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The X-ray Crystal Structure of an Eight Co-ordinate Cyanide Complex of Niobium, $K_4[Nb(CN)_8]\cdot 2H_2O$

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Few octacyano complexes are known, the only established examples being those of molybdenum and tungsten, and the recently discovered complexes of niobium [1], $[Nb(CN)_8]^{4-}$ and $[Nb(CN)_8]^{5-}$. We have determined the X-ray crystal structure of $K_4[Nb(CN)_8]\cdot 2H_2O$, the first such study on an octacyanoniobate, both to extend our knowledge of the stereochemistry of ML_8 systems in which the ligands impose no steric restraints on the structure, and because E.P.R. [1] and vibrational spectroscopic [2] data suggests that the $[Nb(CN)_8]^{4-}$ ion is an Archimedean antiprism in solution and dodecahedral in the solid state.

The yellow crystals were obtained by the published method [1] and were recrystallised from a water–methanol mixture in the dark under nitrogen. The crystals are orthorhombic, space group $Pna2_1$; $a = 16.899(10)$, $b = 8.821(5)$, $c = 11.754(7)$ Å, $U = 1752.1$ Å^3, $Z = 4$. Data were measured on a Philips four-circle diffractometer with graphite-monochromated MoKα radiation (λ = 0.7107 Å) for θ between 3 and 30°. Of 2655 reflexions measured, 2408 were classed as observed: $I > 2.0\sigma(I)$. A Patterson map gave the coordinates of the Nb atom and confirmed that the structure was almost identical with that of $K_4[Mo(CN)_8]\cdot 2H_2O$ [3b]. The structure was refined by block-diagonal least squares to R = 0.031 anisotropically. A difference Fourier map now revealed the positions of the H atoms of the water molecules. The H atoms were included and R converged to 0.0295 for the 2408 observed data (full details of the refinement and the relationship of the crystal structure to that of the Mo analogue will be published separately by M.L. and G.G.).

The anion is dodecahedral, the mean Nb–C distance of 2.255 Å being significantly longer than the 2.163(5) Å found for Mo–C in $K_4[Mo(CN)_8]\cdot 2H_2O$ [3a]. As in the latter salt [3a], all eight Nb–C distances aere equal within the limits of experimental error. Although our E.P.R. data [1] suggested that the solid salt, doped in $K_4[Mo(CN)_8]\cdot 2H_2O$, was dodecahedral, the possibility could not be excluded that this symmetry was imposed on $[Nb(CN)_8]^{4-}$ by the host lattice of dodecahedral $[Mo(CN)_8]^{4-}$ ions, present in vast excess for the E.P.R. experiment. The present study shows that the anion in $K_4[Nb(CN)_8]\cdot 2H_2O$ is indeed dodecahedral. It appears therefore that the $[Nb(CN)_8]^{4-}$ in $K_4[Nb(CN)_8]\cdot 2H_2O$ is the first fully authenticated example of an octacyano complex changing its stereochemistry from the solid to the solution phase. Previous claims for such a change, in $K_3[Mo(CN)_8]$ and $K_3[W(CN)_8]$ [4], were made on the basis of E.P.R. data alone, without supporting X-ray evidence for the solid and without an isomorphous host lattice for the paramagnetic species.

The adoption by $K_4[Nb(CN)_8]\cdot 2H_2O$, a d_1 species, of a dodecahedral (D_{2d}) rather than an antiprismatic (D_{4d}) structure found in another d_1 species, $Na_3[W(CN)_8]\cdot 4H_2O$ (and presumably in the isomorphous $Na_3[Mo(CN)_8]\cdot 4H_2O$) [5] is probably due to crystal packing rather than to electronic factors. The suggestion that d^0 and d^1 octacyano species tend to a 'hard sphere model' with antiprismatic coordination and d^2 to a 'most favourable polyhedra' model [6] is seen not to be a universal rule; another d^1 complex which has slightly distorted dodecahedral symmetry is $(Bu^n_4N)_3[Mo(CN)_8]$ [7].

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