The Octacyanoniobate(IV) Ion

By P. M. KIERNAN, J. F. GIBSON, and W. P. GRIFFITH*
(*Department of Inorganic Chemistry, Imperial College, London* SW7 2AY)

Summary Salts of $[Nb(CN)_8]^{4-}$ have been prepared; it appears that the anion of the potassium salt is dodecahedral in the solid state and probably antiprismatic in solution.

REDUCTION of a methanolic solution of niobium pentachloride at a mercury pool cathode followed by reaction with concentrated aqueous potassium cyanide yields orange crystals of the stable salt $K_4[Nb(CN)_8],2H_2O$ (I); further reduction leads to the less stable red $K_5[Nb(CN)_8]$. The salt (I) is paramagnetic ($\mu_{eff} = 1{\cdot}69$ B.M. at 293 K) and is the first unsubstituted cyano complex of niobium to be reported.

The structure of the anion in solid (I) appears to be dodecahedral (D_{2d}). *X*-Ray studies show that (I) and K_4-$[Mo(CN)_8],2H_2O$ (II) are isomorphous; the latter is known to contain a dodecahedral anion.[1] The e.s.r. spectrum of a magnetically dilute solid solution of (I) in (II) at 100 and 293 K is anisotropic with two ten-line sets of hyperfine features. Analysis, allowing for second-order effects, gives $g_\perp = 1{\cdot}992$ and $g_\parallel = 1{\cdot}976$ with $A_\perp = 0{\cdot}0075\ cm^{-1}$ and $A_\parallel = 0{\cdot}0154\ cm^{-1}$. Thus $g_\perp > g_\parallel$ (both less than the free-spin value) and $A_\perp < A_\parallel$, consistent[2] with a dodecahedral structure for the anion. Such a structure has been found by e.s.r.[2] and *X*-ray determination[3] for salts of the iso-electronic $[Mo(CN)_8]^{3-}$ ion.

The structure of $[Nb(CN)_8]^{4-}$ in solution, however, appears to be different. The e.s.r. spectrum in glycerol at 340 K gives $g_{iso} = 1{\cdot}980$ and $A_{iso} = 0{\cdot}0097$ cm^{-1}; similar results are found for methanolic and aqueous solutions at 293 K. These values differ significantly from the corresponding parameters for the solid, for which $g_{iso} = 1{\cdot}987$ and $A_{iso} = 0{\cdot}0101$ cm^{-1}, the error limits being $\pm 0{\cdot}0005$ for g-values and $\pm 0{\cdot}00002$ cm^{-1} for A-values. A glycerol glass of (I) at 100 K gave $g_{\perp} = 1{\cdot}970$ and $A_{\perp} = 0{\cdot}0121$ cm^{-1}. Values for the partially masked parallel features were calculated from the isotropic and perpendicular values, giving $g_{\parallel} = 2{\cdot}000$ and $A_{\parallel} = 0{\cdot}0049$ cm^{-1}. The fact that $g_{\perp} < g_{\parallel}$ and $A_{\perp} > A_{\parallel}$, the reverse of the situation for the solid, again implies a structural change on solution, probably to an antiprismatic (D_{4d}) configuration, as has been proposed for $[Mo(CN)_8]^{3-}$.[2] The proximity of $g_{\parallel}$ for (I) in glycerol to the free-spin value of 2·0023 is also consistent with an antiprismatic structure. The vibrational spectra of (I) in water, though they differ considerably from those of the solid, are insufficiently well resolved to complement these findings.

We thank the S.R.C. for a grant (to P.K.).

(*Received*, 13*th August* 1973; *Com.* 1156.)

---

[1] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, 1968, **90**, 3177.

[2] B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476; R. G. Hayes, *J. Chem. Phys.*, 1966, **44**, 2210.

[3] B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, 1970, **9**, 356.