

## Synthesis and Structural Characterization of Three Homotrinnuclear Metal Complexes Stabilized by tetradentate N-isopentylidene hydrazinedithiocarbamate Schiff base Ligand

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### ABSTRACT

The new tetradentate Schiff base ligand (L), which was used as stabilizers for homotrinnuclear metal complexes were prepared from condensation of 3-pentanone and ammonium hydrazinedithiocarbamate have been used into in situ reactions with metal chlorides in molar ratio of 3 : 2 (M : L) in ethanol, leads to the Schiff base homotrinnuclear metal complexes of the general formula  $[M_3(L)_2Cl_2(H_2O)_2]$  where L = N-isopentylidene hydrazinedithiocarbamate and M= Co (II), Ni(II) and Cu(II), which have been characterized by elemental analysis, molar conductivity and magnetic susceptibility measurements, FT-IR and UV-Vis spectroscopy as well as MM2 calculation by using CsChem3D Ultra program package. The spectroscopic evidences and magnetic data exhibits presence of mixed properties for both the square planar configuration around the center metal ion and the tetrahedral configuration around the two terminal metal ions within the homotrinnuclear units.

### INTRODUCTION

Coordination chemistry of Schiff bases derived from dithiocarbamate with various metal ions leading to mono- or poly-nuclear complexes [1,2]. A successful of this strategy allowing for the control of the nuclearity consists in the ingenious use of compartmental ligands [3,4] 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 [5]. Transition metal complexes of Schiff bases containing nitrogen and sulfur and other donors have been widely studied due to M-S, M-N and other bonds in their structure and the effects of the bonding on diversified applications basically in biological field [6,7]. In the 70s, M. Iskander and L. El. Sayd. used hydrazinedithiocarboxylic acid, as a precursor for the synthesis of Schiff base which behaved as monobasic bidentate ligand and giving only mononuclear nickel (II) complex containing a new Schiff base type N-isopropylidene hydrazinedithiocarbamate [8]. In this study we synthesized the homotrinnuclear metal complexes containing a new tetradentate Schiff base type N-isopentylidene hydrazinedithiocarbamate by in situ reactions with metal chlorids, Co (II), Ni(II) and Cu(II), in 3 : 2 molar ratio metal ions to ligand (Fig. 1). The spectroscopic and magnetic data confirm the 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 within homotrinnuclear units.

## EXPERIMENTAL

### Chemicals

Hydrazine hydrate, carbon disulphide, ammonium hydroxide,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 3-pentanone and ethanol (96%) were of analytical reagent grade (BDH, Aldrich or Fluka).

### Instruments

The Schiff base homotrinnuclear 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  $4000\text{-}200\text{ cm}^{-1}$ . 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  $200\text{-}1100\text{ nm}$ ), model 160 Koyoto (Japan) using acetonitrile as a solvent. Conductivity measurements were carried out on  $10^{-3}\text{ M}$  solutions of the complexes in acetonitrile at room temperature on a digital conductivity meter, model 4070 (Jenway). The optimized geometry, steric energy and MM2 calculated of the prepared complexes were done using CsChem3D Ultra program package.

### Preparation of the ligand

Ammonium hydrazinedithiocarbamate ( $\text{NH}_2\text{NHCS}_2\text{NH}_4^+$ ) was prepared by the reaction of hydrazine hydrate with carbon disulphide in presence of ammonium hydroxide by known method [9].

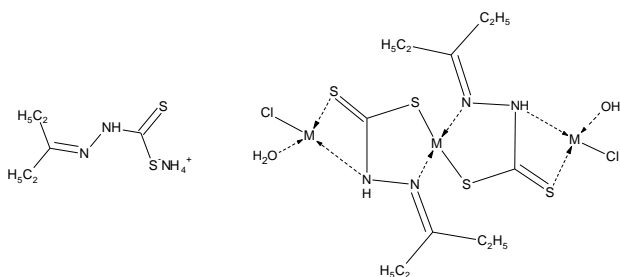
### Preparation of the complexes

0.033 mol of the hydrated metal chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) was added to an ethanolic solution of the 0.022 mol of the ammonium hydrazinedithiocarbamate 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  $\text{P}_2\text{O}_5$  in a desiccator vacuum for 24 hr.

## RESULTS AND DISCUSSION

### Syntheses and physical Properties

The physical properties of the homotrimeric metal complexes are tabulated in Table 1, the FT-IR data are listed in Table 2 and the UV-Vis and molar conductivities of the complexes are listed in Table 3. The elemental composition of the prepared complexes  $[M_3(L)_2Cl_2(H_2O)_2]$  is shown in Fig. 1, which is corresponds to 3 : 2 (metal : ligand). These complexes are insoluble in most organic solvent but are soluble in DMSO and DMF. They are quite stable in air and decompose above 250 °C as shown in Table. 1.



**Figure 1:** The Schiff base ligand and the suggested structures of complexes, where M=Co(II), Ni(II) and Cu(II).

### Molar conductivity measurements

The conductivity of the three complexes are showed values ranging between 14.4-19.5  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  and are listed in Table 3, indicating non-electrolyte in DMSO [10].

**Table 1.** Physical properties of the Schiff base complexes.

Com. Seq.	Complex	Color	M.P (°C)	% Analysis, found (calcd)			$\mu_{\text{eff}}$ (B.M)
				C%	H%	N%	
1	$[Co_3(L)_2Cl_2(H_2O)_2]$	Gray	250	20.88 (21.54)	3.08 (3.29)	7.96 (8.37)	2.92
2	$[Ni_3(L)_2Cl_2(H_2O)_2]$	Brown	300	21.32 (21.56)	3.17 (3.29)	8.19 (8.37)	3.85
3	$[Cu_3(L)_2Cl_2(H_2O)_2]$	Brown	260	20.78 (21.10)	3.17 (3.20)	7.98 (8.20)	1.02

### IR spectra and mode of bonding

IR spectra and the mode of bonding values are shown in Table. 2. The significant increase and decrease in the absorption IR bands  $\nu(C=N)$  and  $\nu(C-S)$  and the appearing of a new bands  $\nu(M-N)$  and  $\nu(M-S)$  the most important band which appeared at  $1663-1652\text{ cm}^{-1}$

due to the  $\nu(\text{C}=\text{N})$  stretching in the homotrinnuclear metal complexes, the shifted to the lower frequency which proves very clearly that the Schiff base had been formed during their in situ reactions with the metal chloride [10-14]. Another important band which at 1040-1025  $\text{cm}^{-1}$  due to  $\nu(\text{C}-\text{S})$  stretching in the all complexes [14], the shifted to the higher frequency, which indicated that the ligand has a coordinate with two or more metal ions [15]. Addition support to this the appearance of new bands in the region 450-430 and 380-363  $\text{cm}^{-1}$  due to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$ , respectively, are further evidence of coordination [16,17]. These spectra also show bands in the region 280-247 and 510-483  $\text{cm}^{-1}$  which may be due to  $\nu(\text{M}-\text{Cl})$  and  $\nu(\text{M}-\text{OH}_2)$  stretching frequencies[18,19].

**Table 2:** Selected IR bands ( $\text{cm}^{-1}$ ) of the complexes

Com. Seq.	$\nu(\text{C}-\text{S})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}=\text{N})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
1	1040 m	973 s	1482 s	1652 m	483 s	448 s	363 m	270 m
2	1025 w	978 m	1467 s	1663 m	510 w	450 m	380 s	280 m
3	1032 m	980 s	1464 m	1658 m	496 m	430 s	367 s	247 m

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

## UV-VIS spectra and magnetic susceptibility

### Measurement

The magnetic properties with  $\mu_{\text{eff}}$  value of cobalt (II) complex 1 is 2.92 B.M. (Table. 1), which is in good agreement with the structure complex of both the square planer configuration around the central cobalt ion (Low spin) and the tetrahedral configuration around the two terminal cobalt ions (High spin) [20-25]. The slightly lower value is due to antiferromagnetic exchange interaction occurred when the ligand is coordinated with three cobalt ions. The electronic spectral band of the complex appearing at 11534  $\text{cm}^{-1}$  (Table. 3), which attributed to the transition  $d_{xy} \rightarrow d_{yz}$  in the square planer configuration [26,27] could be attributed to the tetrahedral configuration, which is the transition  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$  ( $\nu_2$ ). The strong bands appeared at 13106-18021  $\text{cm}^{-1}$  which attributed to the transition  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  ( $\nu_3$ ) in the distorted tetrahedral configuration and could be also attributed to the square planer configuration, which is the transition  ${}^2\text{A}_1\text{g} \rightarrow {}^2\text{E}_1\text{g}'$ .

The nickel (II) complex 2 gave  $\mu_{\text{eff}}$  of 3.85 B.M. (Table. 1), the proportion higher value due to some orbital contributions for both the two terminal nickel ions (High spin) in the tetrahedral configuration, whereas the central nickel ion (Low spin) appeared to be diamagnetic [20,21,23]. This argument was supported by electronic spectral of obtained for this complex in the Table. 3. The electronic spectral bands at 13003-16320  $\text{cm}^{-1}$  attributed to the transition  ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$  ( $\nu_3$ ), which is again assigned to a distorted tetrahedral configuration and could be also attributed to the square planer configuration, which is the transition  ${}^1\text{A}_1\text{g} \rightarrow {}^1\text{A}_2\text{g}$  [28]. A single band at 21490  $\text{cm}^{-1}$  due to transition  ${}^1\text{A}_1\text{g} \rightarrow {}^1\text{B}_1\text{g}$  in the square planer configuration [29,30].

The copper (II) complex 3 showed magnetic properties with  $\mu_{\text{eff}}$  value of 1.02 B.M. (Table. 1) [31], the lower value may be attributed to antiferromagnetic exchange interaction occurred on the adjacent copper ions within homotrinnuclear units. The electronic spectra of

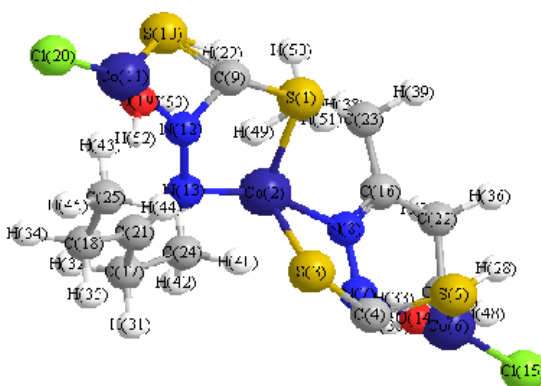
complex ( Table. 3) showed one band at  $16025\text{ cm}^{-1}$  attributed to the transition  ${}^2B_{1g} \rightarrow {}^2E_g$  in the square planer configuration [31,32], since the tetrahedral structure does not, usually, give electronic band in the range  $10000\text{--}20000\text{ cm}^{-1}$ .

**Table 3:** Electronic spectra and molar conductivity of the complexes (in DMSO).

Com. Seq.	Spectra ( $\text{cm}^{-1}$ )	$\Delta_M$ $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
1	11534, 13106, 14934, 18021, 21834, 27100, 28490, 29239, 32274, 35222	15.6
2	13003, 14341, 16320, 21490, 25706, 27027, 29498, 32467, 33222	19.5
3	11086, 16025, 28985, 32467, 34222	14.4

### Molecular modeling studies

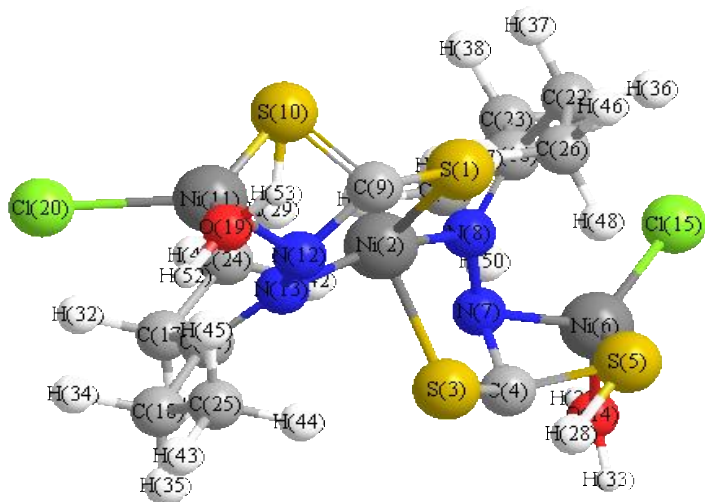
In order to get finer structural details of these complexes, we have optimized and MM2 calculated the molecular structure of complexes. Therefore we could obtain the optimized geometry for each complex by competing the minimum steric energy and the theoretical physical parameters, such as bond lengths and bond angles using CsChem3D Ultra program package. The optimized structures of complexes 1 and 2 (Fig. 3 and 4) were some selected calculated parameters in coordination sphere (Table. 4 and 5). 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 geometry around the central metal ion and the tetrahedral geometry around the two terminal metal ions. All three studied complexes reveals minimum steric energies values ( $7.75\text{ kcal/mol}$  for Schiff base ligand,  $59.78\text{ kcal/mol}$  for complex 1,  $52.28\text{ kcal/mol}$  for complex 2 and  $86.236\text{ kcal/mol}$  for complex 3) associated with mixed properties geometries. MM2 calculated is in good agreement with the experimental results and confirms the expected of mixed properties geometry.



**Figure 2:** Optimized structure of cobalt (II) complex 1

**Table 4.** Some selected calculated parameter of the cobalt (II) complex. 1.

Bond lengths Å (Central ion)		Bond lengths Å (Terminal ions)			
S(7)-Co(1)	2.18	Co(10)-O(17)	0.60	N(5)-Co(13)	1.84
Co(1)-S(6)	2.18	Co(10)-Cl(16)	2.15	Co(13)-O(15)	0.60
N(4)-Co(1)	1.84	N(3)-Co(10)	1.84	Co(13)-Cl(14)	2.15
Co(1)-N(2)	2.16	S(7)-Co(1)	2.18	S(12)-Co(13)	1.88
Bond angles° (Central ion)		Bond angles° (Terminal ions)			
S(7)-Co(1)-S(6)	169.2	N(3)-Co(10)-O(17)	168.52	N(5)-Co(13)-O(15)	168.12
S(7)-Co(1)-N(4)	90.00	N(3)-Co(10)-Cl(16)	24.55	N(5)-Co(13)-Cl(14)	21.76
S(7)-Co(1)-N(2)	90.00	N(3)-Co(10)-S(11)	65.45	N(5)-Co(13)-S(12)	68.24
S(6)-Co(1)-N(4)	90.00	O(17)-Co(10)-Cl(16)	143.9	O(15)-Co(13)-Cl(14)	146.36
S(6)-Co(1)-N(2)	79.17	O(17)-Co(10)-S(11)	126.1	O(15)-Co(13)-S(12)	123.64
N(4)-Co(1)-N(2)	90.00	Cl(16)-Co(10)-S(11)	90.00	Cl(14)-Co(13)-S(12)	90.00

**Figure 3:** Optimized structure of nickel (II) complex 2

**Table 5:** Some selected calculated parameter of the **nickel (II)** complex. **2.**

Bond lengths Å (Central ion)		Bond lengths Å (Terminal ions)			
N(8)-Ni(2)	2.13	N(7)-Ni(6)	1.83	O(19)-Ni(11)	1.79
N(13)-Ni(2)	1.83	Ni(6)-Cl(15)	2.14	S(10)-Ni(11)	1.91
S(3)-Ni(2)	2.17	S(5)-Ni(6)	1.69	Ni(11)-N(12)	1.83
S(1)-Ni(2)	2.17	O(14)-Ni(6)	1.79	Ni(11)-Cl(20)	2.14
Bond angles° (Central ion)		Bond angles° (Terminal ions)			
N(8)-Ni(2)-N(13)	96.49	O(14)-Ni(6)-S(5)	129.24	O(19)-Ni(11)-S(10)	131.4
N(8)-Ni(2)-S(3)	76.92	O(14)-Ni(6)-N(7)	129.24	O(19)-Ni(11)-N(12)	131.4
N(8)-Ni(2)-S(1)	109.5	O(14)-Ni(6)-Cl(15)	93.07	O(19)-Ni(11)-Cl(20)	91.83
N(13)-Ni(2)-S(3)	160.5	S(5)-Ni(6)-N(7)	72.62	S(10)-Ni(11)-N(12)	67.93
N(13)-Ni(2)-S(1)	90.00	S(5)-Ni(6)-Cl(15)	117.7	S(10)-Ni(11)-Cl(20)	118.6
S(3)-Ni(2)-S(1)	109.5	N(7)-Ni(6)-Cl(15)	117.7	N(12)-Ni(11)-Cl(20)	118.6

## CONCLUSION

New N-isopentylidene hydrazinedithiocarbamate Schiff base ligand with their of the type  $[M_3(L)_2Cl_2(H_2O)_2]$  were synthesized. The mixed properties structures of the homotrimeric metal complexes were characterized by FT-IR and UV-Vis spectroscopy and magnetic susceptibility measurement in addition to MM2 calculation by using CsChem3D Ultra program package. The spectroscopic and magnetic data confirms presence of mixed properties for both the square planar configuration and the tetrahedral configuration. The tetradentate Schiff base is used as stabilizer ligand for homotrimeric metal complexes and according to the measurements and MM2 calculations, the Co (II), Ni(II) and Cu(II) complexes have mixed properties for both the square planer geometry around the central metal ion and the tetrahedral geometry around the two terminal metal ions. The MM2 calculations were performed to obtain the theoretical information on the geometry which is identical with the experimental results.

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## تحضير و تشخيص ثلاثة من المعقدات الفلزية ثلاثية النوى المتجانسة استقرت بليجاندا قاعدة شيف الرباعية السن n-ايزوبنتليدين هيدرازين ثنائي ثايوكارباميت

باسل مكر<sup>1</sup> و عبدالحفيظ علي عبدالله<sup>2</sup>

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### ملخص

ليجاندا قاعدة شيف الجديدة رباعي السن (L) استعملت لاستقرار المعقدات الفلزية ثلاثية النوى المتجانسة. حيث تم تحضيرها بالتفاعل موضعيا و ذلك بتكثيف 3-بننانون و هيدرازين ثنائي ثايوكارباميت الامونيوم مع كلوريد الفلزات وبنسبة مولية 2 : 3 (فلز : ليجاند) في الايثانول, تمتلك المعقدات الفلزية ثلاثية النوى المتجانسة الصيغة العامة  $[M_3(L)_2Cl_2(H_2O)_2]$  حيث  $n = L$ - ايزوبنتليدين هيدرازين ثنائي ثايوكارباميت و  $M = Co(II), Ni(II) \text{ and } Cu(II)$ . لقد تم تشخيص المعقدات عن طريق التحليل الدقيق للعناصر و التوصيلية المولارية الكهربائية و الحساسية المغناطيسية و اطياف الاشعة تحت الحمراء و الاطياف الالكترونية بالإضافة الى حساب MM2 عن طريق (CsChem3D Ultra program package). إذ دلت القياسات المغناطيسية و الطيف الالكتروني على وجود خليط من ترتيب المربع المستوي حول ايون الفلز الوسطي و ترتيب الرباعي السطوح حول ايوني الفلز في الاطراف ضمن وحدات ثلاثي النوى المتجانسة.