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STRUCTURE ELUCIDATION OF Co (II) AND Ni (II) COMPLEXES OF MONOBASIC TRIDENTATE (SOO DONOR) AND TETRADENTATE (SOON DONOR) LIGANDS

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ABSTRACT

The ligands α-mercaptophenylacetohydroxamic acid (MPA-H) and α-mercapto-2-amino phenylacetohydroxamic acid (MAPA-H) and their four novel complexes with Co (II) and Ni (II) with specific formulae have been synthesized and characterised by elemental analyses, magnetic and conductance measurements, IR and electronic spectral studies. The ligand MPA-H and MAPA-H were found to behave in monobasic tridentate (SOO donor) and tetradentate (SOON donor) manner, respectively. All the synthesized complexes were non-electrolyte with magnetic moment ranging from 3.18 B.M. to 5.4 B.M. All the complexes were found to have octahedral geometry.

Key words : Hydroxamic acids, Tridentate ligand, Tetradentate ligand, Octahedral complex, Magnetic moment, Cobalt (II), Nickel (II).

INTRODUCTION

Hydroxamic acids are versatile reagents for organic and inorganic analyses[1,2]. Their derivatives are biochemically highly active and find applications in medicinal use[3]. The sulphur containing derivatives of hydroxamic acid have aroused considerable interests over decades[4]. Despite the ligational potentiality associated with sulphur derivatives of hydroxamic acid, the studies made on the metal complexes of these ligands are limited[5]. The study of coordination compounds of sulphur donor ligands is of biochemical interests due to their carcinostatic (anticancer)[6] antibacterial[7] and antifungal[8] activities. Sulphur donor compounds are expected to be the most effective anticancer agents as they usually confer lipid solubility on the metal complex. The sulphur donor ligands have also been widely used as agro-chemicals and favorable environmental degradation. In continuation[9-11] of our work on the complexes with the mentioned ligands, we report here

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the synthesis and structural characterization of two new ligands, α-mercapto-2-aminophenylacetohydroxamic acid (MAPA-H) and α-mercapto phenylacetohydroxamic acid, (MPA-H) (Fig. 1) and their complexes with Co (II) and Ni (II).

(MAPA-H) (MPA-H)

Fig. 1

EXPERIMENTAL

Materials

All the chemicals and reagents used were of AnalaR grade. Anhydrous grade alcohols, DMF, and DMSO were obtained from Fischer Scientific. Hydroxylamine hydrochloride and α-mercapto phenyl acetate were obtained from Fluka (Germany). The metal chlorides used in the present investigation were of BDH AR grade. All reactions and experimental manipulations were carried out at 300 K.

Instrumentation

Elemental analysis (C, H and N) of ligand and complexes was carried out in micro analytical laboratory on Carl-Ebra 1106 elemental analyzer. Metals, chloride and sulphur in the complexes were estimated following standard procedures [12].

The molar conductance measurements were carried out for the 10^{-3} M solutions of complexes in DMF solvent at 300 K using a Systronics direct reading digital conductivity bridge-304 with a dip type cell. The magnetic measurements of the complexes at 300 K were made by Gouy magnetic balance using Hg $[Co(NCS)_4]$ as calibrant. The measured susceptibilities were corrected for diamagnetic susceptibility of the ligand.

The IR spectra of ligand and the complexes as nujol-mull smears were recorded in the region 4000-200 cm^{-1} on a Perkin-Elmer 577 spectrophotometer. The electronic spectra of the complexes were recorded on Systronics UV-Visible spectrophotometer Type –119 PC based (λ = 200 – 1000 nm and band width 2 nm) using ethanol as the solvent.

Synthesis of ligand (MAPA-H)

To a mixture of alcoholic KOH and hydroxylamine hydrochloride solution at 35-45 ºC temperature, 0.175 mole of α-mercapto- 2-aminophenyl acetate in methanol was added to get the K-salt of acid. The free acid was obtained by treating the K-salt with acetic acid. Yellow brown crystals of the ligand (MAPA-H) were obtained with melting point 191 – 193 ºC (decomposition point).

Synthesis of ligand (MPA-H)

To a mixture of methanolic KOH and hydroxylamine hydrochloride solution at 45 ºC, 0.35 mole of α-mercapto phenyl acetate was added with constant shaking and then solution was filtered immediately through suction. The filtrate was kept for 48 hours in Elmer Flask and the K-salt of the acid was filtered, washed with absolute alcohol and then dried in vacuum. The product was then mixed with 80 mL 0.25 N acetic acid and heated with stirring until a clear solution was obtained. The light brown crystals of MPA-H ligand were obtained on keeping the solution in ice-bath.

Synthesis of complexes

0.041 moles of metal (II) chloride were dissolved in 40 mL of distilled water and added to an aqueous ethanolic solution of the ligand (0.040 moles in 35 mL ethanolic water) slowly with constant shaking. The colored heavy mass was separated out. It was filtered and washed with distilled water until free from chloride and dried at 110 – 115ºC in vacuo.

RESULTS AND DISCUSSION

All the synthesized complexes were stable and non-hygroscopic solids. These were soluble in ethanol, DMF and DMSO but insoluble in water.

The following chemical equations represent the formation of ligand and the complexes:

$$\mathrm{Ph(NH_2)\ CH\ (SH)\ COOEt + NH_2OH.HCl \longrightarrow \underset{(MAPA\text{-}H)}{Ph(NH_2)CH\ (SH)\ CONHOH} + EtOH + HCl}$$

$$\mathrm{CoCl_2.6H_2O + MAPA\text{-}H \xrightarrow{EtOH} \underset{Brown}{[Co\ (MAPA)\ Cl\ H_2O]} + HCl + 5\ H_2O}$$

$$\mathrm{NiCl_2.6H_2O + MAPA\text{-}H \xrightarrow{EtOH} [Ni(MAPA)\,Cl\,H_2O] + HCl + 5\,H_2O}$$

Yellow

$$\mathrm{PhCH(SH)COOMe + NH_2.OH.HCl \xrightarrow{Alc.\ KOH} PhCH(SH)CONHOH + HCl + MeOH}$$

MPA-H (Brown)

$$\mathrm{CoCl_2.6H_2O + MPA\text{-}H \xrightarrow{EtOH} [Co(MPA)Cl\,(H_2O)_2] + HCl + 4\,H_2O}$$

Reddish brown

$$\mathrm{NiCl_2.6H_2O + MPA\text{-}H \xrightarrow{EtOH} [Ni(MPA)Cl\,(H_2O)_2] + HCl + 4\,H_2O}$$

Pale yellow

Elemental analysis data (Table 1) and molecular weight suggested 1 : 1(metal : ligand) stoichiometry and monomeric nature of the complexes.

Table 1. Analytical and physical data of complexes

Compound	Found (calculated) %						μ_{eff}	Λ_M
	C	H	N	S	Cl	M		
MPA-H (L)	52.55	4.90	7.64	17.50	-	-	-	-
Brown	(52.56)	(4.92)	(7.65)	(17.48)				
[CoLCl $(H_2O)_2$]	30.68	3.86	4.50	10.20	11.38	18.90	5.13	28
Reddish brown	(30.73)	(3.84)	(4.48)	(10.24)	(11.36)	(18.86)		
[NiLCl $(H_2O)_2$]	30.70	3.90	4.46	10.30	11.40	18.80	3.20	32
Pale yellow								
MAPA-H (L')	48.50	5.04	14.15	16.15	--	--	--	
Brown	(48.48)	(5.05)	(14.14)	(16.16)				
[CoL'ClH_2O]	31.01	3.57	9.08	10.35	11.50	19.02	5.11	18
Brown	(31.03)	(3.55)	(9.05)	(10.34)	(11.48)	(19.05)		
[NiL'ClH_2O]	31.08	3.58	9.02	10.32	11.50	18.95	3.18	32
Yellow	(31.05)	(3.56)	(9.05)	(10.35)	(11.48)	(18.98)		

(μ_{eff} is in B.M. and Λ_M is in $\Omega^{-1}cm^2\ mol^{-1}$) and L and L' are MPA and MAPA, respectively

The molar conductance values for complexes in DMF (10^{-3}M) showed their non-electrolytic nature[10].

IR spectral studies

The structural possibilities of the complexes depend upon the mode of coordination of the ligands. The IR spectral studies are quite useful in determining the mode of coordination of ligands. On critically examining the position and direction of the shifts of the frequencies of the ligands in the complexes, as compared to their positions in the free state, the mode of coordination can be suggested for all the synthesiszed complexes. The IR spectral studies show that the ligand MAPA-H acts as uninegative tetradentate ligand in all the synthesized complexes, bonding through the carbonyl oxygen, alcoholic oxygen, thioalcoholic sulphur and amino nitrogen. The IR spectral studies showed that the ligand, MPA-H acted as a mono-negative tridentate ligand in all the synthesized complexes, bonding through the carbonyl O, alcoholic O and thioalcoholic S. The IR spectrum of the ligand showed a medium intensity band at 2570 cm^{-1} for ν(S-H). Absence of this band in complexes indicates the destruction of the S-H bonding followed by complexation of S with metals after deprotonation [13]. This is further supported by a downward shift in ν(C-S) by 15-25 cm^{-1} in the complexes and the disappearance of a low intensity band at 275-295 cm^{-1} due to M-S stretches. The band at 3275 cm^{-1} due to ν (N-H) mode remains intact in complexes indicating the non-participation of N-H of hydroxamic acid group in coordination. Further the IR spectra of the complexes showed the band attributed to ν (NH_2) of the coordinated amino group, which appeared at $\Delta\nu > 50$ cm^{-1} than in the spectrum of MAPA-H (a medium intensity band around 1525 – 1535 cm^{-1}). The ν(C=O) stretch shifts to lower side in the complexes by 15-25 cm^{-1}, suggesting involvement of carbonyl oxygen in coordination [14]. This is further supported by the appearance of new low intensity bands around 450-500 cm^{-1} in the spectra of complexes due to the ν (M-O) stretch. The ν (O-H) stretch shifts to lower frequency in the complexes by 20-30 cm^{-1} suggesting coordination of hydroxamic acid group through O-H group with metals [15]. The appearance of a low intensity band around 220-230 cm^{-1} in Co (II) complexes indicated the coordination of Cl with metals [ν (M-Cl)]. Further Co (II) complexes exhibit characteristic bands due to coordination of water molecule [16] around 800-850 cm^{-1}. Comparison with the IR spectrum of the ligands, the complexes showed new bands in the far IR regions 450-500, 350-400 and 275-295 cm^{-1} assignable to M-O, M-N, and M-S stretching vibrations, respectively[17].

The IR spectral studies showed that the ligand, MPA-H acted as mononegative tridentate ligand in all the synthesized complexes, bonding through the carbonyl O, alcoholic O and thioalcoholic S. IR spectrum of the ligand showed a medium intensity band at 2560 cm^{-1} for ν (S-H). Absence of this band in the complexes indicated the destruction of the S-H bonding followed by complexation of S after deprotonation. This was further supported by a downward shift in ν (C-S) by 10 - 15 cm^{-1} in the complexes and the appearance of new low intensity bands at 270-280 cm^{-1} due to M-S stretching vibrations.

The band at 3265 cm^{-1} due to ν (N-H) mode remained intact in the complexes indicating the non-participation of N-H of hydroxamic acid group in coordination. The ν (C=O) stretch shifted to lower frequency in the complexes by 18-30 cm^{-1}, suggesting involvement of O (C=O) in coordination. This was further supported by the appearance of low intensity bands at 480-495 cm^{-1} in the spectra of complexes due to the ν (M-O) stretch. The ν (O-H) stretch shifted to lower frequency in the complexes by 15-25 cm^{-1} suggesting coordination of hydroxamic group through O-H group with metals. The IR spectral studies indicated the coordination of Cl [ν (M-Cl)] at 220-230 cm^{-1} with metals. In addition, Co and Ni complexes exhibited characteristic bands due to coordination of water molecules around 1560 – 1600 and 800 – 850 cm^{-1}. In the far IR spectral region, the additional bands in the regions 435-480 cm^{-1} and 290-355 cm^{-1} were assigned to ν (M-O) and ν (M-S) stretching vibrational modes, respectively in the complexes. It was observed that ν (M-O) frequency shifted downward with increasing mass of the metals [18].

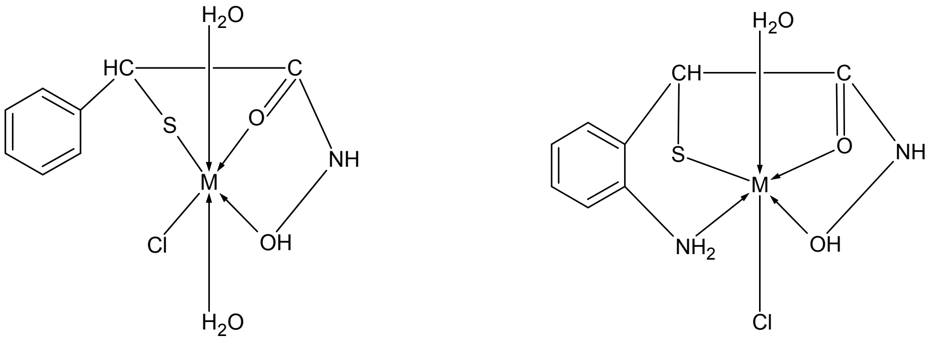
Electronic spectral studies

The study of magnetic and electronic spectral data is quite informative in characterizing the geometry of the complexes. The monomeric nature of the complexes was confirmed by their magnetic moment values.

The electronic spectrum of Co (II) complex exhibited three bands at 9990, 16120 and 22135 cm^{-1}, assigned to– $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, which predicted the high-spin octahedral geometry of the complexes that was confirmed by the observed magnetic moment values (5.11 to 5.13 B.M.). These higher values of magnetic moments than the spin –only value (3.89 B.M.) for three unpaired electrons and may be ascribed to substantial orbital contribution to the moment [19].

The electronic spectrum of Ni (II) complex exhibited three weak bands at 11105, 15890 and 23120 cm^{-1} which are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, which favoured octahedral geometry of the complexes. The observed magnetic moment values (3.18 to 3.20 B.M.) for the complexes confirmed the presence of two unpaired electrons and an octahedral environment.

On the basis of these evidences, the proposed structures for the complexes are presented in Fig. (a) and (b)



(a) **(b)**

Proposed octahedral structures of [ML’ClH_2O] (M = Co and L = MAPA) and (b) [MLCl $(H_2O)_2$] M = Co {L = MPA}

CONCLUSIONS

Four complexes of the ligands MPA-H and MAPA-H with Co^{2+} and Ni^{2+} have been synthesized and characterized. The IR spectral studies revealed that the ligands MPA-H and MAPA-H acted as a mononegative tridentate (SOO donor) and tetradentate (SOON donor), respectively in all the complexes. The magnetic, conductance and electronic spectral studies revealed that the complexes were paramagnetic with octahedral geometries. All the investigated complexes were non-electrolyte and monomer.

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