

Monochelate Complexes of Copper(II) with α -(3,5-Dimethyl-1-pyrazolyl)acetohydrazide

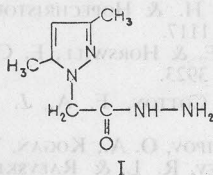
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Solid monochelate complexes of copper (II) with α -(3,5-dimethyl-1-pyrazolyl) acetohydrazide (PAH), $\text{Cu}(\text{PAH})\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{SCN}, \text{NO}_3, \text{ClO}_4, \text{BF}_4$; $n = 1$ or 2), have been characterised by various physico-chemical techniques. The complexes are best regarded as polymeric octahedral molecules in terms of their magnetic, electronic and vibrational spectral data. IR spectra of the ligand and the metal complexes tentatively suggest the carbonyl oxygen and the amino nitrogen atoms of the hydrazide residue (with a ketonic structure) together with the iminic nitrogen of the pyrazole ring as potential donor sites in complex formation; the anions are also shown to be preferentially coordinated in the solid state.

IN continuation¹⁻⁶ of our studies on the coordination behaviour of pyrazole-based ligands, we report in the paper the preparation and characterization of the mono-chelate complexes of copper (II), $\text{Cu}(\text{PAH})\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{SCN}, \text{NO}_3, \text{ClO}_4$ and BF_4 ; $n = 1$ or 2) with α -(3,5-dimethyl-1-pyrazolyl) acetohydrazide [I, PAH]. The synthesis of the ligand (I) has been described in an earlier publication⁵.



Materials and Methods

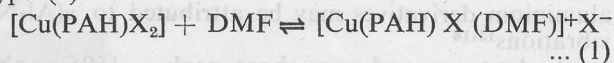
$\text{Cu}(\text{PAH})\text{X}_2 \cdot n\text{H}_2\text{O}$ [$\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4$ and BF_4 ; $n = 1$ or 2]—Hot ethanolic solutions of the hydrated Cu(II) salt, $\text{CuX}_2 \cdot n\text{H}_2\text{O}$ (0.01 mole) and of the ligand (0.01 mol) were mixed and the resulting solution ($\text{pH} \approx 3$) was heated at water-bath temperature for 5–10 min. with occasional stirring and then left at room temperature. In each case, the coloured compound (blue or green) separated out within an hour. This was collected on a filter, washed well with water and ethanol and finally dried in a desiccator.

$\text{Cu}(\text{PAH})(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ —On mixing aqueous alcoholic solutions of copper chloride dihydrate (0.01 mol) and of the ligand (0.01 mol) a deep bluish green solution resulted. To this reaction mixture was added an aqueous solution of ammonium thiocyanate (0.02 mol) when an olive green compound immediately separated out. This was collected and dried as above.

Results and Discussion

The present copper(II) complexes conforming to

the general composition, $\text{Cu}(\text{PAH})\text{X}_2 \cdot n\text{H}_2\text{O}$ (Table 1) are normally insoluble in water and in common organic solvents, but they are fairly soluble in coordinating solvents like DMF, DMSO etc. The molar conductance (Δ_M) values (Table 2) of the compounds ($1 \times 10^{-3}M$) in DMF at 30° indicate their behaviour as 1:1 electrolytes⁷. This may be ascribed to a partial solvolysis phenomenon leading to the release of an anion due to a possible equilibrium of the type (1).



The room temperature magnetic moments of most of the complexes (Table 2) are close to the spin only value of 1.73 B.M. required for an $S = 1/2$ system. In the case of the chloride and perchlorate complexes the somewhat subnormal magnetic moment values can be attributed to the antiferromagnetic exchange between the interacting Cu^{2+} ions; thus dimerisation or polymerisation in the solid state either through Cu^{2+} - Cu^{2+} interaction or through ligand participation⁸ cannot be ruled out in the present case.

The electronic spectra (both reflectance and DMF or DMSO solution) show a broad asymmetric band around 14.0–16.5 kK, often accompanied with shoulders on the low/high frequency region indicating distorted octahedral environment for the complexes. This observation is consistent with the recent investigations on the electronic spectra of Cu(II) complexes which have indicated that three transitions ${}^2B_1 \rightarrow {}^2A_1$ (ν_1), ${}^2B_1 \rightarrow {}^2B_2$ (ν_2) and ${}^2B_1 \rightarrow {}^2E$ (ν_3) are close in energy and often give rise to a single broad envelope. The origin of an additional band (both in reflectance and in solution spectra) around 25,000–27,000 cm^{-1} in the chloride and thiocyanate complexes is due to the symmetry forbidden ligand-metal charge transfer transition rather than due to the binuclear species^{9,10}. The shift of the main spectral bands to lower frequency regions in solution (as compared to those in solid

TABLE 1 — ANALYTICAL DATA FOR Cu (PAH) X₂.nH₂O

Sl. No.	Complex ^a	Colour	Cu (%)		N (%)		Anion (%)		H ₂ O (%)	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1.	Cu(PAH)Cl ₂ .2H ₂ O ^b	Bluish green	18.76	18.69	16.54	16.50	20.93	20.76	10.64	10.50
2.	Cu(PAH)Br ₂ .2H ₂ O ^b	Greyish green	14.86	14.77	13.10	13.15	37.38	37.19	8.43	8.31
3.	Cu(PAH)(SCN) ₂ .2H ₂ O ^c	Olive green	16.55	16.63	21.90	21.84	16.70 ^d	16.53	9.39	9.26
4.	Cu(PAH)(NO ₃) ₂ .H ₂ O ^e	Deep blue	17.00	17.11	22.49	22.52	—	—	4.82	4.75
5.	Cu(PAH)(ClO ₄) ₂ .H ₂ O	Deep blue	14.16	14.09	12.48	12.43	15.81 ^e	15.62	4.01	4.00
6.	Cu(PAH)(BF ₄) ₂ .2H ₂ O	Green	14.40	14.38	12.70	12.73	—	—	8.16	8.29

(a) Copper was estimated iodometrically after decomposition of the complex with nitric acid-sulphuric acid mixture.

(b) Halogen estimated as silver halide.

(c) Nitrogen analyses include percentage nitrogen present in thiocyanate and nitrate.

(d) Percentage sulphur estimated as BaSO₄.

(e) Percentage chlorine estimated as AgCl

(f) Estimated by heating at 110° ± 5° for 3 hr in an air-oven.

TABLE 2 — MOLAR CONDUCTANCES, MAGNETIC MOMENTS AND OUT-OF-PLANE BENDING VIBRATIONS OF PYRAZOLE RING

Complex*	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} B.M. (302 K)	Out-of-plane vibrations [†] (cm ⁻¹)
1	45.60	1.58	755 (s), 700 (ms) 630 (s)
2	49.00	1.75	760 (s), 685 (ms), 650 (ms)
3	46.20	1.83	770 (w), 700 (ms), 655 (s)
4	83.30	1.71	760 (ms), 685 (ms), 635 (ms)
5	48.70	1.62	760 (s. sh), 635 (ms), 650 (ms)
6	51.80	1.78	760 (s), 690 (m), 640 (ms)

*Sl Nos. refer to compounds listed in Table 1.

†The ligand shows bands at 735 sh, 680 s and 630w

state) suggests appreciable degree of solvation, indicating at the same time that although there is no gross change in the stereochemistry of the compounds on dissolution, the overall symmetry is lower than O_h.

The most significant changes that occur in the IR spectra (ν_{max} in cm⁻¹ throughout) of the metal complexes, as compared to the free ligand, is the negative shift of the amide-I band appearing at 1615 in the complexes (ligand shows amide-I ~ 1660–1630), and the positive shifts of the amide-II ($\Delta\nu$ ~ 30–50 cm⁻¹) and amide-III ($\Delta\nu$ ~ 20 cm⁻¹) bands which being contrary to our previous observation^{5,6} with bis-Ni(II) and Co(II) complexes, point to the carbonyl oxygen atom (amidic oxygen) as a potential donor site^{11,12}. The ligand exhibits amide-II and amide-III at 1520s and 1265s sh respectively.

The IR bands in the 3 μ region are complex probably due to the mixing of the NH and NH₂ stretching vibrations with the —OH mode of vibrations of water molecules (present in the complexes) associated with intra or/and intermolecular hydrogen bonding. A very broad band in the region 3500–3200 and a weak broad band around 3100 appearing in most of the complexes, may be taken to be, although not convincing, as a negative shift of the ν_{NH} and ν_{NH_2} (as compared to the free ligand), indicating the end nitrogen atom of the —NHNH₂ group as a point of attachment^{13–15}; this is further supported by far IR data (see later). Moreover, the $\nu(N-N)$ of the hydrazide residue appearing at 910 in the free ligand mole-

cule undergoes a large positive shift and appears ~ 1040 in the copper (II) complexes; this observation indicates the involvement both the N-atoms of the hydrazide residue in complexation^{16–18}. The attachment of both the N-atoms to the same metal ion being highly improbable due to steric reasons, the simultaneous coordination of the terminal amine nitrogen and the amidic oxygen to a Cu(II) ion resulting in a stable five-membered ring is proposed as a first step and the amide-nitrogen may then be logically considered to coordinate to another Cu(II) ion of an adjacent molecule finally giving rise to polymeric structures for the present complexes; the formation of such polymeric species with hydrazine derived ligands has been proposed by several authors^{17,18}.

The participation of the ring nitrogen atom of the pyrazole moiety in complex formation, although unequivocally inferred from X-ray crystallographic studies of a number of pyrazole-metal complexes, is suggested in the present case from the noticeable positive shifts of the out of-plane bending vibrations of the ring system in the complexes as compared to the free ligand molecule (Table 2). The conclusion is compatible with earlier observations^{22–24}. Moreover, reasonable support for the participation of the ring nitrogen of the pyrazole moiety and amidic oxygen of the hydrazide residue) in complexation is provided by the far IR spectral data on the nitrate and fluoborate complexes. The bands appearing at 320(s) and 350(s) in the IR spectra of Cu(PAH)(NO₃)₂.H₂O and Cu(PAH)(BF₄)₂.2H₂O respectively can safely be assigned to the Cu-N (pyrazole ring) stretching vibration^{25,26}. The band/bands appearing in the region 400 [390 (ms); 405 (ms) for the nitrate complex and 420 (ms) cm⁻¹ for the fluoborate complex] may be ascribed to Cu-O (amidic) vibration^{24,27,28}. The additional IR band appearing in the region 480–490 (s) can be attributed to Cu-N (hydrazide residue) vibration^{29–31} thus giving tacit support for the participation of the nitrogen of —NHNH₂ group in coordination as outlined before.

The broad diffused band around 3500 in all these Cu(II) complexes implies the presence of lattice water molecules in the complexes; but the absence of any recognisable bands for rocking and wagging modes of vibrations due to water molecules indicate their non-

coordinating nature. The lattice nature of the water molecules is further substantiated from the thermal treatment of the compounds, which on heating at $110^{\circ} \pm 5^{\circ}\text{C}$ suffer mass loss corresponding to the respective equivalent of water molecules (Table 1).

The diagnostic IR band frequencies of the anions with probable assignments indicate the monodentate nature of the anions, viz., the thiocyanate (N-bonded)³², nitrate (in C_{2v} symmetry)³³, perchlorate (in C_{3v} symmetry)³⁴ and fluoborate³⁵ group in the present monochelates of Cu(II).

In the absence of complete far IR data, Cu-X vibrations could not be located, but it appears that the anions are preferentially coordinated in the solid Cu(II)-complexes and the ligand molecules (PAH) be have primarily as a neutral tridentate ligand in forming species of empirical composition Cu(PAH) $X_2 \cdot nH_2O$. In line with the proposition made by Nagano *et al.*³⁶, in the case of Cu (II) complexes of picolinoylhydrazide, the present Cu(II) complexes are, however, best regarded as polymeric octahedral species, the polymerisation being affected probably through ligand participation as gathered from IR data and this polymeric nature of the complexes can well account for their insolubility in common organic solvents as well as somewhat subnormal magnetic moments in a few cases.

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