

## X-Ray Structure of the Pentacyanocobaltate(II) Anion in Diethyl-di-isopropylammonium Pentacyanocobaltate

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*Summary* The crystal and molecular structure of the  $[\text{Co}(\text{CN})_5]^{3-}$  anion has been determined; the complex has square-pyramidal geometry with a *trans*  $\text{C}_{\text{basal}}\text{-Co-C}_{\text{basal}}$

angle of  $164.7(4)^\circ$  and  $\text{Co-C}_{\text{apical}}$  and  $\text{Co-C}_{\text{basal}}$  bond lengths of 2.01 and 1.89 Å, respectively.

DESPITE many solution studies on the cobalt-cyanide system and the  $[\text{Co}(\text{CN})_5]^{3-}$  anion,<sup>1</sup> prompted in many cases by its activity as a hydrogenation catalyst,<sup>2</sup> little is known about the  $[\text{Co}(\text{CN})_5]^{3-}$  anion in the solid state, since it dimerizes from aqueous solution to the violet  $[\text{Co}_2(\text{CN})_{10}]^{6-}$

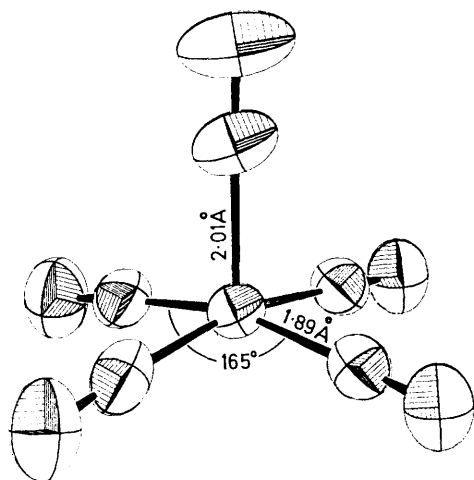


FIGURE. Structure of the pentacyanocobaltate(II) anion.

ion whose structure was recently characterized.<sup>3</sup> A green solution of  $\text{Li}_3[\text{Co}(\text{CN})_5]$  in ethanol, gave a white monomeric solid form of  $[\text{Co}(\text{CN})_5]^{3-}$ ,<sup>4</sup> and more recently, a yellow form of  $[\text{Co}(\text{CN})_5]^{3-}$  was reported in dimethylformamide (DMF) and a yellow solid was isolated.<sup>5</sup> We report here the X-ray structure of diethyl-diisopropylammonium pentacyanocobaltate(II).

A solution (ca. 0.5M) in DMF of  $\text{NEt}_2\text{Pr}_2\text{CN}$  and an-

hydrous  $\text{CoCl}_2$  (5:1 mol. ratio) was slowly cooled to  $-20^\circ$  to yield yellow crystals of  $[\text{NEt}_2\text{Pr}_2]_3[\text{Co}(\text{CN})_5]$ . The crystals are extremely sensitive to air and water; for X-ray studies, single crystals were sealed in thin-walled glass capillaries. *Crystal data:*  $\text{C}_{35}\text{H}_{72}\text{CoN}_8$ , space group  $P2_1/m$ ,  $a = 17.766(6)$ ,  $b = 10.674(4)$ ,  $c = 10.676(4)$  Å,  $\beta = 105.85(1)^\circ$ ,  $Z = 2$ ,  $D_c = 1.15$  g cm<sup>-3</sup>,  $D_m = 1.14$  g cm<sup>-3</sup>. Intensity data were collected by automated diffractometer methods. At the present stage of refinement  $R = 9.7\%$  for 1498 reflections with  $F^2 > 3\sigma(F^2)$ .

The  $[\text{Co}(\text{CN})_5]^{3-}$  anion (Figure) is situated on a mirror plane with three crystallographically independent ligands, the apical and two basal cyanides. The average Co-C<sub>basal</sub> distance is 1.894(8) Å compared to the elongated Co-C<sub>apical</sub> distance of 2.01(1) Å. The C-N distances for all the ligands were constrained to be 1.15 Å.<sup>6</sup> The *trans* C<sub>basal</sub>-Co-C<sub>basal</sub> angle is  $164.7(4)^\circ$ . The average C<sub>apical</sub>-Co-C<sub>basal</sub> angle is  $97.5^\circ$ . The Co atom lies 0.251(7) Å above the plane of the four basal carbons. No atoms were found in the open position *trans* to the apical cyanide, thus eliminating the possibility of distortion of the square pyramid as has been observed in the  $[\text{Co}(\text{CNPh})_5]^{2+}$  cation.<sup>7</sup>

All three  $[\text{NEt}_2\text{Pr}_2]^+$  cations are also situated on the mirror plane. The thermal motion exhibited by some of the carbon atoms is highly anisotropic.

The structure reported here shows that, for the yellow form, the  $[\text{Co}(\text{CN})_5]^{3-}$  anion is truly five-coordinate. Comparison with the green form of the isoelectronic  $[\text{Co}(\text{CNPh})_5]^{2+}$  ion<sup>7</sup> implies that the green form of the  $[\text{Co}(\text{CN})_5]^{3-}$  ion is weakly co-ordinated in the sixth, axial position. The analogous  $d^8$   $[\text{Ni}(\text{CN})_5]^{3-}$  anion and other five-coordinate transition-metal complexes have also been reported.<sup>8</sup>

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<sup>1</sup> A. W. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710; N. K. King and M. E. Winfield, *ibid.*, 1961, **83**, 3366; A. Haim and W. K. Wilmarth, *ibid.*, p. 509; K. G. Caulton, *Inorg. Chem.*, 1968, **7**, 392; J. M. Pratt and R. J. P. Williams, *J. Chem. Soc. (A)*, 1967, 1291; M. G. Burnett, P. J. Connolly, and C. Kembell, *ibid.*, p. 800; J. P. Maher, *ibid.*, 1968, 2918; F. D. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 3760; W. P. Griffith and J. R. Lane, *J.C.S. Dalton*, 1972, 158; J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *Austral. J. Chem.*, 1963, **16**, 954.

<sup>2</sup> J. Kwiatek, *Catalysis Rev.*, 1967, **1**, 37.

<sup>3</sup> L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, 1972, **94**, 7664; G. L. Simon, A. W. Adamson, and L. F. Dahl, *ibid.*, p. 7654.

<sup>4</sup> G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discuss. Faraday Soc.*, 1968, 110.

<sup>5</sup> D. A. White, A. J. Solodar, and M. M. Baizer, *Inorg. Chem.*, 1972, **11**, 2160.

<sup>6</sup> S. Z. Goldberg, and K. N. Raymond, *Inorg. Chem.*, 1973, **12**, 2923.

<sup>7</sup> F. A. Jurnak, D. R. Greig, and K. N. Raymond, submitted for publication to *Inorg. Chem.*

<sup>8</sup> K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362; F. A. Jurnak and K. N. Raymond, *ibid.*, 1974, **13**, 2387; L. Sacconi, *Coordination Chem. Rev.*, 1972, **8**, 351.