra of the cobalt (II) complex is shown in Figure 8, the appearance of a band at 11,534 cm^{-1}, is attributed to the transition $^2A_1g(F)\rightarrow{}^2E_1g$ in the square planer configuration around the central metal ion (Low spin) and could be also attributed the band in the transition $^4A_2(F)\rightarrow{}^4T_1(P)$ (ν_2) in the distorted tetrahedral configuration around the two terminal metal ions (High spin) [34,35]. The bands in the range 14749-18281 cm^{-1} are due to the transition $^4A_2(F)\rightarrow{}^4T_1(P)$ (ν_3) characteristic of strong distorted tetrahedral configuration [36,37]. The magnetic properties of the nickel (II) complex 2, display μ_{eff} value of 3.80 B.M in the Table 1, the higher value may be attributed to orbital contribution occurred between the two terminal nickel while the central metal ion is diamagnetic, which is strongly supported that complex is homotrinuclear units [23, 29, 31, 38-40]. The electronic spectra of the nickel (II) complex is shown in Figure 9, the appearance of a band at 15151 cm^{-1}, it is due to the transition $^3T_1(F)\rightarrow{}^3T_1(P)$ (ν_3) in the distorted tetrahedral configuration around the two terminal nickel ions and could be also attributed to the transition $^1A_1g\rightarrow{}^1A_2g$ in the square planer configuration around the central nickel ion [41,42,43]. The band at 22062 cm^{-1} is ascribed to the transition $^1A_1g\rightarrow{}^1B_1g$, which is again assigned to the square planer configuration [41,42]. The copper (II) complex 3, showed magnetic properties with μ_{eff} value of 0.97 B.M in the Table 1 [44], the lower value is clearly indicating that antiferromagnetic interaction occurred between three copper ions, which is strongly supported that the complex is homotrinuclear. The electronic spectra of the copper (II) complex is shown in Figure 10, the band is observed at 16611 cm^{-1}, which certainly indicating the square planer configuration around the central copper ion, which the transition $^2B_1g\rightarrow{}^2Eg'$. [44,45], since the tetrahedral configuration does not, usually, give electronic band in the range 10000-20000 cm^{-1}.

Table 3: Electronic spectra and molar conductivity of the complexes

Compound	Spectra (cm^{-1})	Λ_M $ohm^{-1}\,cm^2mol^{-1}$
1	11,534, 14749, 16749, 18281, 26737, 28490, 29239, 32467, 33222	11.5
2	15151, 16025, 16313, 18975, 24100, 28490, 29498, 32362, 33222	14.5
3	11363, 16611, 30030, 32362, 33112	13.5

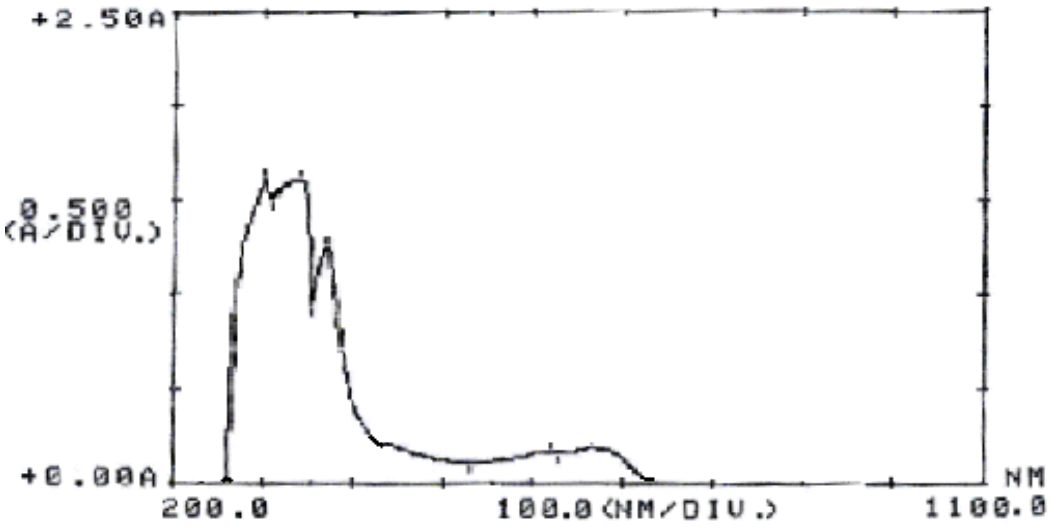


Figure 8: Electronic spectrum for Schiff base cobalt complex 1

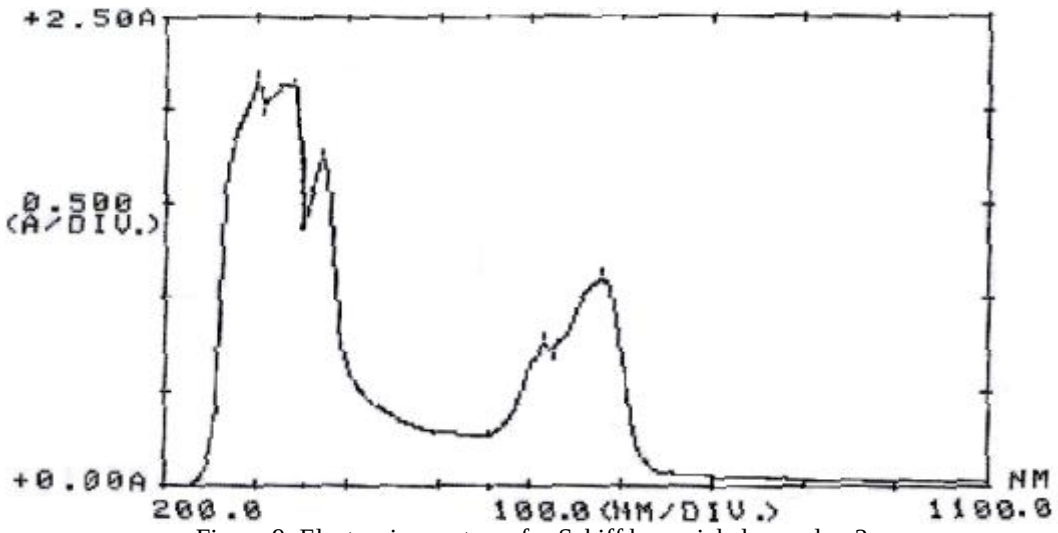


Figure 9: Electronic spectrum for Schiff base nickel complex 2

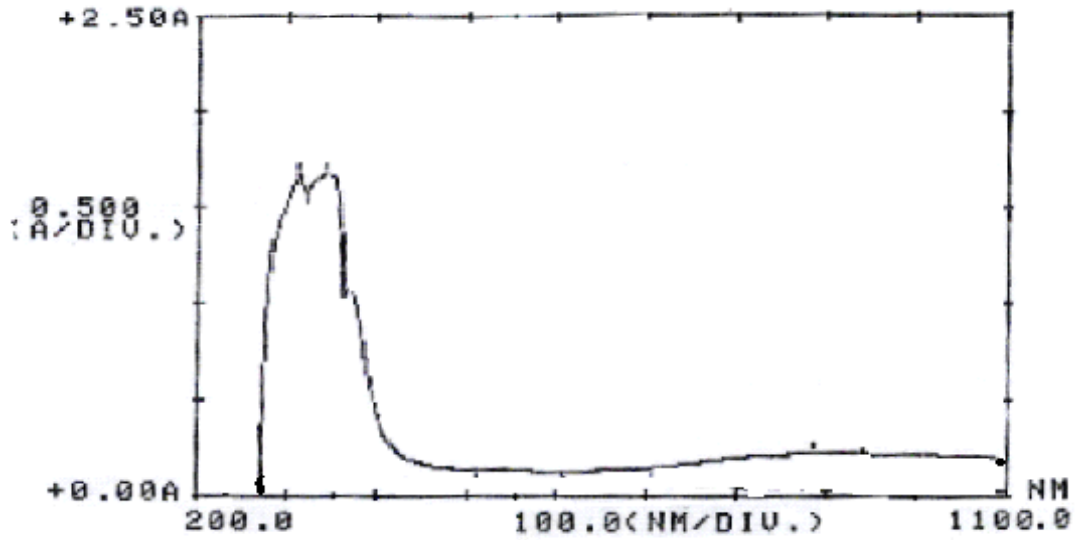


Figure 10: Electronic spectrum for Schiff base copper complex 3

Molecular structure and analysis of bonding modes: I have optimized and MM2 calculated the molecular structure of the ligands and Schiff base complexes by using CsChem3D Ultra program package [13]. Therefore we could obtain the optimized geometry for each complex by competing the minimum steric energy and the theoretical physical parameters, such as bond lengths and bond angles. The optimized structures of the complexes are observed in the Figures 11-13, which were some selected calculated parameters in coordination sphere in the Tables 4-6. In complexes, coordination by chelation involving the various modes of sulfur, nitrogen, oxygen and chloride are possible. These results reveal presence of mixed properties for both the square planar configuration around the central metal ion and the tetrahedral configuration around the two terminal metal ions. All three studied of the ligand and three complexes reveals minimum steric energies values (3.032 kcal/mol^{-1} for Schiff base ligand, 59 kcal/mol^{-1} for complex 1, 62 kcal/mol^{-1} for complex 2 and 74 kcal/mol^{-1} for complex 3). MM2 calculated is in good agreement with the experimental results and confirms the expected of the structures.

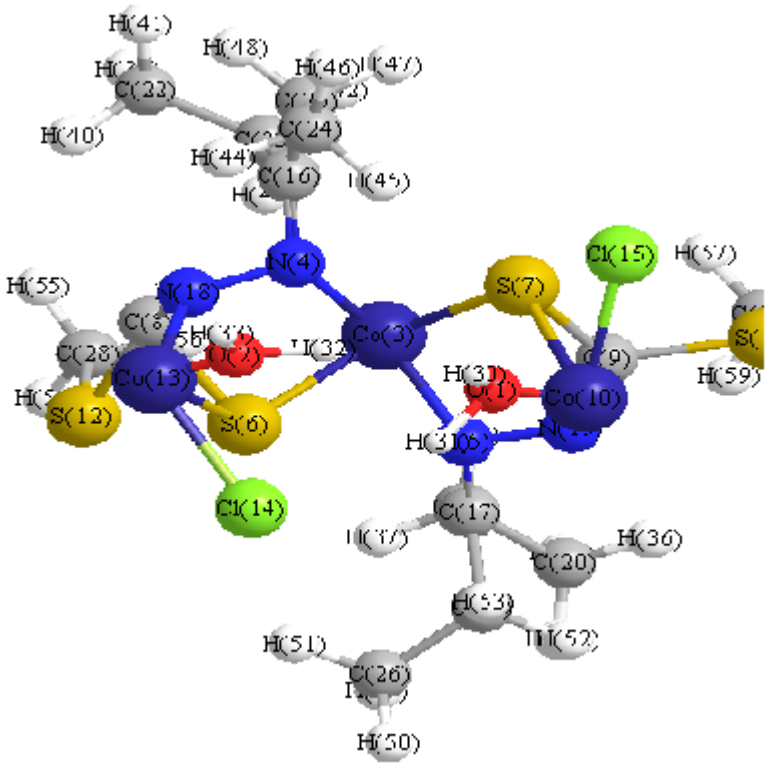


Figure 11: Optimized structure of the cobalt complex 1

Table 4 : Some selected calculated parameter of the cobalt complex 1

Bond lengths Å					
S(6)-Co(13)	2.2016	N(19)-Co(10)	1.8558	Co(3)-N(5)	1.8554
S(7)-Co(10)	2.2184	Co(10)-Cl(15)	2.1490	N(4)-Co(3)	1.8539
N(18)-Co(13)	1.8607	Co(3)-S(7)	2.1897	Co(13)-O(2)	1.1158
Co(13)-Cl(14)	2.1548	S(6)-Co(3)	2.1903	Co(10)-O(1)	1.1103
Bond angles°					
S(6)-Co(13)-N(18)	59.7127	S(7)-Co(10)-N(19)	63.4107	S(7)-Co(3)-S(6)	118.3300
S(6)-Co(13)-Cl(14)	63.2486	S(7)-Co(10)-Cl(15)	62.5563	S(7)-Co(3)-N(5)	74.4663
S(6)-Co(13)-O(2)	95.9363	S(7)-Co(10)-O(1)	78.1118	S(7)-Co(3)-N(4)	79.8408
N(18)-Co(13)-Cl(14)	119.6060	N(19)-Co(10)-Cl(15)	119.4500	S(6)-Co(3)-N(5)	76.8983
N(18)-Co(13)-O(2)	87.5401	N(19)-Co(10)-O(1)	103.6900	S(6)-Co(3)-N(4)	72.2294
Cl(14)-Co(13)-O(2)	79.9617	Cl(15)-Co(10)-O(1)	90.0597	N(5)-Co(3)-N(4)	123.0520

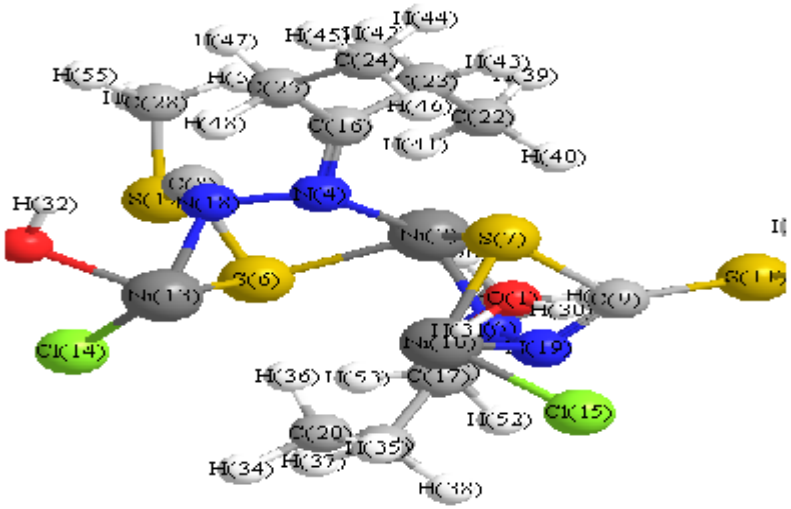


Figure 12: Optimized structure of the nickel complex 2

Table 5 : Some selected calculated parameter of the nickel complex 2

Bond lengths Å					
S(6)-Ni(13)	2.1790	N(19)-Ni(10)	1.8478	Ni(3)-N(5)	1.8452
S(7)-Ni(10)	2.1867	Ni(10)-Cl(15)	2.1480	N(4)-Ni(3)	1.8478
N(18)-Ni(13)	1.8513	Ni(3)-S(7)	2.1840	Ni(13)-O(2)	1.8354
Ni(13)-Cl(14)	2.1441	S(6)-Ni(3)	2.1764	Ni(10)-O(1)	1.8349
Bond angleso					
S(6)-Ni(13)-N(18)	60.3072	S(7)-Ni(10)-N(19)	64.6546	S(7)-Ni(3)-S(6)	121.5613
S(6)-Ni(13)-Cl(14)	70.8254	S(7)-Ni(10)-Cl(15)	113.9388	S(7)-Ni(3)-N(5)	73.1641
S(6)-Ni(13)-O(2)	108.1125	S(7)-Ni(10)-O(1)	75.2499	S(7)-Ni(3)-N(4)	72.0953
N(18)-Ni(13)-Cl(14)	112.4713	N(19)-Ni(10)-Cl(15)	77.6998	S(6)-Ni(3)-N(5)	91.3751
N(18)-Ni(13)-O(2)	76.8121	N(19)-Ni(10)-O(1)	111.7577	S(6)-Ni(3)-N(4)	70.9741
Cl(14)-Ni(13)-O(2)	77.4740	Cl(15)-Ni(10)-O(1)	71.1903	N(5)-Ni(3)-N(4)	123.0032

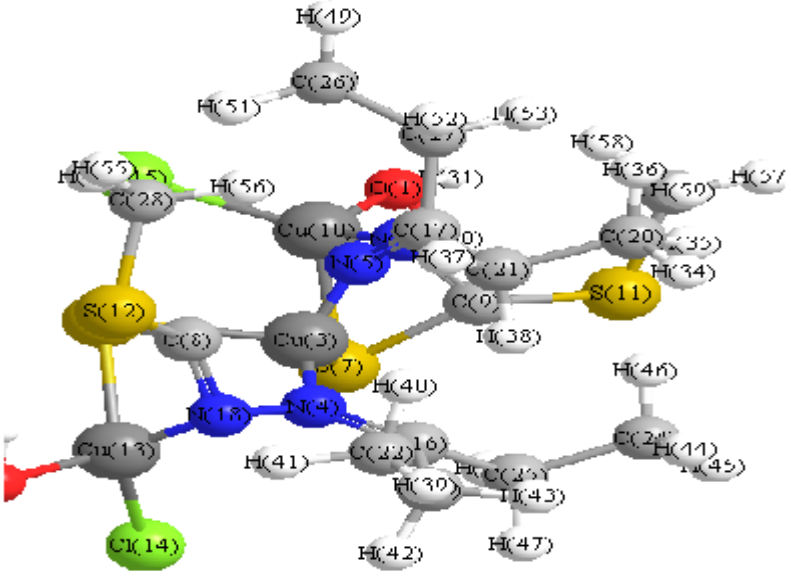


Figure 13: Optimized structure of the copper complex 3

Table 6 : Some selected calculated parameter of the copper complex 3

Bond lengths Å					
S(6)-Cu(13)	2.1951	N(19)-Cu(10)	1.3891	Cu(3)-N(5)	1.3521
S(7)-Cu(10)	2.1955	Cu(10)-Cl(15)	2.1540	N(4)-Cu(3)	1.3492
N(18)-Cu(13)	1.3826	Cu(3)-S(7)	2.2018	Cu(13)-O(2)	1.8346
Cu(13)-Cl(14)	2.1543	S(6)-Cu(3)	2.2076	Cu(10)-O(1)	1.8444
Bond angles°					
N(18)-Cu(13)-Cl(14)	119.0100	N(19)-Cu(10)-Cl(15)	122.6130	S(7)-Cu(3)-N(5)	96.8416
N(18)-Cu(13)-S(6)	77.8002	N(19)-Cu(10)-S(7)	79.0691	S(7)-Cu(3)-N(4)	115.4021
N(18)-Cu(13)-O(2)	112.3746	N(19)-Cu(10)-O(1)	111.0393	S(6)-Cu(3)-N(5)	105.1331
Cl(14)-Cu(13)-S(6)	118.9638	Cl(15)-Cu(10)-S(7)	119.0062	S(6)-Cu(3)-N(4)	93.5251
Cl(14)-Cu(13)-O(2)	110.6854	Cl(15)-Cu(10)-O(1)	111.3920	N(5)-Cu(3)-N(4)	133.4826
S(6)-Cu(13)-O(2)	114.5738	S(7)-Cu(10)-O(1)	109.8159	S(7)-Cu(3)-N(5)	96.8416

Conclusion

A new tetradentate N-isopentylidine hydrazinedithiocarboxylic methyl ester Schiff-base ligand (L) with their homotrinuclear metal complexes of the general formula $[M_3(L)_2Cl_2(H_2O)_2]$ were synthesized. The suggested structures of ligand and their complexes were characterized by using several methods such as elemental analysis, molar conductivities, FT-IR, UV-Vis, magnetic susceptibility and theoretical calculation using MM2 modeling program. The tetradentate Schiff base ligand (L) is used as stabilizer ligand for homotrinuclear metal complexes and according to the measurements and theoretical calculations, the cobalt (II), nickel (II) and copper (II) complexes have mixed properties for both the square planer configuration around the central metal ion and tetrahedral configuration around the two terminal metal ions.

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