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Complex Cyanides of Zirconium(0)

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Curiously there are no known cyanides, simple or complex, of zirconium, and no attempts to stabilize low oxidation states of zirconium with cyanide ions have been reported. Indeed complexes of zirconium in formally low oxidation states are known only with delocalised organic anions [1]. Complex cyanides of titanium have only been prepared using liquid ammonia solutions [2] and we consequently chose this solvent in our attempts to prepare zirconium cyanide complexes. Under conditions which were expected to produce zirconium(III) cyanide complexes we have obtained the zirconium(0) complexes $K_5Zr(CN)_5$ and $Rb_5Zr(CN)_5$.

Results and Discussion

The reaction between zirconium(III) bromide and liquid ammonia gives an adduct $ZrBr_3 \cdot 6NH_3$ with no ammonolysis and with no change in oxidation state of the zirconium. When treated with an excess of either potassium or rubidium cyanides in anhydrous ammonia at –50 °C however, zirconium(III) bromide yields ammonia-insoluble grey compounds of formula $M^I_5Zr(CN)_5$. These compounds are air and moisture sensitive but far less so than the titanium compound $K_4Ti(CN)_4$ [2]. The magnetic moment of $K_5Zr(CN)_5$ is 2.69 BM at room temperature and it gives an e.s.r. spectrum with $g = 1.986$. The possibility of formulating this complex as containing zirconium(III) (d^1) is thus ruled out. Since the reduction potential of zirconium(III) is believed to be more negative than that of potassium in liquid ammonia [3] it is unlikely that zirconium(III) has been reduced by cyanide ion in our reaction. Furthermore we find the filtrate from the reaction contains predominantly zirconium(IV) and that the distribution of zirconium between the insoluble and soluble products of the reaction is in accord with the disproportionation reaction (unsolvated species written for simplicity):

$$4ZrBr_3 + 5KCN + 6NH_3 \longrightarrow K_5Zr(CN)_5 + 3ZrBr_3(NH_2) + 3NH_4Br$$

While such a disproportionation ($4Zr(III) \rightarrow Zr(0) + 3Zr(IV)$) seems remarkable, it is not unknown in zirconium(III) chemistry. Larsen [4] has proposed a disproportionation in the reaction of zirconium(III) chloride with an excess of lutidine, identifying zirconium(IV) but not the other oxidation state of the zirconium.

The X-ray powder photograph on $K_5Zr(CN)_5$ confirms the absence of any free KCN. The infrared spectrum shows at least five bands in the C≡N stretching region at 2195, 2173, 2112, 2097 and 2073 cm^{-1} (unfortunately the compound is not amenable to Raman study). A rather low symmetry to the $Zr(CN)_5$ grouping is thus indicated (D_{3h} and C_{4v} structures would give rise to only two and three bands respectively in this region). Possible structures include a distorted trigonal bipyramidal structure (C_{2v}) for which $3A_1 + 1B_1 + 1B_2$ modes are expected and a bridging octahedral dimer (C_{2h}) for which there would be $1A_u + 4B_u$ i.r. active modes. The compounds are not soluble in solvents with which they do not react. The diffuse reflectance spectrum of $K_5Zr(CN)_5$ shows bands at 45 800, 36 100(sh), 29 400, 21 000, 18700 and 10 000 cm^{-1}.

Experimental

Zirconium(III) bromide was prepared from zirconium(IV) bromide and aluminium powder at 300°C. In the reaction of $ZrBr_3$ with liquid ammonia, a brown insoluble product formed which became dark brown and crystalline upon evacuation at room temperature (Found: NH_3, 23.2; Br, 55.8; Zr, 21.4; $ZrBr_3(NH_3)_6$ *requires* NH_3, 23.59; Br, 55.35; Zr, 21.06%).

Preparation of $K_5Zr(CN)_5$ and $Rb_5Zr(CN)_5$

Liquid ammonia (100 cm^3) was condensed onto a mixture of $ZrBr_3$ (~ 2 g) and an excess of the alkali metal cyanide (~ 10–12 mol ratios) and the reaction mixture warmed to around – 50 °C. The dark precipitate which formed was then filtered off from the brown filtrate *in vacuo* and washed many times with redistilled liquid ammonia to remove soluble materials. The solid was then evacuated at room temperature for 6 hours prior to removal from the vacuum line under an atmosphere of dried nitrogen to yield a grey powder. *Anal.* Found, using KCN; C, 14.57; N, 16.33; K, 46.71; Zr, 21.60; $K_5Zr(CN)_5$ requires C, 14.41; N, 16.80; K, 46.91; Zr, 21.88%; using RbCN; C, 9.13; N, 10.61; Rb, 65.63; Zr, 13.85; $Rb_5Zr(CN)_5$ requires C, 9.26; N, 10.80; Rb, 65.88; Zr, 14.06%. In the $K_5Zr(CN)_5$ preparation the distribution of zirconium between the insoluble and soluble reaction products was: insoluble 23.4; soluble

76.6% (the disproportionation 4Zr(III) → Zr(0) + 3Zr(IV) requires insoluble 25.0, soluble 75.0%). The i.r. spectrum on the dried filtrate showed the presence of NH_4^+ and was typical of ammoniated transition metal amides. The electronic spectrum of this filtrate showed bands at 47 500 and 28 500 cm^{-1} with no bands at lower energies as are found in Zr(III) spectra and in $K_5Zr(CN)_5$.

References

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