The Structure of the Adduct of Perfluoroethylene and the Hydridopentacyanocobaltate(III) Ion

By R. MASON and D. R. RUSSELL

(Department of Chemistry, The University, Sheffield)

THE reaction of tetrafluoroethylene with the hydridopentacyanocobaltate(III) ion and the pentacyanocobaltate(II) ion in aqueous solution has been described by Mays and Wilkinson[1] and is of interest in connection with the nature of the reduced cyanocobalamin (vitamin B_{12s}) species.[2] The structure of the $[(CN)_5CoCF_2CF_2H]^{3-}$ ion has now been determined by a three-dimensional X-ray analysis of single crystals of $K_3[(CN)_5CoC_2F_4H]$ ($R = 0.088$ for 1573 non-equivalent reflexions) and is shown in the Figure.

The average equatorial cobalt–carbon (cyanide) bond length is 1·894 Å (e.s.d. 0·014 Å), the axial cobalt–carbon (cyanide) bond length being 1·927 Å. The metal–carbon (C_2F_4H) bond length is 1·990 Å, the difference (0·063 Å) in length between the two axial metal–carbon bonds being that which

is to be expected simply on the basis of the differing σ-orbital radii of the two carbon atoms. The *total* bond orders of the two axial cobalt–carbon bonds are therefore essentially equal and somewhat less than their equatorial counterparts.

The relative stability of metal–alkyl and -fluoroalkyl complexes can be discussed from two points of view which are not necessarily mutually exclusive. An essentially electrostatic model would imply that the bonding of the fluoroalkyl group to the metal may lead to considerable metal orbital contraction and a stronger metal–carbon σ-bond than for the case of the equivalent alkyl complex. A second explanation is based on the possible π-acceptor properties of the fluoroalkyl group with respect to filled metal orbitals. In both these descriptions a shortening

[1] M. J. Mays and G. Wilkinson, *Nature*, 1964, **203**, 1167.
[2] J. W. Collat and J. C. Abbot, *J. Amer. Chem. Soc.*, 1964, **86**, 2308.

of the metal–carbon (fluoroalkyl) bond length compared with the metal–carbon (alkyl) value is expected. In the only perfluoroalkyl complex previously studied by crystallographic methods, Churchill[3] has found such a shortening.

The covalent radius of octahedral cobalt(III)[4] may be estimated as 1.30 ($\pm$ 0.03 Å) from the bond lengths in $Co(NH_3)_3(NO_2)_2Cl$;[5] as 1.27 Å from the Co–N bond lengths in azidopentamminecobalt(II) azide[6] and as 1.28 Å from the mean Co–N bond length in trans-dichlorobis-(−)-propylenediamine-cobalt(III) chloride hydrochloride dihydrate.[7] The sum of the Co^{III}–$C(sp^3)$ σ-covalent radii is therefore 2.05 ± 0.02 Å, 0.06 Å (4σ) greater than the observed cobalt–carbon (C_2F_4H) bond length. The Co–C_α–C_β bond angle is 119.7 ($0.9°$) compared with the Rh–C_α–C_β bond angle of $117°$ in iodo-carbonyl-π-cyclopentadienylpentafluoroethylrhodium,[3] values which are also consistent with the view that the metal–carbon (fluoroalkyl) bond has some double-bond character. The concept of the π-acceptor role of fluoroalkyl groups[8,9] therefore seems reasonably well established although the relative contributions of σ- and π-bonding to the
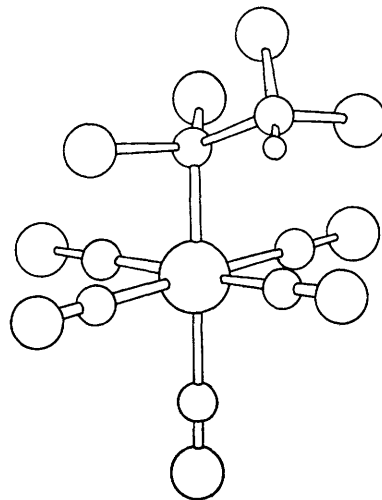
total bond order of the metal–carbon bond remains difficult to assess in any detailed way.

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[5] Y. Tanito, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1953, **26**, 420.
[6] G. J. Palenik, *Acta Cryst.*, 1964, **17**, 360.
[7] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, 1962, **35**, 1131.
[8] F. A. Cotton, *Inorg. Chem.* 1964, **3**, 702.
[9] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.