

Preparation and Characterization of Homo and Heterobinuclear Complexes of Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2} with Tetramethylthiurammonosulfide

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Abstract:

Some new homo and heterobinuclear complexes of Co(II) , Cu(II) , Ni(II) , Zn(II) Cd(II) and Hg(II) with tetramethylthiurammonosulfide have been prepared in 2:2 molar ratio. The prepared complexes were characterized by their metal contents (Co , Ni , Cu , Zn , Cd and Hg), IR, electronic spectra, conductivity and magnetic measurements.

Conductivities data showed that the complexes were non electrolytes assigning the formulae $[\text{M}_2(\text{L})_2\text{CL}_4]$ or $[\text{MM}'(\text{L})_2\text{CL}_4]$. Explanation for the structural elucidation of these complexes on the bases of magnetic and electronic measurements indicated that the complexes had tetragonal geometry with tetrahedral environment.

تحضير وتشخيص المعقدات المتجانسة وغير المتجانسة ثنائية النوى

Co^{+2} و Ni^{+2} و مع رباعي مثيل ثايورام احادي الكبريتيد Hg^{+2}
و Cd^{+2} و Zn^{+2} و Cu^{+2}

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ملخص البحث:

يتضمن هذا البحث تحضير بعض المعقدات الجديدة المتجانسة وغير المتجانسة ثنائية النوى لـ Co(II) و Ni(II) و Cu(II) و Zn(II) و Cd(II) بالإضافة إلى Hg(II) مع ليكند رباعي مثيل ثايورام أحادي الكبريتيد بنسبة مولية 2:2 (فلز : ليكند). شُخصت المعقدات باستخدام قياس المحتوى الفلزي (الكوبلت، النيكل، النحاس، الكاديوم، الخارصين، الزئبق) وقياس طيف الأشعة تحت الحمراء وطيف الأشعة المرئية - فوق البنفسجية وقياس التوصيلية الكهربائية والقياسات المغناطيسية. أشارت قيم التوصيلية للمعقدات بأنها غير موصلة، وتمتلك صيغ عامة $[\text{M}_2(\text{L})_2\text{CL}_4]$ أو $[\text{MM}'(\text{L})_2\text{CL}_4]$ وتم بيان الصيغ التركيبية للمعقدات اعتماداً على قيم العزم المغناطيسي وقياس الطيف الإلكتروني حيث تبين أن المعقدات رباعية التناسق تمتلك بنية رباعية السطوح.

Introduction

There is considerable interest in the unusual structures adopted by chalcogenolate complexes of transition metals and group 12 elements ^[1-2] the (thiuramsulfides $R_2NC(S)_nC(S)NR_2$ ($n=2$)(R_4tds) tetramethylthiuram disulfides) ^[3] have been known on account of their biological activities, which lead to applications as fungicides, rubber vulcanization, accelerator agent of alcoholism therapy ^[4-5], as well as their ability to stabilize high oxidation states in transition metals ^[6].

The mono sulfides ($n=1$) tetramethylthiurammonosulfide (R_4tms) , (perhaps because the lack of wide breadth of applications as known for the disulfides in agriculture and experimental medicine) , ligand have been much less extensively studied, and where such studies deal with the subject of interaction of mono sulfide with metal species, the field remained virtually unexplored ^[7]. The preparation and characterization of 1: 1 adducts of silver halides AgX ($X= Cl^-, Br^-, I^-$) with N, N, N', N' tetramethylthiurammonosulfide have been reported. The products were characterized by elemental analysis, magnetic measurements and IR and Raman spectroscopy ^[8].

The reactions of $CoCl_2$ and $NiCl_2$ with tetramethylthiurammonosulfide in boiling ethanol produced $[Co(dtc)_3]$ and $[Ni(dtc)_2]$ ($dtc=$ dithiocarbamate) through ascession of C-S-C and the metal ions were not oxidized, which were studied by *Ojima et al.* ^[9]. *Victoriano et al.* ^[10-11] showed that the reaction of acetonitrile solutions of copprous iodide and tetraethylthiurammonosulfide (Et_4tms) lead to the formation of a crystalline solid of composition $[(CuI)_5(Et_4tms)_2]$.

Some new Co(II), Ni(II), and Cu(II) complexes with tetramethylthiuram - monosulfide and their adducts with monodentate and bidentate donor ligands gave adducts in (1: 1) and (1: 2) molar ratio. The prepared complexes and adducts were characterized by elemental analysis, IR and UV-Visible spectroscopy, conductivity and magnetic measurements ^[12].

In this paper the preparation and characterization of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with tetramethylthiurammonosulfide have been described and characterized physico-chemically .

Experimental

All the chemicals used were of high purity. The metal contents (Co, Ni, Cu, Zn, Cd and Hg) estimated spectrophotometrically using (pye Unicam SPG atomic absorption spectrophotometer) ^[13] measured in department of Biology

Melting points were measured by a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra were recorded using infrared using spectrometer Model Tanser 27 Bruker Co. Germany ($200-4000\text{ cm}^{-1}$) as CsI pellets.

The electronic spectra were recorded on Shimadzu UV-vis spectrophotometer UV-160 using $10^{-3}M$ solution of the ligand and their complexes in DMSO at $25^\circ C$. Conductivity measurements were carried out on $10^{-3}M$ solution of the complexes in DMSO at ambient temperature by PMC₃(JENWAY) Conductivity Model). Magnetic measurements were carried out by the Faradays method using Bruker BM6 instrument.

Preparation of the complexes :

Preparation of $[M_2(L)_2 Cl_4]$ where $M= Zn, Cd, Hg$:

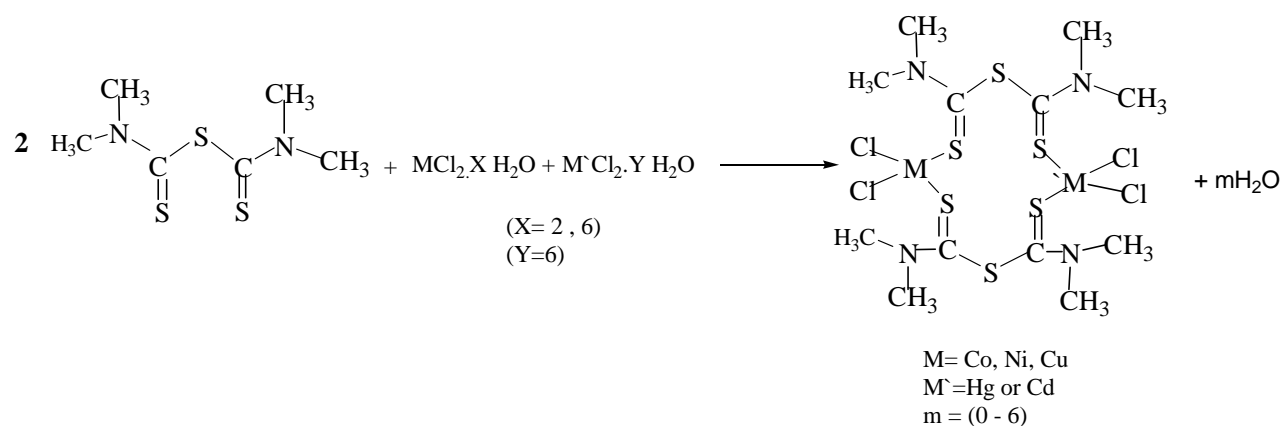
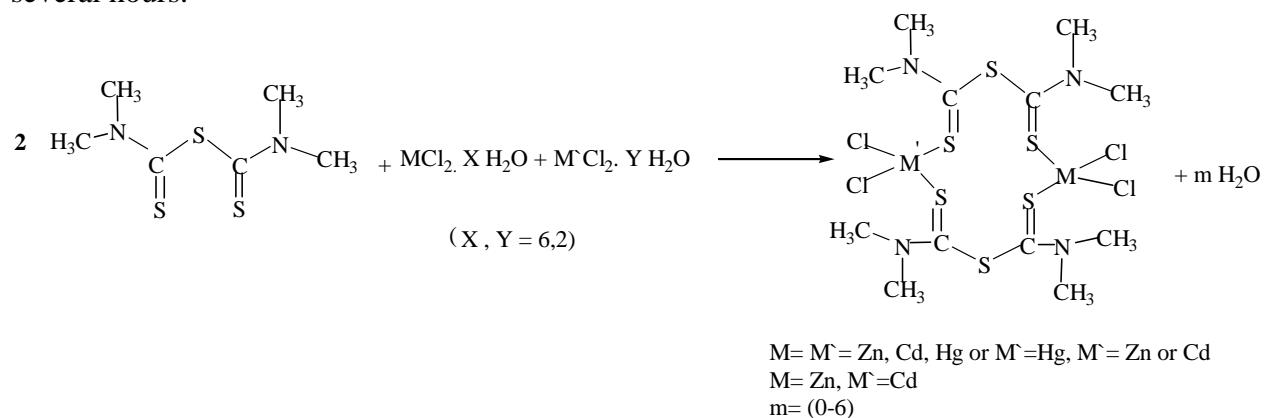
The metal salts $ZnCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol), $CdCl_2 \cdot 6H_2O$ (0.45 g, 2 mmol), $HgCl_2 \cdot 6H_2O$ (0.76 g, 2 mmol) was dissolved in ethanol (15 cm^3) and the resulting solution was filtered through celite the filtrate was added to the solution of ligand (0.42g, 2 mmol) in ethanol (10 cm^3) and the mixture was refluxed for 3h. The solution was reduced in volume (5 cm^3) the solid thus formed, was filtered off washed several times with ethanol and diethylether then dried under vacuum for several hours.

Preparation of $[MM'(L)_2Cl_4]$, $M = Zn$, $M' = Cd$, Hg :

The Zinc chloride (0.24g, 0.001 mol) and cadmium chloride (0.29g, 0.001 mol) dissolved in (15 cm³) ethanol were added to the solution of the ligand (0.42g, 2 mmol) in ethanol (10 cm³) then following the above procedure.

Preparation of $[MM'(L)_2Cl_4]$, $M = Co$, Ni , Cu , $M' = Cd$ or Hg :

Ethanol solution of the ligand (0.42g, 0.002 mol) in ethanol (20 cm³) were mixed with of $CoCl_2 \cdot 6H_2O$ (0.24g, 0.001 mol), or $NiCl_2 \cdot 6H_2O$ (0.24g, 0.001 mol) or $CuCl_2 \cdot 2H_2O$ (0.17g, 0.001 mol) and $CdCl_2 \cdot 6H_2O$ (0.29g, 0.001 mol) or $HgCl_2 \cdot 6H_2O$ (0.38g, 0.001 mol). The solution were heated under reflux for 2h. Then the coloured precipitate was observed, the product was filtered off. The precipitate was washed with ethanol and diethylether for several times, then dried under vacuum for several hours.



Results and discussion

The complexes were prepared by the reaction of metal chloride with tetramethylthiurammonosulfide, however, was found not to decompose to N, N-dimethyldithiocarbamate anion as found by *ojima et.al* [9].

The physical properties of the solid complexes have been listed in (Table 1). The complexes were quite stable in dry air and very slowly affected by moisture, they were fairly stable to heat and found to melt (decompose) at (115-291°C). They were insoluble in most organic solvent except DMF or DMSO.

The molar conductivities of 10⁻³M solution of the complexes (Table 1) indicated that the complexes are non electrolytic in DMSO [14].

The most important IR assignment of the ligand have been studied by a careful comparison of the spectra of the ligand with those of their complexes (Table 2). The IR spectra of the ligand showed medium band at 680 cm⁻¹ assigned to $\nu_{(C-S-C)}$. This

vibration remained unchanged in the spectra of all complexes. Another band appearing at 960 cm^{-1} in the free ligand assigned to $\nu_{\text{(C=S)}}$ was found to be shifted to alower position upon coordination with metal ions ^[15]. Moreover the IR spectra of the complexes showed new band at $350\text{-}380\text{ cm}^{-1}$ which is tentatively assigned to $\nu_{\text{(M-S)}}$ ^[16]. Furthermore, the IR spectra of the complexes showed another new band in the region $280\text{-}330\text{ cm}^{-1}$ which may well due to $\nu_{\text{(M-Cl)}}$ ^[16].

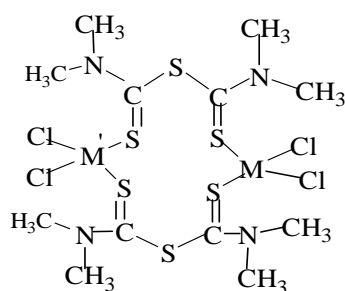
The magnetic moment data of the complexes calculated from the corrected magnetic susceptibilities determined at 25°C are given in Table 1. The magnetic moment values of complexes (1-6) are zero as expected for d^{10} elements, whereas for the complexes (7-12) had values higher than the spin free value of respective metal ion, indicating tetrahedral geometry for the complexes^[17]. The UV-visible spectra of the ligand and their complexes in 10^{-3} M solution (DMSO) were recorded. The results were listed in Table 2, the broad band observed at 35714 cm^{-1} was due to charge transfer transition within the ligand.

The electronic spectra of Co(II) complexes (7,10) recorded showed a broad band at $15528\text{-}15576\text{ cm}^{-1}$ due to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ (ν_3) transition in tetrahedral symmetry as the results ^[18- 20]. The ligand field parameter B and the ligand field splitting energy (10Dq) in case of Co(II) complexes have been calculated, the values of (B, β , ν_2/ν_1) suggested tetrahedral geometry for all the complexes ⁽²¹⁾.

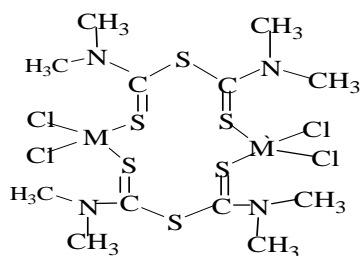
The electronic spectra of Ni(II) complexes (8,11) showed bands at 16181 and 16393 cm^{-1} , respectively, due to ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition (ν_3) in tetrahedral geometry^[22]. The ligand field parameter B and the ligand field splitting energy (10Dq) in case of Ni(II) complexes have been calculated, the values of (B, β , ν_2/ν_1) suggested tetrahedral geometry for all the complexes ⁽²¹⁾.

The electronic spectra of the Cu(II) complexes (9,12) showed bands at 16129 and 16321 cm^{-1} corresponding to the transition ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ and other bands at $28900\text{-}31200\text{ cm}^{-1}$ due to the charge transfer, which is consistent with tetrahedral geometry ^[23].

According to the above measurements, the following structures for the complexes (Fig 1) have been suggested .



M= M' = Zn, Cd, Hg, or M' =Hg, M' = Zn or Cd
M= Zn, M' = Cd



M= Co, Ni, Cu

M' =Hg or Cd

Fig 1 : Suggested structure for the prepared complexes

Table (1)
Some physical properties and some electronic spectral data of the complexes

No.	Compounds	Colour	m.p (°C)	Λ_M (ohm ⁻¹ . mol ⁻¹ .cm ²)	μ_{eff} (B.M)	Metal content Found/(Calculated)
1	[Zn ₂ (L) ₂ Cl ₄]	White	291	13.4	----	9.49 (8.95)
2	[Cd ₂ (L) ₂ Cl ₄]	White	183	19.7	----	14.36 (14.0)
3	[Hg ₂ (L) ₂ Cl ₄]	White	178 ^d	10.7	----	20.9 (19.82)
4	[Zn Cd (L) ₂ Cl ₄]	White	115	18.8	----	Zn 8.89(8.4) Cd 15.27 (15.0)
5	[Zn Hg (L) ₂ Cl ₄]	Pale Yellow	150	11.9	----	Zn 7.93 (7.5) Hg 24.34 (23.1)
6	[Cd Hg (L) ₂ Cl ₄]	Pale Brown	213 ^d	16.7	----	Cd 12.91 (12.3) Hg 23.03 (22.5)
7	[Co Cd (L) ₂ Cl ₄]	Dark green	235	19.4	4.2	Co 8.08 (8.0) Cd 15.41 (15.0)
8	[Ni Cd (L) ₂ Cl ₄]	Dark green	266	14.7	3.2	Ni 8.05(7.95) Cd 15.4 (15.04)
9	[Cu Cd (L) ₂ Cl ₄]	Dark Brown	210	17.2	2.2	Cu 8.66(8.4) Cd 15.31(15.0)
10	[Co Hg (L) ₂ Cl ₄]	Pale green	190	18.3	4.4	Co 7.21 (7.0) Hg 24.53(23.8)
11	[Ni Hg (L) ₂ Cl ₄]	Greenish Yellow	278	16.8	3.01	Ni 7.18 (7.0) Hg 24.54 (23.72)
12	[Cu Hg (L) ₂ Cl ₄]	Brown	240	13.6	1.85	Cu 7.73 (7.4) Hg 24.39 (24.0)

Λ_M = molar conductivity , μ_{eff} = effective magnetic moment , **d**= decomposition point .

Table (2)
IR spectra and electronic spectra of the ligand and their metal compounds

Compounds	IR spectra			Electronic spectra					
	ν (C-S)	ν (M-S)	ν (M-Cl)	ν (cm ⁻¹)	10Dq	ν_2/ν_1	B(cm ⁻¹)	β	C.F.S.E
(C6H12 N2S3)	960(S)	—	—	35714	---	---	---	---	---
1	942	350(w)	290	35971	---	---	---	---	---
2	950	370(w)	300	35211	---	---	---	---	---
3	950	360	310	33783	---	---	---	---	---
4	952	372	320	35971	---	---	---	---	---
5	950	380(w)	330	35881	---	---	---	---	---
6	950	375	320	35971	---	---	---	---	---
7	944	370	310	15528,24032, 28571	15528	1.6	778	0.8	18633
8	948	365	320	16393, 25907, 29412	16393	2.106	995	0.9	13114
9	942	360	310	16129, 22831,28900	---	---	---	---	---
10	950	380	320	15576, 28409	9469	1.67	1038	1.0	11362
11	940	360	330	16181, 25641	7263	2.171	1117	1.0	5810
12	942	370	310	16321,31200	---	---	---	---	---

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