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Synthesis and characterization of ligating properties of organic disulfides complexes with Co^{+2}, Ni^{+2} and Cu^{+2} metal ions

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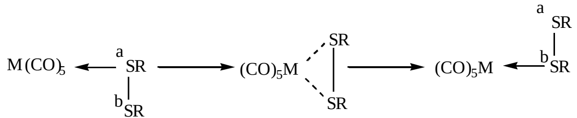
Abstract

A series of new complexes of the type $[M(L)Cl_2]$, $[M(L)_2Cl_2]$ and $[M(L)_2]Cl_2$, where L= L^1 or L^2 , L^1= 2,2`-thiosalyciylic acid disulfide, L^2=dibenzyl disulfide, M=Co^{+2}, Ni^{+2} and Cu^{+2}, were prepared and characterized by molar conductance, IR, UV/Vis spectral studies, magnetic measurements and metal content analysis. Magnetic moment and electronic spectra indicate that the some of the complexes show a tetrahedral geometry and, the others show an octahedral geometry.

Introduction

The recognition of the disulfide group as a potential ligand for metal ions in biological systems has stimulated a number of different studies(1-2). In particular there have been structural studies on several crystalline complexes of simple(3-4) and polyfunctional disulfide(5-7).



Abel et al(8) studied the dynamics of migration of the metal fragment from one sulfur to another in the complexes$[M(CO)_5(RSSR)]$.

A mechanism such as that shown in the following equation was proposed based on NMR studies.

The interactions of new ligands bis (2-bromo phenyl) disulfide $(Brph)_2S_2$ =L with transition metals, Mn(II), Fe(II), Co(II), and Ni(II) were prepared and characterized by physicochemical and spectroscopic method which suggested that. The di(bromo phenyl) disulfide behaves a monodentate ligand giving an octahedral complexes of general formula $[M(L)_2Cl_2(H_2O)_2]$ were studied by Anacona and Mez(9). They showed that the dominant reaction pathway is a second order in metal and inhibited by excess methyl disulfide.

Salivon et al(10) have prepared the compounds $[Cu_2 X_2$ DADS] (where X=Cl or Br DADS= diallyl disulfide) by electrochemical synthesis and their crystal structures were determined. They found that DADS are tetradentated ligand coordinated through sulfur atoms with olefine double bond and the halide atoms forming distorted tetrahedral environment around each Cu (I) centers.

Novel macrocyclic bis (disulfide) tetramine ligands and several Cu(II) and Ni(II) complexes have been synthesized by oxidative coupling of linear tetradentate N_2S_2 tetramines with iodine(11).

The ligand (H_4L) is obtained as a condensation product of bis-(2-aminophenyl) disulfide and 3-formyl salicylic acid and has eight donor sites $N_2S_2O_4$. It acts however as a septadentate side-off ligand using two imine nitrogenes, two phenolato oxygen, one disulfide sulphur and two carboxylato oxygen as donar sites with Cu(II), Zn(II), Ba(II) and UO_2 (V) were studied by Nag et al(12).

The synthesis of bis-(4(2-pyridyl methyl eneimino phenyl) disulfide, having the anrophilic disulfide moiety at one end and the chelating 2-pyridyl methyleneimine at the other. Its complexes with Co(II), Ni(II), and Cu(II) were prepared and their electrochemical properties studied both in solution and, as self-assembled monolayers(13).

The complex $[Ir_2(C_2H_6NS)_2(C_4H_{12}N_2S_2)_2]$ $Br_4.2H_2O$ which was obtained by rearrangement of $[Re\{Ir(aet)_3\}]^{+2}$ (aet=2-aminoethanethiolate) in an aqueous solution, two approximately octahedral $fac[Ir(NH_2CH_2CH_2S)_3]$ unit are linked by two coordinated disulfide bonds (14).

Experimental

IR spectra were recorded in the range 4000-250 cm^{-1} range using CsI discs. The metal content was estimated sphectrophotometrically using Shimadzu AA670 spectrophotometer. Electronic spectra were obtained with a Shimadzu UV/Visible recording UV/160 spectrophotometer at room temperature. The measure-ments were obtained using a concentration of10^{-5}M of the complex in dimethyl sulfoxide (DMSO).

The magnetic measurements were determined at 25C° as a solid by Fararday's method using Bruker BM6 instrument. Conductivity measure-ments were made on 10^{-3}M solution of the complexes in (DMSO) solvent at ambient temperature using conductivity meter model 4070 Jenway.

Synthesis

The 2,2`-thiosalicylic acid disulfide were prepared using the following standard method(15). A suspension of thiosalicylic acid (3.08 g, 0.02 mol) in water was treated with $CuSO_4.5H_2O$ (2.50 g, 0.01 mol) and acidified with 4N HCl (2ml). The mixture was stirred under reflux for 1h. The precipitate was obtained after evaporation of solution to about 1/3 of its volume, which was filtered off, washed with ethanol, ether and recrystallized from acetone. The metal (II) chloride and dibenzyl disulfide (L^2) were used as supplied by Fluka.

Preparation of $[M(L^1)Cl_2]$ and $[M(L^1)_2]Cl_2$

To an ethanolic solution (20 cm^3) of the ligand 2,2`-thiosalicylic acid disulfide (L^1) (0.31 g,1 mmol) or (0.62 g,2mmol) was added an ethanolic solution of $Co.Cl_2.6H_2O$ or $NiCl_2.6H_2O$ or $CuCl_2.2H_2O$ (1 mmol). Then the mixture was refluxed for 2h. with continuous stirring. The precipitates was obtained after evaporation of the solution to a bout 1/3 of its volume, which was filtered out, washed with ethanol and diethyl ether. Then dried under vacuum for several hours.

Preparation of $[M(L^2)_2Cl_2]$

A solution of the ligand dibenzyl disulfide (0.44 g, 2mmol) in ethanol (15 cm^3) was added to a solution $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ or $CuCl_2.2H_2O$ (1 mmol) in (10 cm^3) ethanol. The mixture stirred with heating for 3h. during which time a precipitate was formed. The mixture was cooled to room temperature and the solid thus formed was filtered off, washed with ethanol and diethyl ether then dried under vacuum for several hours.

Results and Discussion

Direct reaction of the ligands 2,2`-disulfide of salicylic acid or dibenzyl disulfide with Co^{+2}, Ni^{+2} and Cu^{+2} in ethanol using 1:1 or 1:2 metal to ligand molar ratio afford complexes of the type $[M(L^1)Cl_2]$,$[M(L^1)_2]Cl_2$ and $[M(L^2)_2Cl_2]$. Ligands were coordinate through sulphur atom according to Hoiduc and Goh(16). These reactions indicated the involvement of simple disulfide or polyfunctional disulfide with metal ions(17-18). The prepared complexes are colored solids, stable in air at room temperature. Chemical analytical data of the synthesized complexes are listed in Table 1. Molar conductances of the complexes in DMSO are within the range 20-32 $ohm^{-1}.cm^2.mol^{-1}$, except complexes number (7-9) which are in the range 70-85 $ohm^{-1}.cm^2.mol^{-1}$ (Table 1) indicating a 1:2 electrolytic nature (19).

IR spectra

The most important diagnostic features of IR spectra are listed in (Table 2). The IR spectra of the ligand recorded using CsI, showed medium bands at 467 and 493,1700-1710,3400 cm^{-1} assigned to υ(S-S), υ(CO) and υ(OH) respectively. The υ(S-S) stretching vibration has been used as a probe for studying the disulfide group(20). The change in υ(S-S) upon coordination vary from 15-35 cm^{-1}. Much larger changes in υ(S-S) were reported by Seff and et al for complexes of amino alkyldisulfide and pridyl alkyl disulfide (21).

The υ(OH) band remained almost unchanged upon coordination with the metal ions which indicates that this group is not involved in the coordination. The frequency of υ(CO) band decreased upon complexation with the metal ions so as the υ(S-S) frequency were shifted to lower position by 15-30cm^{-1} which indicates the it is shared in coordination. Further support for the formation of new complexes were provided by the a appearance of a new bands with in the 340-360 and 551-569 cm^{-1} range characteristic for υ(M-S) and υ(M-O) respectively (22). Furthermore the IR spectra of the complexes No.(1-3) and No(4-6) show a new band with the range 290-310 cm^{-1} which may be due υ(M-Cl)(23).

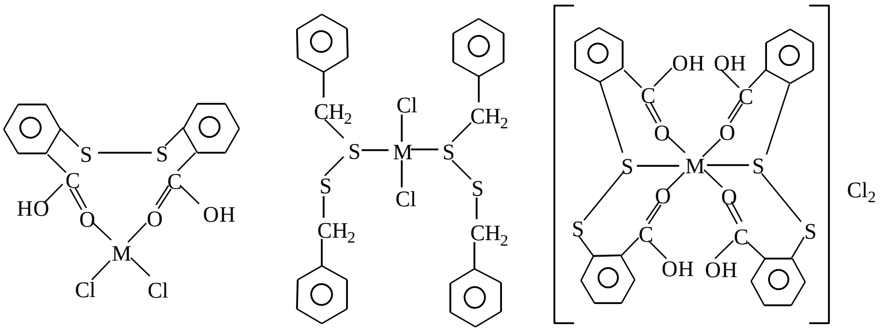
Electronic spectra:

The tentative assignments of the absorption bands from the electronic spectra of the complexes are reported in Table 2. The π-π^* transition in the spectrum of the ligands is observed at 34965-38461cm^{-1}, and a bond at 33333-32258 cm^{-1} which associated with ligand to metal charge transfer transition. The Co(II) complexes (No. 1 & 4) show a band observed in the visible region 15361 and 14286 cm^{-1}, general considered to correspond to a transition $^4A_2(F)\rightarrow {}^4T_{1(p)}g$, these band suggest tetrahedral geometry (24). while complex (7) showed two bands at 10204 and 18868 cm^{-1} which could be assigned to spin-allowed transitions $^{4[}T_1g(F)\rightarrow {}^4T_2g(\upsilon_1)$ and $^4T_1g(F)\rightarrow {}^4T_1g(p)(\upsilon_2)$ respectively (23). The position of these bands indicate an octahedral geometry around Co(II) ion.

The nickel complexes (2 and 5) show a bands at 14792and 13377 cm^{-1} nm due to the transition from $^3T_1(F)\rightarrow {}^3T_1(p)$ in tetrahedral geometry, while the nickel complex (8) show three bands at 10183, 16447and 19011 cm^{-1} corresponding to the transitions $^3A_2g(F)\rightarrow {}^3T_2g(F)$, $^3A_2g(F)\rightarrow {}^3T_1g(F)$ and $^3A_2g(F)\rightarrow {}^3T_2g(p)$ respectively , as expected (22) for octahedral Ni^{+2} ion. The copper complexes (3 and 6) shows the presence of one band at 11792 and 12406 cm^{-1} which correspond to the transition $^2T_2\rightarrow {}^2E$ which consistent with distorted tetrahedral geometry(25), whereas the copper complex (9) show the presence of two bands at 11876 and 13158 cm^{-1} corresponding to the transitions, $^2B_1g\rightarrow {}^2B_2g$ and $^2B_1g\rightarrow {}^2Eg$ in the electronic spectra, point out the distorted octahedral geometry(26).

Magnetic measurements

The results of the magnetic measurements are presented in Table 1. The magnetic moments of cobalt complexes (1 and 4) were 4.11 and 4.23 B.M corresponding to a high spin tetrahedral Co(II) complexes (27-29). Where as the cobalt complex (7) has a magnetic moment of 4.78 B.M which correspond to an octahedral geometry. The magnetic moments of nickel complexes (2 and 5) were 3.90 and 3.98 B.M which suggest the presence of two unpaired electrons, correspond to a tetrahedral geometry. The high value result probably from an orbital contribution(30). The nickel complex (8) has a magnetic moment of 3.10 B.M which correspond to an octahedral geometry. The magnetic moment values of copper complexes (3 and 6) are 1.96 and 1.95 B.M which are in agreement with distorted tetrahedral geometry. The copper complex (9) have a magnetic moment of 2.10 B.M which correspond to an octahedral geometry.



complex No.(1-3) complex No. (4-6) complex No.(7-9)

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

Fig. 1: suggested structure for the complexes

From the above discussion, the structures shown in (Fig. 1) can be suggested for the prepared complexes

Table 1: Physical properties of the complexes

No.	Compound	Color	M.p (C°)	Yield (%)	Analysis found (calcd.) %	Λ Ohm^{-1}. cm^{-1} .mol^{-1}	µeff (B.M)
					M		
1	$[Co(L^1)Cl_2]$	Dark pink	260	86	13.51 (12,39)	20.0	4.11
2	$[Ni(L^1)Cl_2]$	Green	236^d	82	13.47 (14.73)	24	3.90
3	$[Cu(L^1)Cl_2]$	Dark green	$>320^d$	79	14.42 (13.52)	30	1.96
4	$[Co(L^2)_2Cl_2]$	Pink	211^d	75	7.94 (8.38)	22	4.23
5	$[Ni(L^2)_2Cl_2]$	Dark green	206^d	90	7.91 (8.31)	32	3.98
6	$[Cu(L^2)_2Cl_2]$	Green	200^d	77	8.51 (7.92)	23	1.95
7	$[Co(L^1)_2]Cl_2$	Pink	212^d	80	9.47 (10.26)	75	4.78
8	$[Ni(L^1)_2]Cl_2$	Green	289^d	85	9.43 (10.31)	70	3.20
9	$[Cu(L^1)_2]Cl_2$	Dark blue	150^d	90	10.14 (9.32)	80	2.10

d = Decomposition temperature .

Table 2: Electronic and IR spectral data of the complexes

No.	IR band assignments (cm^{-1})						UV.Visible band λ_{max} (cm^{-1})
	υ(S – S)	υ(C=O)	υ(OH)	υ(M-S)	υ(M–O)	υ(M– Cl)	
1	463_m	1680_S	3400_m	---	551_m	298_m	38461,33333,15361
2	467_S	1633_m	3425_b	---	564_m	300_m	37037,32786,14792
3	467_m	1670_S	3390_m	---	569_m	290_m	35714,33333,11792
4	450_m	---	3400_b	350_w	---	310_w	35714,32258,14286
5	440_m	---	3401_b	355_w	---	300_w	36363,32467,13477
6	445_m	---	3401_b	345_w	---	305_w	37037,33333,12406
7	461_m	1681_S	3400_b	360_w	551_m	---	35714,33333,18868,10204
8	467_m	1681_S	3400_b	350_w	552_m	---	32258,19011,16447,10183
9	467_m	1650_S	3400_b	340_w	554_m	---	33333,13158,11876

s = strong **m** = medium **b** = broad

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الملخص

تم تحضير مجموعة من المعقدات ذوات الصيغ العامة $[M(L)Cl_2]$، $[M(L)_2Cl_2]$ و $[M(L)_2]Cl_2$ حيث $L = L^1$ أو L^2 وان $L^1 =$ `2-2 حامض ثايوسالسيليك ثنائي الكبريتيد وان $M = Co^{+2}$ و Ni^{+2} و Cu^{+2} وتم تشخيص المعقدات المحضرة بواسطة قياسات التوصيلية الكهربائية وأطياف الأشعة تحت الحمراء وفوق البنفسجية كذلك القياسات المغناطيسية وتعيين المحتوى الفلزي. بينت قياسات الأطياف الالكترونية والعزم المغناطيسي بأن قسم من المعقدات تمتلك بنية رباعية السطوح والاخر يمتلك ثمانية السطوح.