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Homo- and hetero- trinuclear complexes of platinum group metals with disubstituted thioethane ligands

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ABSTRACT

The new disubstituted thioethane ligands $RSCH_2CH_2SR$ { where R= $(CH_2)_{11}CH_3(L^1)$ and R=$CH_2Ph(L^2)$}, react with one, or a mixture of the metal salts, $NiCl_2.6H_2O$, Na_2PdCl_4 or K_2PtCl_4 in (3:2) metal to ligand molar ratio respectively, to yield homo or hetero trinuclear complexes. Unexpected complexes of a general formula $[NiPd(L)_2Cl_4]$ ($L=L^1\&L^2$) and they were successfuly isolated . Adducts of the complexes were prepared by their reaction with triphenylphosphine. The complexes and adducts were characterized by C,H, metal content , I.R, U.V/Vis spectroscopy, conductivity and magnetic measurements. Conductivity data showed that some of the complexes were non-electrolytes, and some of them were 1:2 electrolytes. Electronic and magnetic measurements indicate that some of the complexes have square planar or octahedral geometry and others contain a mixture octahedral and square planar geometry. Explanation of the structural elucidation of the complexes are given.

Key words: Trinuclear complexes, platinum and thioethane ligands.

INTRODUCTION

A number of research groups have investigated the coordination chemistry of thioether ligands, and work continues to progress in several areas including transition metal complexes, main group compounds and organometallic complexes[1]. One particularly active area of focus involves thioether complexes of platinum (II) due to high stability of Pt-S bonds and the relevance of this type of bond in catalysis and pharmacodynamics of cis-platin[2-3]. Theses thioether complexes contain unusual structural features. Multimetallic complexes, having communication between adjacent metal ions are becoming of increasing interest because of their catalytic properties[4].

Gürol *et al.*[5] reported the synthesis of a new dithioglyoxime ligand containing long alkyl chains. Mono, tri- and penta-nuclear complexes as well as polymers have been synthesized by the reaction of dithioglyoxime with a variety of transition metal ions. These complexes and polymers are very interesting due to their solubility in most organic solvents. Homobinuclear complexes of the type $[Cl_2MRC{=}CRMCl_2]$ [M=Ni(II),Pd(II) or Pt(II) and R=5-phenyl-1,3,4-oxadiazole-2-thio,4,5-diphenyl-1,2,4-triazole-3-thiol or mercaptobenzothiazole have been prepared and characterized . Octahedral environment around Ni(II), while square planar geometry around Pd(II) or Pt(II) have been deduced on the bases of magnetic and spectral measurements[6].

Three new nickel complexes have been prepared with the ligands Hbss (4-mercapto-2-thio-1-butylbenzen) and Hbsms (2-benzylsulfanyl)-2-methyl-1-propanethiol). $[Ni(bss)_2]$ is mononuclear complex with S_4 coordination environment. $[Ni_3(bss)_4](BF_4)_2$ and $[Ni_3(bsms)_4](BF_4)_2$ are linear trinuclear complexes. The complex $[Ni_3(bss)_4](BF_4)_2$ were determined using x-ray single crystal by Verhagen *et al*.[7], they showed that the nickel centers are square planar environment.

Palladium (II) and platinum (II) complexes containing the mixed ligands $Ph_2P(CH_2)_nPPh_2$(n=1-4) and benz-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione or benz-1,3-thiazoline-2-thione have been prepared and characterized by elemental analysis, spectral and magnetic studies as well as ^{31}P-{H}-n.m.r. data[8].

Metal complexes with thioether ligand are very important and as continuation of our studies on Pd and Pt metal ions sulfur containing ligand[9-11].

Here in we report the synthesis of new dithio ligands 1,2-bis(dodecanthio)ethane (L^1) and 1,2-bis(benzylthio)ethane (L^2). Mono and tri-nuclear complexes have been synthesis by reaction of the above ligands with platinum metal group in (2:3) (metal to ligand) molar ratio. The most exciting feature of these complexes is their solubility in common organic solvents.

EXPERIMENTAL

All the chemical used were of high purity according to the supplie (Fluka). Analysis of ligand and complexes were carried out using a CHN elemental analyzer model 1100 (Carlo Erba). The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer. Melting point and decomposition temperature were determined on a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra within the range 4000-200cm^{-1} range were recorded on a Perkin-Elmer 580B spectrophotometer, calibrated with polystyrene. The samples measured as CsI discs. Electronic spectra were obtained with a Shimadzu UV/Vis recording UV160 spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3}M of the complexes in DMSO. The magnetic moments were carried out at 25ºC, on the solid state, by Farraday's methods using Brucker BM6 instruments. Conductivities were measured using a conductivity meter model PCM3-Jenway. These measurements were obtained using DMSO over the 10^{-3} M at 25ºC.

Preparation of ligands

Preparation of bis(n-dodecanethio) ethane (L^1)

The reaction of potassium dodecylthiolate {prepared in situ from the reaction of an equivalent amount of KOH (1.12g, 0.02 mol) and dodecyl thiol (4.04g, 0.02mol) in ethanol (30 cm^3)} with 1,2-diobromoethane (1.87g, 0.01 mol). The mixture was boiled under reflux for ca.6h.

After cooling at room temperature, KBr was removed by filtration. The solution was reduced in volume to ca (5 cm^3) and on cooling to 5ºC, a white precipitate was formed, which was washed with ethanol and diethylether and dried under vacuum.

Preparation of bis(benzylthio) ethane (L^2)

Similar procedure was used as above except the amount of benzyl mercaptane was (2.24g, 0.02mol).

Preparation of $[Ni(L^1)_2(OH)_2]_3$

The salt $NiCl_2.6H_2O$ (0.72g, 0.03 mol) was dissolved in hot ethanol (5 cm^3). The resulting solution was added slowly with stirring to a solution of ligands (L^1) (2.50 g, 0.006 mol) in ethanol (10 cm^3). Then a solution of KOH in ethanol was added to the mixture until the pH was (9). The colour changed from to with the appearance of some precipitate. The mixture was refluxed for 2h, the solid thus formed was filtered off, washed with ethanol and dried in vacuum.

Preparation of $[M_3(L^1)_2Cl_6]$ and $[Pt_3(L^1)_2Cl_4]Cl_2$ M= Pd or Pt

The salt Na_2PdCl_4 or K_2PtCl_4 (3 mmol) in (10 cm^3) distilled water was added to a solution of ligand (L^1) (2mmol) in ethanol (15 cm^3). A rapid formation of a coloured precipitate was observed. The mixture was then stirred at room temperature for ca 2h, to ensure the completion of the reaction. The solid obtained by filtration was washed with water (10cm^3), ethanol (2 ×10 cm^3) and ether (10 cm^3) then dried under vacuum.

Preparation of $[M_2M'(L)_2(PPh_3)_4Cl_6]$, $[M_3(L)_2(PPh_3)_4Cl_4]Cl_2$ M=Pd or Pt ,M=Pd ,M'=Pt, L= L^1 or L^2

The complexes were prepared by the reaction of (1mmol) of the complex $[M_2M'(L)_2Cl_6]$ or $[M_3(L)_2Cl_4]Cl_2$ in dimethyl formamide (DMF) (10 cm^3) with triphenylphosphine (1.05 g, 0.004 mol) in ethanol (10 cm^3). The mixture was refluxed for 2h. with continuous stirring. The precipitate that was obtained after evaporation of the residue solution to about 1/3 of its volume, which was filtered out, washed with DMF, ethanol and diethyl ether, then dried under vacuum.

Preparation of $[NiPd(L)_2Cl_4]$

The salt $NiCl_2.6H_2O$ (0.48g; 0.002 mol) was dissolved in (10 cm^3) of ethanol and was added to

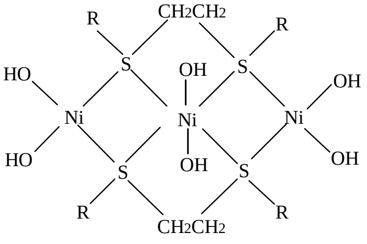
(0.86g, 0.002mol) of (L^1) or (0.55g, 0.002 mol) of (L^2) in ethanol (10 cm^3). A solution of $PdCl_2$ (0.18 g,0.001mol) in (10 cm^3) of distil water was added. The mixture was refluxed for 2h, with continuous stirring. The precipitate that was obtained, was washed with water and ethanol and then dried under vacuum.

RESULTS AND DISCUSSION

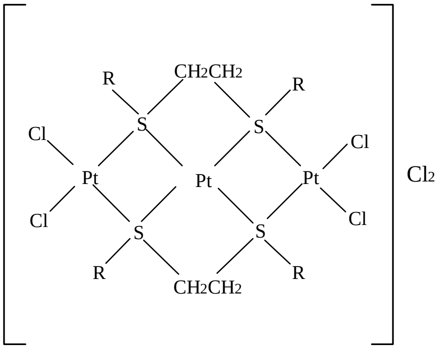
Treatment of n-dodecyl thiol or benzyl mercaptane with 1,2-dibromoethane in a basic medium gives, after recrystallization 80-85% yield of the ligands bis-(dodecylthio) ethane and bis-(benzylthio) ethane. Direct reaction of metal (II) chlorides with the above ligands gave the trinuclear complexes of general formula $[Ni_3(L)_2(OH)_6]$, $[M_3(L)_2Cl_6]$, $[Pt_3(L)_2Cl_4]Cl_2$,$[M_3(L)_2(PPh_3)_4Cl_4]Cl_2$ and unexpected complexes of general form $[NiPd(L)_2Cl_4]$ were L=L^1 and L^2 , M=Pd or Pt .

The nucleophilicity of sulphur atoms in these complexes is responsible for the formation of these complexes . The most fascinating feature of most of these complexes is their solubility in various organic solvents. The complexes are microcrystalline variously coloured powders, whose melting points are higher than that of the pure ligands (Table 1).

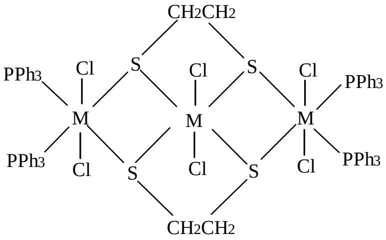
The electrical conductivity of the complexes in 10^{-3}M DMSO solution is within the range 10-21 $ohm^{-1}.mol^{-1}.cm^{-2}$, indicating the neutral nature of the complexes, except the complexes



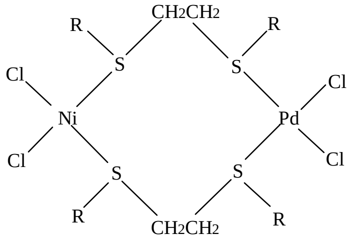
(1)



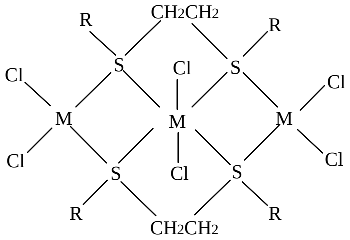
(3,10,12)



(6,9)
M= Pd or Pd Pt



(4,13)



(2,5,7,14,15,16,17)
M= Pt or Pd,Pt and Ni

Table 1: Physical properties of the prapred complexes

No	Complexes	Colour	m.p (ºC)	Analysis found (calc.)					$\Omega ohm^{1}.cm^{2}.$ mol^{-1}	μ_{eff} (B.M)
				C%	H%	Ni %	Pd %	Pt%		
L^1	$CH_3(CH_2)_4SCH_2CH_2$ $S(CH_2)_{11}CH_3$	White	49-51	72.11 (72.49)	12.08 (12.62)	-	-	-	-	-
1	$[Ni_3(L^1)_2(OH)_6]$	Pale brown	350d	54.03 (54.79)	9.77 (10.07)	18.48 (18.01)	-	-	10	3.19*
2	$[Pd_3(L^1)_2Cl_6]$	Yellow	272-274	44.77 (44.82)	7.02 (7.80)	-	22.92 (22.45)	-	6	2.97
3	$[Pt_3(L^1)_2Cl_4]\ Cl_2$	Black	237-234	37.20 (37.64)	6.11 (6.55)	-	-	35.12 (34.75)	74	Di
4	$[NiPd(L^1)_2Cl_4]$	Yellow	242-244	63.12 (53.45)	9.0 (9.30)	5.03 (4.81)	-	-	14	Di
5	$[Pd_2Pt(L^1)_2Cl_6]$	Brown	250-252	42.01 (42.13)	7.00 (7.33)	-	14.37 (13.95)	-	5	2.75
6	$[Pd_3(L^1)_2(PPh_3)_4Cl_4]\ Cl_2$	Pale yellow	250d	60.13 (60.92)	6.21 (6.92)	-	13.07 (12.69)	-	14	2.81
7	$[Pt_3(L^1)_2(PPh_3)_4Cl_4]\ Cl_2$	Gray	276-280	54.27 (54.98)	6.07 (6.24)	2.65 (2.62)	-	21.61 (21.40)	70	2.75
8	$[NiPd(L^1)_2(PPh_3)_4Cl_4]$	Yellow	283-285	66.99 (67.16)	7.24 (7.62)	-	-	-	2	2.85
9	$[Pd_2Pt(L^1)_2(PPh_3)_4Cl_6]$	Yellowish	260	58.22 (58.83)	6.13 (6.68)	-	8.41 (8.31)	-	4	2.97
L^2	$PhCH_2SCH_2CH_2SCH_2Ph$	White	40-42	70.0 (70.02)	6.06 (6.60)	-	-	-		
10	$[Ni_3(L^2)_2Cl_4]Cl_2$	Green	240d	40.99 (41.06)	3.31 (3.87)	18.79 (18.38)	-	-	71	Di
11	$[Pd_3(L^2)_2Cl_6]$	Orange	110	35.27 (35.56)	3.03 (3.35)	-	29.54 (29.05)	-	6	3.09
12	$[Pt_3(L^2)_2Cl_4]\ Cl_2$	Beje	128-130	28.13 (28.53)	2.28 (2.69)	-	-	43.31 (42.99)	78	Di
13	$[NiPd(L^2)_2Cl_4]$	Orange	168-170	44.20	3.99	6.86	-	-	5	Di

				(44.91)	(4.23)	(6.68)				
14	$[Pd_2Pt(L^2)_2Cl_6]$	Dark yellow	190-192	32.07 (32.86)	2.89 (3.09)	-	18.20 (17.82)	-	60	3.20
15	$[Pd_3(L^2)_2(PPh_3)_4Cl_4]\ Cl_2$	Yellow	266-268	58.29 (58.64)	4.11 (4.53)	58.29 (58.64) -	14.98 (14.88)	-	70	2.98
16	$[NiPd(L^2)_2(PPh_3)_4Cl_4]$	Yellow	258-260	65.22 (65.57)	4.97 (5.07)	3.08 (2.95)	-	-	79	2.77
17	$[Pd_2Pt(L^2)_2(PPh_3)_4Cl_4]Cl_2$	Greenish	264-266	56.17 (56.30)	4.08(4.35)	-	9.59(9.38)	-	74	2.83

d= decomposition,* each ion

(3,7,10,12) are (1:2) electrolyte[12]. This is consistent with the stoichiometry assumed for the complexes on the basis of the analytical data.

The most important IR assignment of the ligands as well as its bonding sites (Table 2) have been determined by careful comparison of the spectra of the ligands with those of their metal complexes. The ligands do not show any õ(SH) band in region of 2500-2600 cm^{-1} , in which this stretching frequency is generally expected(13).

The IR spectrum of the free ligands recorded using CsI, showed medium to strong bands at 630-635 cm^{-1}, which may be assigned to the vibration of õ(C-S) group. This apsorption was found at lower frequency in all complexes , indicating that this group was shared in coordination with the metal ions through sulphur atom(9).

The infrared spectra of metal complexes showed a new band at 360-405 cm^{-1} which may be assigned to ν(M-S). they also showed a band in the region 290-330 cm^{-1}, which may be associated to ν(M-Cl) vibration(14). The IR spectra of the adducts showed new bands at 430-455 cm^{-1} assigned to ν(M-P) {M=Pd(II) or Pt(II)} while that for M=Ni was not observed[10].

In order to obtain some information about the coordination properties of the metal ions, the electronic spectrum has been recorded. The tentative assignments of the absorption bands from the electronic spectra of the complexes are reported in Table 2. for the homonuclear complexes (No. 1-3,10-12). The nickel complex (1) shows three d-d transitions (Table 2) indicating the octahedral geometry, while Ni complex (10) shows one d-d transition, which indicates a square planar environment. The Pd complexes (2 and 11) contain a mixture of octahedral and square planar geometry (Table 2). The Pt complexes (3 & 12) have d-d transition belonging to square planer geometry[6] .

The hetronuclear complexes (4,13,8 and 16) comprise nickel and palladium metal ions. The complexes (No.4,13) show a bands that may be assigned square planar geometry around both Ni & Pd ions, while complex (No. 8) shows an octahedral environment around both ions (Table 2). Complex

Table 2: Selected IR bands (cm^{-1}) and electronic spectra of the ligands and their complexes

No.	IR band assignments (cm^{-1})								λmax	Assignment	Geometry
	υ(C – S)	υ(Ni– S)	υ(Pd– S)	υ(Pt–S)	υ(M–Cl)	υ(Pd– P)	υ(Pt– P)	υ(Ni– O)	(cm^{-1})		
L_1	630_S	-	-	-	-	-	-	-	38300		
1	595_S	385_w	-	-	-	-	-	440	10672	$^3A_2g(F)\rightarrow{}^3T_2g(F)(\tilde{o}_1)$	(Oct.) + (Sq.p.)
									12487	$^3A_2g(F)\rightarrow{}^3T_1g(F)(\tilde{o}_2)$	
									24096	$^3A_2g(F)\rightarrow{}^1A_1g$ or	
									29940	$^1A_1g(F)\rightarrow{}^1B_1g$	
2	608_m	-	348_w	-	$316_m 335$	-	-	-	10214	$^3A_2g(F)\rightarrow{}^3T_2g(F)$ or	(Oct.) + (Sq.p.)
									12180	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25125	$^1A_1g\rightarrow{}^1B_1g$	
3	616_S	-	-	372	$300_m 336$	-	-	-	19685	$^1A_1g\rightarrow{}^3A_2g$ or	(Sq.p.)
									27548	$^1A_1g(F)\rightarrow{}^1B_1g$	
									37037	C.T	
4	614_m	380_m	391_m	-	302_w	-	-	-	16863	$^1A_1g\rightarrow{}^1Eg$	(Sq.p.)
									25252	$^1A_1g\rightarrow{}^1B_1g$	
5	611_S	-	347_m	365m	$316_w 330_w$	-	-	-	10993	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct) + (Sq.p.)
									18148	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25510	$^1A_1g\rightarrow{}^1Eg$	
6	613_S	-	347_m	-	320_w	447_w		-	10121	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.) +(Sq.p.)
									14326	$^3A_2g(F)\rightarrow T_1g(F)$	
									25906	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
7	595_S	-	-	384m	$314_w 330_w$	-	455_w	-	11100	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	(Oct.) + (Sq.p.)
									12406	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25773	$A_2g(F)\rightarrow{}^3T_1g(p)$	
									34246	$^1A_1g\rightarrow{}^1Eg$	
8	603_S	363_m	344_m	-	320_m	435_m		-	10214	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	(Oct.)
									12376	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									26385	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
9	608_m	351	376	-	$330_m 310_m$	430_m	452_m	-	10143	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	(Oct.)
									18148	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25510	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	

L_2	635	-	-	-	-	-	-	-	36000		
10	605_m	391	-	-	300_m	-	-	-	25641	$^1A_1g\rightarrow{}^1Eg$	(Sq.p.)
11	615_m	-	405_m	-	$283_w 300_w$	-	-	-	10193	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.) + (Sq.p.)
									14450	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									26525	$^1A_1g\rightarrow{}^1Eg$	
12	614_S	-	-	367m	$292_w 320_w$	-	-	-	16129	$^1A_1g\rightarrow{}^1A_2g$	(Sq.p.)
									26385	$^1A_1g\rightarrow{}^1Eg$	
13	605	383_m	360_m	-	$331_w 301_w$	-	-	-	18832	$^1A_1g\rightarrow{}^1A_2g$	(Sq.p.)
									25188	$^1A_1g\rightarrow{}^1Eg$	
14	608	-	375_m	400_m	$300_w 330_w$	-	-	-	99701	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.) + (Sq.P.)
									17271	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25125	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
									29300	$^1A_1g\rightarrow{}^1Eg$	
15	594_m	400_m	370_m	-	$283_m 300_m$	440_m	-	-	10204	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.) + (Sq.P.)
									11	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25125	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
									29000	$^1A_1g\rightarrow{}^1Eg$	
16	602_S	-	391_m	-	$331_m 450_m$	435_m	-	-	12886	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.)
									1727	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25125	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
17	600_m	-	380_m	402_m	290450_m	445_w	-	-	10090	$^3A_2g(F)\rightarrow{}^3T_2g(F)$	(Oct.) + (Sq.P.)
									17699	$^3A_2g(F)\rightarrow{}^3T_1g(F)$	
									25336	$^3A_2g(F)\rightarrow{}^3T_1g(p)$	
									29096	$^1A_1g\rightarrow{}^1Eg$	

s =strong ,m=medium,w=weak

(16), show octahedral environment around nickel ion and square planar around the palladium ion .

The complexes (5& 14) show the presence of three bands indicating an octahedral environment for central metal ion and a square planer for the terminal metal ions.

The adducts with triphenylphosphine (6, 7, 9, 15 and 17),show three d-d transition bands (Table 2) indicating an octahedral geometry for terminal ions and a square planer geometry for central ion, except complex (9) which shows only octahedral geometry. The adducts (8&16) have three d-d transition bands which belong to an octahedral environment.

The magnetic moment measurements for the prepared nickel complexes and adducts (1,8,10 and 16) gave the values (3.19,2.85,3.24 and 2.77 B.M) meaning the are paramagnetic and having an octahedral geometry(17). On the other hand, the complexes (4 &13) which are diamagnetic and thus have a square plane geometry(16).The palladium complexes number (2,5,6,9, 11,14,15 and 17) their magnetic values (2.97,2.75,2.81,2.97, 3.09, 3.20, 2.98 and 2.83 B.M), may indicate that the central metal ion possesses an octahedral environment while the terminal metal ions are of a square planar geometry[18],except complexes (15&17) where the central metal ion is a square planer and the terminals are of octahedral environment.

The platinum complexes (3,7,12) have the magnetic moment values of (0.0, 2.75 and 0.0 B.M) meaning that the complexes are diamagnetic and indicating a square planar geometry except complex (7) which possesses an octahedral geometry for central metal and a square planar geometry for terminal ions[19].

On the bases of the fore-going studies , the ligands used in this study, coordinate to the metal ions in bidentate or tridentate fashions from the sulphur site of the ligand forming dinuclear and trinuclear complexes as shown in Fig 1.

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