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Bis-chelate Complexes of Co(II) with α -(3,5-Dimethyl-1-pyrazolyl)acetohydrazide

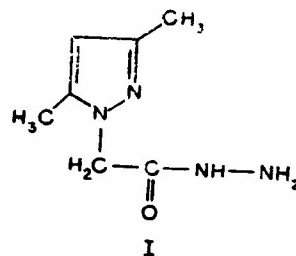
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The chelating behaviour of α -(3,5-dimethyl-1-pyrazolyl) acetohydrazide (PAH) has been reported by complexation with cobalt(II) salts (halide, nitrate, sulphate and thiocyanate). Solid chelate bis-complexes of the type $\text{Co}(\text{PAH})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{SCN}$ and $\frac{1}{2}\text{SO}_4$; $n = 0$ or 2) have been characterized by elemental analysis, magnetic and conductivity measurements and IR and reflectance spectral data. All the cobalt(II) complexes are distorted octahedral as evident from electronic spectral data and the corresponding ligand field parameters calculated in terms of O_h symmetry. IR spectra of complexes together with the ligand indicate the pyrazole-ring nitrogen and the amide nitrogen (involving an 'imidol' structure) of the hydrazide residue as the points of attachment showing neutral bidentate function of the ligand.

THE coordination chemistry of pyrazole-based ligands has been investigated¹ extensively in recent years, because of the biological implications of these heterocyclic bases. In continuation of our studies²⁻⁵ on the coordinating properties of substituted pyrazoles, we wish to report in this note the synthesis and characterization of a few bis-chelates of cobalt(II) salts with α -[3,5-dimethyl-1-pyrazolyl]acetohydrazide (I, herein after abbreviated as PAH), the preparation of which has been reported earlier⁴.



Preparation of cobalt(II) complexes; $\text{Co}(\text{PAH})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \frac{1}{2}\text{SO}_4$; $n = 0, 2$)— The deep pink solution resulting ($\text{pH} \approx 3$) on mixing aqueous ethanolic solutions of the ligand (0.01 mole) and the hydrated cobalt(II) salt (0.005 mole), was heated on a water-bath for 10 min and then kept at room temperature. On stirring well, a pink compound separated out in each case. It was suction-filtered, washed with ethanol and then dried over fused calcium chloride.

$\text{Co}(\text{PAH})_2(\text{NCS})_2$ —Ethanolic solutions of hydrated cobalt(II) nitrate (0.005 mole) and KSCN (0.01 mole) were mixed and the precipitated KNO_3 filtered off. The filtrate was evaporated on a water-bath to a smaller bulk and filtered directly into a hot ethanolic solution of the ligand (0.01 mole). The reaction mixture was stirred well at room temperature when a violet compound settled down. It was filtered off and collected as before.

Cobalt was estimated gravimetrically as anhydrous CoSO_4 , halogens as silver halide and sulphate as BaSO_4 . Nitrogen was estimated by Dumas' method. The conductance, electronic spectra in solution, diffuse reflectance and IR spectra and magnetic susceptibility in the solid state of the compounds were carried out as described earlier⁴.

All these pink complexes are fairly soluble in water and low molecular weight alcohols, except $\text{Co}(\text{PAH})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ which is sparingly soluble in organic solvents; the aqueous and methanolic solutions are highly conducting (Table 1) which show the ionic nature of the complexes $[\text{Co}(\text{PAH})_2(\text{sol})_2]^{2+}$ (for most of the compounds) at least in solution of that solvent.

Magnetic data reveal that all the present cobalt(II) complexes are high spin ($\mu_B = 4.6-4.8$ BM at 29° ; Table 1). The slightly lower magnetic moment values, as compared to those assigned for high spin octahedral Co(II) complexes⁶ imply that the complexes probably belong to an orbital singlet ground state with distorted octahedral environment⁷. This is supported by electronic spectral data (Table 2).

The very much similar reflectance spectra of the complexes are characterized by two main bands at ~ 9000 and ~ 20000 cm^{-1} (with shoulders on both the sides) which may be assigned to $\nu_1[{}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ and $\nu_3[{}^4T_{1g} \rightarrow {}^4T_{1g}(P)]$ transitions respectively in an octahedral field.

However, the splitting of the ν_3 bands into many components in some of the cases makes the assignment difficult; these components may be due to lifting of the degeneracy of the ${}^4T_{1g}$ level either by spin-orbit splitting or by the presence of low symmetry (approximating to C_2) components in the ligand field. Alternatively, the components

TABLE 1 — ANALYTICAL DATA AND PROPERTIES OF THE Co(II) COMPLEXES

Complex	Colour	Co (%)		N (%)		Halogen or S (%)		ΛM ($\text{ohm}^{-1} \text{cm}^2$ mole $^{-1}$)	μ_{eff} BM (302°K)
		Calc.	Found	Calc.	Found	Calc.	Found		
Co(PAH) ₂ Cl ₂ ·2H ₂ O	Deep pink	11.73	11.78	22.32	22.41	14.11	14.20	137.0 ^a 232.7 ^b	4.64
Co(PAH) ₂ Br ₂ ·2H ₂ O	Light pink	9.97	9.93	18.96	18.89	27.04	27.12	131.6 ^a 190.8 ^b	4.59
Co(PAH) ₂ I ₂	do	9.08	9.13	17.27	17.22	39.10	39.21	129.5 ^a 237.9 ^b	4.79
Co(PAH) ₂ (NO ₃) ₂ ·2H ₂ O	do	10.61	10.62	25.23*	25.29	—	—	154.9 ^a 236.0 ^b	4.63
Co(PAH) ₂ (NCS) ₂	Violet	11.52	11.57	27.39†	27.46	12.54	12.45	78.0 ^a 238.3 ^b	4.69
Co(PAH) ₂ SO ₄ ·2H ₂ O	Dirty pink	11.18	11.09	21.28	21.28	18.22	18.16	209.5 ^b	4.64

*Including nitrogen present in nitrate.

†Including nitrogen present in thiocyanate.

(a) In methanol; (b) in conductivity water in 10⁻³M solution.

TABLE 2 — ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Complex	Medium	Absorption maxima (molar extinction coefficient) in cm ⁻¹
I. Co(PAH) ₂ Cl ₂ ·2H ₂ O	(i) Reflectance	5,800 sh; 8,000 wsh; 8,600; 16,000 sh; 18,800; 20,000 ssh; 21,000 ssh
	(ii) Methanol	16,390 sh (2.75); 19,230 (23.77)
II. Co(PAH) ₂ Br ₂ ·2H ₂ O	(i) Reflectance	5,800 sh; 6,200 sh; 9,200; 17,000; 20,200; 20,800 sh; 21,800 sh
	(ii) Methanol	16,390 sh (3.86); 19,610 (17.52)
III. Co(PAH) ₂ I ₂	(i) Reflectance	5,800 sh; 6,400 sh; 9,200; 17,000; 19,800 sh; 20,200; 20,600 sh
	(ii) Methanol	19,610 (16.29)
IV. Co(PAH) ₂ (NO ₃) ₂ ·2H ₂ O	(i) Reflectance	5,800 sh; 6,600; 9,400; 12,800 sh; 17,000 sh; 19,600 sh; 20,800; 22,000
	(ii) Methanol	16,390 sh (1.74); 19,800 (13.24)
V. Co(PAH) ₂ (NCS) ₂	(i) Reflectance	8,800; 15,600 sh; 18,800; 20,000 sh
	(ii) Methanol	16,130 (5.98); 19,420 (19.27)
VI. Co(PAH) ₂ SO ₄ ·2H ₂ O	(i) Reflectance	5,800; 6,200 sh; 9,200; 17,000 sh; 19,800 sh; 20,600; 21,800 sh
	(ii) Water	16,390 sh (1.38); 19,610 (9.33)

sh = shoulder; w = weak; s = strong.

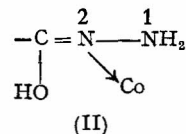
may be due to the presence of a spin-forbidden band or the appearance of the ν_2 transitions⁸.

The values of D_q and B calculated from the known relationships⁹ lie in the regions 1000 and 800 cm⁻¹ respectively, which are in good agreement with those of previously reported cobalt(II) complexes having an average octahedral environment¹⁰. The ν_2 bands have been calculated ($\nu_2 = \nu_1 + 10 D_q$ and are found to lie very close to their respective ν_3 bands and thus the shoulders appearing near the ν_3 transition (in some of the cases) are assigned ν_2 transitions. Furthermore, the calculation suggests that the bands occurring ~ 16000 - 17000 cm⁻¹ are not due to $\nu_2[{}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)]$ and are likely to be the spin-forbidden ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(G)$ transition¹¹.

The electronic spectral data of the complexes in methanol solution [water solution in case of Co(PAH)₂SO₄·2H₂O] indicate that there is no gross change in stereochemistry of the complexes on dissolution. The main band occurring at 19200-19800 cm⁻¹ can safely be assigned to ν_3 transition in O_h symmetry while the corresponding ν_1 bands remain unrecorded due to the limited range of the spectrophotometer (Hilger UVISPEK) used. The shift of the ν_3 transition usually to lower wave-numbers compared to the solid state spectra suggests some degree of solvation. Moreover, the molar extinction values ($< \sim 25$) of the spectral bands give additional

support for a pseudo-octahedral environment of the complexes in solution.

Regarding the participation of the hydrazide group in complexation, the most significant change that occurs in the IR spectra of Co(PAH)₂X₂· n H₂O as compared to the free ligand, is the displacement of the amide-I band with the simultaneous appearance of three newly developed bands ~ 1600 , 1300 and ~ 1070 cm⁻¹. This observation being similar to that of Dutta-Ahmed and Roychoudhuri¹² and our previous observation⁴, points to the participation of the amide nitrogen in coordination with an 'imidol' type structure (II) for the hydrazide residue.



If the assumption is true, the newly developed IR bands at ~ 1600 and ~ 1300 cm⁻¹ (in the metal complexes) are assigned to $\nu_{\text{as}}(\text{C}=\text{N}^2)$ and $\nu_{\text{s}}(\text{C}=\text{N}^2)$ respectively¹² and the band at ~ 1070 cm⁻¹ can then be safely assigned to $\nu(\text{C}-\text{O})$ ¹³ giving tacit support to the 'imidol' structure (II) of the hydrazide group in the ligand during complex formation.

On the other hand, the broad and diffused IR band in the 3μ region (being complicated due to

the overlap of NH and NH₂ stretching frequencies with O-H mode of vibrations of the attached water molecules), shows no appreciable shift to the lower frequency region as compared to the free ligand, suggesting non-involvement of the terminal nitrogen (¹N) atom of the hydrazide residue in complexation. The presence of broad band near 3450-3500 cm⁻¹ and absence of any detectable band around 900 cm⁻¹ indicate attached water molecules in the hydrated complexes.

Although the band due to νM-N (pyrazole ring) could not be located due to the absence of data in the far IR region, nevertheless, definite positive shift by 30-40 cm⁻¹ of ν(C=N) vibration of the pyrazole ring in the metal complexes as compared to the free ligand (at 1520 cm⁻¹), indirectly suggests the tertiary nitrogen atom (of the pyrazole ring) as a possible site of coordination in accordance with earlier observations¹⁴. The X-ray crystallography of several pyrazole-metal complexes¹⁵ showing pyridine nitrogen atom as always a point of attachment in such metal complexes, gives additional support to our above suggestion from the IR data.

The mode of linkage of the attached anions are ascertained from the IR data as follows:

The nitrate compound shows bands at 1390 (bs) (ν₃), 1040 (ms)(ν₁), 835 (ms)(ν₂) and 775 cm⁻¹ (s) (ν₄), which point to the presence of monodentate nitrate group in C_{2v} symmetry¹⁶.

In the thiocyanate compound one very sharp band at 2090 (νC-N) and a medium sharp band at 810 cm⁻¹ (νC-S) suggest N-bonded thiocyanate group in the complex¹⁷.

In the sulphate complexes the appearance of a broad sharp band at 1120 (ν₃) (along with two shoulders at 1150 and 1180 and a weak band at 1050 and a medium sharp band at 990 cm⁻¹ (ν₁)

clearly indicate the presence of sulphate group in C_{2v} symmetry in the compound¹⁸.

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