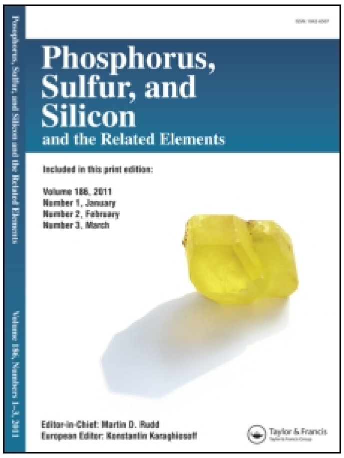

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N_2S_2-Donor Macrocycles with Some Transition Metal Ions: Synthesis and Characterization

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N_2S_2-Donor Macrocycles with Some Transition Metal Ions: Synthesis and Characterization

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A novel series of 15-membered diaza-dithiamacrocyclic complexes (ML_1Cl_2) and (ML_2Cl_2) (M=Fe,Co, Ni, Cu, and Zn) have been prepared by the template condensation reaction of o-thiosalicylic acid with aliphatic or aromatic diamines and diethyl malonate in the presence of transition metal ions in alcoholic medium and have been characterized through IR, ^{1}HNMR and electronic spectral studies, conductivity and magnetic susceptibility measurements. An octahedral geometry has been suggested for all complexes.

Keywords 15-membered diaza-dithiamacrocyclic complexes; template synthesis; Co(II); Cu(II); Fe(II); Ni(II); Zn(II)

INTRODUCTION

Studies on complexes with synthetic macrocyclic ligands have recivevd a new impetus since the discovery of the natural molecules.[1] The chemistry of macrocyclic ligands and their complexes has attracted growing interest because of their applications as catalysts[2] and dioxygen transports,[3] in addition to their biomedical applications,[4] and their use as medical-imaging agents.[5]

Reviews on macrocycles show that a considerable amount of work has been done on sulfur and nitrogen[6–8] or oxygen and nitrogen[9–11] atoms-containing macrocycles. Kimora et al.,[12] have shown that (N_2S_2) macrocyclic ligands in which the two amide and two sulfide units act cooperatively, show high selectivity and efficiency for complex formation with Pt(II), and Pd(II) over Cu(II), Ni(II) and Co(II). I have previously reported the synthesis and characterization of a wide variety of polyaza,[13–19] tetraaza-dithia,[7] and diaza-dioxamacrocyclic complexes.[11] Herein, I report a novel series of diaza-dithiamacrocyclic complexes derived from o-thiosalicylic acid, with ethylene diamine or

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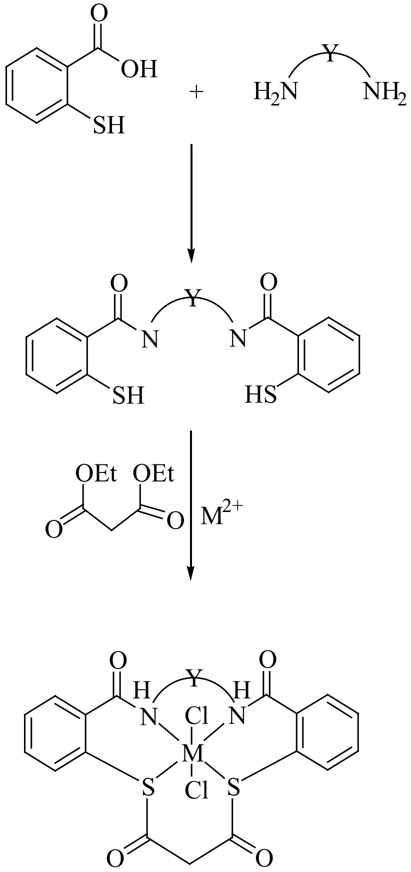
o-phenylene diamine and diethyl malonate in alcoholic medium in the presence of transition metal ions as templates.

RESULTS AND DISCUSSION

The reaction of o- thiosalicylic acid with ethylene diamine or o- phenylene diamine and diethyl malonate in ethanol in the presence of transition metal ions as templates, yielded in each case a novel series of diaza-dithiamacrocyclic complexes as shown in Scheme 1.



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

Y = C_2H_4 or C_6H_4

SCHEME 1

However, the yields in case of (ML_2Cl_2) were found to be comparatively low which may be due to the more stirric hindrance of the o-phenylene diamine than that of ethylene diamine. The color and crystalline habits of the complexes under study indicate that thay are of the same family of compounds. The iron complexes are brownish red. The cobalt complexes are mauve. The nickel complexes are obtained as light green while the color of the copper complexes is dark blue. The zinc complexes are off white as expected.

The low molar conductivity values observed in DMSO of all compounds indicate[20] that they are non-electrolytes (Table I). The overall geometries were inferred from the various spectroscopic studies discussed below.

It is important to note that the reactions were carried out applying stirring with gentle heating to avoid possible formation of H_2S gas.

The elemental analysis are consistent with the proposed formulations (Table I).

IR Spectra

The nature of the macrocyclic ligand complexes was inferred from the appearance of new bands and the disappearance of other bands in their IR spectra (Table II). The absence of NH_2, OH, SH and OET bands and the appearance of four amide bands in the 1680–1720, 1500–1530, 1245–1270 and 640–670 cm^{-1} regions, assignable to amide I ν (C=O), amide II ν (C—N) + δ (N—H), amide III δ (N—H), and amide IV ϕ (C=O) bands, respectively, along with a negatively shifted[21,22] amide NH stretching vibration in the 3235–3260 cm^{-1} region, provide evidence for the skeleton of the macrocyclic moiety. This was further confirmed by the appearance of a strong- intensity band in the 475–510 cm^{-1} region and a medium intensity band in the 380–420 cm^{-1} region, which may be assigned to M—N and M—S stretching modes respectively.[6,23] Bands observed in the 680–710 cm^{-1} region can be assigned to the C—S stretching vibrations,[6] whereas, the bands in 1230–1240, 1000–1025, and 850–870 cm^{-1} regions are the usual modes of disubstituted benzene.

EPR Spectra

The EPR spectra of the copper (II) complexes recorded at 25°C did not show any hyperfine lines which may be due[24] to strong dipolar and exchange interactions between the copper (II) ions in the unit cell. Their spectra exhibited a strong single broad band and their g_{II} and $g_{\perp}$ values appeared in the 2.20–2.23 and 2.07–2.10 regions, respectively,

TABLE I Color, M.P (°C), Yield (%), Elemental Analyses, and Molar Conductivity Data of the Complexes

Compound	Color	M.P (°C)	Yield	M	C	H	N	S	Cl	Molar cond. ($cm^2\Omega^{-1}mol^{-1}$)
FeL_1Cl_2	Brownish Red	210	65	10.55	43.27	3.03	5.28	12.12	13.37	24
				(10.59)	(43.33)	(3.04)	(5.32)	(12.15)	13.47)	
FeL_2Cl_2	Brownish Red	216	40	9.69	47.90	2.77	4.84	11.11	12.31	16
				(9.71)	(48.02)	(2.78)	(4.87)	(11.13)	(12.35)	
CoL_1Cl_2	Mauve	206	65	11.10	42.93	3.01	5.26	12.06	13.38	12
				(11.12)	(43.03)	(3.02)	(5.28)	(12.8)	(13.40)	
CoL_2Cl_2	Mauve	212	45	10.18	47.70	2.76	4.84	11.06	12.26	14
				(10.19)	(47.76)	(2.77)	(4.85)	(11.07)	(12.28)	
NiL_1Cl_2	Light green	198	70	11.10	42.95	3.01	5.26	12.06	13.38	18
				(11.11)	(43.03)	(3.01)	(5.27)	(12.08)	(13.39)	
NiL_2Cl_2	Light green	202	50	10.18	47.71	2.76	4.84	11.06	12.26	15
				(10.19)	(47.67)	(2.76)	(4.84)	(11.07)	(12.28)	
CuL_1Cl_2	Dark blue	198	75	11.87	42.62	2.98	5.24	11.96	13.27	20
				(11.88)	(42.65)	(2.99)	(5.24)	(11.97)	(13.28)	
CuL_2Cl_2	Dark blue	205	50	10.89	47.35	2.74	4.80	11.98	12.18	20
				(10.90)	(47.38)	(2.74)	(4.80)	(11.99)	(12.19)	
ZnL_1Cl_2	Off white	184	60	11.58	42.47	2.98	5.22	11.92	13.22	18
				(11.59)	(42.51)	(2.98)	(5.22)	(11.93)	(13.24)	
ZnL_2Cl_2	Off white	188	40	11.17	47.20	2.73	4.79	10.95	12.14	16
				(11.17)	(47.23)	(2.79)	(4.79)	(10.95)	(12.15)	

TABLE II IR Spectral Data (cm^{-1}) of the Compounds

	ν(N—H)	Amide bands								Ring Vibrations		
Compound	amide	I	II	III	IV	ν(C—S)	ν(M—N)	ν(M—S)	ν(M—Cl)			
FeL_1Cl_2	3250	1700	1510	1260	660	700	500	410	305	1240	1010	850
FeL_2Cl_2	3260	1710	1530	1245	650	705	510	410	320	1235	1000	870
CoL_1Cl_2	3245	1710	1500	1260	660	690	480	420	305	1230	1025	865
CoL_2Cl_2	3255	1720	1520	1250	645	680	485	385	295	1230	1025	860
NiL_1Cl_2	3260	1680	1505	1245	640	710	475	380	310	1240	1020	855
NiL_2Cl_2	3250	1680	1500	1250	660	685	470	415	300	1230	1010	865
CuL_1Cl_2	3235	1690	1510	1270	650	695	480	410	310	1235	1015	860
CuL_2Cl_2	3245	1680	1505	1265	645	700	485	415	320	1230	1020	860

TABLE III Band Position and Their Assignments of the Compounds

Compound	μ_{eft} (BM)	Band position	Assignments
FeL_1Cl_2	5.42	11.650	$^5T_2g \rightarrow ^5Eg$
FeL_2Cl_2	5.45	11.750	$^5T_2g \rightarrow ^5Eg$
CoL_1Cl_2	4.35	21.800	^4T_1g (F) $\rightarrow ^4T_2g$ (p)
		13.800	^4T_1g (F)$\rightarrow ^4A_2g$ (F)
CoL_2Cl_2	4.28	22.000	^4T_1g (F)$\rightarrow ^4T_1g$ (p)
		14.100	^4T_1g (F) $\rightarrow ^4A_2g$ (F)
NiL_1Cl_2	3.23	27.550	^3A_2g (F) $\rightarrow ^3T_1g$(P)
		20.350	^3A_2g (F) $\rightarrow ^3T_1g$(F)
		11.200	^3A_2g (F) $\rightarrow ^3T_2g$(F)
NiL_2Cl_2	3.24	27.700	^3A_2g (F) $\rightarrow ^3T_1g$(P)
		20.300	^3A_2g (F) $\rightarrow ^3T_1g$(F)
		11.150	^3A_2g (F) $\rightarrow ^3T_2g$(F)
CuL_1Cl_2	1.73	20.550	$^2B_1g \rightarrow ^2Eg$
		16.400	$^2B_1g \rightarrow ^2E_2g$
CuL_2Cl_2	1.71	20.300	$^2B_1g \rightarrow ^2Eg$
		16.350	$^2B_1g \rightarrow ^2E_2g$

indicating[25] that the ground state is d x^2–y^2 in which the unpaired electron may be present. It has been reported[26] that for ionic environment $g_{II} > 2.3$ and for covalent environment $g_{II} > 2.3$, which is characteristic of axially distorted octahedral copper (II) complexes as $g_{II} > g_\perp > 2.02$. The g values are related by the expression $G = (g_{II} - 2)/(g_\perp - 2)$ which measures the exchange interaction between the copper centers.

^{1}HNMR Spectra

The ^{1}HNMR spectra of both the zinc (II) complexes recorded in d_6 DMSO showed a multiplet in the 2.14–2.18 ppm regions which may be ascribed[15] to CO—CH_2—CO (2H) protons, along with a broad signal in the 8.36, 8.42 ppm regions, assignable to the amide C—NH—CO (2H) protons. In addition, the ^{1}HNMR spectra of [ZnL_1CL_2] complex showed a multiplet in the 2.52 ppm region which may reasonably be assigned[15] to N—CH_2—CH_2—N (4H) protons. The ZnL_1CL_2 complexes showed a broad muliplet in the 7.22 ppm region and the ZnL_2CL_2 complex in the 7.60 ppm region assignable[6,15] to phenyl ring C_6H_4 (8H) and C_6H_4 (12 H) protons, respectively. All the above along with the absence of any band characteristic of NH_2, SH, or OH protons, support the proposed macrocyclic framework.

The μ_{eff} values (Table III) are normal, suggesting the absence of strony interactions between the electrons of the metal centre units.

UV Vis Spectra

The observed magnetic moments and the positions of the absorption bands (Table III) in the electronic spectra of the iron (II) macrocyclic complexes recorded in DMSO showed a weak intensity band at 11650,11750 cm^{-1} corresponding to high spin d^6 system which may reasonably be assigned[27] to $^5T_2g \rightarrow {}^5Eg$, consistent with an octahedral environment around the iron(II) ion. However, the electronic spectra of the cobalt (II) complexes showed two ligand field bands in the 21800, 22000 and 13800, 14100 cm^{-1} regions which may correspond to high spin d^7 system assignable[27,28] to $^4T_1g(F) \rightarrow {}^4A_2g$ (F) and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions, respectively, consistent with an octahedral geometry around the cobalt(II) ions.

The nickel (II) complexes, each showed a magnetic moment (Table III) correspond to a spin—free complex. Their electronic spectra showed three distinct bands consistent with an octahedral feature around each of the nickel (II) complexes. Two bands around 27550, 27700 and 20300, 20350 cm^{-1} and one broad band around 11150 and 11200 cm^{-1} assignable[19,27] to ^3A_2g (F) $\rightarrow {}^3T_1g$ (P), and ^3A_2g (F) $\rightarrow {}^3T_2g$ (F) transitions, respectively.

The electronic spectra of the capper (II) complexes each showed a main broad band in the 20300, 20550 cm^{-1} region along with a shoulder in the 16350, 16400 cm^{-1} region which may unambiguously be assigned to$^2B_1g \rightarrow {}^2Fg$ and $^2B_1g \rightarrow {}^2B_2g$ transitions, respectively, corresponding[15,16,27] to a distorted octahedral geometry around the copper (II) ions. Their magnetic moment values further support the proposed geometry.

All the above complexes exhibit a strong absorption band around 30000 cm^{-1} characteristic of L→ M charge transfer excitation.

EXPERIMENTAL

The metal salts $FeCL_2$, $CoCL_2.6H_2O$, $NiCL_2.6H_2O$, $CuCL_2.2H_2O$, and $ZnCL_2$ (BDH) were commercially available pure samples. O-thiosalicylic acid, ethylene diamine, o-phenylene diamine (E. Merk) and diethyl malonate (BDH) were used as recieved.

Synthesis of Dichloro-(1,2;8,9-dibenzo-4,6,10,15-tetraoxo-3,7-dithia-11,-14-diazacyclopentadecane Iron(II); [FeL_1Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of iron chloride (0.35 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2; 8,9;12,13-tribenzo-4,6,10,15-tetraoxa-3,7-dithia-11,-14-diazacyclopentadecane Iron (II); [Fe L_2 Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and o-phenylene diamine (0.27 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about one houre.A hot ethanolic solution of iron chloride (0.35 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2;8,9-dibenzo-4,6,10,15-tetraoxo-3,7-dithia-11,-14-diazacyclopentadecane Cobalt(II); [CoL_1Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h.A hot ethanolic solution of cobalt chloride hexahydrate (0.6 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro –(1,2; 8,9;12,13-tribenzo-4,6,10,15-tetraoxa-3,7-dithia-11,-14-diazacyclopentadecane Cobalt (II); [CoL_2Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and o-phenylene diamine (0.27 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of cobalt chloride hexahydrate (0.6 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2;8,9 – dibenzo- 4,6,10,15-tetraoxo-3,7 -dithia -11,-14-diazacyclopentadecane Nickel(II); [NiL_1Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of nickel chloride hexahydrate (0.6 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro –(1,2; 8,9;12,13-tribenzo-4,6,10,15-tetraoxa -3,7-dithia-11,-14-diazacyclopentadecane Nickel (II); [NiL_2Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and o-phenylene diamine (0.27 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of nickel chloride hexahydrate (0.6 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2;8,9-dibenzo-4,6,10,15-tetraoxo-3,7-dithia-11,-14-diazacyclopentadecane Copper(II); [CuL_1Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of copper chloride dihydrate (0.43 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2; 8,9;12,13-tribenzo-4,6,10,15-tetraoxa-3,7-dithia-11,-14-diazacyclopentadecane Copper (II); [CuL_2Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and o-phenylene diamine (0.27 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of copper chloride dihydrate (0.43 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2;8,9-dibenzo-4,6,10,15-tetraoxo-3,7-dithia-11,-14-diazacyclopentadecane Zinc(II); [ZnL_1Cl_2]

A mixture of o-thiosalicylic acid (0.8g, 5mmol) and ethylene diamine (0.15 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h. A hot ethanolic solution of zinc chloride (0.35 g, 2.5 mmol) was then added, followed by the addition of a warm ethanolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Synthesis of Dichloro-(1,2; 8,9;12,13-tribenzo-4,6,10,15-tetraoxa-3,7-dithia-11,-14-diazacyclopentadecane Zinc (II); [ZnL_2Cl_2]

A mixture of o-thiosalicylic acid (0.8 g, 5 mmol) and o-phenylene diamine (0.27 g, 2.5 mmol) dissolved in 50 ml ethanol was gently stirred for about 1 h.A hot ethanolic solution of zinc chloride (0.35 g, 2.5 mmol) was then added, followed by the addition of a warm ethonolic solution of diethyl malonate (0.4 g, 2.5 mmol). The resultant mixture was stirred with gentle heating for a total of 7 h. The solid product was filtered off, washed several times with cold ethanol, and dried in vacuo.

Metals were determined by atomic absorption spectrometer. Chlorides were determind gravimetrically.[29] IR spectra (4000–200 cm^{-1}) were recorded as KBr discs on Shimadzu FTIR- 8201 PC spectrophotometer. ^{1}HNMR spectra were recroded in d_6—DMSO using a JEOL TNM-LA300 – NMR spectrometer with Me4Si as an internal standard. Electronic spectra of the compounds in DMSO were recorded on UV-1601 UV-Vis spectrophotometer at room temperature. The electrical conductivities of 10^{-3} M solution in DMSO were obtained on AC13 CM-30 V conductivity meter at 25°C. Magnetic susceptibility measurements were carried out using a Faraday balance.

CONCLUSION

The procedures outlined for preparing the macrocyclic complexes understudy appear to be facile and proceed smoothly. The resultant complexes may have wide applicability, It should prove useful for investigating complexes of a range of other ligand types, as well as for the study of metal-containing biological molecules such as metallo-enzymes, in addition to their catalytic activity for important industrial applications.

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