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Synthesis and Characterization of Co(II),Ni(II),Cu(II) and Zn(II) Complexes with Mixed Ligands Thioether and Ethylenediamine Ligands

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ABSTRACT

New bimetallic complexes of the types$[M_2LCl_4]$,$[M_2L(en)_2Cl_4]$, $[M_2L(en)_2(TP)_4]$, where M=Co(II),Ni(II),Cu(II) and Zn(II), TP =*p*-aminophenylthiolate were prepared by reacting metal chloride with the ligands 1,1,2,2-tetrakis(*p*-aminophenylthio)ethylene (L), ethylenediamine (en) and in some case with sodium *p*-aminophenylthiolate.

The aryl thioether ligand together with the complexes have been characterized on the basis of microanalysis (N and M), infrared spectra,electronic spectra,magnetic and conductivity measurements.

تحضير وتشخيص معقدات العناصر Co(II) وNi(II) وCu(II) وZn(II) مع خليط ليكاندات الثايوايثر والاثلين ثنائي الامين

الملخص

يتضمن البحث تحضير معقدات ثنائية النوى جديدة ذات الصيغ العامة $[M_2LCl_4]$ و $[M_2L(en)_2Cl_4]$ و $[M_2L(en)_2(TP)_4]$ حيث M= الكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) ، TP= بارا-أمينوثايوفينوليت حيث يتفاعل كلوريد العنصر مع 2,2,1,1 – رباعي (بارا-امينو ثايوفنيل) الاثيلين (L) والاثيلين ثنائي الأمين (en) وفي بعض الأحيان مع بارا-امينوثايوفينوليت الصوديوم.

تم تشخيص الليكاندات والمعقدات المحضرة باستخدام تحليل النايتروجين بطريقة كلدال وتحليل العناصر بالطرق الوزنية وطيف الأشعة تحت الحمراء والطيف الالكتروني فضلاً عن القياسات المغناطيسية والتوصيلية الكهربائية.

INTRODUCTION

Transition metal complexes containing mixed N or S donor ligands are of great interest among coordination complexes because of thier dual ability in acting as either mono or bidentate ligands (Blake et al., 1998; Kersting, 2000; Buttrus et al., 2001; Gurol et al., 1992) .

An interesting preparative features in the chemistry of sulphur containing ligands with zinc group obtained from electrochemical and anodic oxidation of zinc and cadmium in acetonitrile solution containing RSH or R_2S_2,provide an excellent route to the polymeric M(SR) compounds (Said and Tuck, 1982) .

The coordination compounds of 5-methyl-1,3,4-thiodiazole with some group VII metals such as Ru(III),Rh(III),Os(III) and Ir (III) have prepared and studied by (Fabretti and Giusti, 1986).

Phosphino-thiolate ligands containing a phosphine center with thiol functionality, as well as phosphino-thioether ligands are similar in over all appearance but contain a thioether group in place of thiol and their complexes with transition results have been reviewed by (Dilworth and weatly, 2000).

Also several palladium complexes derivid from 2,5-diphenyl complexes of 5-phenyl-1,3,4-oxadiazole-2-thione with Ni(II), Pd(II) and Pt(II) have been reported(AL-Haylay et al., 2002).

In view of the interesting results reported and as a continuation of our comprehensive studies on some transition metal with sulphur contaning ligands (Buttrus et al., 2002;Butrus,1997),we have prepared arylthioethene derivatives and their $[M_2LCl_4]$, $[M_2L(en)_2Cl_4]$ and $[M_2L(en)_2(TP)_4]$ complexes in which M = Co(II), Ni(II),Cu(II) and Zn(II),TP = *p*-aminophenylthiolate.

EXPERIMENTAL

All chemicals were used as reagent grade (BDH,Fluka) and used as such. All solvents were dried by standard methods. 1,1,2,2-tetrakis-(*p*aminophenylthio)ethylene(L) was synthesized using a literature method (Al-Allaf et al., 1997).

Physical measurements:

Analysis of ligand and complexes was carried out using a standard method. Infrared spectra with in the 4000-200cm^{-1} range were recorded as KBr or CsI discs on a Perkin-Elmer 580B spectrophotometer, calibrated with polystyrene.Electronic spectra were obtained with Shimadzu UV/Vis. recording UV160 spectrophotometer at room temperature. The measurement were recorded using a concentration of 10^{-3}M of the complexes in (DMSO).The magnetic moments measurements were carried out at 25°C on the solid states by Faraday's method using Bruker BM6.instrment. Conductivities were measured using a conductivity meter model PCM3-Jenway,on 10^{-3}M solution of the complexes in (DMSO) at 25°C.

Preparation of the complexes

A.Synthesis of dinuclear complexes of the type $[M_2LCl_4]$

M = Co(II),Ni(II),Cu(II) and Zn(II)

A solution of $CoCl_2.6H_2O$, $NiCl_3.6H_2O$,$CuCl_2.2H_2O$ or $ZnCl_2.2H_2O$, (2mmol) in ethanol (10 cm^3) was added to a solution of 1,1,2,2-tetrakis-(*p*-aminophenylthio)ethylene (0.51 g,1 mmole) in ethanol (10 cm^3) was added. The mixture was stirred under reflux for ca 2h. the precipitate formed, was filtered off ,washed with ethanol, diethylether and dried under vacuum for several hours.

B. Synthesis of dinuclear complexes of the type [$M_2L(en)_2Cl_4$]

A solution of 1,1,2,2-tetrakis-(*p*-aminophenylthio) ethylene (0.45 g,1 mmole) in ethanol (10 cm^3) was added to a solution of $NiCl_2.6H_2O$, (0.47g,2mmol) in ethanol (10cm^3).The mixture was refluxed for 3h. with sltirring.The precipitate was filtered off, washed with n-butanol (10cm^3), diethylether (10cm^3) and dried under vacuum for several hours.Similar procedure was used to prepare the Co(II),Cu(II) and Zn(II) complexes.

C. Synthesis of dinuclear complexes of the type [$M_2L(en)_2(TP)_4$]

A solution of the dinuclear complexe of the type [M_2LCl_4](1.0 mmol) dissolved dimethyl formamide DMF (10 cm^3) was added with constant stirring to a solution of ethylenediamine (0.48 g,2 mmol) in ethanol (15 cm^3).The mixture was stirred under reflux for 1h. To this mixture a solution of potassiumthiophenoxide prepared from equimolar quantities of a *p*-aminothiopenol (0.28g,2 mmol) and KOH (0.11g,2 mmol) (15 cm^3) ethanol was added,with stirring under reflux for 2h.,the resulting solution was reduced in volume to ca 1/3. the precipitate,formed was filtered off washed with DMF (10 cm^3),ethanol (10 cm^3) diethylether (10 cm^3) and dried under vacumm over P_2O_5.

RESULTS AND DISCUSSION

The reaction of 1,1,2,2-tetrakis-(*p*-aminophenylthio) ethylene with Co(II), Ni(II), Cu(II) or Zn(II) in a (1:2) ligand to metal moler ratio gave the neutral metal (II) chelates in which the ligand behaves as tetradentate chleated to metal (II) via four sulfur atoms giving the dinnclear metal (II) complexes.

The complexes of the types [$ML(en)_2Cl_4$] and [$M_2L(en)_2(TP)_4$] were prepared by addition of two moles of ethylene diamine or four moles of potassiumthiophenoxide to [M_2LCl_4] complexes. The isolated complexes and their physicochemical properties are listed in Table (1). In general the prepared complexes are soluble dimethyl sulfoxide (DMSO).The molar conductance in 10^{-3}M (DMSO) solution are in the (10-20) ohm^{-1} cm^2 mol^{-1} range indicating a non-electrolytic nature of the complexes except complex No.5,which is 1:2 electrolytes. This is in consistent with the stoichiometry assumed for the complexes on the basis of the analytical data.

The ligand dose not show an υ(SH) band in the region of 2600-2500 cm^{-1},in which this stretching frequency generally expected (Rao, 1963). The characteristic band in the infrared spectra of the ligands occur at 3300-3400,1660 and 695 cm^{-1} due to the υ(NH_2) , υ(C═C) and υ(C – S) resepectively (AL-Allaf et al., 1997). The i.r.spectrum of [M_2LCl_4] complexes, showed a lowering in the frequnciesof the υ(C – S) bands, indicating that this group is involved in the coordination (Table 2). The infrared of these complexes show new bands at 410-415 and 290-305 cm^{-1} assingned to υ(M–S) and υ(M–Cl) respectively (Stoicoscu et al., 2001). The i.r.specta of the [$M_2L(en)_2Cl_4$] and [$M_2L(en)_2(Tp)_4$] complexes showed similar observation,except that of the ethylenediamine ligand were found to coordinate to the metal via NH_2 donor site . This is clear from the drastic decrease of the absorption of NH_2 groups by 90-110 cm^{-1} upon coordination (Table 2).Similar results were found elsewhere (Buttrus, 2002).The absence of any band due to υ(M–Cl) absorption in complexes No.3,6,9,12 indicates the absence of the chlorid ion in the complexes.This observation was also confirmed by sodium fussion test.

Magnetic measurements and electronic spectra:

Cobalt (II) complexes:

The values of magnetic moments of Co(II) complexes (No.1-3) are 3.9,4.1 and 4.0 B.M respectively. The electronic spectrum (Table 2) of Co(II) complex (No.1) shows a broad band at 16400 cm^{-1} due to $^4A_2 \rightarrow {}^4T_1p$ (υ_3) transition ,due to spin-orbit coupling (Bayoumi et al., 2001) similar to those reported for $[CoCl_4]^{-2}$ and $[CoI_4]^{-2}$ suggesting a tetrahedral geometry .The complexes (No. 2 and 3) shows two bands each at 15300 , 21500 and 15400, 19800 cm^{-1} assigned to $^4T_2g(F) \rightarrow {}^4A_2g(F)(\upsilon_2)$ and $^4T_1g(F) \rightarrow {}^4T_2g\ (p)(\upsilon_3)$ .Those are typical for octahedral structure.

Ni(II) complexes:

The Ni(II) complexe No.4 shows a magnetic moment of 3.5 B.M. This value agree will with a high-spin configuration and indicats the presence of a tetrahedral environment (Mustafa et al., 2002).

The electronic spectra of Ni(II) complex No.4 shows a band at 13000 cm^{-1} which correspond to the transition $^3T_1(F) \rightarrow {}^3T_1(p)(\upsilon_3)$ in tetrahedral geometry.The Ni(II) complex (No.5) was diamagnetic and its electronic spectrum showed two bands (Table 3) were assigned to $^1A_1g \rightarrow {}^1B_2g$ and $^1A_1g \rightarrow {}^1Eg$ transitions respectively . These results suggest a square planner structure around the nickel ions.The Ni(II) complex (No.6) shows a magnetic moment of 3.2 B.M at room temperature, This value is in tune with a high-spin configuration and indicates the presence of an octahedral environment around Ni(II) ions (Chandra and Gupta, 2001).The electronic spectrum of the complex shows three band at 11000,13000 and 25400 cm^{-1}correspend to the three spin-allowed transition$^3A_2g(F) \rightarrow {}^3T_2g(F)$ (υ_1),$^3A_2g(F) \rightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)(\upsilon_3)$ An examination of these band suggstan octahedral geometry.

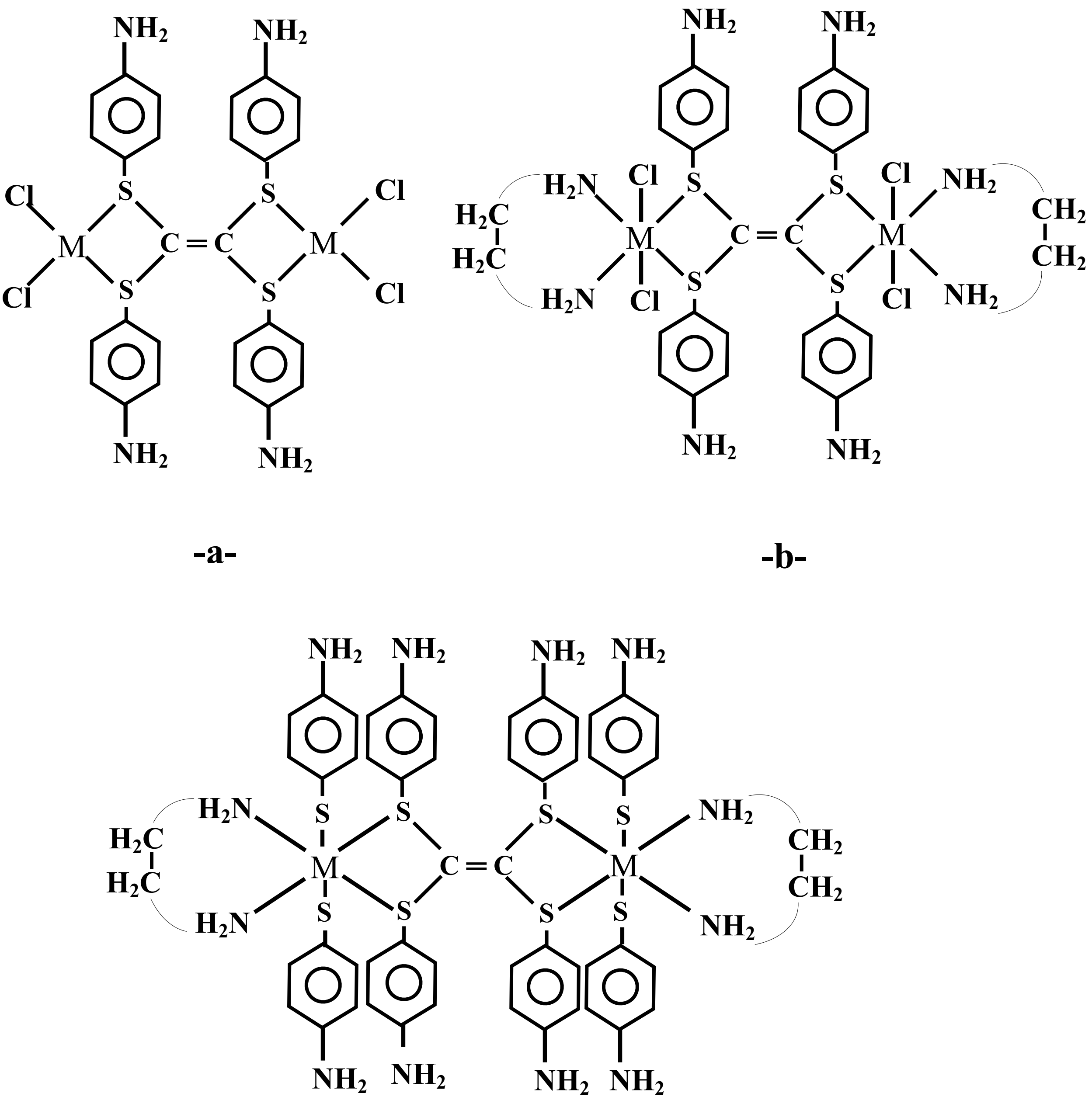
Cu(II) complexes:

The Cu(II) complex (No. 7) shows a magnetic moment of 1.9 B.M.The electronic spectrum showed a broad band centered at 13600 cm^{-1} correspond to the transition $^2B_1g \rightarrow {}^2A_1g$ or $^2B_1g \rightarrow {}^2Eg$ for distorted square planner geometry around Cu(II) (Comba et al., 1996).

The complex (No. 8 and 9) have magnetic moments (2.00 B.M).The electronic spectrum of Cu(II) complex show broad bands centered at 15730,13000,14480 cm^{-1} assigned to the $^2E_2g \rightarrow {}^2T_2g$ transition in a distorted octahedral structure around Cu(II) (Lever, 1968).

As the spectrum of Zn(II) complexes is not well resolved, it is not interpreted but its μ_{eff} value shows that they are diamagnetic as expected.

On the basis of the above discussions we propose the following structures for the metal(II) complexes as showen in Fig (1).



-a-

-b-

-c-

M = Co(II),Ni(II),Cu(II) or Zn(II)

Fig. 1: Suggested structures for the prepared complexes

Table 1: Physical properties and elemental analysis of the complexes (1)-(12)

Compound	Colour	M.P (^oC)	Yield (%)	Found (Calc) (%)		
				N	M	Molar conduc (Ω^{-1} cm^2 mo
$Cl_4]$	Black	351	75	6.95 (7.19)	15.00 (15.14)	9
$(en)_2Cl_4]$	Brown	400	70	12.20 (12.47)	12.89 (13.03)	13
$(en)_2(Tp)_4]$	Black	410	68	10.95 (11.02)	11.50 (11.59)	11
$Cl_4]$	Green	306	38	7.01 (7.20)	15.22 (15.10)	16
$en)_2]Cl_4$	Yellow	320	36	12.16 (12.47)	13.21 (13.07)	60
$en)_2(Tp)_4]$	Pale green	330	40	13.10 (13.40)	9.21 (9.36)	14
$Cl_4]$	Black	255	47	7.00 (7.11)	16.00 (16.14)	7
$(en)_2Cl_4]$	Black	318	57	11.98 (12.34)	13.90 (14.00)	11
$(en)_2(Tp)_4]$	Black	294	70	12.93 (13.30)	10.00 (10.06)	13
$Cl_4]$	White	365	60	7.11 (7.08)	16.45 (16.53)	18
$(en)_2Cl_4]$	Gray	340	55	12.31 (12.29)	14.31 (14.35)	21
$(en)_2(Tp)_4]$	White	333	48	12.05 (12.13)	9.26 (9.44)	16

Table 2: Selected I.R bands and the magnetic values of the prepared metal complexes (1)-(12)

npund	υ(M – S) cm^{-1}	υC – S cm^{-1}	υ(N – H) cm^{-1}	υ (M –N) cm^{-1}	υ (M –Cl) cm^{-1}	μ_{eff} B.M	d – d transition cm^{-1}	Co
ligand		695	3350				16400	
1	410	630	3250		290	3.9	15300,21500	
2	415	625	3225	530	300	4.1	15400,19800	
3	410	615	3350	540		4.0	11460,13000,18580	
4	412	630	3350		305	3.5	17100,27600	
5	415	625	3250	530		D	12400,13000,25400	
6	414	618	3250	530		3.2	11000,13000,25300	
7	418	625	3355		300	3.8	13600	
8	410	620	3200	529	305	2.0	15730,13000	
9	414	630	3255	524		2.0	14480	
10	410	625	3350		306	D		
11	414	620	3260	520	300	D		
12	414	618	3240	510		D		

D = Diamagnetic ,Td = tetrahedral,Oh = octahedral,Sq.pl. = sequare planer

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