

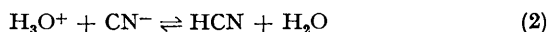
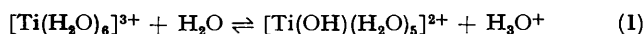
The Complex Cyanides of Titanium

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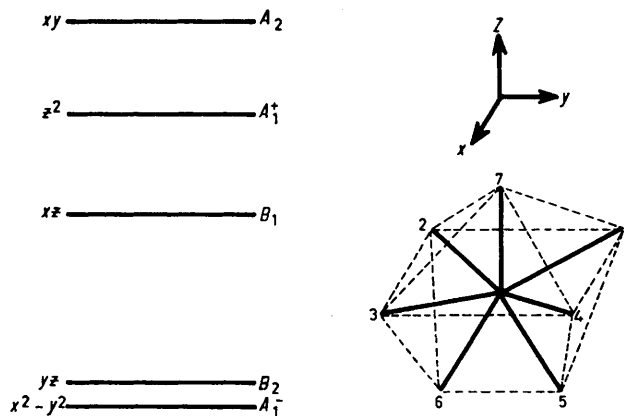
Summary The reported preparation of $K_3Ti(CN)_6$ in aqueous solution has not been confirmed, but we now confirm the preparation of $K_5Ti(CN)_8$ in liquid ammonia and give evidence for the formulation $K_4Ti(CN)_7 \cdot KCN$ with a C_{2v} seven co-ordinate anion; the Ti^0 complex $K_4Ti(CN)_4$ has also been isolated.

SEVERAL authors¹⁻³ have indicated the need for reinvestigations in the field of titanium(III)-cyanide complexes. We report here a preliminary account of our findings in these systems.

Heintz⁴ has reported a dark-blue octahedral complex cyanide of titanium(III), $K_3Ti(CN)_6$, as well as a compound formulated as $K_3Ti(CN)_6 \cdot KCN$. These complexes were claimed to have been isolated from aqueous solutions of $TiCl_3$ and KCN under conditions that might be expected to produce only titanium(III) hydroxide. We have repeated Heintz's preparations, and find the only titanium product of these reactions to be the dark-blue hydroxide, HCN being displaced by the stronger acid $[Ti(H_2O)_6]^{3+}$ [equations (1) and (2)].



We do confirm, however, that the reaction between $TiBr_3$ and KCN in liquid ammonia⁵ produces a grey-green precipitate of formula $K_5Ti(CN)_8$. There has been much debate^{1,2,5,6} about the structure of this complex; the



original workers⁵ preferring the formulation $K_3Ti(CN)_6 \cdot 2KCN$, whilst others⁶ have favoured the eight co-ordinate structure $[Ti(CN)_8]^{5-}$. We find that the complex gives a

reflectance spectrum having $d \leftrightarrow d$ transitions at 22,400, 16,800 and 9700 cm^{-1} , and is magnetically dilute having a room temperature magnetic moment of 1.71 B.M. The reflectance spectrum rules out the possibility of a six-coordinate structure (*i.e.* one containing $[\text{Ti}(\text{CN})_6]^{3-}$). We find, however, that the X-ray powder photograph shows the presence of KCN in this compound which excludes the possibility of the eight co-ordinate species $[\text{Ti}(\text{CN})_8]^{5-}$. Complexes of stoichiometry ML_7 have only been found with pentagonal bipyramidal (D_{5h})^{7,8} and mono-capped trigonal prismatic (C_{2v})⁸⁻¹⁰ structures. The D_{5h} structure (recently found for $[\text{V}(\text{CN})_7]^{4-}$)⁴⁻⁷ can be eliminated, since only two $d \leftrightarrow d$ bands would be observed for a d^1 system.¹¹ However, the C_{2v} structure would give three $d \leftrightarrow d$ bands, as shown in the energy level diagram (which was derived using a standard approach¹² assuming a slight distortion of

the structure.¹³ A similar C_{2v} structure has recently been postulated for solid $\text{K}_4\text{Mo}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$.¹⁴

The reaction between TiBr_3 (3.4 g), KCN (8.4 g) and potassium (5 g) in liquid ammonia (150 cm^3) results in the precipitation of the black complex, $\text{K}_4\text{Ti}(\text{CN})_4$, which is stable under dry argon. This is the first example of the stabilisation of Ti^0 with an inorganic anion. The powder is pyrophoric in air, and reacts violently with water to produce NH_3 (the other products are as yet unidentified). The i.r. spectrum of the complex contains a strong cyanide stretching band at 1943 cm^{-1} , with a weaker band at 2012 cm^{-1} : the room temperature magnetic moment is 2.17 B.M. The reflectance spectrum shows only a broad unresolved band in the $d \leftrightarrow d$ region.

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