

## Synthesis and Structural Characterization of Transition Metal(II) Complexes with Monobasic Tetradentate (NOOS donor) Ligand

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The  $\alpha$ -mercapto-2-amino phenylacetohydroxamic acid (MAPA-H) and its coordination compounds with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions have been synthesized and characterized on the basis of elemental analyses, magnetic and conductance measurements, IR and electronic spectral studies. The shifts of carbonyl  $\nu(\text{C}=\text{O})$ , thioalcoholic  $\nu(\text{C}-\text{S})$ , alcoholic  $\nu(\text{O}-\text{H})$  and amino  $\nu(\text{N}-\text{H})$  stretches in complexes indicated the monobasic tetradentate (NOOS donor) nature of the ligand (MAPA-H). The Co(II) and Ni(II) complexes were paramagnetic and possessed octahedral geometry. The Cu(II) complex was paramagnetic with distorted octahedral geometry. The Zn(II) and Cd(II) complexes were diamagnetic and tetrahedral.

**Key Words:** Hydroxamic acids, Tetradentate ligand, Transition metals, Magnetic moment.

### INTRODUCTION

Hydroxamic acids are versatile reagents for organic and inorganic analyses.<sup>1,2</sup> Their derivatives are biochemically highly active and find applications in medicinal use<sup>3</sup>. The sulphur containing derivatives of hydroxamic acid have aroused considerable interest over decades<sup>4</sup>. Despite the ligational potentiality associated with sulphur derivatives of hydroxamic acid, the studies made on the metal complexes of these ligands are limited<sup>5</sup>. The study of coordination compounds of sulphur donor ligands is of biochemical interest due to their carcinostatic, antibacterial<sup>7</sup> and antifungal<sup>8</sup> 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 favourable environmental degradation.

We report the synthesis and structural characterization of a new ligand,  $\alpha$ -mercapto-2-amino phenylacetohydroxamic acid (MAPA-H) (Fig. 1) and its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions.

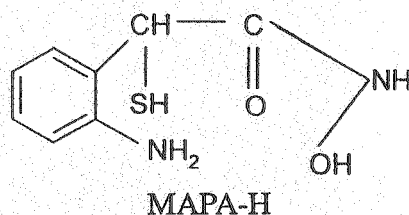


Fig. 1

### EXPERIMENTAL

All the chemicals and reagents used were of AnalaR grade. These were from Aldrich, E. Merck and BDH (AR) in the present investigation. All reactions and experimental manipulations were carried out at 300 K in air.

Elemental analyses (C, H and N) of the ligand and complexes were carried out in microanalytical laboratory on Carlo-Erba 1106 elemental analyzer. Metals, chloride and sulphur in the species were estimated following standard procedures<sup>9</sup>.

Molar conductance measurements were carried out for the  $10^{-3}$  M solutions of the 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  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as calibrant.

The IR spectra of ligand and the complexes in nujol-mull were recorded in the region  $4000\text{--}200\text{ cm}^{-1}$  on a Perkin-Elmer 577 spectrophotometer. The electronic UV-Vis spectra of complexes were recorded on Systronics UV-Vis spectrophotometer type-119 PC based (wavelength  $200\text{--}1000\text{ nm}$  with bandwidth  $2\text{ nm}$ ) using ethanol as the solvent.

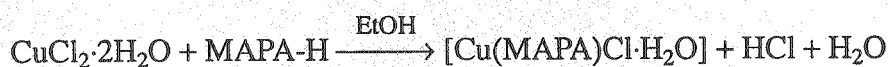
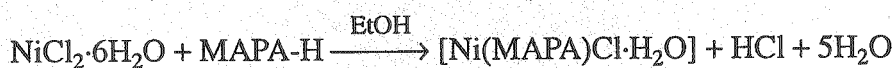
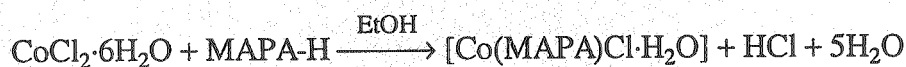
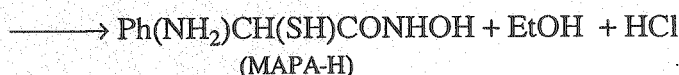
**Synthesis of Ligand (MAPA-H):** To a mixture of alcoholic KOH and hydroxylamine hydrochloride solution at  $35\text{--}45^\circ\text{C}$  temperature,  $0.175\text{ mol}$  of  $\alpha$ -mercapto-2-amino phenyl acetate in methanol was added to get the potassium-salt of acid. The free acid was obtained by treating the potassium-salt with acetic acid. Yellow brown crystals of the ligand (MAPA-H) were obtained with melting point  $191\text{--}193^\circ\text{C}$  (decomposition point).

**Synthesis of Complexes:**  $0.041\text{ mol}$  of metal(II) chloride was dissolved in  $40\text{ mL}$  of distilled water and added to an aqueous ethanolic solution of the ligand ( $0.040\text{ mol}$  in  $35\text{ mL}$  ethanolic water) slowly with constant shaking. A coloured heavy mass separated out. It was filtered and washed with distilled water until free from chloride and dried at  $110\text{--}115^\circ\text{C}$  *in vacuo*.

### RESULTS and DISCUSSION

All the synthesized complexes were nonhygroscopic solids and were stable in air. These were soluble in ethanol, DMF and DMSO but insoluble in water.

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



Elemental analyses data (Table-1) and molecular weight determination suggest 1 : 1 (metal: ligand) stoichiometry and monomeric nature of the complexes. The molar conductance values for Co(II), Ni(II) and Cu(II) complexes in DMF ( $10^{-3}$  M) showed their non-electrolytic nature<sup>10</sup> but Zn(II) and Cd(II) complexes behaved as 1 : 1 electrolytes.

**IR spectral studies:** The IR spectral studies show that the ligand MAPA-H acts as a uninegative tetradentate in all the synthesized complexes, bonding through the carbonyl oxygen, alcoholic oxygen, thioalcoholic sulphur and amino nitrogen. The IR spectrum of the ligand showed a medium intensity band at  $2570\text{ cm}^{-1}$  for  $\nu(\text{S—H})$ . Absence of this band in all the metal complexes indicates the destruction of the (S—H) bonding followed by complexation of S with metals after deprotonation<sup>11</sup>. This is further supported by a downward shift in  $\nu(\text{C—S})$  by  $15\text{--}25\text{ cm}^{-1}$  in the complexes and the disappearance of a new low intensity band at  $295\text{--}275\text{ cm}^{-1}$  due to (M—S) stretches.

The band at  $3275\text{ cm}^{-1}$  due to  $\nu(\text{N—H})$  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  $\nu(\text{NH}_2)$  of the coordinated amino group, which appeared at  $\Delta\nu > 50\text{ cm}^{-1}$  than in the spectrum of MAPA-H (a medium intensity band around  $1525\text{--}1535\text{ cm}^{-1}$ ). The  $\nu(\text{C=O})$  stretch shifts to lower in the complexes by  $15\text{--}25\text{ cm}^{-1}$ , suggesting involvement of carbonyl oxygen in coordination<sup>12</sup>. This is further supported by the appearance of new low intensity bands around  $500\text{--}450\text{ cm}^{-1}$  in the spectral complexes due to the  $\nu(\text{M—O})$  stretch. The  $\nu(\text{O—H})$  stretch shifts to lower frequency in the complexes by  $30\text{--}20\text{ cm}^{-1}$  suggesting coordination of hydroxamic acid group through O—H group with metals<sup>13</sup>. The appearance of a low intensity band around  $230\text{--}220\text{ cm}^{-1}$  in Co(II), Ni(II) and Cu(II) complexes indicates the coordination of Cl with metals [ $\nu(\text{M—Cl})$ ]. Further Co(II), Ni(II) and Cu(II) complexes exhibit characteristic bands due to coordination of water molecule<sup>14</sup> around  $850\text{--}800\text{ cm}^{-1}$ . Comparison with the IR spectrum of the ligand, complexes showed new bands in the far IR regions  $500\text{--}450$ ,  $400\text{--}350$  and  $295\text{--}275\text{ cm}^{-1}$  assignable to (M—O), (M—N) and (M—S) stretching vibrations

respectively<sup>12</sup>. It was observed that  $\nu(\text{M—O})$  frequency shifted downward with increasing atomic mass of the metals<sup>14</sup>.

TABLE-I  
ANALYTICAL AND PHYSICAL DATA OF LIGAND AND COMPLEXES

Species	Colour	Analysis (%), Found (Calcd.)						$\mu_{\text{eff}}$	$\Lambda_M$
		M	C	H	N	S	Cl		
MAPA-H	Brown	—	48.50 (48.48)	5.04 (5.05)	14.15 (14.14)	16.15 (16.16)	—	—	—
[CoLCIH <sub>2</sub> O]	Brown	19.02 (19.05)	31.01 (31.03)	3.57 (3.55)	9.08 (9.05)	10.35 (10.34)	11.50 (11.48)	5.11	18
[NiLCIH <sub>2</sub> O]	Yellow	18.95 (18.98)	31.08 (31.05)	3.58 (3.56)	9.02 (9.05)	10.32 (10.35)	11.50 (11.48)	3.18	32
[CuLCIH <sub>2</sub> O]	Blue	20.22 (20.23)	30.55 (30.57)	3.53 (3.50)	8.40 (8.42)	10.20 (10.19)	11.30 (11.31)	1.92	38
[ZnL]Cl	Cream	21.98 (21.95)	32.24 (32.23)	3.01 (3.02)	9.38 (9.40)	10.70 (10.74)	11.88 (11.92)	0.00	84
[CdL]Cl	White	32.55 (32.59)	22.86 (22.83)	2.60 (2.60)	8.11 (8.12)	9.29 (9.28)	10.28 (10.28)	0.00	82

[Magnetic moment in B.M. and molar conductance in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \times 10^{-3} \text{ M}$ ]

The electronic spectrum of Co(II) complex exhibited three bands at 9990, 16120 and 22135  $\text{cm}^{-1}$ , assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively which predicted the high spin octahedral geometry of the complex that was confirmed by the observed magnetic moment value 5.09 B.M. This value of magnetic moment is higher than the spin-only value (3.89 B.M.) for three unpaired electrons and may be ascribed to substantial orbital contribution to the moment<sup>15</sup>.

The electronic spectrum of Ni(II) complex exhibited three weak bands at 11105, 15890 and 23120  $\text{cm}^{-1}$  which are assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  transitions respectively which favoured octahedral geometry of the complex. The observed magnetic moment value 3.15 B.M. for the complex confirmed the presence of two unpaired electrons and octahedral environment to it.

The electronic spectrum of the Cu(II) complex showed two bands at 17950 and 23210  $\text{cm}^{-1}$  due to the envelope of  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{2g}$ ,  ${}^2\text{B}_{2g}$  and  ${}^2\text{E}_g$  transitions (*d-d*) and charge transfer respectively, suggesting a distorted octahedral geometry<sup>16</sup> with  $\text{D}_{4h}$  symmetry in terms of Jahn-Teller effect for the complex. The observed magnetic moment value (at 300 K) of 1.92 B.M. also supported the distorted octahedral geometry<sup>17</sup> of the complex.

The Zn(II) and Cd(II) complexes were found to be diamagnetic as expected for  $d^{10}$  system. These complexes were suggested to be four-coordinated having

tetrahedral geometry based on analytical, IR and conductance studies. On the basis of the forgoing evidences, the proposed structures for the complexes are presented in Figs. 2 and 3.

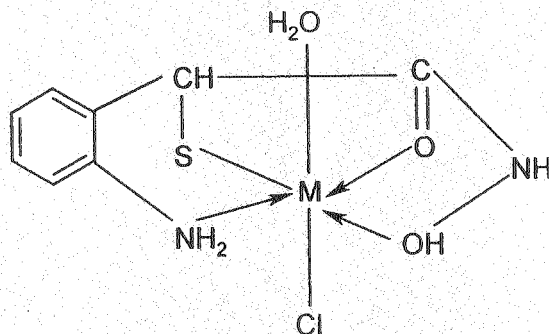


Fig. 2. Proposed octahedral structure of  $[MLClH_2O]$  ( $M = Co, Ni$  and  $Cu$  and  $L = MAPA$ )

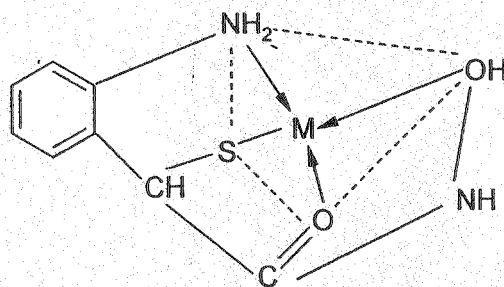


Fig. 3. Proposed tetrahedral structure of the complexes  $[ML]Cl$  ( $L = MAPA, M = Zn$  and  $Cd$ )

## Conclusions

The monobasic quadridentate ligand MAPA-H and its five metal-coordination compounds have been synthesized. The magnetic, conductance and spectral studies revealed that  $Co(II)$  and  $Ni(II)$  complexes were octahedral, but  $Cu(II)$  complex was distorted octahedral and all were paramagnetic and monomer. The  $Zn$  and  $Cd$  complexes were tetrahedral, monomer and diamagnetic but (1 : 1) electrolytes. The octahedral complexes were non-electrolytes.

## ACKNOWLEDGEMENT

The authors are very much thankful to the authorities of the J.P. University, Chapra, India for encouragement and helpful attitude.

## REFERENCES

1. Y.K. Agrawal, *Russ. Chem. Rev.*, **48**, 1773 (1979).
2. Y.K. Agrawal and S.A. Patel, *Rev. Anal. Chem.*, **4**, 237 (1980).
3. W.H. Prusoff, *Biochim. Biophys. Acta*, **32**, 295 (1959).
4. V.G. Kartsev, *Oxygen and Sulphur Containing Heterocycles*, Vols. 1 and 2, IBS Press, Moscow (2003).

5. S. Padhaye and G.B. Kauffman, *Coord. Chem. Rev.*, **63**, 127 (1985).
6. M. Mohan, A. Agrawal and N. Jha, *J. Inorg. Biochem.*, **34**, 41 (1981).
7. A. Maiti, A.K. Guha and A. Gosh, *J. Inorg. Biochem.*, **41**, 13 (1988).
8. N.K. Kaushik and A.K. Mishra, *Indian J. Chem.*, **42A**, 276 (2003).
9. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 6th Edn., Wiley, NY (1996).
10. J. Lewis and T.D.O. Donoghue, *J. Chem. Soc., Dalton Trans.*, 736 (1980)
11. S.E. Livingstone, M.A. Ali and D.J. Phillips, *Inorg. Chim. Acta*, **5**, 119 (1971).
12. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordinate Compounds*, 4th Edn., Wiley-Interscience, NY (1986).
13. R.J. Kulawiec and R.H. Crabtree, *Coord. Chem. Rev.*, **99**, 89 (1990).
14. P. Kofod, *Inorg. Chem.*, **34**, 2768 (1990).
15. M. Gerloch, *Coord. Chem. Rev.*, **99**, 117 (1990).
16. E.I. Solomon and A.B.V. Lever, *Inorganic Electronic Structure and Spectroscopy*, Vol. 1, John Wiley & Sons Inc., NY (1999).
17. R.L. Dutta and A. Syamal, *Elements of Magnetochemistry*, 2nd Edn., Elsevier, New Delhi (1992).

(Received: 17 October 2005; Accepted: 14 June 2006)

AJC-4951