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Perchlorate and Tetrafluoroborate Complexes of Mn(II), Ni(II), Co(II) and Cu(II) with Tetrabenzo-(b,e,l, o)-4,14-Dithia-1,7,11,17-Tetraaza-8,10,18,20-Tetramethyl-cylodedeca-7,10,17,20-Tetraene

P. R. SHUKLA, NIHAL AHMAD* AND ASHISH K. PATHAK

Department of Chemistry, Lucknow University
Lucknow-226 007, India

Eight macrocyclic complexes have been prepared by the template condensation reaction between di(2-aminopenyl) sulphide and acetylacetone. These complexes have the general formula $[M(L)]X_2$ and $[M'(L)(H_2O)_2]X_2$ where L = tetrabenzo-(b,e,l,o)-4,14-dithia-1,7,11,17-tetraaza-8,10,18,20-tetramethylcyclodedeca-7,10,17,20-tetraene, M = Ni(II), Cu(II); M′ = Mn(II), Co(II) and X = ClO_4^-, BF_4^-. The complexes have been characterized on the basis of analytical data, conductance measurements, IR, ^{1}H NMR, magnetic and electronic spectral studies and are assigned to have either square planar or octahedral geometries.

INTRODUCTION

A wide variety of coordination complexes of nitrogen donor macrocyclic ligands with first row transition metals have been reported from this laboratory[1–4]. The present work deals with the preparation and characterisation of first row transition metals with the title ligand which is a N_4 donor macrocycle. The complexes were prepared by the condensation of di(2-aminophenyl) sulphide and acetylacetone in 1 : 1 molar ratio in presence of different metal salts. The geometries for the complexes are assigned on the basis of analytical and conductance data, magnetic susceptibility measurements and spectroscopic studies *viz.* IR, ^{1}H NMR and electronic spectra. The ^{1}H NMR spectral studies are used only for the characterisation of ligand.

EXPERIMENTAL

Di(2-aminophenyl) sulphide was prepared as reported earlier[4]. For the preparation of the complexes a methanolic solution of di(2-aminophenyl) sulphide (4.90 gm, 0.02 mole), containing metal(II) salts (0.01 mole), also in methanol (20 ml) was refluxed for 30 min. To this solution, acetylacetone (0.2 gm, 0.02 mole) in 5 ml of methanol was added dropwise and the solution was further refluxed for *ca.* 15 hrs. The complexes were crystallised out by distilling off the solvent and treating the residue either with pet-ether (40–60°C) or with pet-ether-acetone mixture. The complexes were purified by running over TLC plates, recrystallised by appropriate solvent mixtures and analysed Table 1). The free macrocyclic ligand was obtained by extricating nickel from the $[Ni(L)](ClO_4)_2$ as follows: To the methanolic solution of complex $[Ni(L)](ClO_4)_2$ (0.82 gm, 0.001 mole) was added aqueous solution of KCN (0.27 gm). The solution was stirred for *ca.* 4 hrs. The resulting $[Ni(CN)_4]^{2-}$ precipitate was filtered off and the filtrate was concentrated to reduce the volume to minimum. The residue was treated with pet-ether-acetone mixture several times and crystallised. The ligand thus obtained was purified by running over TLC plates, recrystallised and characterised as follows: Found/(Calcd.)

TABLE 1

ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Complexes	Found (calcd.) %				Molar conductance (10^{-3} M) en (BMF) (Ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (BM)
	%M	%C	%H	%N		
$[Mn(L)H_2O)_2](ClO_4)_2$	6.39	47.92	4.02	6.49	148.54	5.80
	(6.45)	(48.00)	(4.23)	(6.58)		
$[Mn(L)(H_2O)_2](BF_4)_2$	6.55	49.42	4.32	6.72	144.72	5.88
	(6.65)	(49.48)	(4.36)	(6.79)		
$[Ni(L)](ClO_4)_2$	7.13	49.79	3.87	6.74	154.37	—
	(7.18)	(49.89)	(3.91)	(6.85)		
$[Ni(L)](BF_4)_2$	7.29	51.42	4.01	7.02	156.59	—
	(7.40)	(51.49)	(4.04)	(7.07)		
$[Cu(L)](ClO_4)_2$	7.68	49.51	3.80	6.71	138.74	1.92
	(7.72)	(49.60)	(3.89)	(6.80)		
$[Cu(L)](BF_4)_2$	7.91	51.02	3.94	6.97	140.05	2.05
	(7.97)	(51.18)	(4.01)	(7.02)		
$[Co(L)(H_2O)_2](ClO_4)_2$	7.08	49.72	3.84	6.80	158.34	4.80
	(7.20)	(49.88)	(3.91)	(6.84)		
$[Co(L)(H_2O)_2](BF_4)_2$	7.38	51.34	3.97	7.01	152.57	5.08
	(7.43)	(51.48)	(4.03)	(7.06)		

%C	%H	%N	Mol. wt.
72.60	5.98	10.41	535
(72.85)	(5.71)	(10.08)	(560)

Characteristic IR bands (cm^{-1}) νCN (1660), νCS (752), aromatic vibrations (1600, 1580, and 1470), ^1H NMR chemical shifts: CH_3 protons at 1.21 ppm (singlet) CH_2 protons at 1.41 ppm (singlet) aromatic protons at 7.18 ppm (multiplet).

The reaction of the isolated ligand with NiX_2 ($X = ClO_4^-$, BF_4^-), although with poor yields also gave the same complexes as prepared above, supporting the *in situ* synthesis.

RESULT AND DISCUSSION

The analytical data alongwith the molar conductance value of the complexes suggest their general formulae to be $[M(L)]X_2$ and $[M'(L)(H_2O)_2]X_2$ where M = Ni(II) and Cu(II), M' = Mn(II) and Co(II) L = tetrabenzo-(b,e,l,o)4,14-dithia-1,7,11,17-tetraaza-8,10,18,20-tetramethyl cyclodedeca-7,10,17,20-tetraene and $X = ClO_4^-$ and BF_4^-. Thus the complexes behave as electrolytes.

The absence of carbonyl stretching at 1700 cm^{-1} shows the formation of macrocycle by the condensation of amino and carbonyl group. A considerable negative shift in azomethine stretching frequency suggests the coordination of azomethine nitrogen atoms to metal[5,6]. The positive shift in the aromatic ring vibrations also suggests the nitrogen coordination to metal[7]. The non-participation of the S-atom is evidenced[18] by the C–S stretch in the complexes which appears at 750 cm^{-1}. It is observed in case of free ligand at identical positions. Moreover the molecular models also indicate that the S-atoms cannot assume the expected apical positions because of steric reasons. The presence of uninegative perchlorate and tetrafluoroborate is evidenced by the absence of ν_1 and ν_2 transitions which are IR inactive in the case of uninegative ionic perchlorate and tetrafluoroborate in T_d symmetry. The IR active ν_3 and ν_4 transitions are observed at 1050–1170 cm^{-1}, 620–630 cm^{-1} and 1010–1025 cm^{-1}; 530 cm^{-1} for perchlorate and tetrafluoroborate uninegative anions respectively[9,10]. Two bands which are seen at the position of 900 ± 10 cm^{-1} and 760 ± 20 cm^{-1} in case of Mn(II) and Co(II) complexes are due to rocking and wagging vibrations of coordinated water molecule[11] whereas the negatively shifted band at 3460–3400 cm^{-1} corresponding to O–H stretch also shows the coordination of water molecule to the metal atom[12].

The diffuse reflectance spectra of Mn(II) complexes show bands at 18,500 ± 200 cm^{-1}; 24,950 ± 200 cm^{-1} and 29500 ± 200 cm^{-1} which are due to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g(D)$ transitions corresponding to the octahedral geometry which is also confirmed by their μ_{eff} values appearing in the range 5.80–5.90 BM. The Co(II) complexes show three bands around 21,000, 15,500 and 8,500 cm^{-1} assigned to be $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions. These transitions along with the μ_{eff} values in the range of 4.80–5.10 BM confirms the octahedral geometries for the complexes[14]. The bands at 18,500 and 27,000 cm^{-1} in the electronic spectra of Cu(II) complexes are assigned to be $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in square planar geometry[15, 16]. The electronic spectra of the Ni(II) complexes also indicate a square planar geometry by showing bands at 21,200 and 16,400 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions. The magnetic moment values of Cu(II) complexes lie in the range of 1.95–2.05 BM whereas the Ni(II) complexes are found to be diamagnetic[16].

Thus it is concluded on the basis of the above physico-chemical studies that the Mn(II) and Co(II) complexes have octahedral structures obtained by the coordination of four azomethine nitrogens and the two water molecules whereas the Ni(II) and Cu(II) complexes possess square planar geometries. The perchlorate and tetrafluoroborate anions, because of their bulky nature, remain outside the coordination sphere.

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