

MAGNETIC AND SPECTRAL STUDIES ON COPPER(II) COMPLEXES WITH α -PYRIDYL-THIOSEMICARBAZIDE

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ABSTRACT

A new series of copper(II) complexes with recently synthesised α -pyridyl-thiosemicarbazide (APT) (pyridinic-N and thioketo-S as donors) having square-planar and distorted octahedral stereochemistry around the metal ion with the general formula $[\text{Cu}(\text{APT})(\text{X})_2]$ and $[\text{Cu}(\text{APT})_2(\text{X}')_2]$ respectively (where $\text{X} = \text{Cl}, \text{Br}, \text{CN}$ and $\text{X}' = \text{NO}_3, \text{ClO}_3, \text{BrO}_3, \text{CH}_3\text{COO}$) have been isolated and characterised by magnetic and spectral (electronic and i.r.) measurements.

HETEROCYCLIC thiosemicarbazides and thiosemicarbazones are bacteriostatic and of vital pharmacological significance¹. Their activity has frequently been thought to be due to their ability to check trace-metals² and hence the chemistry of the metal chelates derived from these organic compounds has been a subject of considerable interest. In the present communication a series of copper(II) complexes with recently synthesised^{3,4} α -pyridyl-thiosemicarbazide ($\text{C}_6\text{H}_8\text{N}_4\text{S}$) abbreviated as 'APT' have been isolated and characterised by chemical analysis, molar conductance, magnetic and spectral (electronic and i.r.) measurements in order to evaluate their stereochemistry.

EXPERIMENTAL

General procedures for the preparation and isolation of copper (II) complexes with 'APT'.

(A) *Di-(Chloro/Bromo/Cyano)-mono-(APT) Copper(II)*:

The ethanolic soln. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10 m. moles) was mixed with 'APT' (20 m. moles) in the same solvent and the green precipitate obtained was digested, cooled, filtered and washed with small amounts of ethanol, acetonitrile and acetone. The product was dried at 80–90° C for 20 min. Dark green cyano and bromo derivatives were obtained by adding 10% aq. KCN soln. (5 ml) and 2 g. NaBr respectively into the refluxing ethanolic soln. of 'APT' just prior to the addition of metal-salt-soln. All the three complexes were insoluble in various organic solvents (ethanol, acetone, acetonitrile, nitrobenzene, DMF and dioxane).

(B) *Di-(Nitrate/Chlorate) (Bromate/Acetate)-bis-(APT) Copper(II)*:

Nitrate and acetate derivatives were obtained by using the corresponding copper(II) salts and following the procedure (A), while chlorate and bromate derivatives were obtained by adding 2 g of $\text{KClO}_3/\text{KBrO}_3$ into the refluxing ethanolic solution of 'APT' just

prior to the addition of the metal salt soln. All the dark-green coloured crystalline products were soluble in acetone, DME, dioxane, acetonitrile and dimethyl sulphoxide. The molar conductance in 10^{-3} M DMF soln. (27.13; 21.74 and 33.58 mhos for chlorate, bromate and acetate derivatives respectively) indicated their non-electrolytic nature.

'Analar' grade chemicals were used throughout. Elemental analysis for all of the complexes was in good agreement with the calculated values indicating the metal to ligand stoichiometric ratio as 1:1 or as 1:2. The diffuse reflectance spectra using MgO as a reference (complexes 1–3) and absorption spectra in acetone medium (complexes 4–7) were recorded on UNICAM-SP-700 U.V. and visible and UNICAM-SP-500 spectrophotometers respectively. Magnetic measurements and i.r. spectra of the complexes were undertaken as described earlier⁵. Thermal, magnetic, electronic and i.r. spectral data for the present copper(II) complexes are recorded in Table I.

RESULTS AND DISCUSSION

No significant conclusion concerning the stereochemistry of copper (II) can be drawn from the magnetic data. The first three complexes (Table I, Nos. 1–3) have the magnetic moment around 1.40–1.55 BM. The bands observed in the regions 15680–16000 cm^{-1} (${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$) and 24900–25700 cm^{-1} (${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$) are attributed to the d-d transitions, which support the sq. planar geometry for these complexes. The band around 25000 cm^{-1} is due to the enhanced d-d transition, assigned to S \rightarrow Cu (termed as 'blue band') and its shifting towards higher energy may be due to axial-coordination to the metal⁶, as it involves bonding through 4s- and 4p- wave functions and the sulphur is more polarizable than nitrogen. The present green coloured copper (II) complexes also possess the broad band around 25000 cm^{-1} as previously reported⁷ for copper (II) sq. planar complexes.

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TABLE I

Thermal, magnetic, electronic and infra-red spectral data for copper(II) complexes with α -pyridyl-thiosemicarbazide ($C_6H_8N_4S$)

Sl. No.	Compound and M.P. °C	$\mu_{eff.}$ BM $300 \pm 2^\circ K$	Electronic spectral bands in cm^{-1}	I.R. bands in cm^{-1} and their assignments				
				$[\nu(C=C) + \nu(C=N)]$ of py. ring	$[\nu(C=S) + \nu(C=N) + \nu(CN)]$	$\nu(C=S)$	$\nu(Cu-S)$ $\nu(Cu-Cl/Br)$ $\nu(Cu-Py. N)$	(*) (*) (*)
	$C_6H_8N_4S$ (APT)	1550 s 1516 s	1333 s 1308 s	760 vs
			${}^2B_{1g} \rightarrow {}^2E_g$ ${}^2B_{1g} \rightarrow {}^2A_{1g}$					
1.	[Cu (APT) Cl ₂] qs-265°	1.55	15680 24800	1575 s 1500 sh	1385 s 1345 m	695 s	400 m 320 m 285 m	(2.430) (1.373) (0.549)
2.	[Cu (APT) Br ₂] qs-265°	1.46	16000 26700	1590 mb 1540 m 1510 m	1400 m 1325 s	700 mb 680 sh	442 w 225 m 280 m	(2.453) (0.679) (0.530)
3.	[Cu (APT) (CN) ₂] qs-265°	1.40	15800 25400	1600 m 1520 m	1400 m 1350 m	730 m 710 w	438 m .. 298 ms	(2.408) .. (0.600)
			${}^2A_1 \rightarrow {}^2E$ ${}^2E \rightarrow {}^2E$					
4.	[Cu (APT) ₂ (NO ₃) ₂] d-200°	1.94	6000 13000	1580 s 1565 mb 1530 m++	1400 m 1390 s 1270 m++	720 m ..	442 m .. 300 m	(2.452) .. (0.608)
5.	[Cu (APT) ₂ (ClO ₄) ₂] m-210°	1.97	6500 15000	1575 m 1560 mb	1385 s 1355 sh	685 s ..	444 mb .. 305 m	(2.474) .. (0.628)
6.	[Cu (APT) ₂ (B ₁ O ₃) ₂] m-215°	2.00	6800 17000					
7.	[Cu (APT) ₂ (CH ₃ COO) ₂] m-205°	1.98	7000 17300					

++ Bands due to nitrate coordination.

b = broad, m = medium, s = sharp, sh = shoulder, w = weak.

(*) Data in parenthesis are the corresponding stretching force constants $\times 10^{-6}$ dynes cm^{-1} , qs = quite stable, d = decomposition before melting, m = melting point.

Magnetic moments around 2 BM. observed in the complexes 4-7 are in agreement with the reported values for six-coordinated copper (II) compounds^{8,9}. The slight increase in the magnetic moment may presumably be due to the distortion of octahedral symmetry and electron delocalization of the ligand⁷. Absorption spectra of these copper (II) complexes show considerable Jahn-Teller distortions and show

bands in the region 6000-7000 cm^{-1} and 13000-17000 cm^{-1} assigned to ${}^2A_1 \rightarrow {}^2E$ and ${}^2E \rightarrow {}^2E$ transitions respectively, supporting pseudo-distorted octahedral geometry^{8,9} around copper (II) ion.

A comparison of i.r. spectra of the free ligand (APT) and its copper(II) complexes reveals the bidentate nature of the ligand and the coordination through pyridinic-nitrogen and thioceto sulphur.

The symmetric and antisymmetric [ν (C = C) + ν (C — N)] vibrations of the pyridine ring of 'APT' are shifted to higher wave numbers on complexation, implying pyridinic nitrogen-metal bond. The absorption bands at 1333 and 1308 cm^{-1} assigned to [ν (C = C) + ν (C = N) + ν (CN)] show the upward shift of frequencies while the band at 760 cm^{-1} (in the free ligand) assigned to ν (C = S) shows a considerable decrease in frequency ($\sim 75 \text{ cm}^{-1}$), indicating the sulphur coordination to the metal¹⁰. In cyano and nitrate complexes, the band at 2210 cm^{-1} may be assigned to the cyano group frequency indicating the coordination through nitrogen, while the medium intensity absorption peaks at 1530 and 1270 cm^{-1} are assigned to the ν (Cu-NO₃) vibrations¹¹.

The medium intensity bands observed in the far-i.r. region 454-425 cm^{-1} and 315-280 cm^{-1} are assigned to ν (Cu-S) and ν (Cu-Py. N) vibrations respectively, while in the complexes (1 and 2), ν (Cu-Cl) and ν (Cu-Br) are observed at 320 and 225 cm^{-1} respectively supporting sq. planar geometry around the copper (II) ion. In complexes (5 and 6) ClO₃ and BrO₃ are coordinated to the metal through the oxygen as -O-ClO₂ and -O-BrO₂ respectively as the ν (Cu-

Cl/Br) band is not observed. In the complex 7, CH₃COO is coordinated through ketonic oxygen. Metal ligand stretching force constants (K-values) for ν (Cu-S), ν (Cu-Cl/Br) and ν (Cu-Py. N) are given in Table I.

1. Aggarwal, K. C., Booth, B. A. and Moore, E. C., *Biochem. Pharmacol.*, 1974, 23, 2421.
2. Ginner, S. A. and Longley, C. J., *J. Med. Chem.*, 1973, 16 (9), 984.
3. Jain, C. L., Saxena, R. C. and Saxena, B. S., *Ind. J. Chem.* (Communicated).
4. —, *Doctoral Dissertation*, Meerut University, Meerut 250 002, India, 1977.
5. Saxena, R. C., Jain, C. L. and Rastogi, S. C., *Inorg. Chim. Acta*, 1975, 16, 103.
6. Belford, R. L. and Belford, G. G., *Theor. Chim. Acta*, 1965, 3, 465.
7. Akbar Ali, M. and Phillips, D. J., *J. Inorg. Nucl. Chem.*, 1974, 36, 2229.
8. Campbell, M. J. M., *Coord. Chem. Rev.* 1975, 15, 279.
9. Akbar Ali, M. and Livingston, S. E., *Ibid.*, 1974, 13, 101.
10. Muto, Y., *Bull. Chem. Soc. Japan*, 1960, 33, 1242.
11. Gatehouse, B. M., Livingston, S. E. and Nyholm, R. S., *J. Chem. Soc.*, 1955, 77, 5476.

COMPLEXES OF Cu(II), Ni(II) AND Co(II) WITH SCHIFF BASE DERIVED FROM 2-AMINO-5-METHYLPYRIDINE AND SALICYLALDEHYDE

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ABSTRACT

Complexes of Cu(II), Ni(II) and Co(II) with a Schiff base derived from 2-amino-5-methylpyridine and salicylaldehyde have been prepared and characterised. Based on elemental analysis, infrared and electronic absorption spectra, a square planar structure for Cu(II) complex and tetrahedral structures for Ni(II) and Co(II) have been proposed.

INTRODUCTION

A VARIETY of Schiff base complexes of transition metal ions have received considerable attention¹ and some have been shown to exhibit reversible oxygenation behaviour². Since the geometrical arrangements play a significant part in their spectroscopic, magnetic, substitution and redox³ properties, the Schiff base derived from 2-amino-5-methylpyridine and salicylaldehyde and the geometrical arrangements of its complexes with Cu(II), Ni(II) and Co(II) have been reported in this study.

EXPERIMENTAL

The free ligand was prepared by refluxing equimolar quantities of 2-amino-methylpyridine and salicylaldehyde in ethanol for 30 min. and keeping the reaction mixture stirred at ca. 20° C for ca. 6 h. The recrystallisation from ethanol of the deep yellow crystals gave the ligand in the pure form.

The bis-salicylaldehydato complexes of the metal ions were prepared according to literature methods⁴ and 0.005 mole of the complexes was refluxed in methanol or chloroform (50 ml) for 1 h. While