

Synthesis and characterisation of cobalt(II) and nickel(II) complexes with acetophenone-5(3)-methylpyrazole-3(5)-carbohydrazone

Nityananda Saha* & Saroj Sinha

Department of Chemistry, University College of Science,
Calcutta 700 009

Received 13 January 1989; revised and accepted 5 June 1989

Complexes of Co(II) and Ni(II) with acetophenone-5(3)-methylpyrazole-3(5)-carbohydrazone (AMPCH) have been synthesised and characterised. These complexes have the general formula, $M(\text{AMPCH})_2X_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Co/Ni}$; $X = \text{Cl, Br, ClO}_4, \text{BF}_4, \text{NO}_3, 1/2\text{SO}_4$; $n = 0/1/2/4$). Magnetic moment and electronic spectral data indicate that most of the complex species are grossly octahedral except the halo ($X = \text{Cl, Br}$) complexes of Co(II), which possibly exist as a mixture of octahedral and tetrahedral species. The IR spectra indicate that the ligand acts as a neutral tridentate (NON) one and the counterion (X) retains its ionic character.

As a part of our programme to study the coordination modes of pyrazole based carbohydrazides and the corresponding carbohydrazones with transition metal ions^{1,2}, we report here the isolation and characterisation of the bis-complexes of nickel(II) and cobalt(II) with the title ligand.

Experimental

The ligand (AMPCH) was prepared by condensing equimolar amounts of 5(3)-methylpyrazole-3(5)-carbohydrazone and acetophenone in ethanol on a steam-bath as reported earlier¹. Its purity was checked by elemental analysis and melting point determination. The complexes were prepared by mixing ethanolic solutions of the metal salt, $\text{MX}_2 \cdot n\text{H}_2\text{O}$ (0.01 mol) and the ligand (0.02 mol) at pH 3-5 and refluxing for an hour. The refluxate was concentrated to a small volume by heating on a water-bath and cooled to room temperature ($\sim 27^\circ\text{C}$) when coloured complexes precipitated. The complexes were filtered, washed with ether or benzene and dried *in vacuo* over fused calcium chloride. The carbon, hydrogen and nitrogen contents of the ligand and the metal complexes were estimated micro-analytically and the metal contents by conventional methods of volumetry and gravimetry. The halogen contents of the complexes were determined as silver halides and the sulphur

contents as BaSO_4 (Ref. 3). The equivalent conductances, magnetic susceptibilities and electronic (d.r.s. and solution) and vibrational spectra of the complexes were recorded as described earlier¹.

Results and discussion

The analytical and some other physicochemical data are given in Table 1. Co(II) and Ni(II) form bis-species. The molar conductance (Λ_M) values in DMF for the Co(II) complexes and those of the Ni(II) complexes in methanol classify them as 1:2 electrolytes⁴. The magnetic moment values of $\text{Co}(\text{AMPCH})_2X_2$ ($X = \text{Cl, Br, ClO}_4, \text{NO}_3$) complexes lie in the range 4.52-5.13 B.M. (25°C) and are consistent with a six-coordinate pseudo-octahedral geometry^{5a}. The low μ_{eff} value (4.27 B.M.) for the fluoborate complex may be qualitatively attributed to incomplete quenching of the orbital contribution to magnetic moment^{5,6}. The μ_{eff} values of the Ni(II) bis-species lie in the range 2.98-3.07 B.M. which indicate magnetically normal six-coordinate spin-free octahedral geometry⁶. The reflectance spectra of the halo complexes ($X = \text{Cl, Br}$) of Co(II) exhibit bands around 8.2-9.1, 15.3-15.4 and 20.5-21.0 kK which can be assigned to ν_1 in O_h , ν_3 in T_d and to ν_3 in O_h symmetries respectively. The halo-species may, thus, be considered as mixtures of both tetrahedral and pseudo-octahedral varieties^{7a,7b} in the solid state. The rest of the bis-species of Co(II) ($X = \text{ClO}_4/\text{BF}_4/\text{NO}_3$) exhibit reflectance spectral bands in the regions 8.8-9.2 (ν_1) and 20.0-20.4 kK (ν_3) in an overall octahedral symmetry^{7c}. The calculated values of Dq ($1000\text{-}1044\text{ cm}^{-1}$), B ($798\text{-}850\text{ cm}^{-1}$) and β (0.82-0.87) for these bis-species are consistent with those observed for spin-free octahedral Co(II) complexes as reported earlier⁸.

DMF solutions of all these Co(II) species exhibit bands around 18.9-20.1 kK (ν_3) suggesting that the halo derivatives are totally converted into octahedral species on dissolution in the said solvent. The lower molar extinction values ($\epsilon \approx 10.6\text{-}39.8$) are also in good agreement with their octahedral environment in solution.

The diffuse reflectance spectra of all the Ni(II) species are characterised by two main bands around 9.9-10.3 (ν_1) and 16.3-16.7 kK (ν_2) in an idealised octahedral symmetry⁹. The ν_3 band in O_h symmetry appears around 27.9-29.4 kK often mixed up with

Table 1—Analytical data and other physicochemical data of the complexes

Compound	Colour	Found (Calc.) %					$\mu_{\text{eff.}}$ (B.M.) (302°K)	Λ_M (ohm ⁻¹ cm ² mol ⁻¹) (Solvent)
		M	N	Anion	C	H		
Co(AMPCH) ₂ Cl ₂	Pink	9.70 (9.60)	18.12 (18.24)	11.93 (11.53)	51.20 (50.82)	4.66 (4.56)	4.76	175 (DMF)
Co(AMPCH) ₂ Br ₂	Brown	8.48 (8.38)	15.55 (15.93)	22.90 (22.76)	44.57 (44.39)	4.02 (3.95)	4.52	160 (DMF)
Co(AMPCH) ₂ (ClO ₄) ₂	Reddish brown	8.03 (7.94)	15.52 (15.03)	9.76 (9.57)*	42.28 (42.05)	3.81 (3.70)	4.98	155 (DMF)
Co(AMPCH) ₂ (BF ₄) ₂	Pink	8.12 (8.22)	15.39 (15.62)	—	43.24 (43.53)	3.98 (3.80)	4.27	163 (DMF)
Co(AMPCH) ₂ (NO ₃) ₂	Reddish brown	8.91 (8.83)	21.20 (20.99)†	—	46.38 (46.78)	4.22 (4.10)	5.13	148 (DMF)
Ni(AMPCH) ₂ Cl ₂ · 2 H ₂ O	Green	9.23 (9.03)	17.54 (17.24)	11.21 (10.92)	48.58 (48.02)	4.82 (4.92)	3.03	180 (Methanol)
Ni(AMPCH) ₂ Br ₂ · 2 H ₂ O	Light	8.03 (7.94)	15.01 (15.16)	21.98 (21.66)	42.43 (42.20)	4.30 (4.33)	2.98	176 (Methanol)
Ni(AMPCH) ₂ (ClO ₄) ₂ · H ₂ O	Green	7.80 (7.72)	14.62 (14.74)	9.43 (9.34)*	41.27 (41.02)	3.83 (3.94)	3.07	143 (DMF)
Ni(AMPCH) ₂ (BF ₄) ₂ · 4 H ₂ O	Sky blue	7.51 (7.44)	14.54 (14.20)	—	39.88 (39.46)	4.67 (4.56)	3.01	172 (Methanol)
Ni(AMPCH) ₂ (NO ₃) ₂ · 4 H ₂ O**	Green	7.87 (7.94)	19.31 (18.95)†	—	42.53 (42.03)	4.95 (4.87)	3.05	—

* Percentage of chlorine; † Including nitrogen present in nitrate; ** Λ_M could not be measured due to the insolubility of the complex.

C.T. absorption except for the chloride complex. The ν_2/ν_1 ratio (1.59-1.65) also supports an O_h environment suggesting strong T_{1g} term interactions¹⁰. The calculated values of Dq (997-1030 cm^{-1}), B (808-1035 cm^{-1}) and β (0.74-0.95) give reasonable support to the proposed O_h geometry^{10b} for these Ni(II) species. Methanol or DMF solutions of the Ni(II) species exhibit spectral bands around 10.2-10.5 (ν_1) and 16.4-17.0 kK (ν_2) and their lower molar extinction values ($\epsilon \approx 8.5$ -20.2) suggest the bis-species to be pseudo-octahedral.

IR spectra

The ligand (AMPCH) shows strong bands at 3400-3415 (bs), and 3260-3280(bs) due to ν N-H (hydrogen bonded)¹ and at 1700 (vs) cm^{-1} due to amide-I (ν C=O)¹¹⁻¹³. The absorption band at 1610 (vs) may be attributed to ν C=N¹¹⁻¹³ of the schiff base linkage while bands at 1570 (vs) and 1410(s) cm^{-1} may be ascribed to ν C=N^{1,2} of the pyrazole ring. The band at 690(ms) cm^{-1} may be due to in-plane deformation of the pyrazole^{1,2} ring. The metal complexes show a negative shift ($\Delta\nu \approx 10$ -40 cm^{-1}) of the amide-I (ν C=O)^{2,13} band suggesting the coordination of the carbonyl oxygen, while a new band at 360-410 cm^{-1} in the far IR spectra of some representative complexes may be

assigned to ν M-O^{2,14} of the hydrazone residue. A positive shift ($\Delta\nu \approx 10$ -30 cm^{-1}) of the azomethine band (ν C=N) points out to the participation of the azomethine¹³ nitrogen in coordination. Such increase in ν C=N on complexation may be due to the presence of electron repelling -CH₃ group on the keto component, which increases the electron density over the azomethine nitrogen. The appearance of a new non-ligand band at 485-510 cm^{-1} may be due to ν M-N (azomethine)¹³ mode. The positive shifts ($\Delta\nu \approx 10$ -20 cm^{-1}) of ν C=N (ring) and in-plane deformation ($\Delta\nu \approx 5$ -15 cm^{-1}) modes of the pyrazole ring in these complexes suggest that the tertiary (ring) nitrogen atom is one of the bonding sites¹⁴⁻¹⁶. In the far IR spectra of some representative complexes, a band around 280-310 cm^{-1} further supports this conjecture; the band is assigned to ν M-N (ring)^{2,17}. The diagnostic IR band frequencies of the counterion (X) indicate that the ClO₄⁻ (bands \sim 1070-1100, 625-630 cm^{-1} in T_d symmetry)¹⁸, BF₄⁻ (band \sim 1030-1070 in T_d)¹⁹ and NO₃⁻ (bands \sim 1350-1375, 830-835 cm^{-1} in D_{3h})²⁰ retain their ionic characters. It appears, therefore, that the ligand (AMPCH) behaves as a neutral tridentate (NON) donor coordinating through the tertiary ring nitrogen of the pyrazole moiety, the ketonic oxygen and

azomethine nitrogen of the hydrazone component. The anionic counterpart (X) retains its ionic character in these Co(II) and Ni(II) bis-chelates.

References

- 1 Saha N & Datta K M, *J inorg nucl Chem*, 43 (1981) 1405 and reference therein.
- 2 (a) Saha N, Datta K M & Sinha S, *Indian J Chem*, 25A (1986) 629 and references therein.
(b) Saha N & Sinha S, *Indian J Chem*, 24A (1985) 203.
- 3 Vogel A I, *A textbook of quantitative inorganic analysis* (ELBS, London) 1962, p. 460, 568, 573.
- 4 Geary W J, *Coord chem Rev*, 7 (1971) 81.
- 5 (a) Figgis B N & Lewis G N, *Progr inorg Chem*, 6 (1964) 37.
(b) Selwood P W, *Magnetochemistry* (Interscience, New York) 1953, 159.
6. Cotton F A & Wilkinson G, *Advanced inorganic chemistry* (Interscience, New York) 1968, 738.
- 7 (a) Iskander M F, Sayed L El & Lasheen M A, *Inorg chim Acta*, 16 (1976) 49, 147.
(b) Saha N & Datta K M, *Inorg nucl chem Lett*, 15 (1979) 331.
(c) Carlin R L, *Transition met Chem*, 1 (1969) 3.
- 8 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam) 1968, 357.
- 9 Liehr A D & Ballhausen C J, *Ann Phys*, 6 (1959) 134.
- 10 (a) Patel K C & Goldberg D E, *J inorg nucl Chem*, 34 (1972) 637.
(b) Lever A B P, *Coord Chem Rev*, 3 (1968) 119.
- 11 Srivastava K M, Das S & Lal R A, *Indian J Chem*, 25A (1986) 85.
- 12 Allan J R, Baillie G M & Baird N D, *J coord Chem*, 13 (1984) 83.
- 13 (a) Matho C B, *J Indian chem Soc*, 57 (1980) 485.
(b) Singh N K, Agarwal N & Aggarwal R C, *Indian J Chem*, 23A (1984) 1011.
(c) Maurya P L, Dube P & Aggarwala B V, *Indian chem Soc*, 59 (1982) 1400.
- 14 Paul R C, Chopra R S & Singh G J, *Inorg chim Acta*, 14 (1975) 105.
- 15 Ferraro J R, *Appl Spectrosc*, 23 (1969) 160.
- 16 (a) Reedijk J, Stork-Blaisse B A & Verschoor G C, *Inorg Chem*, 20 (1971) 2594.
(b) Poddar A, Dattagupta J K, Saha N & Saha A, *Z fur Kris*, 175 (1986) 151 and references cited therein.
- 17 (a) Mani G & Scapacci S, *Inorg chim Acta*, 16 (1976) 163.
(b) Vos J G & Grone M Veld, *Inorg chim Acta*, 24 (1977) 123.
- 18 Hathaway B J & Underhill A E, *J chem Soc*, 36 (1974) 230.
- 19 (a) Buffagni S, Vallarino L M & Quaglino J V, *Inorg Chem*, 3 (1964) 480, 671.
(b) Greenwood N N, *J chem Soc*, (1959) 3811.
- 20 Curtis N F & Curtis Y M, *Inorg Chem*, 4 (1965) 804.