

The Hexacyanotitanate Ion: Synthesis and Crystal Structure of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$

William R. Entley, Christopher R. Treadway, Scott R. Wilson, and Gregory S. Girolami*

Contribution from the School of Chemical Sciences, The University of Illinois at Urbana—Champaign, 601 South Goodwin Avenue, Urbana, Illinois 61801

Received August 8, 1996. Revised Manuscript Received April 28, 1997[⊗]

Abstract: The hexacyanotitanate salt, $[\text{Et}_4\text{N}]_3[\text{Ti}(\text{CN})_6] \cdot 4\text{MeCN}$, has been prepared by addition of tetraethylammonium cyanide to the titanium(III) triflate salt $\text{Ti}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$. The orange crystalline product has been characterized by X-ray diffraction, and the d^1 anion is only slightly distorted from ideal O_h symmetry. The anion resides on a center of symmetry and is characterized by the following parameters: $\text{Ti}-\text{C} = 2.195(2)$, $2.197(3)$, and $2.213(3)$ Å; $\text{C}-\text{N}(\text{av}) = 1.141(4)$ Å; $\text{C}-\text{Ti}-\text{C}(\text{cis}) = 88.01(9)$, $88.02(9)$, $89.02(9)$, and $89.78(9)^\circ$; $\text{C}-\text{Ti}-\text{C}(\text{trans}) = 180^\circ$. In addition to the crystallographic study, details of the IR ($\nu_{\text{CN}} = 2071 \text{ cm}^{-1}$), EPR, and UV-vis spectra ($\Delta_o = 22800 \text{ cm}^{-1}$) are given. Crystal data for $[\text{Et}_4\text{N}]_3[\text{Ti}(\text{CN})_6] \cdot 4\text{MeCN}$ are as follows: monoclinic, space group $I2/a$, $a = 18.171(6)$ Å, $b = 12.200(4)$ Å, $c = 20.989(5)$ Å, $\beta = 91.17(2)^\circ$, $V = 4652(2)$ Å³, $Z = 4$, $wR^2 = 0.2054$ for 3831 data, 27 restraints, and 318 parameters.

Introduction

The preparation of new molecular-based magnetic materials has become one of the fastest growing areas of inorganic and materials chemistry today.^{1–3} Recent work has convincingly shown that molecular magnets with magnetic ordering temperatures approaching (and sometimes exceeding) 300 K can be prepared by using cyanometalates of stoichiometry $[\text{M}(\text{CN})_6^{n-}]$ as molecular building blocks.^{4,5} Such anions can be treated with a variety of paramagnetic transition metal cations to prepare magnetic materials that are analogues of the well-known solid Prussian blue. Generally, solids with higher magnetic ordering temperatures are obtained if early transition metal cyanometalates such as $[\text{V}(\text{CN})_6^{4-}]$ and $[\text{Cr}(\text{CN})_6^{3-}]$ are employed as building blocks.^{4,5} In part, this correlation reflects the higher energies of the d-orbitals in early transition metals and the consequent greater degree of delocalization of spin density onto the cyanide ligands.

In view of this correlation, it would be of interest to prepare titanium-substituted analogues of Prussian blue. Before this can be accomplished, however, it is necessary to synthesize a hexacyanotitanate building block. Hexacyanometalate complexes of stoichiometry $[\text{M}(\text{CN})_6^{n-}]$ have long been known for every first-row transition metal between vanadium and cobalt; in contrast, although the reactions of titanium(III) with cyanide salts have been the subject of much discussion, the identities of the products obtained are far from firmly established.

In 1906 Grossman reported that titanium trichloride and excess potassium cyanide react in aqueous solution to give an immediate black precipitate.⁶ No analytical data were presented, but Grossman stated that the precipitate could not be $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (which should be soluble in water as judged from the properties of other hexacyanometalates); instead he proposed that the product was $\text{Ti}(\text{OH})_3$.

In 1963, Heintz reported that the reaction of stoichiometric amounts of titanium trichloride and potassium cyanide in water, under rigorously anaerobic conditions, gave a deep blue product of stoichiometry $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ as judged from microanalytical data.⁷ When the reaction was carried out in the presence of excess cyanide, a deep blue product of stoichiometry $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot \text{KCN}$ was obtained. Successive washings with distilled water gave the original reaction product $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$. Heintz did not comment on the unexpected finding that his product was insoluble in water.

In 1961 Schläfer and Götz reported that titanium tribromide and potassium cyanide reacted in liquid ammonia to give a dark green complex which analyzed well for $\text{K}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$.⁸ The authors argued that the dark green product was an octahedral cyanide complex best represented by the formula $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 2\text{KCN}$. In 1962 Golding and Carrington suggested that this dark green complex was actually eight-coordinate based on the similarity of its EPR spectrum to those of the known eight-coordinate cyano compounds $\text{K}_3[\text{W}^{\text{V}}(\text{CN})_8]$ and $\text{K}_3[\text{Mo}^{\text{V}}(\text{CN})_8]$.⁹ In 1969 Bose and Basu concluded that $\text{K}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$ was eight-coordinate based on magnetic susceptibility and UV-vis data, but that the EPR spectrum was more consistent with a six-coordinate structure.¹⁰

More recent investigations of the reaction products of titanium(III) and cyanide have been carried out by Nicholls and co-workers.¹¹ In 1974, these authors repeated Heintz's aqueous preparation but found that the only titanium product obtained was the dark blue titanium(III) hydroxide. Nicholls et al. also reinvestigated the work of Schläfer and Götz; they suggested that the dark green reaction product of stoichiometry $\text{K}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$ was actually a seven-coordinate monocapped trigonal prismatic complex of formula $\text{K}_4[\text{Ti}^{\text{III}}(\text{CN})_7] \cdot \text{KCN}$. In 1980,

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

(1) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385–415.

(2) Kahn, O. *Molecular Magnetism*; VCH Publishers, Inc.: New York, 1993.

(3) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series E, Vol. 198; Plenum: New York, 1991.

(4) Ferlay, S.; Mallah, T.; Ouahés, R.; Veillet, P.; Verdager, M. *Nature* **1995**, *378*, 701–703.

(5) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397–400.

(6) Grossman, H. *Chem.-Ztg.* **1906**, 907.

(7) Heintz, E. A. *Nature* **1963**, *197*, 690.

(8) Schläfer, H. L.; Götz, R. *Z. Anorg. Allg. Chem.* **1961**, *309*, 104–109.

(9) Golding, R. M.; Carrington, A. *Mol. Phys.* **1962**, *5*, 377–385.

(10) Bose, S. K.; Basu, S. *J. Chim. Phys. (Paris)* **1969**, *66*, 1985–1986.

(11) Nicholls, D.; Ryan, T. A.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1974**, 635–636.

Nicholls and co-workers also prepared the gray-green insoluble rubidium and cesium compounds $\text{Rb}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$ and $\text{Cs}_4[\text{Ti}^{\text{III}}(\text{CN})_7]$ by treating TiBr_3 with excess RbCN or CsCN in liquid ammonia, respectively.¹² The authors reiterated their conclusion that each of these complexes contains the C_{2v} monocapped trigonal prismatic $[\text{Ti}^{\text{III}}(\text{CN})_7^{4-}]$ anion.

Nicholls and co-workers also claimed that heating $\text{K}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$ to 280 °C in vacuo caused the gray-green solid to become dark gray.¹² Extraction with liquid ammonia gave a black residue that analyzed as $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$. The powder X-ray diffraction pattern of this material suggested that it was not isomorphous with the known hexacyanometalates $\text{K}_3[\text{M}^{\text{III}}(\text{CN})_6]$, where M is Cr, Mn, or Fe.

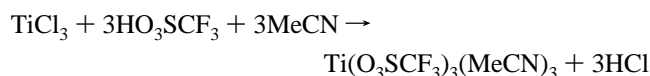
Finally, Alexander and Gray have discussed the electronic spectrum of $[\text{Ti}(\text{CN})_6^{3-}]$, but apparently based their discussion on the data reported by Schläfer and Götz.¹³

Thus, the current view of homoleptic titanium(III) cyanide anions is that they are either six-, seven-, or eight-coordinate, and are either dark blue, dark green, or black in color. We now report the synthesis and crystal structure of the first well-documented titanium(III) hexacyanometalate. In contrast to previous reports, $[\text{Et}_4\text{N}]_3[\text{Ti}(\text{CN})_6]$ is pale orange when crystalline and bright yellow when powdered. Octahedral d^1 ions are of considerable theoretical interest but remain rather rare; the present salt is the first in which a d^1 ion is in a strong ligand field. The present paper focuses on the physical and spectroscopic properties of this species; descriptions of our efforts to prepare Prussian blue analogues from this building block will be described elsewhere.

Results and Discussion

Synthesis of $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$. As pointed out by Nicholls and co-workers, the high acidity of the titanium(III) cation in aqueous solution prevents the formation of a titanium cyanide complex in water, titanium(III) hydroxide and hydrogen cyanide being formed instead.^{11,12} Thus, cyanotitanates must be prepared in non-aqueous media if they are to be prepared at all. Some workers have investigated the preparation of cyanotitanates in liquid ammonia,^{8,11,12} but this solvent is less than ideal owing to its ability to coordinate strongly to transition metals. We have taken a different approach and have investigated the preparation of cyanotitanates in organic media such as acetonitrile.¹⁴

Our first need is a source of titanium(III), preferably halide free, which is soluble in acetonitrile; a trifluoromethanesulfonate derivative would be ideal but is unknown for titanium(III).¹⁵ We find that treatment of titanium(III) chloride with neat trifluoromethanesulfonic acid affords a light blue-white solid. This reaction is rather slow and is complete only after about 72 h at 25 °C. Heating the solution above 50 °C must be avoided: at higher temperatures, the resulting mixture turns black. Recrystallization of the light-blue solid from acetonitrile yields the dark-purple "triflate" salt $\text{Ti}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$.



(12) Nicholls, D.; Ryan, T. A. *Inorg. Chim. Acta* **1980**, *41*, 233–237.
(13) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260–4271.

(14) The synthesis of cyanotitanates in acetonitrile has previously been suggested but not implemented: Chadwick, B. M.; Sharpe, A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83–176.

(15) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 243–250.

Table 1. Crystal Data for $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$ (**1**·4MeCN) at –75 °C

space group: $I2/a$	$V = 4652(2) \text{ \AA}^3$
$a = 18.171(6) \text{ \AA}$	$Z = 4$
$b = 12.200(4) \text{ \AA}$	mol wt = 758.99
$c = 20.989(5) \text{ \AA}$	$\rho_{\text{calcd}} = 1.084 \text{ g cm}^{-3}$
$\beta = 91.17(2)^\circ$	$\mu_{\text{calcd}} = 2.23 \text{ cm}^{-1}$
$\alpha = \gamma = 90^\circ$	size = $0.35 \times 0.30 \times 0.20 \text{ mm}$
diffractometer: Enraf-Nonius CAD4	
radiation: Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$	
monochromator: graphite crystal, $2\theta = 12^\circ$	
scan range, type: $3.86 < 2\theta < 48.94^\circ$, ω/θ	
scan speed, width: $3\text{--}16^\circ \text{ min}^{-1}$, $\Delta\omega = 1.00[1.00 + 0.35 \tan \theta]^\circ$	
rfltns: 3948 total, 3834 unique, 2893 with $I > 2\sigma(I)$	
internal consistency: $R_1 = 0.0239$	
$R_1 [I > 2\sigma(I)] = 0.0521^a$	variables = 318
$wR_2[\text{all data}] = 0.2054^b$	constraints = 27

$$^a R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

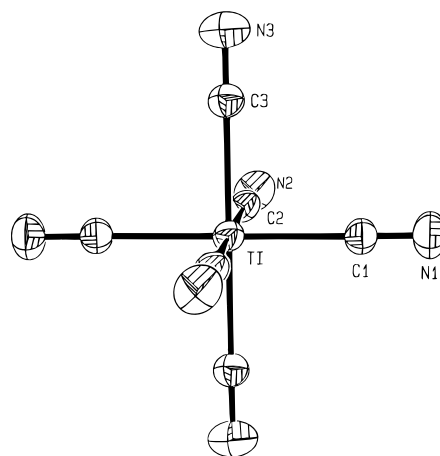
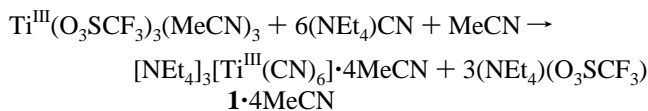


Figure 1. ORTEP diagram of the $[\text{Ti}^{\text{III}}(\text{CN})_6^{3-}]$ anion. The 35% probability density surfaces are shown.

Treatment of $\text{Ti}^{\text{III}}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$ with excess $(\text{NEt}_4)\text{CN}$ in acetonitrile at 45 °C for 10 min followed by cooling to –20 °C gives pale orange prisms of the hexacyanotitanate(III) salt $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$ (**1**·4MeCN). This reaction must be carried out at 45 °C or below: refluxing the reaction mixture causes decomposition of the product. The crystals readily desolvate to give $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**). The unambiguous characterization of this hexacyanotitanate(III) anion is described below.



Crystal Structure of $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6] \cdot 4\text{MeCN}$. Single crystals of **1**·4MeCN were obtained by cooling saturated acetonitrile solutions to –20 °C. The orange prisms lose solvent readily, and quickly become amorphous unless they are handled while still wet with the supernatant. Crystal data are collected in Table 1, and selected bond distances and angles are presented in Table 2.

The overall stoichiometry of the crystals is $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6] \cdot 4\text{MeCN}$. Compound **1**·4MeCN crystallizes in the monoclinic space group $I2/a$ with four formula units per unit cell; the asymmetric unit contains 1.5 cations, 0.5 anions, and 2 acetonitrile molecules. The unique $[\text{Ti}(\text{CN})_6^{3-}]$ anions reside on crystallographic inversion centers (Figure 1) and are ordered. Of the three $[\text{NEt}_4^+]$ cations in each formula unit, two are related

Table 2. Selected Distances (Å) and Angles (deg) for $[\text{NET}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$ (1·4MeCN)

Distances			
Ti—C(1)	2.197(3)	N(7)—C(71)	1.521(4)
Ti—C(2)	2.195(2)	N(7)—C(73)	1.492(4)
Ti—C(3)	2.213(3)	N(7)—C(75)	1.499(3)
C(1)—N(1)	1.143(4)	N(7)—C(77)	1.530(3)
C(2)—N(2)	1.139(3)	C(61)—C(62)	1.533(9)
C(3)—N(3)	1.142(3)	C(63)—C(64)	1.518(7)
N(6)—C(61)	1.517(6)	C(65)—C(66)	1.518(9)
N(6)—C(63)	1.513(8)	C(67)—C(68)	1.520(6)
N(6)—C(65)	1.512(6)	C(71)—C(72)	1.516(5)
N(6)—C(67)	1.514(8)	C(73)—C(74)	1.534(5)
		C(75)—C(76)	1.538(5)
		C(77)—C(78)	1.496(4)
Angles			
C(1)—Ti—C(2)	89.02(9)	C(71)—N(7)—C(73)	111.8(2)
C(1)—Ti—C(3)	90.22(9)	C(71)—N(7)—C(75)	106.2(2)
C(2)—Ti—C(3)	88.02(9)	C(71)—N(7)—C(77)	109.3(2)
Ti—C(1)—N(1)	178.9(2)	C(73)—N(7)—C(75)	112.1(3)
Ti—C(2)—N(2)	177.4(2)	C(73)—N(7)—C(77)	106.0(2)
Ti—C(3)—N(3)	178.9(2)	C(75)—N(7)—C(77)	111.5(2)
C(61)—N(6)—C(63)	111.0(4)	N(6)—C(61)—C(62)	113.8(7)
C(61)—N(6)—C(65)	106.4(6)	N(6)—C(63)—C(64)	115.2(5)
C(61)—N(6)—C(67)	111.1(4)	N(6)—C(65)—C(66)	114.1(7)
C(63)—N(6)—C(65)	111.6(4)	N(6)—C(67)—C(68)	114.9(5)
C(63)—N(6)—C(67)	105.8(6)	N(7)—C(71)—C(72)	114.9(3)
C(65)—N(6)—C(67)	111.0(4)	N(7)—C(73)—C(74)	115.3(3)
		N(7)—C(75)—C(76)	114.1(3)
		N(7)—C(77)—C(78)	114.5(2)

by symmetry: these reside on general positions and are ordered. The third $[\text{NET}_4]^+$ cation lies almost exactly on a 2-fold axis and is disordered. There are no unusually short contacts between the cations and anions. The acetonitrile molecules are solvates of cocrystallization and are well separated from the titanium centers. A stereoview down the *b* axis of the unit cell is shown in Figure 2.

The $[\text{Ti}(\text{CN})_6]^{3-}$ anions adopt nearly ideal octahedral geometries. The cis C—Ti—C angles all lie between 88.0(1) and 92.0(1)°; the trans C—Ti—C angles are exactly 180° by symmetry. The Ti—C—N linkages are almost precisely linear: the three independent Ti—C—N angles are 178.9(2), 177.4(2), and 178.9(2)°. One of the three independent Ti—C distances is very slightly longer than the other two: Ti—C(1) = 2.195(2) Å, Ti—C(2) = 2.197(3) Å, and Ti—C(3) = 2.213(3) Å. The crystallographic inversion center ensures that the two longest Ti—C distances are mutually trans. Thus, the structure of the $[\text{Ti}(\text{CN})_6]^{3-}$ anion may be described as a nearly ideal octahedron that shows (at best) an almost vanishingly small tetragonal elongation of 0.017 Å.

The carbon—nitrogen distances within the cyanide ligands are nearly identical and average 1.141(3) Å. This distance is essentially identical with those of other transition metal cyanide complexes in the series $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$, where M is chromium,^{16–21} manganese,^{16,22–23} iron,^{16,24–27} or cobalt^{16,28–31} (Table 3).

(16) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic: New York, 1976.

(17) Jagner, S.; Ljungström, E.; Vannerberg, N. G. *Acta Chem. Scand., Sect. A* **1974**, *28*, 623–630.

(18) Figgis, B. N.; Reynolds, P. A. *Inorg. Chem.* **1985**, *24*, 1864–1873.

(19) Figgis, B. N.; Reynolds, P. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1747–1753.

(20) Figgis, B. N.; Forsyth, J. B.; Reynolds, P. A. *Inorg. Chem.* **1987**, *26*, 101–105.

(21) Iwata, M. *Acta Crystallogr., Sect. B* **1977**, *33*, 59–64.

(22) Gupta, M. P.; Milledge, H. J.; McCarthy, A. E. *Acta Crystallogr., Sect. B* **1974**, *30*, 656–661.

(23) Ziegler, B.; Hagele, R.; Babel, D. Z. *Naturforsch. B* **1989**, *44*, 896–902.

(24) Vannerberg, N. G. *Acta Chem. Scand.* **1972**, *26*, 2863–2876.

The metal—carbon bond lengths decrease from 2.20 Å in hexacyanotitanate(III) to 1.89 Å in hexacyanocobalt(III).^{16–31} By taking the metal—carbon bond distance and subtracting the metal ionic radius, one obtains a parameter Δ that is corrected for the different sizes of the metals in the series; Δ corresponds to the effective radius of the carbon atom of the cyanide group. Table 3 shows that Δ is largest for $[\text{Ti}(\text{CN})_6]^{3-}$ and smallest for $[\text{Co}(\text{CN})_6]^{3-}$. The trend suggests that, upon proceeding from Ti to Co, either there is an increase in metal-to-ligand π -back-bonding, an increase in ligand-to-metal σ -bonding, or both. As usual, the synergism of σ - and π -bonding effects makes it difficult to determine which of these phenomena is most important.

In hexacyanometalates, π -back-bonding is known to play a role as shown by changes in metal—carbon bond lengths upon oxidation of the metal center.^{16,32,33} For example, the metal—carbon bond length increases upon oxidation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ despite the smaller ionic radius of Fe^{III} .^{34–36} An analogous situation has been observed in the manganese derivatives $[\text{Mn}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$.^{22,36,37} The decrease in Δ from Ti to Co is consistent with an increase in the total amount of metal—cyanide π -back-bonding as the number of t_{2g} electrons on the metal centers increases from 1 (Ti) to 6 (Co). If this view is correct, then the total amount of π -back-bonding in $[\text{Ti}(\text{CN})_6]^{3-}$ is rather small. Nevertheless, it is likely that the single t_{2g} electron in this complex is delocalized into the cyanide π^* orbitals to a greater degree than are the t_{2g} electrons of hexacyano derivatives of later transition metals, owing to the high energy of the d-orbitals of Ti^{III} relative to those of later M^{III} centers.

The decrease in Δ from Ti to Co, however, could also reflect changes in the ligand-to-metal σ bonding; as the energies of the metal orbitals drop from Ti to Co, donation from the cyanide 5σ orbital should increase and the metal—carbon bond should become relatively shorter. This latter explanation is more consistent with the IR spectroscopic results (see below).

The trivalent chromium and cobalt hexacyanometalates both adopt nearly ideal octahedral structures as expected since these ions are not susceptible to Jahn—Teller distortions. The trivalent manganese and iron hexacyanometalates (which have electronically degenerate t_{2g}^4 and t_{2g}^5 ground states, respectively) are susceptible to Jahn—Teller distortions, but in fact the structures are only weakly distorted and the degree of distortion is cation dependent. The $[\text{Ti}(\text{CN})_6]^{3-}$ anion, which has a t_{2g}^1 ground state, should also show a Jahn—Teller distortion but again its structure has nearly ideal O_h symmetry. These observations illustrate that the t_{2g} orbitals are at best weakly bonding even

(25) Figgis, B. N.; Skelton, B. W.; White, A. J. *Aust. J. Chem.* **1978**, *31*, 1195–1198.

(26) Figgis, B. N.; Kucharski, E. S.; Raynes, J. M.; Reynolds, P. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3597–3604.

(27) Capparelli, M. V.; Murgich, J. *Acta Crystallogr., Sect. C* **1995**, *51*, 356–358.

(28) Barkhatov, V.; Zhdanov, H. *Acta Physicochim. URSS* **1942**, *16*, 43–58.

(29) Kohn, J. A.; Townes, W. T. *Acta Crystallogr.* **1961**, *14*, 617–621.

(30) Chadwick, B. M.; Sharpe, A. G. *J. Chem. Soc. A* **1966**, 1390–1391.

(31) Curry, N. A.; Runciman, W. A. *Acta Crystallogr.* **1959**, *12*, 674–678.

(32) Sano, M.; Kashiwagi, H.; Yamatera, H. *Inorg. Chem.* **1982**, *21*, 3837–3841.

(33) Jones, L. H. *Inorg. Chem.* **1963**, *2*, 777–780.

(34) Swanson, B. I.; Ryan, R. R. *Inorg. Chem.* **1973**, *12*, 283–286.

(35) Swanson, B. I.; Hamburg, S. I.; Ryan, R. R. *Inorg. Chem.* **1974**, *13*, 1685–1687.

(36) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.

(37) Tullberg, A.; Vannerberg, N. G. *Acta Chem. Scand., Sect. A* **1974**, *28*, 551–562.

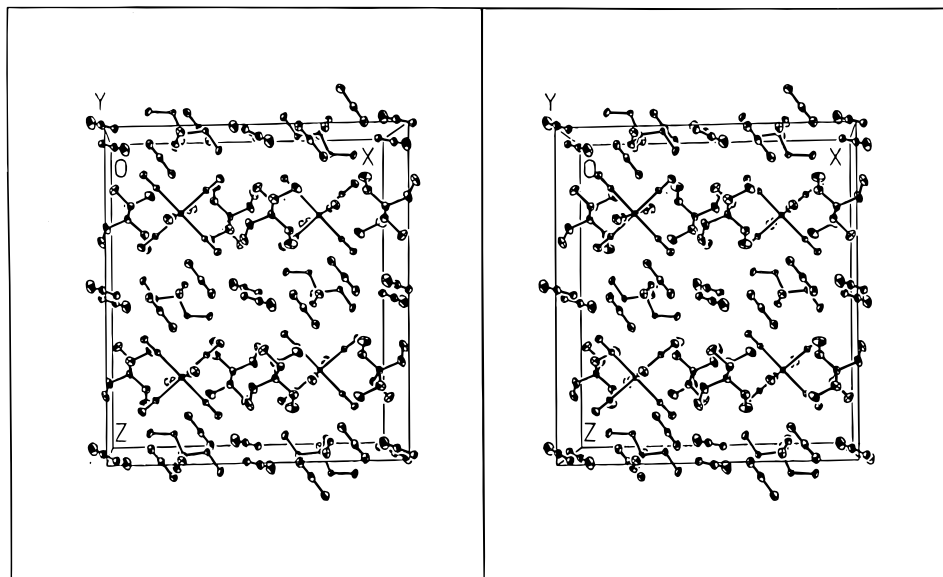


Figure 2. Stereoview of the unit cell contents down the *b* axis, showing the packing of the cations and anions and the acetonitrile solvate molecules.

Table 3. Structural and Spectroscopic Data for $[M^{III}(\text{CN})_6]^{3-}$ Complexes

compd	d_{CN} (Å)	d_{MC} (Å)	r_{M}^a (Å)	Δ^b (Å)	$\nu_{\text{C}\equiv\text{N}^c}$ (cm^{-1})	$\nu_{\text{M}-\text{C}^c}$ (cm^{-1})	$\delta_{\text{M}-\text{CN}^c}$ (cm^{-1})	$10Dq^d$ (cm^{-1})
$[\text{NEt}_4]_3[\text{Ti}^{III}(\text{CN})_6]$ (1)	1.141(3)	2.202	0.81	1.392	2071	300	390	22800
$\text{K}_3[\text{Cr}^{III}(\text{CN})_6]$	1.14 ^e	2.077 ^e	0.755	1.322	2128	339	458	26600
$\text{K}_3[\text{Mn}^{III}(\text{CN})_6]$	1.15 ^f	1.98 ^f	0.72	1.260	2112	361	483	34000
$\text{K}_3[\text{Fe}^{III}(\text{CN})_6]$	1.14 ^g	1.95 ^g	0.69	1.260	2118	389	506	34950
$\text{K}_3[\text{Co}^{III}(\text{CN})_6]$	1.15 ^h	1.89 ^h	0.685	1.205	2129	416	564	34500

^a Reference 36. ^b $\Delta = d_{\text{MC}} - r_{\text{M}}$. ^c Reference 45. ^d Reference 13. ^e References 17–21. ^f References 22–23. ^g References 24–27. ^h References 28–31.

in these cyanometalate complexes (as opposed to the strongly metal–ligand antibonding character of the e_g orbitals).

The single crystal structures of other titanium(III) complexes with six equivalent ligands also have essentially identical metal–ligand bond lengths. For example, the titanium(III) centers in the β -alum $\text{CsTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ are octahedrally coordinated to six water molecules in sites of nearly perfect O_h symmetry.³⁸ Hexakis(urea)titanium(III) iodide and perchlorate also adopt structures in which all of the titanium–oxygen bonds are equal in length.^{39,40} The titanium(III) centers in the latter two compounds, however, do not adopt perfect octahedral coordination geometries. Instead, the coordination polyhedra of the titanium(III) centers are trigonally distorted: one face of the octahedron is rotated by ca. 5° relative to the other about a pseudo- C_3 axis. Although these complexes adopt nearly ideal octahedral geometries, their electronic spectra clearly show that they are Jahn–Teller distorted (see below).^{41–43}

Reactions of $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$. Once $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$ crystallizes out of solution it is difficult to redissolve. Attempts to dissolve desolvated crystals of **1** in acetonitrile or acetonitrile solutions of tetraethylammonium cyanide resulted in the formation of a gray precipitate; at no point was the clear orange color characteristic of the mother liquor observed. Attempts to

redissolve the solvated crystals (**1**·4MeCN) in acetonitrile gave a similar gray precipitate, but the solution did develop a slight orange color.

Addition of deoxygenated water to crystalline samples of **1** instantly results in the formation of dark-blue titanium(III) hydroxide and hydrogen cyanide. Over time, the dark-blue material turns into a white solid (presumably titanium dioxide). This behavior agrees with the observations of Nicholls and co-workers, who noted that deep-blue titanium(III) hydroxide was the only product obtained by treatment of titanium trichloride with potassium cyanide in water.^{11,12}

Spectroscopic Characterization of $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$. The infrared spectrum of **1** taken as a Nujol mull displays a very strong $\text{C}\equiv\text{N}$ stretch at 2071 cm^{-1} ; weak features are also noted at 2200, 2103, and 2093 cm^{-1} (Figure 3). The feature at 2200 cm^{-1} is assigned to acetonitrile, while the strong 2071-cm^{-1} band must be assigned to the t_{1u} stretching mode of the $[\text{Ti}(\text{CN})_6]^{3-}$ anion. (For comparison, the black solid of empirical formula $\text{K}_3[\text{Ti}^{III}(\text{CN})_6]$ prepared by Nicholls and Ryan displayed a single $\text{C}\equiv\text{N}$ stretch at 2088 cm^{-1} .¹²) The appearance of additional weak $\text{C}\equiv\text{N}$ stretches in the solid-state IR spectrum of **1** is a common feature of crystalline hexacyanometalate complexes, and reflects the low site symmetry of the anion in the solid state lattice.^{16,44–46}

The $\text{C}\equiv\text{N}$ stretching frequency for $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$ (**1**) is lower than those of other $\text{K}_3[\text{M}^{III}(\text{CN})_6]$ salts, where M is Cr, Mn, Fe, or Co (Table 3).⁴⁵ This result supports the proposal that ligand-to-metal donation from the 5σ orbital of the cyanide

(38) Sygusch, J. *Acta Crystallogr., Sect. B* **1974**, *30*, 662–665.

(39) Davis, P. H.; Wood, J. S. *Inorg. Chem.* **1970**, *9*, 1111–1116.

(40) Figgis, B. N.; Wadley, L. G. B. *Aust. J. Chem.* **1972**, *25*, 2233–2234.

(41) Clark, R. J. H. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeleus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, 1973; pp 355–417.

(42) The elpasolite-type compounds $\text{Rb}_2\text{Na}[\text{Ti}^{III}\text{Cl}_6]$ and $\text{Cs}_2\text{K}[\text{Ti}^{III}\text{Cl}_6]$ behave similarly: they show electronic but not structural consequences of a Jahn–Teller effect.⁴³

(43) Ameis, R.; Kremer, S.; Reinen, D. *Inorg. Chem.* **1985**, *24*, 2751–2754.

(44) The appearance of multiple bands in the $\text{C}\equiv\text{N}$ stretching region is even more common for the divalent hexacyanometalates.¹⁵

(45) Griffith, W. P.; Turner, G. T. *J. Chem. Soc. A* **1970**, 858–862.

(46) Trageser, G.; Eysel, H. H. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 65–70.

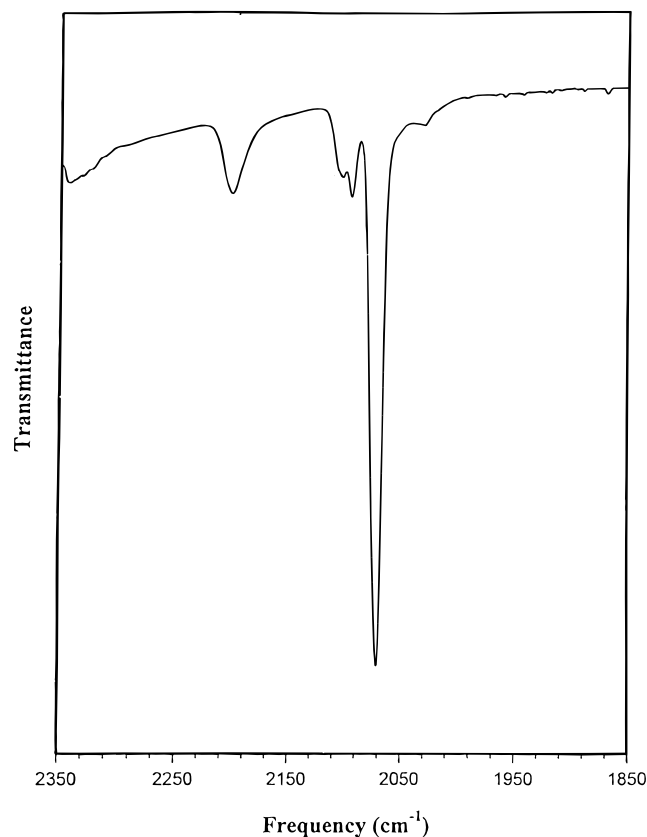


Figure 3. The infrared spectrum of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot x\text{MeCN}$ (**1**· $x\text{MeCN}$) as a Nujol mull. The band at 2200 cm^{-1} is due to residual acetonitrile.

ligands is weakest for titanium and strongest for cobalt: donation from this orbital (which is weakly carbon–nitrogen antibonding) is known to increase the C–N stretching frequencies.⁴⁷ The trivalent titanium center has the highest-energy orbitals in this series owing to its smaller effective nuclear charge compared to other trivalent hexacyanometalates, so that ligand-to-metal donation is disfavored. While a low ν_{CN} frequency might also be rationalized in terms of strong metal-to-ligand π -back-bonding, such an explanation would not explain the long Ti–C bond (see above) or the low frequency of the Ti–C stretch (see below).

In the region between 250 and 450 cm^{-1} , the IR spectra of hexacyanometalates typically show two bands: a lower-frequency metal–carbon stretch and a higher-frequency metal–cyanide deformation mode.^{33,45} In the trivalent hexacyanometalates of chromium, manganese, iron, and cobalt the metal–carbon stretching and metal–cyanide bending frequencies correlate well with the metal–carbon bond lengths:^{44,48,49} as the metal–carbon bond length decreases, the frequencies increase (Table 3). The IR spectrum of **1** features a strong band at 390 cm^{-1} and a medium intensity feature at 300 cm^{-1} . As judged from the trends discussed above, we assign these bands to the titanium–cyanide bending mode and the titanium–carbon stretching vibration, respectively. The low frequencies of these modes are consistent with the rather long metal–carbon bond length observed for **1**. In contrast, the black residue of empirical formula $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ prepared by Nicholls and Ryan showed bands at 434 and 311 cm^{-1} , which these investigators assigned to the cyanide bending and Ti–C stretching modes, respectively.¹² These results are not consistent with our observations.

(47) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed.; Wiley: New York, 1986; pp 272–280.

(48) Jones, L. H. *J. Chem. Phys.* **1964**, *41*, 856–863.

(49) Jones, L. H. *J. Chem. Phys.* **1962**, *36*, 1209–1215.

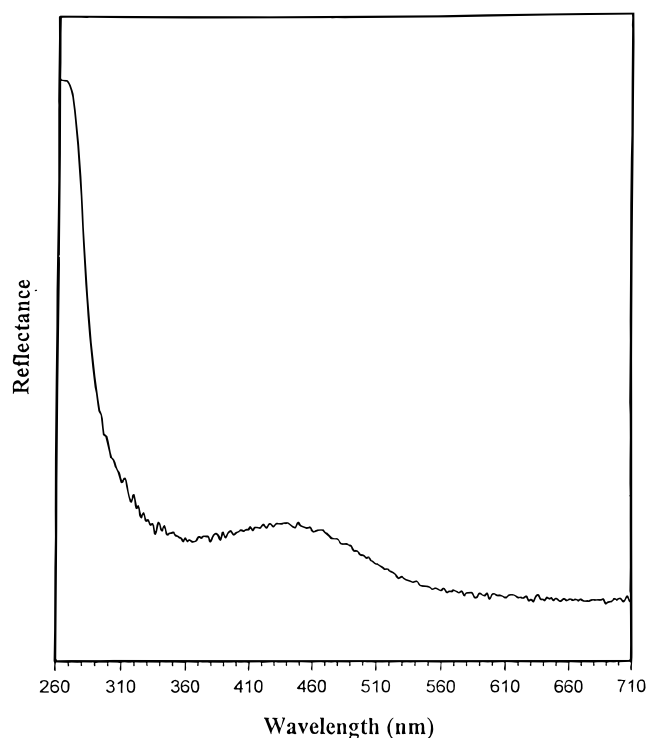


Figure 4. The reflectance electronic spectrum of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**) as a Nujol mull.

The reflectance electronic spectrum of **1**· 4MeCN as a Nujol mull is shown in Figure 4. The intense feature at 260 nm (38500 cm^{-1}) is assigned to the M \rightarrow L charge transfer band, as judged from the studies of other hexacyanometalate anions by Alexander and Gray.¹³ The reflectance spectrum also shows a broad d–d absorption centered at 439 nm , which is assigned to the ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition. The ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ band should be split if the $[\text{Ti}(\text{CN})_6]^{3-}$ anion is Jahn–Teller distorted, but we do not see such a splitting in the solid state spectrum.

The energy of the ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition is a direct measure of the d-orbital splitting: $10Dq$ is calculated to be 22800 cm^{-1} . As expected, this value is larger than those seen for other $\text{Ti}^{\text{III}}\text{L}_6$ complexes in which the ligands are lower in the spectrochemical series: the $10Dq$ values for $[\text{Ti}^{\text{III}}(\text{H}_2\text{O})_6]\text{Cl}_3$,⁵⁰ $(\text{NH}_4)_3[\text{Ti}^{\text{III}}\text{F}_6]$,⁵¹ and $(\text{C}_5\text{H}_6\text{N})_3[\text{Ti}^{\text{III}}\text{Cl}_6]$ ⁵² are $18\,600$, $17\,100$, and $11\,800\text{ cm}^{-1}$, respectively. In the trivalent hexacyanometalates, Alexander and Gray have demonstrated that $10Dq$ increases across the first row from chromium ($10Dq = 26600\text{ cm}^{-1}$) to cobalt ($10Dq = 34500\text{ cm}^{-1}$).¹³ The $22\,800\text{-cm}^{-1}$ value we observe for **1** is completely consistent with this trend (Table 3).

A solution UV–vis spectrum was obtained from a sample generated by adding tetraethylammonium cyanide to $\text{Ti}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$ in acetonitrile. This spectrum displays two features at 384 (26050 cm^{-1}) and 423 nm (23650 cm^{-1}). This spectrum differs from that seen for solid samples of $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$, and we cannot rule out the possibility that in solution a species such as $[\text{Ti}(\text{CN})_5(\text{MeCN})_2]^{-}$ is present. Alternatively, if the spectrum is actually that of the $[\text{Ti}(\text{CN})_6]^{3-}$ ion, then the splitting of the d–d band into two components separated by 2400 cm^{-1} reflects the presence of vibronic coupling between the excited electronic ${}^2\text{E}_g$ state and the ϵ_g normal vibration; equivalently, the single electron in the e_g^* orbital will induce a

(50) Hartmann, H.; Schläfer, H. L.; Hansen, K. H. *Z. Anorg. Allg. Chem.* **1956**, *284*, 151–161.

(51) Nassiff, P. J.; Couch, T. W.; Hatfield, W. E.; Villa, J. F. *Inorg. Chem.* **1971**, *10*, 368–373.

(52) Hartmann, H.; Hansen, K. H.; Schläfer, H. L. *Z. Anorg. Allg. Chem.* **1957**, *289*, 40–69.

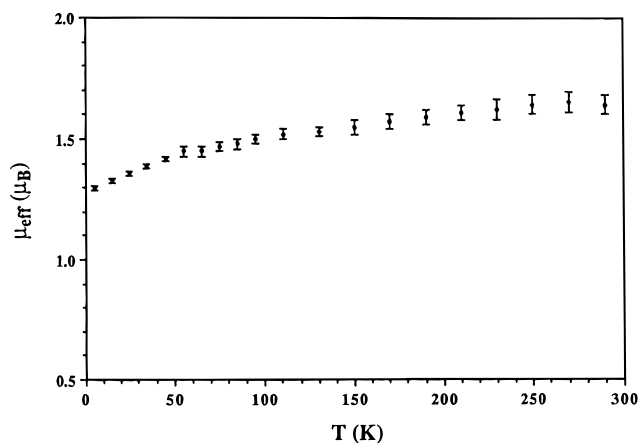


Figure 5. Temperature dependence of μ_{eff} per formula unit of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**) in an applied magnetic field of 500 G.

Jahn–Teller distortion, and the splitting represents the consequent lifting of the degeneracy.^{53,54} For comparison, other well-characterized $\text{Ti}^{\text{III}}\text{L}_6$ complexes exhibit electronic spectra that contain two bands split by 1500 to 3100 cm^{-1} .⁴¹

Electronic spectra have been reported for some of the other compounds claimed over the years to be cyanotitanates: Schläfer and Götz reported that “ $\text{K}_5[\text{Ti}^{\text{III}}(\text{CN})_8]$ ” in liquid ammonia displayed two bands at 22 300 and 18 900 cm^{-1} ,⁸ and Nicholls and Ryan reported that the black “ $\text{K}_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ ” residue they obtained displayed a band at 22 100 cm^{-1} and a shoulder at 18 300 cm^{-1} .¹² The general appearance of these spectra suggests that these workers may have obtained solids that contained the $[\text{Ti}(\text{CN})_6]^{3-}$ anion, but the dark colors of their bulk samples certainly do not agree with the yellow to orange color we observe for **1** and its acetonitrile solvate. Most likely, previous samples thought to contain the $[\text{Ti}(\text{CN})_6]^{3-}$ anion were probably contaminated with other titanium(III) species or with titanium(IV) centers, in which case charge transfer processes could explain the dark colors noted.

Magnetic Susceptibility. The temperature dependence of the magnetic moment per formula unit of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**) in an applied magnetic field of 500 G is shown in Figure 5; the curve is qualitatively identical with that found for many other octahedral titanium(III) complexes.^{51,55–62} At room temperature, the magnetic moment of 1.64(4) μ_B falls in the typical range of 1.50–1.70 μ_B observed for other magnetically-dilute pseudooctahedral titanium(III) complexes.⁶³ As the temperature is lowered, μ_{eff} slowly decreases and ultimately reaches a value of 1.30(1) μ_B at 5 K. Plots of χ^{-1} vs T are linear between 290 and 170 K; the Weiss constant θ , determined from the equation $\chi = C/(T - \theta)$, is -45 K (Figure 6).

The magnetic data are completely in accord with the presence of a single unpaired electron in $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$. The magnetic moments of virtually all titanium(III) salts decrease with

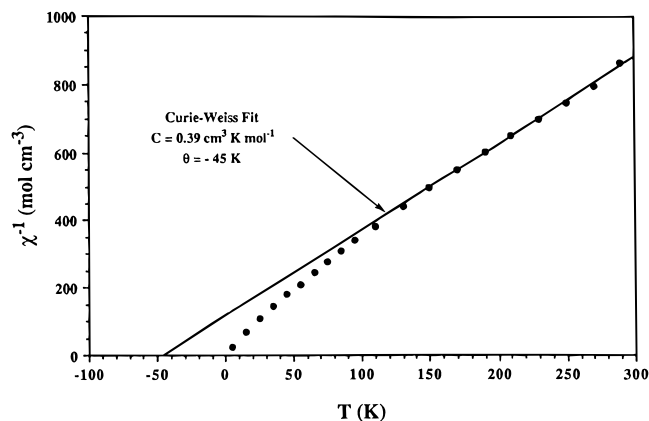


Figure 6. Temperature dependence of the reciprocal susceptibility of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**). The Curie–Weiss fit is shown by the straight line through the data points.

temperature; this may be a consequence of second-order Zeeman perturbations.^{2,64,65} It is difficult to distinguish this effect, however, from the presence of weak antiferromagnetic intermolecular interactions, which have been observed in other octahedral titanium(III) complexes in the solid state.⁴³ Analyses of magnetic data for d^1 complexes are commonly carried out according to Figgis’s method, which involves three fitting parameters: k (the orbital angular momentum reduction factor), δ (the splitting within the ${}^2\text{T}_{2g}$ level), and λ (the reduced spin–orbit coupling pertinent to the lowest term for the free ion).⁶⁶ The magnetic data for $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ correspond approximately to the following values for these parameters: $k \approx 0.75$, $\delta \approx 450$ cm^{-1} , and $\lambda \approx 150$ cm^{-1} . The positive value of δ implies that the orbital singlet ${}^2\text{B}_{2g}$ derived from ${}^2\text{T}_{2g}$ is the ground state of the $[\text{Ti}(\text{CN})_6]^{3-}$ ion, as it is for essentially all titanium(III) species. It is important to point out, however, that the magnetic data do not necessarily provide unique values for the fitting parameters: Carlin has shown that several quite different sets of values can give equally good fits to the data for titanium(III) complexes.⁶²

The magnetic moment of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (**1**) above 100 K is slightly field dependent: in an applied magnetic field of 1000 G, the room temperature magnetic moment is 1.55(5) μ_B . Thus for this compound the susceptibility decreases with increasing field. While the origin of this field dependence is unclear, similar magnetic behavior has been observed for some other titanium(III) complexes: the susceptibilities of several adducts of TiCl_3 with nitrogen donors decrease with increasing field, with the field dependence becoming less pronounced at lower temperatures.⁵⁶

Electron Paramagnetic Resonance Spectra. The EPR spectrum of the orange-colored acetonitrile solution prepared by adding $(\text{Et}_4\text{N})\text{CN}$ to $\text{Ti}(\text{MeCN})_3(\text{O}_3\text{SCF}_3)_3$ consists of a single isotropic signal at $g = 1.984$ (line width = 9 G) at 4 K. We cannot rule out the possibility that this signal is due to a species of lower symmetry such as $[\text{Ti}(\text{CN})_5(\text{MeCN})_2]^-$ (see above). The EPR spectrum of a powdered sample of **1** at 25 °C shows an isotropic resonance at $g = 1.971$ (peak-to-peak line width = 30 G). This g value is consistent with those of other titanium(III) species, although usually relaxation effects make it difficult to observe EPR spectra for such species at room temperature.^{43,61,65,67,68} When the powdered sample is cooled,

(64) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(65) Carlin, R. *Magnetochemistry*; Springer-Verlag: New York, 1986.

(66) Figgis, B. N. *Trans. Faraday Soc.* **1961**, *57*, 198–203.

(67) Gladney, H. M.; Swalen, J. D. *J. Chem. Phys.* **1964**, *42*, 1999–2010.

(53) Jorgensen, *Acta Chem. Scand.* **1957**, *11*, 73–85

(54) Liehr, A. D.; Ballhausen, C. J. *Ann. Phys. (New York)* **1958**, *3*, 304–319

(55) Clark, R. J. H.; Lewis, J.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379–387.

(56) McDonald, G. D.; Thompson, M.; Larsen, E. M. *Inorg. Chem.* **1968**, *7*, 648–655.

(57) Baker, J.; Figgis, B. N. *Aust. J. Chem.* **1980**, *33*, 2377–2385.

(58) Davis, P. H.; Wood, J. S. *Chem. Phys. Lett.* **1969**, *4*, 466–468.

(59) Baker, J.; Figgis, B. N. *Aust. J. Chem.* **1975**, *28*, 439–442.

(60) Schläfer, H. L.; Lenz, W.; Staab, J. Z. *Phys. Chem. (Munich)* **1968**, *62*, 290–311.

(61) Gigenbach, W.; Brubaker, C. H., Jr. *Inorg. Chem.* **1969**, *8*, 1131–1137.

(62) Carlin, R. L.; Terezakis, E. G. *J. Chem. Phys.* **1967**, *47*, 4901–4906.

(63) Brant, P.; Tornqvist, E. G. M. *Inorg. Chem.* **1986**, *25*, 3776–3779.

the signal at $g = 1.971$ broadens slightly (peak-to-peak line width = 55 G) but otherwise remains unchanged. In addition, however, two smaller resonances grow in: one near $g = 1.897$ becomes apparent at temperatures below 250 K, and a second near $g = 1.779$ becomes apparent at temperatures below 100 K. At 3.2 K, these two resonances appear at $g = 1.901$ (line width = 70 G) and 1.778 (line width = 140 G). These resonances are tentatively ascribed to an axially-distorted $[\text{Ti}(\text{CN})_6^{3-}]$ ion. For comparison, $\text{Rb}_3[\text{TiCl}_6]$ also gives an axial EPR spectrum, and the effects of the Jahn–Teller distortion on the electronic structure of this ion have been analyzed.⁴³

Concluding Remarks. Numerous investigators have sought to prepare cyanotitanate(III) complexes, but the results until now have been doubtful, inconclusive, or contradictory. By treating titanium(III) triflate with tetraethylammonium cyanide in acetonitrile, we have obtained the first authentic hexacyanotitanate(III) complex $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$. The magnetic and spectroscopic data clearly are consistent with the presence of a hexacyanotitanate(III) anion in this salt. Single-crystal X-ray diffraction studies unequivocally establish the presence of an almost undistorted octahedral structure for the $[\text{Ti}^{\text{III}}(\text{CN})_6^{3-}]$ anion in the solid state. Our attempts to use this hexacyanotitanate(III) salt as a building block for the construction of molecular magnets will be reported in due course.

Experimental Section

All operations were carried out in vacuum or under argon. Acetonitrile and toluene were distilled under N_2 from CaH_2 and Na, respectively, before use. Distilled water was sparged with argon prior to use. HO_3SCF_3 (Lancaster) was distilled in vacuum (bp 20 °C at 1 Torr) to remove colored impurities before use. $(\text{NEt}_4)\text{CN}$ was prepared according to the method of Andreades and Zahnow.⁶⁹ Anhydrous TiCl_3 (Cerac) was used as received.

Microanalyses were performed by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 1750 FTIR instrument. Far-IR spectra were recorded as Nujol mulls between CsI plates on a Nicolet 750 Magna-IR Spectrometer employing a Solid Substrate beamsplitter and a DGTS polyethylene detector. Reflectance spectra were recorded on a Hitachi U-3300 spectrophotometer equipped with an integrating sphere. Magnetic measurements were carried out with a low-field (1 T) Quantum Design MPMS² SQUID magnetometer. The diamagnetic correction for $[\text{NEt}_4]_3[\text{Ti}(\text{CN})_6]$ was estimated by using Pascal's constants:^{64,65} $\chi_{\text{dia}} = -410 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The X-band EPR spectra were recorded on a Bruker ESP 300 spectrometer.

Tris(acetonitrile)titanium(III) Trifluoromethanesulfonate $\text{Ti}^{\text{III}}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$. To TiCl_3 (1.0 g, 6.5 mmol) at -78°C was added trifluoromethanesulfonic acid (2.2 mL, 25 mmol). The dark-purple reaction mixture was slowly warmed to room temperature and then heated to 30 °C for 48 h (heating to higher temperatures causes decomposition). The resulting light blue–white precipitate was contaminated with a significant amount of unreacted dark-purple TiCl_3 . An additional aliquot of trifluoromethanesulfonic acid (2.0 mL, 23 mmol) was added, and the mixture was heated to 30 °C for an additional 24 h. The solvent was removed by vacuum distillation at 25 °C, and the resulting turquoise solid was extracted into acetonitrile (40 mL). The purple extract was filtered, and the filtrate was concentrated to ca. 7 mL and stored at -20°C for 12 h to give a sticky dark-purple solid. This solid was recrystallized from acetonitrile to give analytically pure material. Yield: 2.43 g (60%). Anal. Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{F}_9\text{O}_9\text{Ti}$: C, 17.48; H, 1.47; N, 6.80; Ti, 7.75. Found: C, 17.42; H, 1.45; N, 7.16; Ti, 7.68. IR (cm^{-1}): 3235 (s), 2322 (vs), 2293 (vs), 1653 (m), 1356 (vs), 1239 (vs), 1200 (vs), 1156 (vs), 972 (vs), 813 (w), 769 (m), 634 (vs), 605 (vs), 570 (w), 534 (m), 506 (s). The excess triflic acid must be removed from the crude pale-blue product in vacuum since the

standard procedure of washing the solid with diethyl ether dissolves the crude product.¹⁴ The infrared spectrum of the recrystallized triflate salt contains a noticeable OH stretch; this is most likely due to the presence of traces of water or triflic acid in the recrystallized product.

Tetraethylammonium Hexacyanotitanate(III) $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (1). To a purple solution of $\text{Ti}^{\text{III}}(\text{O}_3\text{SCF}_3)_3(\text{MeCN})_3$ (0.70 g, 1.1 mmol) in acetonitrile (22 mL) was added a clear solution of NEt_4CN (1.42 g, 9.1 mmol) in acetonitrile (40 mL). A dark brown–black precipitate formed immediately. The reaction mixture was warmed to 45 °C for ca. 10 min (higher temperatures result in decomposition of the product); at this point the solution was cloudy and orange. The solution was filtered, concentrated to ca. 50 mL, layered with toluene (2 mL), and stored at -20°C . After 24 h, a large crop of clear orange crystals was isolated. If crystallization does not occur within 24 h, additional toluene should be layered on top of the clear orange solution and cooling should be continued. The clear orange crystals were dried in vacuum, at which point they desolvated and turned into a yellow powder. Powdered samples of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6]$ (1) are extremely air sensitive and rigorous precautions must be taken to avoid exposing the sample to the atmosphere. Yield: 0.50 g (74%). Mp: 250 °C dec. Anal. Calcd for $\text{C}_{30}\text{H}_{60}\text{N}_9\text{Ti}$: C, 60.6; H, 10.17; N, 21.2; Ti, 8.05. Found: C, 60.2; H, 10.32; N, 20.4; Ti, 7.88. IR (cm^{-1}): 2200 (m), 2103 (w), 2093 (w), 2071 (vs), 1400 (vs), 1306 (s), 1272 (m), 1186 (vs), 1175 (vs), 1080 (m), 1033 (s), 1006 (vs), 792 (vs), 669 (w), 639 (w), 606 (m).

Crystallographic Studies.⁷⁰ Single crystals of $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$ grown from acetonitrile were mounted while still wet with the mother liquors on glass fibers with Paratone-N oil (Exxon) and immediately cooled to -75°C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and inspection of the diffraction pattern confirmed the crystal symmetry. Least-squares refinement of 25 reflections yielded the cell dimensions given in Table 1.

Data were collected in one quadrant of reciprocal space ($\pm h, -k, -l$) by using the measurement parameters listed in Table 1. Systematic absences for hkl ($h + k + l \neq 2n$) and $h0l$ ($h, l \neq 2n$) were consistent with space groups Ia and $I2/a$. The average values of the normalized structure factors suggested the centric choice $I2/a$, which was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.945 and 0.907. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data.

The structure was solved by using direct methods (SHELXS-86) and weighted difference Fourier methods. The correct positions for the Ti atom and the non-hydrogen atoms of one of the tetraethylammonium cations were deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms including two independent solvate molecules. The $[\text{Ti}(\text{CN})_6^{3-}]$ anion resides on an inversion center, and one of the $[\text{NEt}_4^+]$ cations (N6A–C68A) is disordered about a 2-fold axis. The N–C and C–C distances of the disordered $[\text{NEt}_4^+]$ cation were restrained to 1.52 and 1.54 Å, respectively, and chemically equivalent 1,3 C···C distances were restrained to be equal with an effective standard deviation of 0.01 Å. Methyl hydrogen atom positions were optimized by rotation about the C–C bond with idealized C–H, C···H, and H···H distances. The remaining hydrogen atoms were included as fixed idealized contributors with C–H = 0.99 Å. Non-hydrogen atoms were refined anisotropically, while the displacement parameters for hydrogen atoms were set to 1.2 times U_{eq} for the adjacent non-hydrogen atom. The relative site occupancy factor for the disordered acetonitrile positions (C81A–N8A) converged at 0.819(8). The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.1429P)^2 + 0.8085P]$ with $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected

(68) McGarvey, B. R. In *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 3, pp 89–201.

(69) Andreades, S.; Zahnow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 4181–4190.

(70) For a description of the crystallographic procedures and programs employed, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977–4982.

for both real and imaginary components of anomalous dispersion. Successful convergence was indicated by the maximum shift/error of 0.009 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final difference Fourier difference map ($0.441 \text{ e } \text{\AA}^{-3}$) was located in the vicinity of N7; the map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Acknowledgment. We thank the Department of Energy under Grant DEFG02-91ER45439 for support of this work and

Quantum Chemicals, E. I. DuPont de Nemours, and Amoco for fellowships to W.R.E.

Supporting Information Available: Tables of positional parameters, anisotropic displacement parameters, and full listing of bond distances and angles for $[\text{NEt}_4]_3[\text{Ti}^{\text{III}}(\text{CN})_6] \cdot 4\text{MeCN}$ (7 pages). See any current masthead page for ordering and Internet access instructions.

JA962773M