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The Crystal and Molecular Structure of Bis(4-methylpyridine)phthalocyaninatocobalt(II)

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In the course of our studies on the mono- and biadducts of phthalocyaninato Co(II) (CoPc) with base molecules it seemed interesting to determine the structure of the title compound by X-ray diffraction methods with the aim of both checking the planarity of the equatorial ligand and finding structural reasons for its thermal behaviour.[1] In fact the deviation from planarity of the equatorial coordination geometry is a key factor in the determination of the chemical properties of this class of adducts with base molecules and is related to the tendency of CoPc to gain different coordination numbers.[2] The particular interest of the bis(4-methylpyridine) adduct lies in the strong similarity of its absorption properties[1] with the ones of the haemoglobin molecule.

The product was synthesized by a method already described[1] and crystals (light-blue platelets),

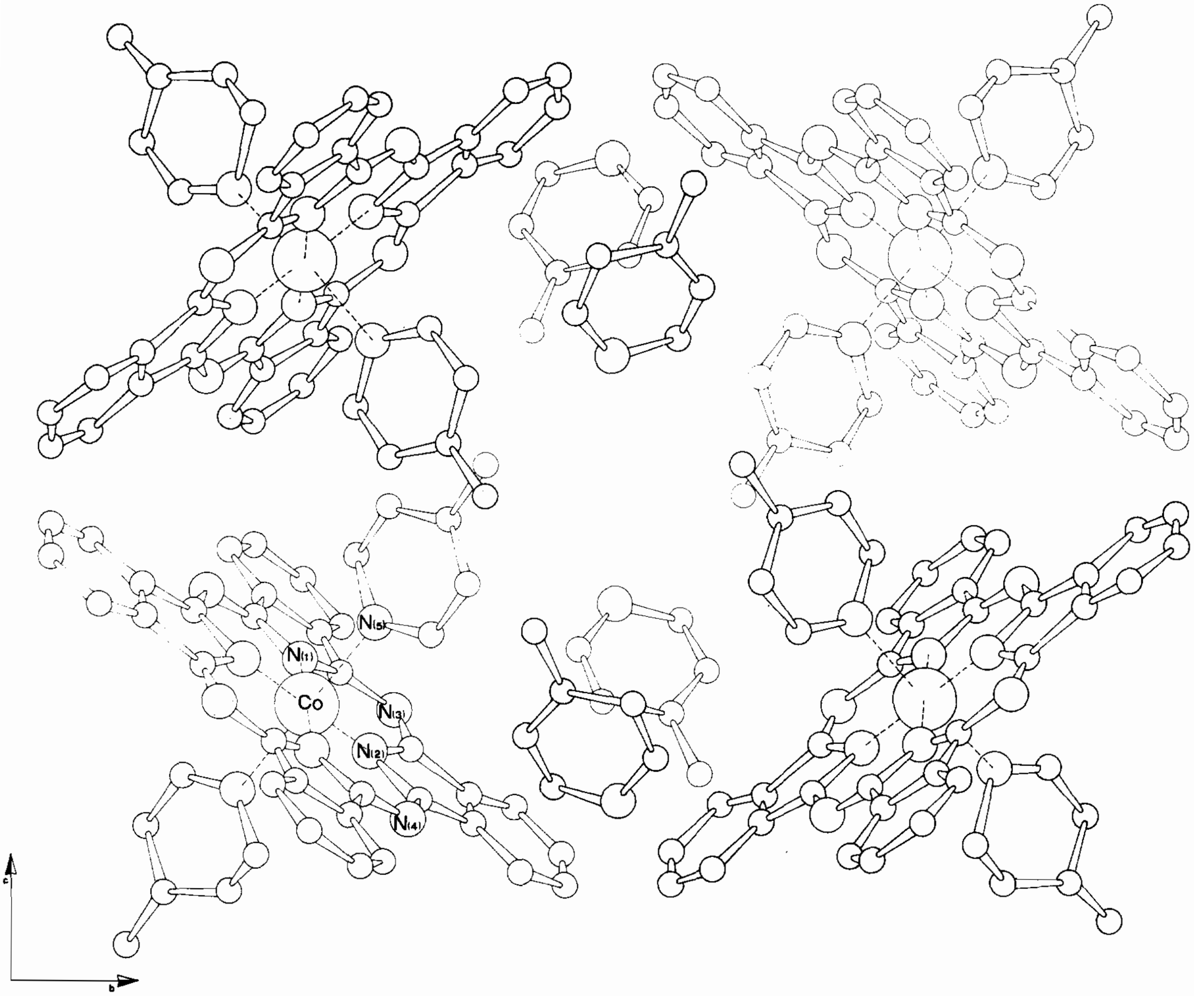

Fig. 1. Molecular packing. For convenience only four of the eight non-coordinated picoline molecules are shown.

suitable for X-ray analysis, were obtained by slow evaporation, in a period of about 15 days, of a concentrated solution of CoPc(4-methylpyridine)$_2$ in 4-methylpyridine at 40 °C.

Crystal data: a = 10.395(2), b = 25.069(4), c = 17.992(3) Å; space group Pbca; 4 molecules per unit cell with the Co atoms lying on inversion centers. The calculated density is d = 1.073 g cm^{-3}. The intensities of 3777 reflections were measured by an automated four-circle diffractometer up to a sin θ/λ value of 0.60 Å^{-1}. Graphite-monochromated MoKα radiation was used and, since the crystal was very small, no absorption correction was applied.

The structure was solved by Patterson and Fourier methods and the least-squares refinement, using anisotropic temperature parameters, gave a value of 0.094 for the conventional R factor based on the 1503 observed reflections. Before the least-squares refinement a Fourier difference map showed the existence of eight non-coordinated 4-methylpyridine molecules in the unit cell. The abnormally high temperature parameters obtained at the end of the least-squares refinement for these solvated picoline molecules may indicate that librational components are active in their thermal motion and may explain the relatively high R value.

The four molecules in the unit cell are centrosymmetric with the Co atoms lying at the inversion centers at 0,0,0; 1/2,1/2,0; 0,1/2,1/2; 1/2,0,1/2 (see Figure 1). The coordination polyhedron is a slightly distorted tetragonal bipyramid. The cobalt atom and the four coordinated phthalocyanine nitrogens lie on a plane, as imposed by the crystallographic local symmetry, and the direction defined by the coordinated picoline nitrogen atoms is slightly off the perpendicular to that plane (about 1.5°). The coordination bond distances and angles are given in Table I. It is interesting to note that the Co–N(5)(picoline) distance (2.295 Å) is significantly longer than the Co(II)–N(pyridine) distance (av. 2.10 Å) found in similar complexes.[3,4] This result is in agreement with the findings of the thermal analysis[1] showing an easy cleavage of the 4-methylpyridine ligands. The structure of the phthalocyanine ligand is essentially identical to the one found by others (see, *e.g.*, Fischer *et al.*[5]).

TABLE I. Coordination Bond Distances (Å) and Angles (°).

Co–N(1)	1.915 (8)
Co–N(2)	1.912 (7)
Co–N(5)	2.295 (8)
N(1)–Co–N(2)	90.9 (2)
N(1)–Co–N(5)	88.6 (2)
N(2)–Co–N(5)	88.6 (2)
N(3)–Co–N(5)	88.7 (2)

No significant structural difference was detected between the picoline ligand and the solvated picoline molecule, but no conclusion can be drawn, due to the already mentioned abnormally high terminal parameters.

The molecular packing, conditioned by the solvated molecules, is rather loose with the implication of considerable distances among the complex units. This result is relevant to the solution of the problems created by our previous observations[1] of the peculiar thermal behaviour shown by various phthalocyaninato Co(II) adducts with base molecules. In fact the products obtained by thermal dissociation of these adducts were α- or β-CoPc, depending on both the nature and the number of the coordinated base molecules. Further work is planned with the aim of determining possible structural relationships among all these adducts and α- and β-CoPc, and of clarifying the role of the solvated molecules in the dissociation process.

Acknowledgements

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References

1 F. Cariati, D. Galizzioli, F. Morazzoni and C. Busetto, *J. Chem. Soc., Dalton Trans.*, in press.
2 H. A. Hill, J. M. Pratt and R. J. Williams, *Discuss. Faraday Soc.*, *47*, 165 (1969).
3 M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografija*, *4*, 239 (1960).
4 M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc.*, *A*, 2411 (1970).
5 M. S. Fischer, D. H. Templeton, A. Zalkin and M. Calvin, *J. Am. Chem. Soc.*, *93*, 2622 (1971).