------ Raf. J. Sci., Vol. 25, No.1 pp. 53-61, 2014------

Synthesis and Characterization of Mn(II), Fe(II) and Co(II) Complexes with 4-Hydroxypiperidinedithiocarbamate and their Adducts with Neutral Bases

Saad E. Al- Mukhtar
Department of Chemistry
College of Science
University of Mosul

Hasan A. Mohammed*
Department of Chemistry
College of Science
University of Kirkuk

***Email**: Hassanahmed88@yahoo.com

(Received 21/ 1 / 2013 ; Accepted 8 / 4 / 2013)

ABSTRACT

A new coordination complexes and adducts of the general formulas $[M(hpipdtc)_2]$ and $[M(hpipdtc)_2L_n]$ where M= Mn(II), Fe(II), Co (II), (hpipdtc)=4-hydroxypiperidinedithiocarbamate, n=1 L= 1, 10phen, en, n=2 L=4-picoline, 3,5-luitidine, triphenylphosphine have been prepared and characterized by metal analyses, infrared, molar conductance measurements, electronic absorption spectra, and susceptibility measurements. Magnetic moments and electronic spectra, suggested tetrahedral geometry for complexes of the type $[M(hpipdtc)_2]$ and an octahedral geometry for their base adducts.

Keywords: Dithiocarbamate, Manganese (II), Iron(II), Cobalt(II),

---

تحضير وتشخيص معقدات المنغنيز (II) والحديد (II) والكوبلت (II) مع 4- هيدروكسي بابيريدين داي ثايوكاربميت و مركبات الإضافة مع القواعد المتعادلة

الملخص

حضرت معقدات جديدة ومركبات الإضافة ذات الصيغ العامة $[M(hpipdtc)_2]$ و$[M(hpipdtc)_2L_n]$، حيث M= Mn(II) وFe(II) وCo(II) ولوحظ أن هذه المعقدات رباعية التناسق $[M(hpipdtc)_2]$ تتفاعل بدورها مع عدد من القواعد النتروجينية وثلاثي فنيل الفوسفين لتكوين معقدات اضافة سداسية التناسق من النوع $[M(hpipdtc)_2L_n]$ عندما n=2 فأن L= ثلاثي فنيل فوسفين او 5,3-ليوتيدين او 4-بيكولين. وعندما n =1 فأن L=10,1- فينانثرولين او اثيلين ثنائي الامين. وشخصت هذه المعقدات بواسطة قياسات التوصيلية الكهربائية المولارية والأطياف الالكترونية وأطياف الأشعة تحت الحمراء والحساسية المغناطيسية وقياسات الامتصاص الذري، إذ دلت القياسات المغناطيسية والطيف الالكتروني على اتخاذ المعقدات ذات الصيغة $[M(hpipdtc)_2]$ شكل رباعي السطوح في حين أن المعقدات سداسية التناسق ذات الصيغة $[M(hpipdtc)_2L_n]$ اتخذت شكل ثماني السطوح.

INTRODUCTION

Dithiocarbamates (R_2CNS_2 - or DTCs) are monoanionic 1,1-dithio ligands they have been reviewed many times (Coucouvanis, 1970 ; Coucouvanis, 1979; Karlin, 2005). Among the ligands coordinating through sulfur atoms, dithiocarbamates are deserving much attention in recent years, and a large number of dithiocarbamate complexes have been synthesized so far; these compounds are being investigated in order to gain insight into the nature of the sulfur-metal bond in many biomolecules (Benigno *et al.*, 2002). Dithiocarbamates derived from secondary amines are the most studied ones because they are stable and possess interesting electrochemical and optical properties (Onwudiwe and Ajibade, 2010). Dithiocarbamate complexes of divalent transition metals, in which the central atom is partially coordinatively unsaturated, are able to reversibly link molecules of organic S-, N-, P-donor bases. The resulting intermolecular heteroleptic complexes are generally called adducts (Tatyana *et al.*, 2011). Dithiocarbamates are organosulfur compounds of robust synthetic and chemical properties (Siddiqi *et al.*, 2007) and are produced in great quantities (Nabipour, 2011; Khwaja *et al.*, 2006). The chemical properties of dithiocarbamates are due to the presence of one or more active group in their structures. This functional group can form complexes with almost all elements, including metal atoms of metal-containing enzymes, thus blocking their catalytic activity (Sanchez-Cortes *et al.*, 1998). In this paper we present new dithiocarbamate complexes of some transition metals and their base adducts.

EXPERIMENTAL

Materials and Methods

All reagents and solvents were commercially available high grade materials (Fluka A.G., Riedel-de Haën, BDH) and used as received, Infrared spectra were recorded on a Brucker Tensor 27co. FTIR spectrophotometer in the 400-4000 cm^{-1} range using KBr discs Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMF using conductivity meter PCM3 Jenway at an ambient temperature. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer UV-160 for 10^{-3}M solutions of complexes in DMF as solvent at 25°C using 1 cm quartz cell. Metal content was determined spectrophotometrically using AA670 atomic absorption spectrophotometer. Melting points were recorded on an Electrothermal 9300 apparatus. The magnetic measurements were carried out at 25°C on the solids by Faraday's method using Brucker BM6 instrument.

I.A. Preprationof sodium 4-hydroxypiperidine dithiocarbamate,Na(4-hpipdtc)

4-hydroxypiperidine (10.1 g, 0.1 mol) was dissolved in 30 ml of water containing sodium hydroxide (4.0 g, 0.1 mol). The resulting solution was cooled in an ice bath, and carbon disulfide (7.6 g, 0.1 mol) was added dropwise with stirring. The mixture was stirred for 30 min, then allowed to be warmed to room temperature and stirred for an additional hour. The yellowish white precipitate formed, was filtered off, washed with diethyl ether and dried in vacuum.

I.B. Synthesis of the complexes [M(4-hpipdtc)$_2$]
M=Mn(II), Fe(II), Co(II),

A solution of sodium 4-hydroxypiperidine dithiocarbamate (1.99 g, 0.01 mol) in 15 ml of (1:4,v/v) water: methanol mixture was added to aqueous solution of $MnCl_2.4H_2O$. (0.98 g, 0.005 mol) or $FeCl_2.4H_2O$, (0.99g, 0.005 mol) or $CoCl_2.6H_2O$ (1.15 g, 0.005 mol) dropwise with a constant stirring at a room temperature in 100 ml round bottom flask. After 30 min, the precipitate formed was filtered off, washed with 10ml of(1:4,v/v) water: methanol mixture and dried under vacuum.

I.C. Synthesis of the complexes [M(4-hpipdtc)$_2$L$_2$]
L= 4-picoline, 3, 5-lutidine, triphenylphosphine

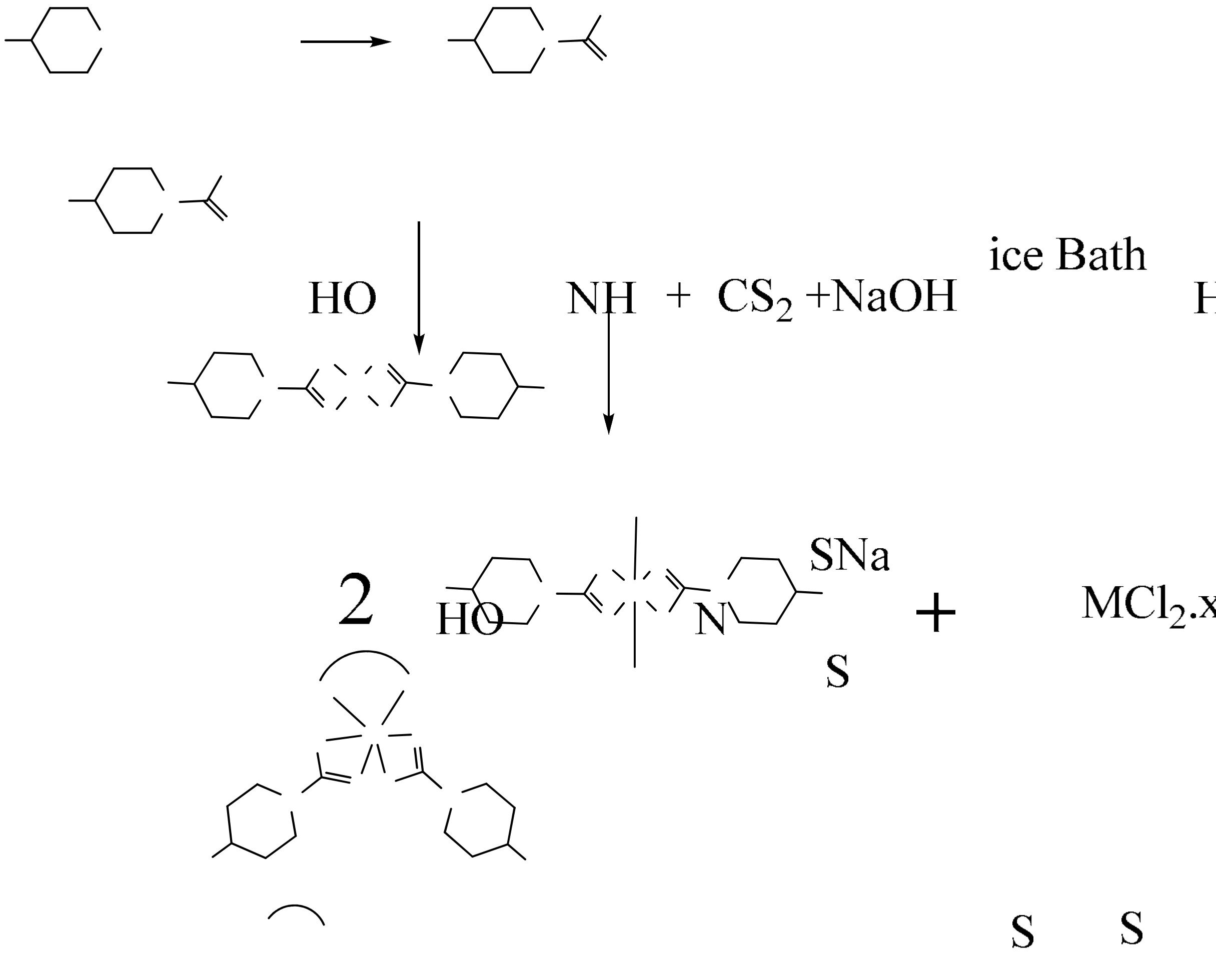
Prepared as in procedure (I.B) above and after the formation of the precipitate, (0.01mol) of (4-picoline) or (3,5-lutidine) or (triphenylphosphine) was added with continuous stirring for 30min, the complexes separated out, were filtered, washed with methanol 10 ml then dried under vacuum.

I.D. Synthesis of adducts[M(4-hpipdtc)$_2$L]
L=1, 10-phenanthroline, ethylenediamine

Prepared similarly as in procedure (I.B) and after the formation of the precipitate, (0.005 mol) of (1,10-phenanthroline or ethylenediamine) was added with continuous stirring for 30 min.The complex formed was filtered and washed with methanol 10 ml, then dried under vacuum.

RESULTS AND DISCUSSION

The ligand was prepared by the reaction of carbon disulfide with the secondary amine 4-hydroxypiperidine in the presence of sodium hydroxide and the complexes were prepared by direct addition of the aqueous solution of the corresponding metal chloride to the ligand solution in aqueous methanol, using 1:2 (metal: ligand) molar ratio. The base adducts were prepared by adding the base to the prepared bis-complexes in (1:2) or (1:1) molar ratios. (Scheme 1).



Scheme 1: Synthesis of ligands, Mn(II), Fe(II), Co(II) dithiocarbamate complexes, and adducts

The composition and analytical data for all complexes are given in Table (1); IR and UV- Visible spectra data are shown in Table (2). The low values of molar conductivities of the complexes in DMF (0.9 –16.3 ohm^{-1}.cm^{2}.mol^{-1}) indicate that all the prepared complexes and adducts are non - electrolytes. (Geary, 1971)

Infrared spectral studies:

The most significant bands recorded in the IR spectra of the ligand and its complexes are reported in Table (2). For dithiocarbamate compounds, three main regions in the IR spectra are of interest. First the 1580–1450 cm^{-1} region, which is primarily associated with the stretching vibration of C–N group of (N–C) moiety (Srinivasan *et al.*, 2010). The ligand shows a strong absorption at (1479) cm^{-1}, which is assigned to the C-N stretching frequency. The complexes show an absorption at (1486 -1516) cm^{-1}, which is assigned to the ν(C=N) stretching frequency. Compared with the ligand, the ν(C-N)band of the complex is indeed shifted towards a higher frequency by (7-37) cm^{-1}. The υ(C=N)ring of 4-picoline,3,5-lutidine and 1,10-phenthroline observed in the range (1441-1522) cm^{-1} (De Lima *et al.*, 2011).

Second the (1060–940) cm^{-1} region, which is associated with ν (C-S) vibrations and a single absorption band observed in this region, suggests a bidentate behavior in dithio ligand. The complexes show bands at (966-1018) cm^{-1} assigned to ν (C-S) vibrations (Serrano *et al.*, 2003).

Third, the (478–519) cm^{-1} region associated with ν (M–S) vibrations (Sarwar *et al.*, 2007), the ν (M-S), occurring in the far-IR region depends on the nature of the metal ion and the substituents attached with the sulfur. We have observed ν (M-S) in the (478-517) cm^{-1} range which is in agreement with the literature data (Serrano *et al.*, 2003). The (543-579) cm^{-1}, (1432-1437) cm^{-1} region assigned to υ (M–N), υ($P\text{-}C_{aryl}$) vibrations respectively, (Mohamed *et al.*, 2009). ν (M-P) stretching vibration occurs below 200 cm^{-1}, in the region of about (150-180)cm^{-1} which is out of the spectrophotometer range, (Saha *et al.*, 2012). The band at (3200-3247) cm^{-1}region assigned for ν (O-H), (Raptopoulou *et al.*, 2000), in the spectra of the free ligand and complexes indicating the non-involvement of hydroxyl group in coordination.

Electronic spectral studies:

The UV-Visible spectra of the ligands and their complexes in 10^{-3} M DMF solution were recorded; the results are listed in Table (2). The UV-Visible spectra of the Mn(II) complex give absorption bands at (31643-34013 cm^{-1}), which corresponds to charge transfer transition. In the high spin d^5 manganese (II) configuration, the (d-d) electronic transitions are spin forbidden and laporate forbidden, due to the presences of five unpaired electrons. Therefore the absorption intensities decrease by a factor of about 100 compared to the usual (d-d) absorption band thus the spectra are not observed in the visible region (Al-Mukhtar and Mustafa , 1988).

The Fe(II) complex (8) give an absorption band at (11025, 32467 cm^{-1}), which corresponds to ($^5E \rightarrow {}^5T_2$) and charge transfer transition in an tetrahedral geometry (Nicholls, 1973). Complexes (9-13) show an absorption band at the range (10039-11139 cm^{-1}), (30874-32894 cm^{-1}) which were assigned to ($^5T_2g \rightarrow {}^5Eg$) and charge transfer transitions (Coucouvanis and Fackler, 1967).

The Co(II) complex (14) exhibited an absorption band at (15527 cm^{-1}) region, which was assigned to ($^4A_2(F) \rightarrow {}^4T_1(P)$) transition (Siddiqi and Nishat, 2000), in tetrahedral configuration. The absence of ($^4A_2(F) \rightarrow {}^4T_2(F)$) and ($^4A_2(F) \rightarrow {}^4T_1(F)$ transitions, are due to their low energy which is out of the range of the instrument. Complexes (15-19) show three absorption bands at the range (9803-10372 cm^{-1}), (14928-15625 cm^{-1}) and (24038-25215 cm^{-1}), which were assigned to ($^4T_1g(F) \rightarrow {}^4T_2g(F)$), ($^4T_1g(F) \rightarrow {}^4A_2g(F)$) and ($^4T_1g(F) \rightarrow {}^4T_1g(P)$) transitions in an octahedral configuration (Martel, 1971; Lever, 1984).

Magnetic susceptibility measurements

The magnetic moments of the complexes Table (1), were measured at (25 °c). The magnetic moments for Mn(II), Fe (II), Co (II) complexes (2, 8 and 14) are (5.70,5.02 and 4.10 B.M) respectively suggest a tetrahedral geometry (Nicholls, 1973). The magnetic moments values of the other complexes of Mn(II)(3-7), Fe (II)(9-13) and Co (II)(15-19) were in the range (5.75-5.96, 4.81-5.06, 4.03-4.76) B.M respectively suggest a high spin octahedral geometry (Nicholls, 1973). The high values of magnetic moments for complexes (16-19) are due to the orbital contribution for Co(II) in octahedral complexes.

Table 1: Analytical and some physical properties of the prepared complexes

Comp. no.	Chemical formula	Color	m.p °C	M% Cal/found	^	Yield %	μ_{eff}
1.	Na (4-hpipdtc)	yellowish white	113		-----		-----
2.	[Mn (4-hpipdtc)$_2$]	black	160-162	13.51 (12.63)	1.4	91	5.70
3.	[Mn (4-hpipdtc)$_2$(1,10- phen)]	orange	148-250	9.37 (8.43)	4.4	82	5.76
4.	[Mn (4-hpipdtc)$_2$en]	black	195-198	11.82 (10.67)	1.1	60	5.88
5.	[Mn (4-hpipdtc)$_2$(4-pic)$_2$]	Brown	300<	9.27 (10.38)	1.2	51	5.95
6.	[Mn (4-hpipdtc)$_2$(3,5-lutid)$_2$]	Brown	180-183	8.85 (9.87)	1.2	48	5.75
7.	[Mn (4-hpipdtc)$_2$(PPh$_3$)$_2$]	White	162-165	5.90 (5.19)	1.2	40	5.96
8.	[Fe (4-hpipdtc)$_2$]	black	163-165	13.68 (12.92)	2.5	89	5.02
9.	[Fe (4-hpipdtc)$_2$(1,10- phen)]	Greenish yellow	155-158	9.49 (10.38)	6.4	42	4.94
10.	[Fe (4-hpipdtc)$_2$en]	Black	170-172	11.97 (11.26)	16.3	71	4.96
11.	[Fe (4-hpipdtc)$_2$(4-pic)$_2$]	Dark red	300<	9.39 (9.97)	3.7	44	4.81
12.	[Fe (4-hpipdtc)$_2$(3,5-lutid)$_2$]	Black	225-227	8.97 (9.40)	1.1	38	4.89
13.	[Fe (4-hpipdtc)$_2$(PPh$_3$)$_2$]	black	300<	5.98 (6.83)	3.3	59	5.06
14.	[Co (4-hpipdtc)$_2$]	Dark green	298-300	14.33 (14.83)	1.1	87	4.10
15.	[Co (4-hpipdtc)$_2$(1,10- phen)]	Dark green	300<	9.96 (9.27)	1.4	51	4.03
16.	[Co (4-hpipdtc)$_2$en]	Dark olive	300<	12.56 (12.16)	4.1	55	4.76
17.	[Co (4-hpipdtc)$_2$(4-pic)$_2$]	Dark green	300<	9.86 (8.20)	0.9	61	4.43
18.	[Co (4-hpipdtc)$_2$(3,5-lutid)$_2$]	Dark green	297-300	9.42 (10.53)	4.3	64	4.56
19.	[Co (4-hpipdtc)$_2$(PPh$_3$)$_2$]	Dark green	300<	6.30 (7.54)	1.1	35	4.53

Table 2: IR bands (cm^{-1}) and electronic spectral data of ligand and prepared complexes

No.	compound	ν(C-S)	ν(C====N)	υ(C = N) ring	ν(M-N)	ν(M-S)	ν(O-H)	UV-Vis. spectra cm^{-1}
1.	Na (4-hydpipdtc)	949(s)	1479(s)	-----		-	3211	31847,33212
2.	[Mn (4-hpipdtc)$_2$]	976(m)	1489(s)	-----	------	492(w)	3200	33557
3.	[Mn (4-hpipdtc)$_2$(1,10-phen)]	966(w)	1516 (s)	1491	543(w)	498(w)	3240	32645
4.	[Mn (4-hpipdtc)$_2$en]	976(s)	1489(s)	-----	553(w)	482(w)	3231	32924
5.	[Mn (4-hpipdtc)$_2$(4-pic)$_2$]	975(s)	1497(m)	1467	577(w)	491(w)	3208	34013
6.	[Mn (4-hpipdtc)$_2$(3,5-lutid)$_2$]	972(m)	1516(m)	1460	569(w)	486(w)	3214	32894
7.	[Mn (4-hpipdtc)$_2$(PPh$_3$)$_2$]	976(m)	1495(s)	-----	-----	478(w)	3222	31643
8.	[Fe (4-hpipdtc)$_2$]	1018(m)	1489(s)	-----	------	480(w)	3246	11025, 32467
9.	[Fe (4-hpipdtc)$_2$(1,10-phen)]	997(s)	1486(s)	1452	546(w)	517(w)	3215	11139, 32894
10.	[Fe (4-hpipdtc)$_2$en]	997(m)	1495(s)	-----	579(w)	478(w)	3232	10418, 30874
11.	[Fe (4-hpipdtc)$_2$(4-pic)$_2$]	999(s)	1506(m)	1456	557(w)	478(w)	3217	10345, 31386
12.	[Fe (4-hpipdtc)$_2$(3,5-lutid)$_2$]	1018(m)	1503(m)	1441	575(w)	480(w)	3206	10039, 32678
13.	[Fe (4-hpipdtc)$_2$(PPh$_3$)$_2$]	1005(w)	1502(m)	-----	-----	488(w)	3247	10343, 31708
14.	[Co (4-hpipdtc)$_2$]	972(w)	1491(m)	-----	------	480(w)	3234	15527, 32894
15.	[Co (4-hpipdtc)$_2$(1,10-phen)]	995(w)	1495(s)	1440	551(w)	478(w)	3226	9823, 15625 25125,
16.	[Co (4-hpipdtc)$_2$en]	999(m)	1500(s)	-----	553(w)	484(w)	3212	10372, 14928 24124, 31250
17.	[Co (4-hpipdtc)$_2$(4-pic)$_2$]	999(m)	1498(s)	1448	586(w)	482(w)	3223	9803, 15527 25215, 30120
18.	[Co (4-hpipdtc)$_2$(3,5-lutid)$_2$]	1001(w)	1491(s)	1468	577(w)	478(w)	3219	9876, 15527 24038, 31446
	[Co (4-hpipdtc)$_2$(PPh$_3$)$_2$]	995(w)	1495(s)	-----	-----	485(m)	3227	9813, 15479 24509, 32258

s= strong, m=medium, w= weak

From the results obtained from different physical measurement and electronic spectra, the complexes and their adducts structures are suggested in Fig. 1, 2, 3.

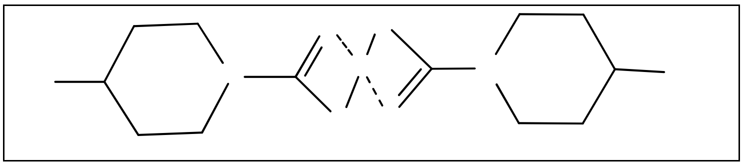


Fig. 1: Suggested structure for [M (4-hpipdtc)$_2$] M =Mn(II),Fe(II),Co(II)

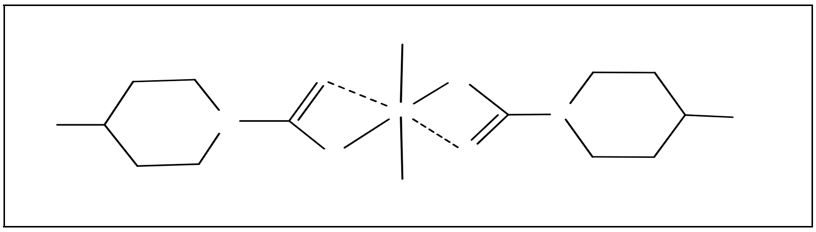


Fig. 2: Suggested structure for [M(4-hpipdtc)$_2$L$_2$]complexes, L=PPh$_3$, 4- picoline, 3, 5-luitidine

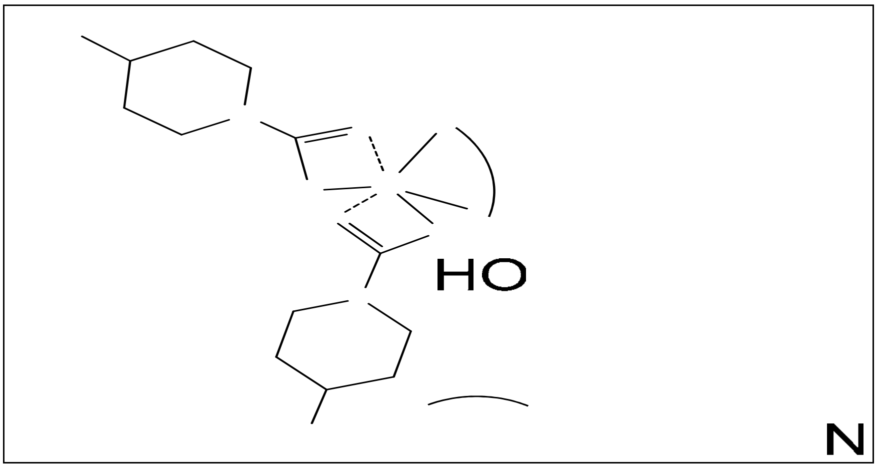


Fig. 3: Suggested structure for [M(4-hpipdtc)$_2$L] complexes. L= 1, 10-phen, en

REFERENCES

Al-Mukhtar, S.E.; Mustafa, I.A. (1988). "Inorganic and Coordination Chemistry". (Arabic version), Mosul University Press, Mosul.

Benigno, M.; María, V.V.; Eduardo, C.; Silvia, M.V.; Alfonso, C.; Joaquín, B. (2002). Copper complexes with dithiocarbamates derived from natural occurring amino acids. Crystal and molecular structure of [Cu(en)(EtOH)(H_2O)$_3$][Cu(dtc-pro)$_2$]. *Polyhedron.*, **21**, 1899-1904.

Coucouvanis, D. (1970). Coordination chemistry of dithio ligands in Prog. *Inorg. Chem.*, **11**(233), 197.

Coucouvanis, D. (1979). Coordination chemistry of dithio ligands in Prog. *Inorg. Chem.*, **26**(301), 274.

Coucouvanis, D.; Fackler, J.P. (1967). Square-planar sulfur complexes VI. reactions of bases with xanthate, dithiocarbamates, and dithiolates of nickel(II). *Inorg. Chem.*, **6**, 2047-2053

De Lima, M.; Menezes, C.; Camila, A.C.; Jaqueline, A.F.; dos Santos; Isabella, P.F.; Eucler, B.P.; James, L.W.; Solange, M.S.; Wardell, K.K.; Isolda, C.M.; Heloisa, B. (2011). Synthesis, characterization and biological aspects of copper(II) dithiocarbamate complexes, [Cu{$S_2CNR(CH_2CH_2OH)$}$_2$], (R = Me, Et, Pr and CH_2CH_2OH). *J. Mol. Struct.*, **988**, 1–8

Geary, W.J. (1971). The use of conductivity measurements in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.*, **7**, 81-122

Karlin, K. (2005). Transition Metal Dithiocarbamates in. *Pro. Inorg. Chem.*, **53**, 71,237

Khwaja, S.S.; Shahab, A.A.N.; Lutfullah, C.; Yonas, C. (2006). Template synthesis of symmetrical transition metal dithiocarbamates. *J. Barz. Chem. Soc.*, **17**, 107–112.

Lever, A.B.P. (1984). "Inorganic Electronic Spectroscopy". 2nd ed., Elsevier, Amsterdam, 357 p.

Martel, A.E. (1971). "Coordination Chemistry". Vannostran Reinhold, New York., 1p.

Mohamed, G.G.; Ibrahim, N.A.E.; Attia, H.A. (2009). Synthesis and anti-fungicidal activity of some transition metal complexes with benzimidazole dithiocarbamate ligand. *Spectrochim. Acta, A.*,**72**, 610–615.

Nabipour, H. (2011). Synthesis of a new dithiocarbamate cobalt complex and its nanoparticles with the study of their biological properties. *Int. J. Nano. Dim.*, **1**(3), 225-232.

Nicholls, D. (1973)."The Chemistry of Iron, Cobalt and Nickel". Pergamon press,Oxford,1st ed.,1037 p.

Onwudiwe, D.C. ; Ajibade, P.A. (2010). Synthesis and characterization of metal complexes of N-alkyl-N-phenyl dithiocarbamates. *Polyhedron*, **29**, 1431-1436.

Raptopoulou, C.P.; Tangoulis, V.; Psycharis, V. (2000). Synthesis and structural, spectroscopic, and magnetic characterization of $(NH_4)[Fe_3$(í3-OH)$(H2L)_3(HL)_3]$ (H3L) Orotic Acid) presenting two novel metal-binding modes of the orotate ligand: the case of a spin-frustrated system. *Inorg. Chem.*, **39**(20), 4452-4459.

Saha, G.; Sarkar, K.K.; Mondal, T.K.; Sinha, C. (2012). Synthesis, spectra, structure, redox properties and DFT computationof copper(I)–triphenylphosphine–pyridyl Schiff bases. *Inorg. Chem. Acta.*, **387**, 240-247.

Sanchez-Cortes, S.; Vasina, M.F.; Garcia-Ramos, O. (1998). Raman and surface enhanced Raman spectroscopy of dithiocarbamate fungicides. *Vib. Spectr.*, **17**, 133–144.

Sarwar, M.; Ahmed, S.; Sajjad, A.; Ali, S.; Awan, A.S. (2007). Copper(II) complexes of pyrrolidine dithiocarbamate., *Trans. Met. Chem.*, **32**,199–203.

Serrano, J.L.; Garcı´a, L.; Peŕez, J.; Peŕez, E.; Sǎnchez, G.; Garcıǎ, J.; Lo´pez, G.; Garcı´a, G.; Molins, E. (2003). New dithiocarbamate and xanthate complexes of nickel(II) with Iminophosphines. *Inorg. Chem. Acta*, **355**, 33-40.

Siddiqi, K.S.; Sadaf, K.; Shahab, A.A.N.; El-ajaily, M.M. (2007). Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates. *Spectrochem. Acta. A.* **67**, 995–1002.

Siddiqi, K.S.; Nishat, N. (2000). Synthesis and characterization of succinimide and phthalimide dithiocarbamate and their complexes with some transition metal ions. *Synth. Reac. Inorg. Met-Org. Chem.,* **30**(8), 1505 -1518.

Srinivasan, N.; Valarmathi, P.; Thirumaran, S.; Ciattini, S. (2010). Synthesis and spectral studies on NiS_4, NiS_2PN, NiS_2P_2chromophores: single-crystal X-ray structure of [Ni(dbpdtc)2] (dbpdtc: 5 benzyl(4-(benzylamino)phenyl)dithiocarbamate). *Trans. Met. Chem.*, **35**, 815–819.

Tatyana, A.R.; Alexander, V.I.; Andrey, V.G.; Maxim, A.I.; Anna, S.Z.; Tatyana, S.P.; Oleg, N.A. (2011). A pyridine adduct of bis (di-iso-butyldithiocarbamato-S,S) cadmium(II): multinuclear (^{13}C, ^{15}N, ^{113}Cd) CP/MAS NMR spectroscopy, crystal and molecular structure, and thermal behavior. *Inorg. Chem. Acta.*, **368**, 263–270.