

High-spin Five-coordinate Cobalt(II)

THE tridentate ligand 1,3-bis(2'-pyridyl)-2,3-diaza-1-propene, (paphy), when reacted with cobalt(II) chloride in ethanolic solution, yields several products. Two of these complexes are formulated as $\text{Co}(\text{paphy})\text{Cl}_2$: one (designated α -) forms red plates and the other (β -) dark green needles. The β -isomer may readily be converted to the α -compound by heating in ethanolic medium.

The magnetic properties over a temperature range and the visible and near infra-red spectra have been suggested as a method of differentiating between octahedral and tetrahedral stereochemistries for $\text{Co}(\text{II})$ complexes. It is important to emphasize that this procedure allows a differentiation between these two stereochemistries, but may not finally establish either of them. The compounds discussed here may be used to elaborate this point.

The magnetic moment (5.04 B.M. at 293° K, $\theta = 13^\circ$) and diffuse reflectance spectrum [absorption at 7,900 (4T_2); 17,300 (4A_2); 19,000, 20,500 cm^{-1} (4T_1)] of the α -isomer lead us to believe that it contains $\text{Co}(\text{II})$ in octahedral environment, probably with chloride bridging of adjacent octahedra to attain CoN_3Cl_2 co-ordination. It is isomorphous with the corresponding compound $\text{Ni}(\text{paphy})\text{Cl}_2$. However, the co-ordination stereochemistry for β - $\text{Co}(\text{paphy})\text{Cl}_2$ is not clearly revealed by the spectral and magnetic data. The most intense absorptions in the reflectance spectrum occur at 4,500, 7,700 and 15,750 cm^{-1} and would most closely indicate strong field tetrahedral co-ordination (with parameters $D_q = 450 \text{ cm}^{-1}$, $B' = 670 \text{ cm}^{-1}$). But there are weaker bands at 12,200 and 20,000 cm^{-1} and the magnetic moment (4.84 B.M. at 294° K, falling to 4.56 B.M. at 80° K) is about 0.25 B.M. greater than that predicted for these parameters. We have therefore determined the crystal structure of this compound.

The complex, β - $\text{Co}(\text{paphy})\text{Cl}_2$, crystallizes in the monoclinic system with cell constants: $a = 8.72$; $b = 11.93$; $c = 12.64 \text{ \AA}$; $\beta = 98^\circ 2'$ and $Z = 4$. From systematic absences, the space group was uniquely determined as $P2_1/n$. Visual estimation of the intensity data collected by the Weissenberg multiple-film technique yielded 1,257 independent reflexions. The phase problem was solved by the 'heavy-atom' procedure using three-dimensional Patterson and Fourier syntheses. Isotropic least-squares refinement of the atomic parameters led to a value for R of 0.12, while the subsequent inclusion of anisotropic temperature factors has reduced this index further, to 0.095.

The stereochemistry of the molecule is illustrated in Fig. 1, from which the essentially square pyramidal geometry around the cobalt is apparent. The metal atom is 0.39 Å above the basal plane which contains all other atoms except the chlorine atom Cl(2). The average Co—N bond length is 2.12 Å and the angles $\text{N}(1)\text{CoN}(2)$ and $\text{N}(3)\text{CoN}(2)$ are both 74° . Angle $\text{N}(2)\text{CoCl}(1)$ is 157° ;

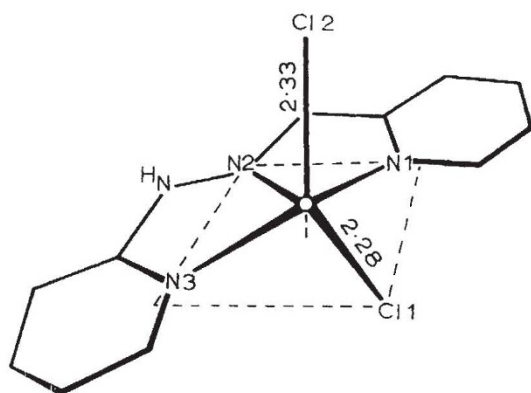


Fig. 1

$\text{N}(2)\text{CoCl}(2)$ is 94° . There are no close inter-molecular interactions and the cobalt-cobalt vector is 4.62 Å.

Two other ML_3X_2 complexes with this stereochemistry, $\text{Ni}[\text{CH}_3\text{As}(\text{CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2)_2]\text{Br}_2$ (ref. 1) and $(\text{C}_{14}\text{H}_{13}\text{P})_3\text{PdBr}_2$ (ref. 2), have apical $M-X$ bonds considerably longer than the basal $M-X$ bonds, but in the present compound this difference is statistically just significant.

It is interesting to note that the ligand 2,2',2''-terpyridyl, (terpy), which presents a tridentate nitrogen donor sequence closely corresponding to that of paphy, also forms a crystalline complex $\text{Co}(\text{terpy})\text{Cl}_2$ (ref. 3). This is high-spin with a near infra-red and visible reflectance spectrum similar to that of β - $\text{Co}(\text{paphy})\text{Cl}_2$. A comparison of the unit cell parameters and about 80 X-ray intensities from crystals of $\text{Co}(\text{terpy})\text{Cl}_2$ and of $\text{Zn}(\text{terpy})\text{Cl}_2$, in which there is trigonal bipyramidal stereochemistry⁴, indicates that these two compounds are isostructural. A full three-dimensional refinement of both these terpy structures is in progress⁵. Trigonal bipyramidal geometry for $\text{Co}(\text{terpy})\text{Cl}_2$ would be in contrast to the square pyramidal geometry for β - $\text{Co}(\text{paphy})\text{Cl}_2$, but we believe that intermolecular crystal forces are a major factor influencing the co-ordination stereochemistry in these two compounds.

It is important to emphasize that a differentiation between a trigonal bipyramidal and a tetragonal pyramidal arrangement in molecules of this type is very often difficult and a reassessment of the geometry of $\text{Zn}(\text{terpy})\text{Cl}_2$ implies a very close relationship with the paphy derivative reported here.

These complexes also provide further examples of high-spin five-co-ordinate cobalt(II), in addition to the compounds $[\text{Co}(\text{Ph}_2\text{MeAsO})_4\text{ClO}_4]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (ref. 6), *bis*(*N*-methylsalicylaldimato)cobalt(II) (ref. 7) and *bis*(*N*- β -diethylaminoethyl-5-chlorosalicylaldimato)cobalt(II) (ref. 8).

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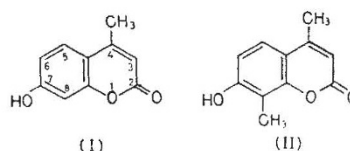
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Estimation of Nitrate by Nitration of 7-Hydroxy-4,8-dimethyl Coumarin

SKUJINS¹ proposed a colorimetric method of nitrate estimation using 7-hydroxy-4-methyl coumarin (I) as the reagent for nitration. The 3, 6 and 8 positions are activated for electrophilic substitution, but there is steric restriction to the entry of NO_2^+ to the 3 position.



A mixture of products using Skujins's reagent and nitrate in a molar ratio of 4.5 : 1, and following the analytical procedure to be outlined later, was extracted with chloroform, and the resultant nitro derivatives subjected to paper chromatography using *n*-butanol-ammonia-water (8 : 30 : 62 v/v) as developing solvent. Three spots were observed with R_F values in agreement with 6-nitro,