

## Ligational Behaviour of a Tridentate NNS Donor Ligand towards Salts of Co(III), Ni(II) & Cu(II)

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Synthesis of a new tridentate NNS donor ligand, 4-phenylthiosemicarbazone of biacetylmonoxime ( $H_2A$ ) and preparation and characterisation of its complexes with Co(III), Ni(II) and Cu(II) are described. At different pH values the tridentate ligand behaves as  $H_2A$  (pH 2-3),  $HA^-$  (pH 3.5-4) and  $A^{2-}$  (pH 6-8). Elemental analyses, spectroscopic (UV-visible, IR), and magnetic and conductivity measurements have been used to arrive at the geometry of the ligand environment around the metal ion and to elucidate the bonding-sites of the ligands with the central metal ions.

The coordination chemistry of the thiosemicarbazones has assumed new dimensions because of the antibacterial and antitumour activities exhibited by some thiosemicarbazones and their metal complexes<sup>1-6</sup>. This prompted us to undertake the study of the ligational behaviour of a new thiosemicarbazone oxime i.e. 4-phenylthiocarbazonate of biacetylmonoxime ( $H_2A$ ) towards Cu(II), Ni(II) and Co(III) ions. Depending on the pH the ligand can act as (i)  $H_2A$ , (ii)  $HA^-$  and (iii)  $A^{2-}$ . In all these cases it is found to behave as a tridentate ligand, bonding through the imine-nitrogen, the oxime-nitrogen and the thioketone/deprotonated thiol sulphur atom.

### Materials and Methods

All the chemicals used were of either AR (BDH) grade or chemically pure. 4-Phenylthiosemicarbazide was prepared by a modification of the procedure used by Sen and Gupta<sup>7</sup>. It was condensed with biacetylmonoxime as follows: A solution of 4-phenylthiosemicarbazide (16.7 g, 0.1 mol) and biacetylmonoxime (10.1 g, 0.1 mol) in dry ethyl alcohol (150 ml) was refluxed for 6 hr and then overnight at room temperature. The pale yellow crystals which separated out, were filtered, washed with ethanol and dried over fused  $CaCl_2$ . The elemental analyses (C,H,N,S) of the pale yellow crystalline compound (m.p. 165°) agreed well with the calculated values.

### Preparation of metal complexes

Copper(II) complexes of the type  $Cu(H_2A)X_2 \cdot 3H_2O$  (where  $X = Cl^-, Br^-, NO_3^-, ClO_4^-, \frac{1}{2}SO_4^{2-}$ ) were prepared by reacting equimolar quantities of the appropriate copper salt and the ligand in aqueous alcoholic medium (pH 2-3). In the case of the sulphato complex, a solution of the metal salt in minimum volume of water was used.

The complexes of the type  $Cu(A).4H_2O$  were prepared as follows: To an alcoholic suspension of  $Cu(H_2A)X_2 \cdot 3H_2O$ , ammonium hydroxide was added till the pH of the solution became 7.5-8.0. This solution was heated on a water-bath when a brownish complex separated out.

Nickel(II) complexes of the type  $Ni(HA)X \cdot 2H_2O$  (where  $X = Cl^-, ClO_4^-, Br^-$ ) were prepared by reacting the metal salts and the ligand in 1:1 molar ratio (pH ~ 4) in aqueous ethanolic medium.

$Ni(H_2A)SO_4 \cdot 3H_2O$  and  $Ni(A)H_2O$  were prepared by the procedures similar to those adopted in the cases of the corresponding Cu(II) complexes.

The complex  $Ni(H_2A)_2(NO_3)_2 \cdot 2H_2O$  was prepared by reacting  $Ni(NO_3)_2 \cdot 6H_2O$  and the ligand in 1:2 molar ratio in aq. ethanol, the pH of the solution being adjusted to ~ 3 with dil.  $HNO_3$ .

The complex  $Ni(HA)_2 \cdot 4H_2O$  was prepared as follows: A suspension of  $Ni(H_2A)_2(NO_3)_2 \cdot 2H_2O$  in hot ethyl alcohol was treated with  $NH_4OH$  until the pH of the solution reached 6.5-7.0. A granular brown precipitate separated out.

The Co(III) complexes except  $Co(HA)SO_4 \cdot 3H_2O$  were obtained by dissolving the appropriate cobalt(II) salt and the ligand in 1:2 molar ratio in 1:2 aq. ethyl alcohol (pH ~ 4) and heating the solution on a water-bath for 2.5-3 hr when spontaneous aerial oxidation took place leading to the isolation of the Co(III) complexes. In the case of complex containing the sulphate ion the metal to ligand ratio was 1:1 and an aqueous solution of  $CoSO_4 \cdot 5H_2O$  was used.

All the complexes were filtered, washed with ethanol and dried over fused  $CaCl_2$ . In the case of sulphato complexes the residues were first washed with water.

Magnetic susceptibilities of the complexes were measured at room temperature in a Gouy balance using  $Hg[Co(SCN)_4]$  as the calibrant. Diamagnetic

corrections were made using Pascal's constants<sup>8</sup>. Electrical conductance was measured in conductivity water using a Philips PR-9500 conductivity bridge and a dip-type cell. The infrared spectra of the ligand and complexes in the range 4000-250  $\text{cm}^{-1}$  were recorded on a Beckman IR 20A spectrophotometer as KBr or CsBr disc (100 mg KBr/CsBr + 1-3 mg sample). In a few cases the spectra were recorded as mulls in hexachlorobutadiene. Electronic spectra of the complexes were recorded in the range 370-1000 nm (27,027-10,000  $\text{cm}^{-1}$ ) in nujol on a Pye-Unicam model SP8-150 UV/VIS and a MoM-201 (hungarian) spectrophotometer, as described by Lee *et al.*<sup>9</sup>

## Results and Discussion

The analytical data together with the colour of the complexes are given in Table 1. Most of the complexes are insoluble in common non-coordinating organic solvents, but are highly soluble in coordinating solvents. The molar conductance value of  $\text{Co}(\text{HA})_2\text{Br} \cdot \text{H}_2\text{O}$ , in conductivity water (62.19  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ) suggests that it is a 1:1 electrolyte.

The cobalt(III) complexes are diamagnetic and therefore octahedral. The magnetic moments of  $\text{Ni}(\text{H}_2\text{A})_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{H}_2\text{A})\text{SO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{Ni}(\text{HA})_2 \cdot 4\text{H}_2\text{O}$  lie in the range 2.92-3.2 B.M., generally found for octahedral Ni(II) complexes. The other nickel complexes are diamagnetic and hence square planar. The magnetic moment values of the copper complexes lie in the range 1.73-1.90 B.M. indicating that these complexes may be either distorted octahedral or square planar but not tetrahedral. The magnetic moments of the complexes are summarized in Table 1.

The IR spectra of most of the complexes exhibit a broad band in the region 3300-3000  $\text{cm}^{-1}$  arising from the overlap of the stretching vibrations of the coordinated or lattice water molecules with the  $\nu\text{NH}$  and the  $\nu\text{OH}$  of the ligand. The  $\nu\text{C}=\text{N}$  (imine)<sup>10</sup> band located around 1590  $\text{cm}^{-1}$  in the spectra of the ligand shifts by 10-20  $\text{cm}^{-1}$  to lower wavenumbers in all the metal complexes indicating the involvement of the  $\text{C}=\text{N}$  (imine) in coordination. In all the complexes the participation of the  $\text{C}=\text{N}$  (oxime) moiety in complexation has been ascertained by a positive shift of 10-30  $\text{cm}^{-1}$  of the ligand band around 1440  $\text{cm}^{-1}$  due to  $\nu\text{C}=\text{N}$  (oxime)<sup>11</sup>. The band around 1010  $\text{cm}^{-1}$  (due to  $\nu\text{N}-\text{O}$ )<sup>12</sup> shifts by 30-50  $\text{cm}^{-1}$  to higher frequency suggesting that bonding occurs through the oxime nitrogen atom.

In the case of the complexes of  $\text{H}_2\text{A}$  and  $\text{HA}^-$ , the band at 750  $\text{cm}^{-1}$  (assigned<sup>13</sup> to the  $\nu\text{C}=\text{S}$ ) shifts by 5-20  $\text{cm}^{-1}$  to lower wavenumber indicating the involvement of the thioketone sulphur in coordination. But in the IR spectra of the metal complexes of

the  $\text{A}^{2-}$  from of the ligand, disappearance of the 750  $\text{cm}^{-1}$  band clearly indicates that the thioketone moiety is converted into the corresponding thiol form and the absence of any band around 2500  $\text{cm}^{-1}$  points to the subsequent deprotonation of the thiol.

There exists the possibility of the ligand acting as a bidentate donor (a) by coordinating through two nitrogen atoms (the imine and the oxime nitrogen atoms) and (b) through the imine nitrogen atom and the thioketone sulphur atom. The coordination mode (a) is expected to leave the  $\nu(\text{C}=\text{S})$  unchanged, while the coordination mode (b) is likely to leave the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{N}-\text{O})$  of the oxime moiety unchanged. However, the IR spectra of none of the metal complexes reveal the presence of unchanged  $\nu(\text{C}=\text{S})$  or unchanged  $\nu(\text{C}=\text{N})$  and  $\nu(\text{N}-\text{O})$ . Thus the IR spectra of all the complexes exhibit characteristic features which indicate the simultaneous participation of the two nitrogen atoms and the sulphur atom in coordination. Hence, it may be concluded that in the present case the ligand behaves exclusively as a tridentate NNS donor.

The IR spectra of  $\text{Co}(\text{HA})\text{SO}_4 \cdot 3\text{H}_2\text{O}$  and all the Co(III), Ni(II) and Cu(II) complexes containing nitrate and perchlorate moieties clearly show that these anions are present in the uncoordinated form. But the spectra of Ni(II) and Cu(II) complexes containing sulphate exhibit two bands at 1130 and 1060  $\text{cm}^{-1}$  and two other bands around 960 and 620  $\text{cm}^{-1}$  indicating the presence of monocoordinated sulphate in these species<sup>14</sup>. The bands around 480 and 340  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{M}-\text{N})$ <sup>15</sup> and  $\nu(\text{M}-\text{S})$ <sup>16</sup> respectively.

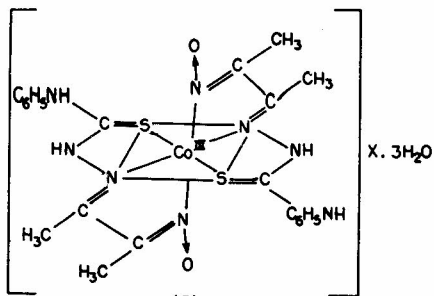
In the IR spectrum of the reddish-brown nickel complex,  $\text{Ni}(\text{A}) \cdot 2\text{H}_2\text{O}$ , the band observed at 415  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{Ni}-\text{O})$  arising out of the coordination of a water molecule<sup>16a</sup> to the fourth position of the coordination square plane around Ni(II). The presence of one coordinated water molecule in  $\text{Ni}(\text{A}) \cdot 2\text{H}_2\text{O}$  is also revealed by the TG-DTA of the compound which exhibit the loss of one rather loosely bound water molecule (lattice water) at 100-110°C but the coordinated water molecule is lost at a much higher temperature (195-98°C).

A band around 410  $\text{cm}^{-1}$  is also observed in the IR spectrum of each of the  $\text{Cu}(\text{H}_2\text{A})\text{X}_2 \cdot 3\text{H}_2\text{O}$  complexes which may be attributed to  $\nu(\text{Cu}-\text{O})$ . The molar conductance value of  $\text{Cu}(\text{H}_2\text{A})\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  in nitrobenzene is 56  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  indicating that both the chlorides are ionic in nature. Hence, the  $\text{Cu}(\text{H}_2\text{A})\text{X}_2 \cdot 3\text{H}_2\text{O}$  type complexes may be either four-coordinated or six-coordinated with three coordination positions being occupied by the ligand and the rest by water molecules.

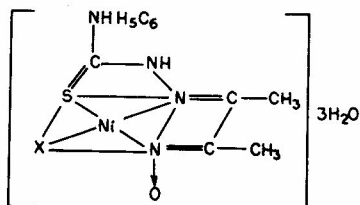
The electronic spectral characteristics (see Table 1) of all the metal complexes lead to the following

Table I—Analytical Data, Colour, Magnetic Moment Values, and Electronic Spectral Data of Complexes

Complex	Colour	Found (Calc.) %					$\mu_{\text{eff}}$ at 302 K	Electronic spectral band (nujol) $\text{cm}^{-1}$	Assignment	Ref.
		C	H	M	N	S				
Co(HA) <sub>2</sub> Cl·H <sub>2</sub> O	Reddish brown	43.26 (43.25)	4.61 (4.59)	9.59 (9.65)	18.42 (18.35)	10.38 (10.48)	5.92 (5.81)	25,000	$^1A_{1g} \rightarrow ^1T_{2g}$	19
Co(HA) <sub>2</sub> Br·2H <sub>2</sub> O	Deep brown	39.29 (39.24)	4.50 (4.46)	8.60 (8.76)	16.76 (16.65)	9.40 (9.51)	11.98 (11.87)	19,610	$^1A_{1g} \rightarrow ^1T_{1g}$	19
Co(HA) <sub>2</sub> ClO <sub>4</sub> ·H <sub>2</sub> O	Reddish brown	39.02 (39.15)	4.27 (4.15)	8.82 (8.74)	16.51 (16.61)	9.54 (9.49)	14.89 (14.75)	25,320	$^1A_{1g} \rightarrow ^1T_{2g}$	19
Co(HA) <sub>2</sub> NO <sub>3</sub> ·2H <sub>2</sub> O	Deep brown	40.45 (40.31)	4.64 (4.58)	9.12 (9.00)	19.09 (19.24)	9.87 (9.77)	—	19,420	$^1A_{1g} \rightarrow ^1T_{1g}$	19
Co(HA)SO <sub>4</sub> ·3H <sub>2</sub> O	Brown	28.79 (28.83)	4.19 (4.15)	12.72 (12.87)	12.12 (12.23)	13.82 (13.97)	20.84 (20.96)	25,640	$^1A_{1g} \rightarrow ^1T_{2g}$	19
Ni(HA)Cl·2H <sub>2</sub> O	Light brown	34.84 (34.81)	4.52 (4.48)	15.42 (15.48)	14.60 (14.77)	8.36 (8.44)	9.24 (9.35)	19,050	$^1A_{1g} \rightarrow ^1T_{1g}$	19
Ni(HA)Br·2H <sub>2</sub> O	Reddish brown	31.19 (31.16)	4.10 (4.01)	13.78 (13.86)	13.10 (13.22)	7.65 (7.55)	18.79 (18.86)	25,000	$^1A_{1g} \rightarrow ^1T_{2g}$	19
Ni(HA)ClO <sub>4</sub> ·2H <sub>2</sub> O	Deep brown	29.81 (29.79)	3.89 (3.84)	13.19 (13.25)	12.59 (12.64)	7.12 (7.22)	22.32 (22.44)	18,870	$^1A_{1g} \rightarrow ^1T_{1g}$	19
Ni(A)·2H <sub>2</sub> O	Deep brown	38.59 (38.52)	4.61 (4.67)	17.09 (17.13)	16.19 (16.34)	9.29 (9.34)	—	25,320	$^1A_{1g} \rightarrow ^1A_{2g} + CT$	19
Ni(H <sub>2</sub> A)SO <sub>4</sub> ·3H <sub>2</sub> O	Deep grey	28.81 (28.78)	4.30 (4.36)	12.69 (12.80)	12.12 (12.21)	13.82 (13.95)	22.32 (20.93)	24,390	$^1A_{1g} \rightarrow ^1A_{2g} + CT$	19
Ni(H <sub>2</sub> A) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Light brown	35.89 (35.83)	4.58 (4.62)	7.90 (7.97)	19.16 (19.00)	8.52 (8.69)	—	24,100	$^1A_{1g} \rightarrow ^1A_{2g} + CT$	19
Ni(HA) <sub>2</sub> ·4H <sub>2</sub> O	Light brown	41.87 (42.00)	5.34 (5.41)	9.27 (9.34)	17.70 (17.81)	10.00 (10.18)	—	24,390	$^3A_{2g} \rightarrow ^3T_{1g}(PKv_3)$	20
Cu(H <sub>2</sub> A)Cl <sub>2</sub> ·3H <sub>2</sub> O	Olive green	30.01 (30.11)	4.62 (4.56)	14.57 (14.49)	12.69 (12.77)	7.10 (7.30)	16.00 (16.17)	15,870	$^3A_{2g} \rightarrow ^3T_{1g}(FXv_2)$	20
Cu(H <sub>2</sub> A)Br <sub>2</sub> ·3H <sub>2</sub> O	Light brown	25.00 (25.03)	3.82 (3.79)	12.12 (12.05)	10.50 (10.62)	6.17 (6.07)	30.50 (30.30)	10,000	$^3A_{2g} \rightarrow ^3T_{2g}(v_1)$	20
Cu(H <sub>2</sub> A)(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Brown	26.76 (26.85)	4.17 (4.07)	13.06 (12.93)	17.22 (17.09)	6.40 (6.51)	—	25,640	$^3A_{2g} \rightarrow ^3T_{1g}(PKv_3)$	20
Cu(H <sub>2</sub> A)SO <sub>4</sub> ·3H <sub>2</sub> O	Light brown	28.40 (28.48)	4.39 (4.31)	13.60 (13.71)	11.96 (12.08)	13.95 (13.81)	20.82 (20.71)	16,390	$^3A_{2g} \rightarrow ^3T_{2g}(v_1)$	20
Cu(H <sub>2</sub> A)ClO <sub>4</sub> ·3H <sub>2</sub> O	Light brown	23.21 (23.30)	3.63 (3.53)	11.02 (11.22)	9.69 (9.89)	5.52 (5.65)	35.00 (35.11)	25,320	$^3A_{2g} \rightarrow ^3T_{1g}(PKv_3)$	20
Cu(A)·4H <sub>2</sub> O	Brown	34.37 (34.42)	5.16 (5.21)	16.42 (16.57)	14.49 (14.60)	8.23 (8.34)	—	16,130	$^3A_{2g} \rightarrow ^1E_g$	20
								13,160	$^3A_{2g} \rightarrow ^3T_{1g}(FXv_2)$	19
								10,310	$^3A_{2g} \rightarrow ^3T_{2g}(v_1)$	20
								16,670	—	20
								16,390	—	19
								16,120	—	19
								16,625	—	19
								17,240	—	19
								15,870	—	19



(I)



(II)

conclusions: (i) the Co(III) ions are present in a pseudo-octahedral environment<sup>17,18</sup>, (ii) the reddish diamagnetic nickel complexes are square planar<sup>19</sup> and paramagnetic nickel complexes are octahedral<sup>19,20</sup>, and (iii) an unambiguous assignment of the broad band<sup>19</sup> observed in the spectra of the Cu(II) complexes around 15,625-17,241 cm<sup>-1</sup> is not possible.

On the basis of the foregoing discussion probable structures of the different types of the complexes reported here may be suggested. The cobalt(III) complexes of the type Co(HA)<sub>2</sub>X.3H<sub>2</sub>O have a pseudo-octahedral structure (I). The complex Ni(HA)<sub>2</sub>.4H<sub>2</sub>O also possess a similar structure. The structure of Ni(H<sub>2</sub>A)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> may be derived from that of Co(HA)<sub>2</sub>X.3H<sub>2</sub>O by replacing Co(III) by Ni(II) and remembering that in this case the ligand in its keto form retains its unenolised thiocarbonyl group and the protonated oxime moiety.

The diamagnetic and square planar complex, Ni(HA)X.3H<sub>2</sub>O may have the structure (II). The structure of the complex Ni(A).2H<sub>2</sub>O may be derived from structure (II) by changing the position of double bond from C=S to C=N-Ph and putting H<sub>2</sub>O in place of X. However, it is not possible to predict, unambiguously, whether the Cu(II) complexes possess distorted octahedral or square planar geometry.

## References

- 1 Orlova N N, Aksenova V A, Selidovkin D A, Bogdanova N S & Perskhin G N, *Russ Pharm Toxic* (1968) 384.
- 2 Johnson C W, Joyner J W & Perry R P, *Antibiotics and Chemotherapy*, 2 (1952) 636.
- 3 Williams D R, *Chem Rev*, 72 (1972) 203.
- 4 Friendlander B L & French F A, *Cancer Res*, 18 (1958) 1286, 1290.
- 5 French F A & Blanz E J, *Cancer Res*, 25 (1965) 1454.
- 6 Idem, *J Med Chem*, 9 (1966) 585.
- 7 Sen A B & Gupta S K, *J Indian chem Soc*, 39 (1962) 628.
- 8 Selwood P W, *Magnetochemistry* (Interscience, New York) 1956, 92.
- 9 Lee R M, Griswold E & Kleinberg J, *Inorg Chem*, 3 (1964) 1278.
- 10 Percy G C & Thornton D A, *Inorg nucl Chem Lett*, 7 (1971) 599.
- 11 Nonoyama M, Tomita S & Yamaski K, *Inorg Chim Acta*, 12 (1975) 33.
- 12 Palm A & Werben M, *Can J Chem*, 32 (1954) 858.
- 13 Bellamy L J, *The infrared spectra of complex molecules* (Chapman & Hall, London) 1975, 400.
- 14 Nakamoto K, *Infrared spectra of inorganic & coordination compounds* (Interscience Publishers) 1970, 173.
- 15 Condrate R A & Nakamoto K J, *Chem Phys*, 42 (1965) 2590.
- 16 Nakamoto K, *Infrared & Raman spectra of inorganic & coordination compounds* (Wiley-Interscience, New York) 1978, 337 & 339.
- 16 (a) Nakagawa & Shimanouchi, *Spectrochim Acta*, 20 (1964) 429.
- 17 Johnson D A & Sharpe A G, *J chem Soc*, (1966A) 798.
- 18 Chen S C & Poon C K, *J chem Soc*, (1966A) 146.
- 19 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, London) 1968, 333; 334; 343; 357; 221-22.
- 20 Jorgensen C K, *Acta chem Scand*, 9 (1955) 1362.