Inorganica Chimica Acta, 41 (1980) 233–237

Complex Cyanides of Titanium

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Received January 17, 1980

The new complex cyanides of titanium(III) $Rb_5Ti(CN)_8$, $Cs_4Ti(CN)_7$ and $K_3Ti(CN)_6$ have been prepared; $K_5Ti(CN)_8$, $Rb_5Ti(CN)_8$ and $Cs_4Ti(CN)_7$ are believed to contain seven coordinated titanium, while $K_3Ti(CN)_6$ probably contains an octahedral anion. A titanium(II) cyanide, $K_2Ti(CN)_4$ has been obtained by reduction of $K_3Ti(CN)_6$ with one equivalent of potassium in liquid ammonia. The extremely reactive titanium(0) cyanide complex $K_4Ti(CN)_4$ has been prepared by potassium reduction of a mixture of titanium(III) bromide and potassium cyanide in liquid ammonia.

Introduction

Despite the interest in the co-ordination chemistry of the cyanide ion, complexes of cyanide with titanium have been reported only in the last twenty years. Schlafer and Gotz [1] were the first to report the reaction between titanium(III) bromide and potassium cyanide in liquid ammonia; the grey-green product of formula $K_5Ti(CN)_8$ was formulated as $K_3[Ti(CN)_6]\cdot 2KCN$ on the basis of its electronic spectrum in ammonia solution and the observation of lines ascribed to KCN in the X-ray powder photograph. Whilst this formulation has been accepted by several authors [2–4], others [5, 6] have preferred an alternative formulation of $K_5[Ti(CN)_8]$. Yet another set of workers [7] have concluded that the average *g*-value of 1.990 (found by Goldring and Carrington) [5] is correctly accounted for by a six co-ordinated titanium(III) ion but that the electronic spectrum and magnetic susceptibility data are better accounted for by an eight coordinated titanium(III) ion. The only other report of a titanium cyanide complex is that by Heintz [3] who claims to have prepared the dark blue $K_3[Ti(CN)_6]$ by the aqueous reaction between titanium(III) chloride and potassium cyanide in the absence of air. A preliminary report of our findings in these systems has been published [9]. Evidence for the formation of titanium(III) cyanide in the reactions between titanium(III) halides and ammonium cyanide in liquid ammonia has recently been published [10].

Results and Discussion

The very high acidity of the $Ti^{4+}(aq)$ ion and the high acidity of the $Ti^{3+}(aq)$ ion relative to that of HCN militate against the preparation of cyanide complexes of titanium(IV) and titanium(III) in aqueous solution. We are unable to confirm the preparation [8] of $K_3[Ti(CN)_6]$ in aqueous solution. The dark blue precipitate we obtained in the reaction between titanium(III) chloride and aqueous potassium cyanide being titanium(III) hydroxide, HCN being displaced from solution by the stronger acid $[Ti(H_2O)_6]^{3+}$:

$$[Ti(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Ti(OH)(H_2O)_5]^{2+} + H_3O^+$$

$$H_3O^+ + CN^- \rightleftharpoons HCN + H_2O$$

In the more basic solvent, liquid ammonia, the titanium(III) halides are not solvolysed [11]. Since complex cyanides of titanium(III) are insoluble in liquid ammonia, it is necessary to use titanium(III) bromide as starting material so that the by-product potassium bromide can be removed by filtration and washing (potassium chloride is very sparingly soluble in liquid ammonia). We confirm that the reaction between $TiBr_3$ and KCN in ammonia yields [1] a grey-green precipitate of formula $K_5[Ti(CN)_8]$. No potassium cyanide can be removed from this material by many washings with liquid ammonia at temperatures in the range –33 to –60 °C (potassium cyanide has a negative temperature coefficient of solubility in liquid ammonia). The X-ray powder photograph of this solid shows amongst its many lines all those expected for KCN; however the reflectance spectrum (Table I) clearly shows three peaks assignable to d–d transitions and cannot be ascribed to the compound $K_3[Ti(CN)_6]\cdot 2KCN$. To clarify this dilemma we carried out the reactions of titanium(III) bromide with excesses of rubidium and caesium cyanides in ammonia; the grey-green insoluble products obtained had the compositions $Rb_5Ti(CN)_8$ and $Cs_4Ti(CN)_7$

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TABLE I. Spectroscopic and Magnetic Properties of Titanium Cyanide Complexes.

Composition	Electronic Spectrum (cm^{-1} × 10^3)		Magnetic Moment μ_{eff} (BM)	Infrared Spectrum (cm^{-1})		
	Charge-transfer	d–d		ν(C–N)	δ(TiCN)	ν(Ti–CN)
$K_5Ti(CN)_8$	47.0, 43.9, 37.3, 35.3	22.4, 16.8, 9.7	1.71	2200(w) 2172(m) 2113(w) 2082(vs) 2042(m)	437(s)	313(s)
$Rb_5Ti(CN)_8$	45.8, 42.7, 37.7, 32.0	22.2, 16.8, 9.2	1.78	2193(w) 2163(w) 2089(vs) 2081(vs) 2040(m)	436(s)	312(s)
$Cs_4Ti(CN)_7$	46.3, 42.8, 35.3, 32.3	22.5, 16.8, 9.7	1.69	2191(w) 2167(m) 2109(m) 2082(s) 2076(s) 2035(w)	434(s)	313(s)
$K_3Ti(CN)_6$	45.1, 36.7, 34.1, 28.1	22.1, 18.3(sh)	1.33	2088(s)	434(s)	311(s)
$K_2Ti(CN)_4$	44.9, 37.2	30.2, 24.3, 15.0	1.19	2073(w) 2035(w) 1945(s)	–	–
$K_4Ti(CN)_4$	46.0	28.0 (broad)	2.17	2012(w) 1943(vs)	–	–

respectively. These compounds have very similar reflectance spectra to that of the potassium salt but their X-ray powder photographs do not show lines due to RbCN or CsCN respectively. The appearance of lines due to KCN in $K_5Ti(CN)_8$ arises fortuitously. An analysis of the lines in the powder photograph of $K_5Ti(CN)_8$ shows the structure to be body-centred cubic. Potassium cyanide is *face*-centred cubic; this is recognisable from the $\sin^2\theta$ values which when divided by a common factor give the numbers 3, 4, 8, 11, 12, 16, 19 and so on. The common factor in this case happens to be numerically equal to the first $\sin^2\theta$ value in $K_5Ti(CN)_8$ and since the lattice of this compound is body centred cubic (and so gives rise to $\sin^2\theta$ ratios which are consecutive integers) then the lines found in KCN will be superimposable throughout the region. The compounds $K_5Ti(CN)_8$ and $Rb_5Ti(CN)_8$ are isomorphous; they have a lattice parameter, a, of 9.18 and 9.22 Å respectively. The caesium compound $Cs_4Ti(CN)_7$ also has a body centred cubic lattice with $a = 9.80$ Å.

In view of the great similarities in the electronic and infrared spectra of these compounds, we believe them all to contain titanium(III) in the same site symmetry and seven co-ordinated titanium(III) seems most likely. Complexes of stoichiometry ML_7 have been found only with pentagonal bipyramidal (D_{5h}) and mono-capped trigonal prismatic (C_{2v}) structures. The D_{5h} structure recently found [12] for $[V(CN)_7]^{4-}$ can be eliminated since only two d–d bands would be expected for a d^1 system [13] and only two infrared bands in the C≡N stretching region. The C_{2v} structure however, is expected to give rise to three bands [9] in the electronic spectrum of the d^1 ion and six infrared bands in the C≡N stretching region. Six cyanide stretching bands are indeed found in the spectrum of $Cs_4Ti(CN)_7$ and five in the spectra of the potassium and ribidium salts (Table I). Unfortunately these compounds are not amenable to Raman spectral studies nor do they dissolve in solvents with which they do not react. In the absence of crystals suitable for crystal structure determinations we are forced to conclude that the most likely structure for these compounds is one containing the C_{2v} $[Ti(CN)_7]^{4-}$ anion. Such a structure is also believed to occur [14] in $[Mo(CN)_7]^{4-}$ although $[Mo(CN)_7]^{5-}$ has recently been shown to contain an anion of D_{5h} symmetry in the sodium salt.

In an attempt to remove any unco-ordinated potassium cyanide from $K_5Ti(CN)_8$ we have studied the thermal decomposition of this material. At 280 °C *in vacuo* the grey-green solid becomes dark grey and extraction of this solid with liquid ammonia at −40 °C yields a filtrate of potassium cyanide and an almost black residue of $K_3Ti(CN)_6$. This shows (Table I) only one ν(CN) and an electronic spectrum typical of octahedrally co-ordinated d^1 ions. We therefore believe this material to contain the $[Ti(CN)_6]^{3-}$ ion; thus we find 10 Dq = 22.100 cm^{-1}. This conclusion is fortuitously in agreement with the earlier result obtained by Schlafer and Gotz [1] who obtained the visible spectrum of $K_5Ti(CN)_8$ but missed the band in the near infrared and hence concluded that $K_5Ti(CN)_8$ should be formulated as $K_3[Ti(CN)_6]$, 2KCN. This value for 10 Dq is in line with the values for other ligands in the spectrochemical series of titanium(III) (H_2O, 20.000 [15], NH_3 [10] ~ 21.000 cm^{-1}) and with the expectation that 10 Dq (and π-bonding) in the complexes $[M(CN)_6]^{3-}$ decreases markedly as the number of t_{2g} electrons decreases from six (M = Co) to one (M = Ti). A corresponding effect is also seen in the far infrared spectra of these complexes; the frequencies of both the M–C stretching and the MCN bending modes decrease steadily (linearly in the former case) as the number of t_{2g} electrons decreases [16, 17] and our data for the d^1 species fits well into these series (we have followed the practice of Jones [15] in quoting ν(Ti–CN) below δ(Ti–CN) but it should be understood that it is not known absolutely which assignment is correct). The low magnetic moment of $K_3Ti(CN)_6$ is presumably due to antiferromagnetic interactions. The X-ray powder photograph of $K_3Ti(CN)_6$ reveals that it has a body centred cubic lattice with a lattice parameter of 9.02 Å. The compound is thus not isomorphous with the complexes $K_3[M(CN)_6]$ (M = Cr, Mn, Fe) which are known to have either orthorhombic or monoclinic crystal structures. The higher symmetry cubic structure is much more akin to the compounds of the type $Cs_2Li[M(CN)_6]$ [16].

The reduction of $K_5Ti(CN)_8$ with potassium in liquid ammonia leads only to heterogeneous products. Treatment of $K_3Ti(CN)_6$ with one equivalent of potassium in liquid ammonia however, yields the titanium(II) species, $K_2Ti(CN)_4$. This has a low ν(CN) in accord with the lower oxidation state of the titanium and in aqueous ammonia affords a gelatinous brown precipitate ($Ti(OH)_2$) which rapidly becomes blue ($Ti(OH)_3$). Whilst the magnetic moment is inexplicable the electronic spectrum (Table I) is assignable to the three octahedral transitions from the $^3T_{1g}(F)$ state to the $^3T_{2g}$ (15.000 cm^{-1}), $^3T_{1g}(P)$ (24,300 cm^{-1}) and $^3A_{2g}$ (30,200 cm^{-1}) states giving a reasonable value of 10 Dq = 16.200 cm^{-1} but a high value of the Racah parameter B = 706 cm^{-1} (Ti^{2+} free ion value for B = 718 cm^{-1}). The i.r. spectrum is in agreement with six co-ordination around titanium in as much as the high cyanide stretching frequencies are assignable to bridging cyanides and the 1945 cm^{-1} peak to terminal cyanide.

The reduction of titanium(III) bromide with potassium in liquid ammonia in the presence of an excess of potassium cyanide produces the black insoluble $K_4Ti(CN)_4$. This paramagnetic material gives an e.s.r. spectrum showing a g value of 1.993 but only very broad absorption in its electronic spectrum. The lowest ν(CN) is below the single band found in $K_4Ni(CN)_4$ (1985 cm^{-1}) [18] and since a greater degree M–C π-bonding is expected in the latter, this would imply different structures for these two compounds. The nickel compound is believed to have a tetrahedral structure; the titanium compound is more likely to have a structure possessing bridging as well as terminal cyanide groups. Whilst $K_4Ti(CN)_4$ is stable under dry argon it is extremely susceptible to oxidation and hydrolysis and is pyrophoric in even traces of air. Hydrolysis by pure water in the absence of air results in reduction of the cyanide ion to methane and ammonia; hydrogen is also evolved and blue $Ti(OH)_3$ remains. In liquid ammonia suspension, $K_4Ti(CN)_4$ does not react with carbon monoxide at atmospheric pressure but reacts with 2,2′-dipyridyl to form a purple solution of K^+dipy^- and leave a brown residue of $KTi(NH)_2$. The tetracyanotitanate(0) is thus an extremely powerful reducing agent; it reduces 2,2′-dipyridyl to its anion becoming oxidised to a titanium(III) species which then undergoes ammonolysis in the presence of K^+dipy^-. Potassium imidotitanate(III) is known [19] to be the product of reaction between potassium amide and potassium hexakis(isothiocyanato)titanate(III) in liquid ammonia.

Experimental

All reactions were carried out using high *vacuum* apparatus and liquid ammonia techniques which are described elsewhere [20]. All compounds were removed from the apparatus and handled subsequently under an atmosphere of dry argon. Microanalyses were by the Alfred Bernhardt Laboratory, Engleskirchen, W. Germany. Titanium(III) bromide was prepared by the standard literature method [21]. Potassium cyanide was dried by evacuation at 100 °C for 24 h. Rubidium and caesium cyanides were prepared by passing hydrogen cyanide through ethanolic solutions of the hydroxides; the crystals so formed were filtered off, washed with ethoxyethane and dried *in vacuo* at 100 °C. X-ray powder photographs were obtained on a 114.6 mm Debye–Scherer camera using nickel filtered Cu-K_α radiation. Magnetic moments were by the Gouy method at room temperature.

Reaction of Titanium(III) Bromide with Potassium Cyanide

Liquid ammonia (200 cm^3) was condensed *in vacuo* on to a mixture of $TiBr_3$ (3.5 g) and KCN (9.7 g) and the mixture stirred at around –40 °C for several hours. After filtration at –60 °C the dark green insoluble product was washed at this temperature eight times with liquid ammonia (100 cm^3). The product was dried by evacuation for eight hours at room temperature to give a grey-green powder. (*Anal.* Found: C, 20.7; N, 24.1; K, 42.3; Ti, 10.2; $K_5Ti(CN)_8$ requires: C, 21.28; N, 24.82; K, 43.30; Ti, 10.61%). X-ray powder photograph d spacings (relative intensities in parentheses): 6.47(20), 4.58(10), 4.06(10), 3.74(50), 3.24(40), 2.92(100), 2.61(10), 2.45(80), 2.30(20), 2.17(10), 2.05(30), 1.96(30), 1.87(10), 1.80(30), 1.66(10), 1.63(10), 1.58(10), 1.49(30), 1.45(10), 1.42(10), 1.35(10), 1.33(10), 1.30(10).

Reaction of Titanium(III) Bromide with Rubidium Cyanide

This was carried out as for the reaction with potassium cyanide but using typically $TiBr_3$ (1.3 g) and RbCN (4.0 g) to obtain a pale grey-green powder (*Anal.* Found: C, 13.8; N, 16.2: Rb, 62.4; Ti, 7.25; $Rb_5Ti(CN)_8$ requires: C, 14.06; N, 16.40; Rb, 62.53; Ti, 7.01%). Powder photograph: 3.77(70), 3.26(30), 2.92(100), 2.56(20), 2.47(80), 2.31(10), 2.18(10), 2.07(70), 1.97(40), 1.89(10), 1.82(70), 1.70(30), 1.64(10), 1.60(10), 1.51(50), 1.47(10), 1.44(20), 1.38(10), 1.35(10), 1.32(10), 1.29(20), 1.27(20).

Reaction of Titanium(III) Bromide with Caesium Cyanide

This was carried out as above but using typically $TiBr_3$ (1.1 g) and CsCN(5.8 g) to obtain a grey-green powder (*Anal.* Found: C, 10.9; N, 12.7; Cs, 69.5: Ti, 6.2; $Cs_4Ti(CN)_7$ requires: C, 11.04; N, 12.87; Cs, 69.80; Ti, 6.29%). Powder photograph: 4.00 (100), 3.10(80), 2.61(90), 2.20(60), 2.09(50), 1.92(70), 1.59(80).

Preparation of Potassium Hexacyanotitanate(III)

$K_5Ti(CN)_8$ was heated *in vacuo* for 6 h at 280 °C when the material became dark grey. Upon cooling and extracting with liquid ammonia until no further soluble material could be extracted, a black residue remained which was evacuated at 70 °C prior to analysis. (*Anal.* Found: C, 22.1; N, 25.9; K, 36.5; Ti, 14.6; $K_3Ti(CN)_6$ requires: C, 22.43; N, 26.16; K, 36.51; Ti, 14.91%). Powder photograph: 6.37(20), 4.5(vw), 3.67(60), 3.21(20), 2.85(100), 2.6(vw), 2.41 (60), 2.25(10), 2.13(10), 2.01(20), 1.92(20), 1.84(20), 1.77(20), 1.65(vw), 1.47(vw).

Preparation of Potassium Tetracyanotitanate(II)

Liquid ammonia was condensed on to a mixture of $K_3Ti(CN)_6$ (1.29 g) and potassium (0.16 g) and the mixture agitated at –33 °C for 15 minutes; after this time the blue colour of the potassium solution had faded considerably. The black residue was filtered off, washed several times with liquid ammonia (100 cm^3) and dried by evacuation at room temperature. (*Anal.* Found: C, 20.3; N, 24.1; K, 33.8; Ti 21.0; $K_2Ti(CN)_4$ requires: C, 20.87; N, 24.34; K, 33.98; Ti, 20.81%). Evaporation of the combined filtrates left a white solid whose i.r. spectrum and qualitative tests indicated it to be potassium cyanide.

Preparation of Potassium Tetracyanotitanate(0)

An excess of potassium (5 g) was added to a mixture of $TiBr_3$ (3.4 g) and KCN (8.4 g) in liquid ammonia (150 cm^3). The deep blue-black mixture was maintained at –78 °C for 15 h and then filtered. The black residue was extracted six times with liquid ammonia (100 cm^3) and then evacuated at 50 °C. (*Anal.* Found: C, 15.3; N, 18.0; K, 50.8; Ti, 15.4; $K_4Ti(CN)_4$ requires: C, 15.58; N, 18.17; K, 50.72; Ti, 15.53%).

Reactions of $K_4Ti(CN)_4$

(i) With Water

Degassed water (10 cm^3) was condensed on to $K_4Ti(CN)_4$ (0.2 g) *in vacuo* at –196 °C. The mixture was allowed to warm slowly and as soon as the ice melted a violent exothermic reaction occurred. The non condensible gases evolved (identified by g.l.c. and mass spectrometry) were methane and hydrogen; the relative amounts of each however varied from experiment to experiment owing to the heterogeneous nature of the reaction. Ammonia was the only condensible gas found and the residues were titanium(III) hydroxide (i.r. and qualitative tests).

(ii) With 2,2'-dipyridyl

A saturated solution of dipy (5 g) in liquid ammonia was added to a suspension of $K_4Ti(CN)_4$ (2 g) in ammonia at –50 °C to produce an intensely purple solution and a dark precipitate. Filtration and repeated extraction of this precipitate left a dark brown pyrophoric powder which was dried *in vacuo* at room temperature. (*Anal.* Found: N, 23.3; K, 32.8; Ti, 39.8; $KTi(NH)_2$ requires: N, 23.93; K. 33.42; Ti 40.94%). I.r. spectrum shows ν(N–H) but no ν(C≡N). The dried filtrate was a purple mixture which became white immediately when exposed to moist air; its i.r. spectrum indicated it to contain KCN and K^+dipy^-; qualitative tests for titanium were negative.

Acknowledgment

We thank the Science Research Council for a maintenance grant (to T.A.R.).

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