The Chemistry of Polyhalozirconates.
Part 1. Zirconium Oxide Chloride, a Source of the Anions $ZrCl_5^-$ and $ZrCl_6^{2-}$

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Abstract

Conductimetric studies of thionyl chloride solutions of $ZrCl_4$ and $ZrOCl_2 \cdot 8H_2O$ indicate that the solvated species in the two solutions are different. From such solutions the synthesis of two types of pentachlorozirconates are reported. The synthesis of hexachlorozirconates from each solution is also reported.

Introduction

Hexachlorozirconates have been prepared previously by treating thionyl chloride solutions of zirconium tetrachloride with quaternary ammonium chlorides [1]. Drake and Fowles report the isolation of only impure products from the addition of quaternary ammonium chlorides to a solution of zirconium tetrachloride, although this can be avoided by saturating the zirconium solution with hydrogen chloride [2]. Clearly such methods are not suitable for the preparation of pentachlorozirconates. We now report the use of thionyl chloride solutions of zirconium oxide chloride and zirconium tetrachloride for the synthesis of pentachlorozirconates and hexachlorozirconates. Similar alkali metal hexachlorozirconates have been isolated from fused salt melts or by the reaction of gaseous zirconium tetrachloride with alkali metal chlorides at elevated temperatures [3, 4]. Recently the isolation of the adduct $ZrCl_4 \cdot SOCl_2$ has been reported from the dehydration of zirconium oxide chloride by thionyl chloride [5]. The only previous reports of the synthesis of a pentachlorozirconate was by a rather inconvenient electrochemical method [6], and the reaction of zirconium tetrachloride with 18-crown-6 to give the product $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl]ZrCl_5$ [7]; an acetonitrile adduct has also been reported [8].

Experimental

Infrared spectra were measured using a Pye Unicam SP3-100 grating instrument and Perkin-Elmer 337, 157G and 521 spectrometers.

Zirconium was determined by precipitation as the tetramandelate followed by pyrolysis to zirconium dioxide [9]. Chloride was determined by Volhards method. Carbon, hydrogen and nitrogen analysis was carried out by Butterworth Microanalytical Consultancy Ltd.

Conductance measurements were made with an Irwin ER 1915 conductance bridge.

Conductimetric Titration Studies

Standard solutions of zirconium(IV) were prepared by stirring the oxide chloride with thionyl chloride until dissolution was complete (12–18 h).

(a) Addition of $(CH_3)_4NCl$ solution to the zirconium(IV) solution derived from $ZrOCl_2 8H_2O$

In a typical experiment a 15 ml aliquot of the zirconium solution (0.1034 M) is diluted with thionyl chloride (50 cm^3) and titrated with tetramethylammonium chloride (0.1068 M) in thionyl chloride. The conductance is recorded after the addition of each 1 cm^3 aliquot of titrant; the results are shown graphically in Fig. 1. As the conductivity falls from the maximum value a cloudy precipitate is formed which appears to reach a maximum opacity after the addition of *ca.* 20 cm^3 of titrant. During further additions of the titrant, the conductivity increases
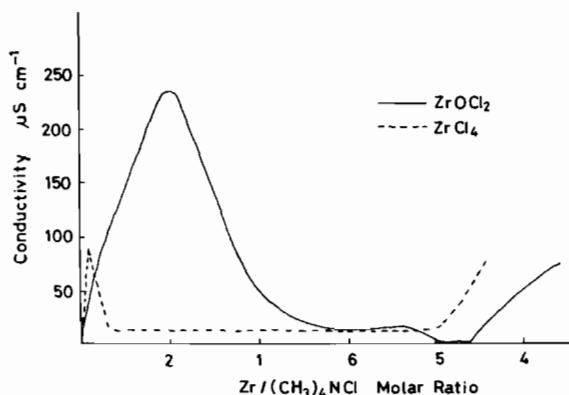

Fig. 1. Conductivity *vs.* Zr/$(CH_3)_4$NCl molar ratio for the titration of zirconium solutions with tetramethylammonium chloride solution.

temporarily but slowly falls back to the equilibrium value.

(b) Addition of zirconium(IV) solution derived from ZrOCl₂·8H₂O to (CH₃)₄NCl solution

In a typical experiment a 10 cm³ aliquot of tetramethylammonium chloride solution (0.1068 M) was diluted with thionyl chloride (30 cm³) and titrated with the zirconium(IV) solution (0.1034 M). The conductance gradually decreases with the addition of titrant until a minimum is reached at a ratio of 2 moles quaternary ammonium salt : 1 mole zirconium.

(c) Addition of (CH₃)₄NCl solution to ZrCl₄ solution

A 10 cm³ aliquot of zirconium tetrachloride solution (0.0969 M) diluted with thionyl chloride (30 cm³) was titrated with tetramethylammonium chloride solution (0.0948 M). The addition of the first two 0.5 cm³ aliquots of the titrant produced an increase in conductance. At this stage the conductance decreased and reached a minimum value after about 15 min with no further additions of titrant. This minimum value persisted with further addition of titrant until 20 cm³ had been added. Further additions of titrant produced a rise in conductance. The results are shown graphically in Fig. 1.

Preparation of Tetramethylammonium Hexachlorozirconate(IV) From Zirconium Oxide Chloride

A solution of tetramethylammonium chloride (24.0 g, 0.22 mol) in thionyl chloride was added slowly to a solution of zirconium oxide chloride (18.0 g, 0.056 mol) in 700 cm³ of thionyl chloride. A precipitate formed immediately, this was separated by filtration, washed with thionyl chloride and dried *in vacuo* to yield a white solid (14.3 g, 56% yield). *Anal.* Found: Zr, 19.26; Cl, 47.8; C, 21.00; H, 5.19; N, 6.38. Calc. for $[(CH_3)_4N]_2[ZrCl_6]$: Zr, 20.2; Cl, 47.1; C, 21.2; H, 6.2; N, 6.19%. The infrared absorption spectrum shows bands at 3040(m, sp), 1655(s, sh), 1478(s, sp), 1441(s, sh), 1435(w, sp), 1410(w, sh), 1282(m, sp), 942(s, sh), 665(w, sp), 655(m, b), 510(w, m), 448(w, sh), 318(s, sh), 302(s, b), 280(s, b), 190(s, b), 173(s, b) cm⁻¹, which was identical with that of a sample of tetramethylammonium hexachlorozirconate(IV) prepared from zirconium tetrachloride in thionyl chloride.

Preparation of Bis(tetramethylammonium) Hexachlorozirconate from Zirconium Tetrachloride

To a solution of zirconium tetrachloride (2.0 g, 8.78×10^{-3} mol in 100 cm³ $SOCl_2$) was added a solution of tetramethylammonium chloride (3.68 g, 0.034 mol in 100 cm³ $SOCl_2$) and the resultant suspension stirred for 2 h to ensure complete

precipitation. The precipitate was separated by filtration, washed with thionyl chloride, and dried *in vacuo* to yield a white solid (3.5 g, 90% yield). *Anal.* Found: Zr, 19.0; Cl, 46.1; C, 21.08; N, 6.38; H, 5.28. Calc. for $[(CH_3)_4N]_2[ZrCl_6]$: Zr, 20.2; Cl, 47.1; C, 21.2; N, 6.19; H, 6.2%.

Preparation of Tetramethylammonium Pentachlorozirconate(IV)

(a) In 'normal' laboratory conditions

A solution of tetramethylammonium chloride (2.04 g, 0.0186 mol) in thionyl chloride (100 cm³) was added slowly to a solution of zirconium oxide chloride octahydrate (6.0 g, 0.0186 mol) in thionyl chloride (100 cm³). An immediate precipitate formed and the solution was stirred for a further 12 h to ensure complete reaction. The product was separated by filtration, washed with thionyl chloride, and dried *in vacuo* to yield a white solid (5.14 g, 85%). *Anal.* Found: Zr, 28.3; Cl, 43.4. Calc. for $[(CH_3)_4N]$-$[ZrCl_4(OH)]$: Zr, 28.1; Cl, 43.8%. Infrared spectroscopic analysis over the range 4000–650 cm⁻¹ showed the following absorption bands: 3230(s, b), 1615(w, b), 1490(s, sh), 1290(w, sh), 952(s, sh).

(b) In a dry atmosphere

A solution of tetramethylammonium chloride (2.0 g, 0.018 mol) in thionyl chloride (50 cm³) was added dropwise with rapid stirring to a solution of zirconium oxide chloride octahydrate (7.0 g, 0.022 mol) in thionyl chloride (100 cm³). The resultant suspension was stirred for 1½ h to ensure complete reaction and the precipitate separated by filtration in a nitrogen atmosphere using Schlenk tubes. The precipitate was dried in a stream of nitrogen and finally dried *in vacuo* to yield a white product (6.2 g). *Anal.* Found: Zr, 26.89; Cl, 50.4; C, 13.81; H, 3.89; N, 4.16. Calc. for $[(CH_3)_4N][ZrCl_5]$: Zr, 26.62; Cl, 51.73; C, 14.02; H, 3.54; N, 4.09%. Infrared spectroscopic bands are observed at 3100–3600(w, b), 1620(w, sp), 1160(w, b), 1045(w, b), 952(s, sp), 725(s, sp), 323(s, sp), 295(s, sh), 288(s, sp), and X-ray powder diffraction data is given in Table I.

(c) From zirconium tetrachloride

A solution of tetramethylammonium chloride (3.2 g, 0.03 mol) in thionyl chloride (30 cm³) was added dropwise with constant stirring to a thionyl chloride (100 cm³) solution of zirconium tetrachloride (7.0 g, 0.03 mol). A white gelatinous precipitate was formed which was separated by filtration in a nitrogen atmosphere. The product was dried under vacuum, during which time the gelatinous appearance faded to leave a white crystalline powder (7.15 g). *Anal.* Found: Zr, 27.2; Cl, 51.6; C, 14.6; H, 3.8; N, 4.09. Calc. for $C_4H_{12}NZrCl_5$: Zr, 26.62; Cl, 51.73; C, 14.02; H, 3.54; N, 4.09%. Infrared spectroscopic

TABLE I. X-ray Powder Data for Two Different Samples of $[(CH_3)_4N]ZrCl_5$

Starting material	d values of product
$ZrOCl_2 \cdot 8H_2O$	7.368(1), 4.667(0.6), 3.862(0.2), 3.704(0.1), 3.422(0.4), 2.882(0.1), 2.492(0.3), 2.148(0.1), 1.893(0.05)
$ZrCl_4$	9.872(1.0), 7.368(0.8). 6.802(0.5), 5.708(0.9), 5.062(0.6), 4.667(0.5), 4.226(0.4), 3.862(0.1), 3.558(0.6), 3.183(0.1), 2.882(0.1), 2.711(0.8), 2.525(0.2), 2.427(0.1), 2.365(0.1), 2.307(1.0), 2.251(0.1), 2.199(0.05), 2.148(0.05), 2.101(0.05)

bands are observed at: 3100–3600(w, b), 1620(w, sh), 1170(w, b), 1040(w, b), 955(s, sp), 728(s, sh), 298(s, b) cm^{-1} and X-ray powder diffraction data is presented in Table I.

Discussion

Zirconium oxide chloride reacts with thionyl chloride in two stages. In the first stage sulphur dioxide and hydrogen chloride are rapidly evolved due to the reaction of interstitial water and some coordinated water with the thionyl chloride, at this stage the compound $ZrOCl_2 \cdot 3H_2O$ may be isolated. During the second state of the reaction sulphur dioxide and hydrogen chloride are evolved much more slowly as the remainder of the coordinated water and the hydroxo bridges react with the thionyl chloride. The adduct $ZrCl_4 \cdot SOCl_2$ may be isolated from the resultant solution [5]. Titration of this solution with tetramethylammonium chloride (TMAC) shows five distinct stages (Fig. 1): an increase in conductance to a maximum value, a fall in conductance to a plateau value, a region of little change in conductance, a small region of virtually zero conductance, and finally a steady rise in conductance with further additions of titrant.

The initial low value of conductance is attributed to the self-ionisation

$$ZrCl_4(SOCl_2)_n \longrightarrow SOCl^+ + ZrCl_5(SOCl_2)_{n-1}^-$$
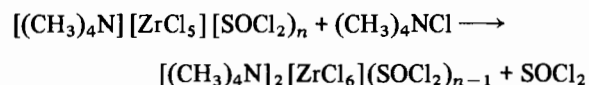
With the addition of titrant the conductance increases to a sharp maximum which is believed to be due to the formation of solvated pentachlorozirconate ions and tetramethylammonium ions:

$$ZrCl_4(SOCl_2)_n + (CH_3)_4NCl \longrightarrow$$
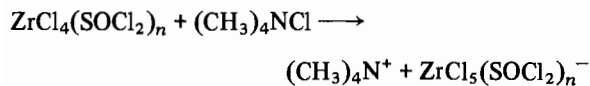
$$(CH_3)_4N^+ + ZrCl_5(SOCl_2)_n^-$$

At the conductance maximum the solubility product of the compound $[(CH_3)_4N][ZrCl_5](SOCl_2)_n$ is exceeded and precipitation begins. Indeed, it appears

most likely that during the period of increasing conductance the solution becomes supersaturated since otherwise a high plateau value would have been expected until all the $ZrCl_4(SOCl_2)_n$ was converted to the pentachlorozirconate salt. This supersaturation is perhaps not surprising since the $ZrCl_5^-$ ion will be heavily solvated with thionyl chloride. Further additions of titrant result in further precipitation and a lowering of the conductance as more and more zirconium is removed from solution as the pentachlorozirconate, a process no doubt aided by the presence of the initially-formed solid. Once the low plateau value of conductance is reached further additions of titrant result in a temporary increase in conductance which soon settles back to the plateau value. This is attributed to a slower reaction of TMAC with the precipitated pentachlorozirconate to give the corresponding hexachlorozirconate

$$[(CH_3)_4N][ZrCl_5][SOCl_2]_n + (CH_3)_4NCl \longrightarrow$$

$$[(CH_3)_4N]_2[ZrCl_6](SOCl_2)_{n-1} + SOCl_2$$

This reaction is complete when Zr:TMAC = 1:2 and the conductance falls to zero. Further additions of titrant show the expected increase in conductance.

In a similar conductimetric study with zirconium tetrachloride solutions quite different results were observed. Thus after the addition of only a few cm^3 of TMAC solution a white precipitate formed and the conductance returned to a low value. Further additions of titrant show a temporary rise in conductance which slowly settles back to the plateau value; this behaviour continues until Zr:TMAC = 1:2.

This contrasting behaviour of zirconium tetrachloride solutions and zirconium oxide chloride solutions suggests that they contain different solvated species. Since zirconium tetrachloride is polymeric in the solid state consisting of a chain of $ZrCl_6$ octahedra sharing a common edge [10, 11], it is likely that short chain polymers exist in solution and that the initial precipitate with TMAC is a TMA salt of a polynuclear anion. Thus if it is assumed, for instance, that the trimeric species $Zr_3Cl_{12}(SOCl_2)_n$ is present in solution then the formation of the salt $[(CH_3)_4N]$-Zr_3Cl_{13} may be envisaged. Such a compound (or similar) would be expected to be less soluble than a pentachlorozirconate and hence the early precipitation from solutions of zirconium tetrachloride is explained. By contrast the species in zirconium oxide chloride solutions are formed from the compound $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 16H_2O$ [12] by a series of reactions with thionyl chloride. In the tetrameric cation each zirconium is eight-coordinate. The first part of the solvation reaction involves reaction of interstitial and coordinated water with thionyl chloride, as the reaction proceeds the rest of the coordinated water reacts with thionyl chloride to give the postulated intermediate $[Zr_4(OH)_4(SOCl_2)_8$-

$Cl_8]^{4+}$. This is followed by thionyl chloride attack on the hydroxo bridges with the formation of further Zr—Cl bonds

$$-Zr-OH + SOCl_2 \longrightarrow -Zr-Cl + SO_2 + HCl$$
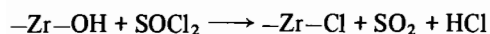
giving finally $ZrCl_4(SOCl_2)_n$. During the course of this reaction the intermediate zirconium species will be solvated with thionyl chloride molecules effectively suppressing the formation of polymeric zirconium species.

These conductimetric studies suggested that thionyl chloride solutions of zirconium oxide chloride could be used for the preparation of hexachlorozirconates and more importantly the much less-readily available pentachlorozirconates. Thus when a solution of TMAC in thionyl chloride is added slowly and dropwise to a thionyl chloride solution of zirconium oxide chloride in a molar ratio of 1:1 a good yield of the compound $[(CH_3)_4N]ZrCl_5$ is obtained; initially this compound has a gelatinous appearance, probably due to loosely coordinated thionyl chloride, but once dried gives a white powder which is very sensitive to moisture. It is important during this preparation to add the TMAC solution carefully and to avoid any risk of localised concentrations of TMAS solution. During an early attempt to prepare a pentachlorozirconate the TMAC solution was poured into the zirconium solution, only to give an impure product the elemental analysis for which was intermediate between the pentachlorozirconate and the corresponding hexachlorozirconate. An attempt to prepare a pentachlorozirconate under 'normal laboratory conditions' gave a product having the formulation $[(CH_3)_4N]ZrCl_4(OH)$ the infrared spectrum of which showed the typical OH absorption at 3230 cm^{-1}. This compound, which has not yet been examined in detail, is probably better formulated as a dimer with bridging hydroxo groups $[(CH_3)_4N]_2[ZrCl_4(OH)_2ZrCl_4]$.

The use of thionyl chloride solutions of zirconium tetrachloride for the synthesis of a pentachlorozirconate has also been explored. Although a product having such an empirical composition may be isolated it is structurally different from the one produced from zirconium oxide chloride solutions.

This is apparent both from X-ray powder data (see Table I) and from infrared spectroscopic measure-ments; and is consistent with the conclusions drawn from the conductimetric data. Thus the $ZrCl_4$-derived product exhibits a single broad absorption at 298 cm^{-1} whereas the $ZrOCl_2$-derived product has bands at 288, 295 and 321 cm^{-1}. All these bands are attributed to Zr—Cl absorptions.

It appears that the two species differ only in the degree of polymerisation of the anion. In the case of the $ZrOCl_2$-derived product, as described above, no opportunity exists for the formation of polymeric zirconium species, although the formation of a dimer can be envisaged after precipitation with the removal of the loosely coordinated thionyl chloride. Zirconium tetrachloride, however, is polymeric in the solid state and short solvated polymeric chains, *i.e.* $Zr_3Cl_{12}(SOCl_2)_n$ and $Zr_4Cl_{16}(SOCl_2)_n$ may be expected to be present in solution. Thus, addition of tetramethylammonium chloride may precipitate salts derived from such polymeric species, e.g. $[(CH_3)_4N]Zr_4Cl_{20}$.

By changing the molar ratio of reactants good yields of the compound $[(CH_3)_4N]_2ZrCl_6$ may be isolated from thionyl chloride solutions of either zirconium oxide chloride or zirconium tetrachloride.

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