Synthesis and characterization of new complexes of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} with (Sodium acetate thio) ethylene ligands

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Abstract :

This research involves the preparation of new ligands 1,1,2,2- tetrakis (sodium acetate thio)ethylene(L^1) and 1,1,2- tris(sodiumacetatethio) ethylene(L^2), through the reaction of disodium thioglycolate) with tetra chloro ethylene or tri chloro ethylene in (1:4) or (1:3) moler ratio . Homodinucliar complexes of general formlu $[M_2(L^1)]$ and $[M_2(L^2)ClH_2O]$, when M= Co(II), Ni(II), Cu (II) and Zn(II) also mono nuclear complexes of general formula $[M(L^2)]$. The prepared complexes were characterized using spectral method (UV/Visible/ IR) , metal content analysis , magnetic and atomic measurements . The spectral and magnetic measurement indicats that some complexes have tetrahedral or square planar complexes environtment .

Key Words : transition metal complexes , acetate thio.

Introduction :

Coordination chemistry of metal - sulfur or oxygen compounds is a source of stimulation to many research workers , due to the fact that it possesses unique metal complexes of ligands containing sulfur or oxygen as donor atoms were studied by many workers. The biological and carcinostatic activitis of metallo sulfur or oxygen compounds have been surveyed for many years [1,2] .

The photo stabilization of poly (vinyl chloride) films by(2-thio acetic acid -5-phenyl -1,3,4- oxadiazole with Sn(II), Ni(II), Zn(II), Cu(II)and Co(II) complexes were investigated. The films containing different concentration of complexes ranging from 0.1% to 0.5% by weights were produced by the same casting method from THF solvent [3].New cobalt (II) dithio curbazats with different mono and dinegative counter ions of general formula $[Co(IN\text{-}DtzH)_2]$ Xn , where (IN-DtzH= isonicotinoyl dithiocarbazic acid, X= Cl , Br , NO_3 , ClO_4 , CH_3COO for n= 2 and X= SO_4 and C_2O_4 for n=1) have been obtained . The prepared complexes have been investigated by elemental analysis UV, IR and magnetic measure mentswere studied by Kalia etal [4].The synthesis and structural characterization of a novel in(III) complexes are described . The reaction between $InCl_3$ with sodium mercaptoacetic acid , affords ($NaSCH_2COOH$) in 4-methyl pyridine (4-Mey) at $25\overset{\circ}{c}$ $[ClIn(SCH_2COO)_2]^{2-}$ $[4MepyH)_2]^{2+}$ (1), X- ray diffraction studies of (1) show it to have a distorted square pyramidal geometry that were studied by Banger etal[5].Yang etal 2002[6] were studied the reaction of $Na_2MoO_4.2H_2O$ with mercapto acetic acid and NH_4Cl in H_2O yielded new complexes $(NH_4)_2$ $[Mo_2O_2(SCH_2COO)_2(SCH_2COO)_2]$. The complexes exhibit a bioctahedral geometry and linked to three dimensional frame work via H-bonds . Using a similar reaction system but , additionally , adding the strong reducing agent $NH_2NH_2.2HCl$, we have now succeeded in isolating a novel tetranuclear mixed valance complex

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$(NH_4)Na_3[Mo_4O_2(SCH_2COO)_6(SCH_2COO)_2]$. $10H_2O$, representing the first example of new class of tetra nuclear Mo-S complexes with a linear metal – metal chain .In new of these interesting results and as continuation of our studies on transition metal complexes with sulfur and oxygen ligands [7,8,9] , we are presenting here the preparation of new ligands and their Co(II), Ni(II), Cu(II) and Zn(II) complexes.

Materials and Methods :

All chemicals that are reagent grade , were used as supplied (Fluka)or (B.D.H).

Metal estimation was done on PyeUnicam SPG Atomic Absorption spectrophotometer . Conductivity measurements for 10^{-3}M solution of the complexes in DMSO were carried out with Jenway 4070 conductivity meter . Infrared spectra were recorded on an FTIR Brucker Tensor 27 Co spectrophotometer in 200-4000 cm^{-1} rang using CsI discs . The UV/Vis spectra were recorded on a shimadzu UV-160 spectrophotometer for 10^{-3} M solution of complexes in DMSO using 1cm quartz cell . Magnetic susceptibility was measured on the solid state by faraday's method using Brucker BM6 instrument at 25C° , all magnetic susceptibilities values were corrected for diamagnetic contribution using Pascal's constant .

Preparation of ligands

1- Preparation of 1,1,2,2- tetrakis (sodium acetatethio) ethylene (L^1):

solution of tetrachloroethlylene (1.02g,0.01mol)in ethanol 10ml was boiled under reflux for 6h with an equivalent amount of 2-mercaptoacetie acid sodium salt (4.56g, 0.04mol) and NaOH (1.60g, 0.04mol) in ethanol (20ml), after cooling to room temperature. NaCl was removed by filtration and the precipitation was washed with ethanol and diethyl ether then dried under vacuum.

2- Preparation of 1,2,2- tris (sodium acetate thio) ethylene (L^2):

this ligand was prepared using similar procedure as above .

3- Preparation of homodinuclear complexes $[M_2(L^1)]$:

A clear solution of the ligand (L^1) (0.489, 0.001mol) in 10 ml ethanol : water (50/50) was added to a solution of $CoCl_2.6H_2O$ (0.48g, 0.002 mol) in 10ml ethanol , the mixture was refluxed for 2h . Then the mixture was left 24h at room temperature to give the precipitate , which was filtered off washed several times with ethanol and diethylether then dried under vacuum .

The rest of the complexes Ni(II), Cu(II) and Zn(II) were prepared similarly .

4- Preparation of $[M_2(L^2)Cl\ H_2O]$ complexes:

These complexes were prepared used the above procedure.

5- Preparation of mononuclear complexes $[M(L^2)]$:

A clear solution of ligand (L^2) (0.36g, 0.001mol)in ethanol : water (50/50) (10ml) was added to $CoCl_2.6H_2O$ (0.24g, 0.001mol) in 10 ml ethanol , the mixture was refluxed for 2h and the precipitate was formed , filtered off washed with ethanol and diethyether.

Results and discussion :

The new ligands (L^1) and (L^2) were prepared by the reaction of disodium thioglycolate with tetrachloro ethylene or trichloro ethylene to give 1,1,2,2-tetrakis (sodium acetate thio) ethylene (L^1) and 1,1,2- tris (sodium acetate thio) ethylene (L^2)in high yield .(Table 1).

Table (1): some physical properties of ligands

No.	Ligands	Colour	Melting point °c	Yield %
L^1	$C_{10}H_8O_8S_4Na_4$	Beige	235-237	74
L^2	$C_8H_7O_6S_3Na_3$	Light yellow	221-223	91

The complexes were prepared through direct reaction of the metal chlorides , $CoCl_2.6H_2O$, $NiCl_2.H_2O$, $CuCl_2.2H_2O$ or $ZnCl_2$ with the above ligands in (1:2) or (1:1) molar ratio . All metal complexes except Zn(II) complexes are colored, all of them are stable toward air and moisture . The metal complexes are insoluble in common organic solvents . They are soluble in DMF or DMSO. The analytical data (Table2) of the metal complexes show that all the metal complexes have (1:1) or (2:1) metal to ligand stoichiometery . Conductance measurements were carried out to ascertain the electrolytical non electrolytic nature of the metal complexes in (10^{-3}M) DMSO solution at room temperature suggest non electrolytic nature for the complexes [10].

Table (2): Analytical , magnetic moments, Conductance and Some physical properties for complexes

No.	Complexes	Colour	Decompose degree	Yield %	%Metal Calc. (Found)	Λ_M(DMSO) ohm^{-1}. cm^2.mol^{-1}	μeff(B.M)
1	$[Co_2(C_{10}H_8O_8S_4)]$	Black	＞350	78	23.17 (23.47)	4	2.59*
2	$[Ni_2(C_{10}H_8O_8S_4)]$	Dark brown	265	90	23.19 (23.41)	8	3.21*
3	$[Cu_2(C_{10}H_8O_8S_4)]$	Green	285	70	24.33 (24.85)	18	1.91*
4	$[Zn_2(C_{10}H_8O_8S_4)]$	White	260	78	25.56 (25.39)	16.	Diamagnetic
5	$[Co_2(C_8H_7O_6S_3)Cl\ H_2O]$	Black	132	82	25.45 (25.26)	13	2.29*
6	$[Ni_2(C_8H_7O_6S_3)Cl\ H_2O]$	Dark brown	290	86	25.09 (25.19)	11	3.47*
7	$[Cu_2(C_8H_7O_6S_3)Cl\ H_2O]$	Olive	195	68	26.52 (26.71)	5	1.83*
8	$[Zn_2(C_8H_7O_6S_3)Cl\ H_2O]$	White	275	82	27.98 (27.27)	13	Diamagnetic
9	$[Co\ (C_8H_7O_6S_3Na)]$	Black	＞350	92	15.67 (15.62)	12	2.33
10	$[Ni\ (C_8H_7O_6S_3Na)]$	Olive	245	83	15.27 (15.58)	15	Diamagnetic
11	$[Cu\ (C_8H_7O_6S_3Na)]$	Black	>350	74	16.81 (16.64)	18	1.65
12	$[Zn\ (C_8H_7O_6S_3Na)]$	White	235	65	17.28 (17.04)	6	Diamagnetic

*For each ion

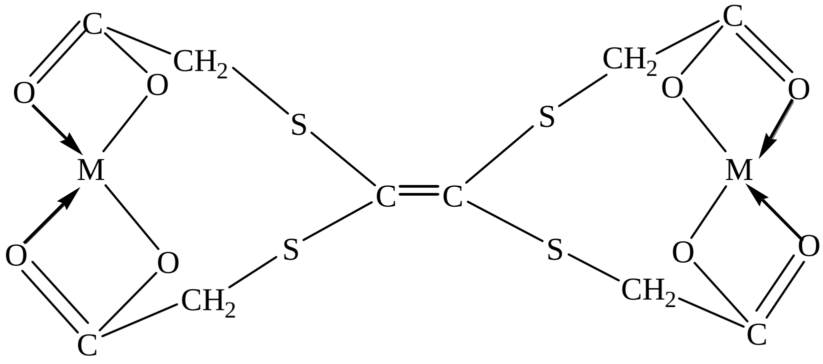
The infrared spectrum of the ligands show characteristic stretching absorption bands at 1583-1584, 1400-1402, (876-884)cm^{-1} assigned to ν asym (COO), ν (COO)sym and ν(C-S) groups.The COO stretching vibrations are important to predict the bonding mode of the ligand . According to[11], the values of Δν [Δν= νasy (COO)- ν sym (COO)] can be divided int 2 groups , a) In compounds where Δν (COO)> 350cm^{-1}, the (COO) groups binds in monodentate fashion b)In compounds where Δν (COO)< 350 cm^{-1} the carboxylate group binds in bidentate fashion . It has been suggested that Δν (COO) value in the chelating mode of the carboxylate are bidentate in all complexes (Table3).The ν(C-S) was not shifted through coordination with the metal ion, this means that it was not shared in coordination with the metal ions . The appearance of additional low frequency bands in the region 275-338, 485-566 and 3510-3552cm^{-1} are assignable to ν (M-Cl), ν (M-O) and coordinated water respectively [12] .The magnetic moments are measured at 25C° . The magnetic moments are (2.29-2.59)B.M for Co(II) complexes (1,5and9) respectively , while for Ni(II) complexes (10) are diamagnetic and(2,6)(3.21 and 3.47) B.M, for Cu(II) complexes (3,7and11) are (1.65-1.91)B.M suggest the presence of one electron , Zn(II) complexes (4,8and12) are diamagnetic . [13] .The UV- visible spectra of the ligands and their complexes in 10^{-3}M solution of DMSO were recorded . The results were listed in Table . The bands observed at 34364 and 35714cm^{-1} were due n → π* or π - π* respectively transition within the ligands. The spectrum of Co(II) complexes (1,5 and 9) show bands at 14641- 14727cm^{-1} which may be assigned to$^2A_1g \rightarrow {}^2B_1g$ (ν_3) transition in square planer geometry [14] .The electronic spectra of Ni(II) complexes (2,6) showed bands at 13986 and 13831 cm^{-1} . There bands assigned to $^3T_1(F) \rightarrow {}^3T_1(P)(\nu_3$) transition while the other two transitions ν_1 and ν_2 could not be observed since they are located below the limits of our instrument. These suggest a tetrahedral enviroment around Ni(II) complexes , while Ni(II) complex (10) shows bands at 15144cm^{-1}and 20118 cm^{-1} which correspond to the transition $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1A_2g$ respectively suggesting a square planer geometry around Ni(II)ion[15] . The electronic spectra of Cu(II) complexes (3,7and11) showed bands at 14044-16366cm^{-1} were assigned to ^{2} $B_1g \rightarrow {}^2Eg$ transition in the suqure planer enviroment [16].The magnetic moment measurements showed that all Zn(II) complexes (4,8and 12) were diamagnetic and the electronic spectra of these complexes do not show any d-d bands.

Table (3): IR absorption (cm^{-1}) and electronic spectra for complexes

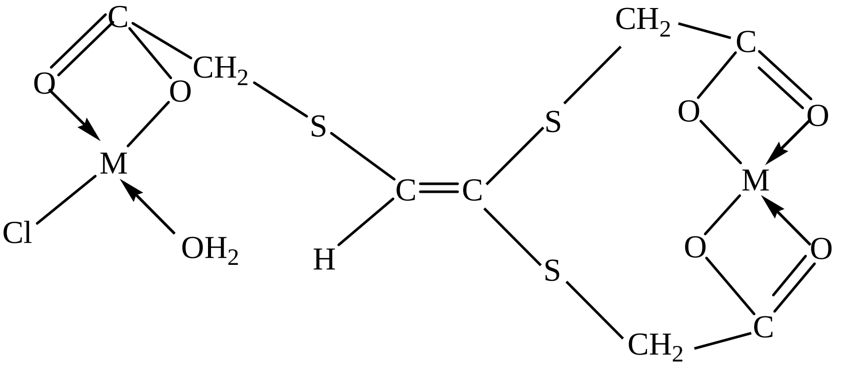
No. of Complex	ν (COO^-)		Δν	ν(M-O)	ν(M-Cl)	ν($M-OH_2$)	UV/ Visible bands Maximam (cm^{-1})	Possible assignments
	νasym	νsym.						
1	1575(s)	1360(m)	215	556(m)	-	-	14641	$^2A_1g \rightarrow {}^2B_1g$
2	1576(m)	1399(m)	177	542(w)	-	-	13986	$^3T_1(F)^3 \rightarrow T_1(P)$
3	1646(m)	1362(s)	284	504(m)	-	-	14044	$^2B_1g \rightarrow {}^2Eg$
4	1625(w)	1412(s)	213	566(s)	-	-	28901 37037	Charge transfer
5	1580(m)	1359(m)	221	490(w)	326(m)	3510	14727	$^2A_1g \rightarrow {}^2B_1g$
6	1573(m)	1400(s)	173	485(m)	310(m)	3525	13831	$^3T_1(F) \rightarrow {}^3T_1(P)$
7	1652(m)	1363(s)	289	504(s)	338(w)	3552	15220	$^2B_1g \rightarrow {}^2Eg$
8	1626(m)	1438(w)	188	494(s)	275(m)	3540	29940 36900	Charge transfer
9	1600(m)	1356(m)	244	520(w)	-	-	14705	$^2A_1g^2 \rightarrow B_1g$
10	1580(s)	1385(s)	195	489(s)	-	-	15144 20118	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1A_2g$
11	1634(w)	1420(w)	214	514(s)	-	-	16366	$^2B_1g \rightarrow {}^2Eg$
12	1625(m)	1377(s)	248	565(s)	-	-	28653 40322	Charge transfer

S= strong , m= medium , w= weak.

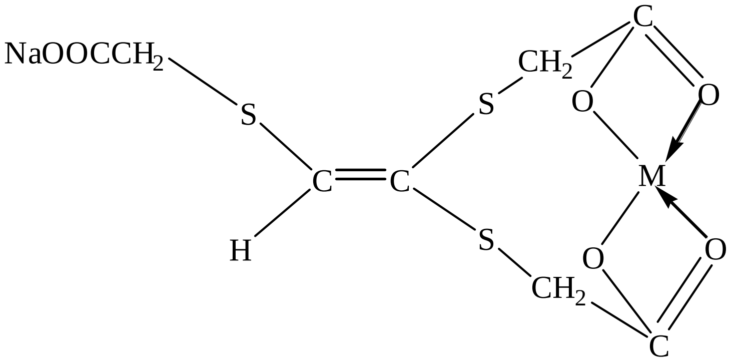
The ligands in this study behave as tetradentate,hexa, or octadentate from the two oxygen atoms of carboxylate group as well as the chloride ion and water molecule present in some of the complexes as in Fig.1:



Dinuclear Complexes (1-4)



Dinuclear Complexes(5-8)



Mononuclear complexes(9-12)

M=Co^{2+},Ni^{2+},Cu^{2+},Zn^{2+}

Fig. (1): suggested structures for the complexes

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تحضير وتشخيص معقدات Co^{+2}، Ni^{+2}، Cu^{+2} وZn^{+2} الجديدة مع ليكاندات(صوديوم خلات ثايو)أثيلين

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الخلاصة:

يتضمن البحث تحضير الليكاندات الجديدة وهي 1,1,2,2 -تتراكس (صوديوم خلاتو ثايو) اثيلين (L^1) و 1,1,2 - تريس(صوديوم خلاتو ثايو) اثيلين (L^2) من خلال تفاعل ثايوكلايكولات ثنائي الصوديوم مع رباعي كلورو اثيلين أو ثلاثي كلورو اثيلين بنسبة مولية (1:4) أو (1:3) .كذلك تم تحضير معقدات ثنائية النوى المتجانسة ذوات الصيغ العامة [$M_2(L^1)$] و [$M_2(L^2)$ Cl H_2O] عندما M= Co(II), Ni(II), Cu(II) وZn(II) وكذلك المعقدات أحادية النوى ذوات الصيغة [$M(L^2)$] .تم تشخيص المعقدات المحضرة باستخدام الطرق الطيفية (الأشعة فوق البنفسجية وتحت الحمراء) تحليل نسبة الفلزات ، القياسات المغناطيسية والقياسات التوصيلية بينت نتائج المغناطيسية والقياسات الطيفية أن بعض المعقدات تمتلك بنية رباعي السطوح والقسم الآخر بنية المربع المستوي .