The Chemistry of Polyhalozirconates.
Part 2. The Preparation of Mixed Chloro–Alkoxo Zirconates

M. D. ATHERTON and H. SUTCLIFFE

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

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Abstract

The preparation of mixed chloro–alkoxo zirconates having the general formula $(C_5H_6N)_2$-$[ZrCl_x(OR)_y]$, where $x = 2$, 4 or 5, $y = 4$, 2 or 1 respectively, and $R = CCl_3CH_2O$, CF_3CH_2O and C_2H_5O, is described. Infrared spectroscopic data are reported and assignments made.

Introduction

Hexachlorozirconates and alkoxozirconates have received intermittent study over the years, from the early work of Wardlaw *et al.* [1–5] to more recent work on the synthesis of hexachlorozirconates and doped hexachlorozirconates as potential phosphors [6, 7]. We have recently been studying new synthetic routes to halozirconates [8, 9] and now report the preparation of mixed chloro–alkoxo species.

Experimental

Most of the compounds handled in this work are sensitive to moisture, they were therefore manipulated in a nitrogen atmosphere using Schlenk tubes or a conventional dry box. Infrared spectra were measured with a Perkin-Elmer 1710 Fourier Transform Infrared Spectrophotometer. Thermal gravimetric analysis was carried out using a Stanton-Redcroft TG 750 thermobalance. Zirconium was determined as described previously [10] and chloride by standard gravimetric procedures.

Elemental analysis was carried out by Butterworths Microanalytical Consultancy Ltd.

Pyridinium hexachlorozirconate was prepared from zirconium tetrachloride or zirconium tetraethoxide as described earlier [3].

Preparation of $(C_5H_6N)_2[ZrCl_5(OCH_2CH_3)]$

Sodium (0.33 g, 14 mmol) was added to ethanol (20 cm^3) and the resultant solution of sodium ethoxide was added dropwise to a suspension of pyridinium hexachlorozirconate (6.8 g, 15 mmol) in ethanol (100 cm^3) at reflux. The hexachlorozirconate was slowly consumed and replaced by a finely divided white precipitate which was removed by filtration. The filtrate was evaporated to dryness to yield a white solid (5.3 g). *Anal.* Found: Zr, 19.6; Cl, 38.2. Calc. for $(C_5H_6N)_2[ZrCl_5(OCH_2CH_3)]$: Zr, 19.3; Cl, 37.4%.

Preparation of $(C_5H_6N)_2[ZrCl_4(OCH_2CH_3)_2]$

A solution of pyridine (4.0 g, 51.5 mmol) in ethanol (25 cm^3) was added, with stirring, to a solution of zirconium tetrachloride (6.0 g, 25.7 mmol) in ethanol (150 cm^3) under nitrogen. A white precipitate slowly formed (5 months) which was separated by filtration and washed with ethanol to give a low yield of a white product (2.4 g). *Anal.* Found: Zr, 13.4; Cl, 20.9. Calc. for $(C_5H_6N)_2[ZrCl_4(OCH_2CH_3)_2]$: Zr, 13.2; Cl, 20.6%.

Preparation of $(C_5H_6N)_2[ZrCl_2(OCH_2CH_3)_4]$

A saturated solution of hydrogen chloride in ethanol (1.2 cm^3, 2.91 mmol HCl) was added to a suspension of zirconium tetraethoxide (0.45 g, 1.6 mmol) in ethanol (75 cm^3) and refluxed for 1 h. The residual solid was removed by filtration and to the filtrate was added slowly a solution of pyridine (0.36 g, 4.5 mmol) in ethanol (25 cm^3) and refluxed for 1 h. The solution was evaporated to dryness to yield a white solid (0.42 g). *Anal.* Found: Zr, 18.4; Cl, 14.0. Calc. for $(C_5H_6N)_2[ZrCl_2(OCH_2CH_3)_4]$: Zr, 18.1; Cl, 14.0%.

Reaction of $(C_5H_6N)_2[ZrCl_5(OCH_2CH_3)]$ with Hydrogen Chloride

Hydrogen chloride gas was bubbled through a solution of pyridinium ethoxypentachlorozirconate (3.0 g, 6.3 mmol) in ethanol (100 cm^3) for *ca.* 30 min. Pyridine (0.5 g, 6.3 mmol) in ethanol (30 cm^3) was added slowly with stirring to give a white suspension. The solid was separated by filtration, washed with ethanol and dried *in vacuo* to yield a white product (2.85 g). *Anal.* Found: Zr, 19.5; Cl, 46.0. Calc. for $(C_5H_6N)_2[ZrCl_6]$: Zr, 19.6; Cl, 45.9%.

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Preparation of $(C_5H_6N)_2[ZrCl_5(OCH_2CCl_3)]$

(a) In acetonitrile from pyridinium hexachlorozirconate

A solution of sodium trichloroethoxide, prepared from sodium (0.35 g, 16.1 mmol) and trichloroethanol (2.4 g, 16.2 mmol) in acetonitrile (25 cm^3), was added dropwise to a suspension of pyridinium hexachlorozirconate (7.5 g, 16.1 mmol) in acetonitrile (100 cm^3) at reflux. The hexachlorozirconate was consumed slowly and replaced by a finely divided precipitate during a 5 h reflux period. The precipitate was removed by filtration, and the filtrate evaporated to dryness to yield a white solid (1.5 g). *Anal.* Found: Zr, 16.0; Cl^-, 31.1. Calc. for $(C_5H_6N)_2\{ZrCl_5(OCH_2CCl_3)\}$: Zr, 15.8; Cl^-, 30.7%.

(b) In ethanol from pydininium hexachlorozirconate

Pyridinium hexachlorozirconate (4.0 g, 8.6 mmol) was suspended in ethanol (50 cm^3) and to this was added sodium trichloroethoxide (1.46 g, 8.5 mmol). After a 1 h reflux period the suspension was filtered and the filtrate reduced in volume by rotary evaporation until a white solid precipitated. Filtration yielded a white crystalline product (3.0 g). *Anal.* Found: Zr, 15.7; Cl^-, 30.5. Calc. for $(C_5H_6N)_2[ZrCl_5(OCH_2CCl_3)]$: Zr, 15.8; Cl^-, 30.7%.

Preparation of $(C_5H_6N)_2[ZrCl_4(OCH_2CCl_3)_2]$

To a suspension of zirconium tetrachloride (5.0 g, 21 mmol) in carbon tetrachloride (100 cm^3) under nitrogen was added a solution of pyridine (3.2 g, 40 mmol) in carbon tetrachloride (25 cm^3), and trichloroethanol (20 cm^3). The resultant white precipitate was separated by filtration, washed with ethanol and dried *in vacuo* to yield a white solid (13.0 g). *Anal.* Found: Zr, 13.6; Cl^-, 21.2; C, 24.50; H, 2.87; N, 4.28. Calc. for $(C_5H_6N)_2[ZrCl_4(OCH_2CCl_3)_2]$: Zr, 13.22; Cl^-, 20.6; C, 24.37; H, 2.34; N, 4.06%.

Preparation of $(C_5H_6N)_2[ZrCl_4(OCH_2CF_3)_2]$

Using an exactly analogous method to that described above, zirconium tetrachloride (5.0 g, 20 mmol), pyridine (3.2 g, 40 mmol) and trifluoroethanol (4.0 g, 40 mmol) gave a white product (10.5 g). *Anal.* Found: Zr, 15.7; Cl, 24.3; C, 28.0; H, 2.4; N, 4.1. Calc. for $(C_5H_6N)_2[ZrCl_4(OCH_2CF_3)_2]$: Zr, 15.4; Cl, 24.0; C, 28.4; H, 2.7; N, 4.7%.

Preparation of $(C_5H_6N)_2[ZrCl_2(OCH_2CH_3)_2(OCH_2CCl_3)_2]$

Sodium (0.33 g, 14 mmol) was added to ethanol (25 cm^3) and the resultant solution of sodium ethoxide added dropwise to a suspension of pyridinium bistrichloroethoxotetrachlorozirconate (4.0 g, 7.4 mmol) in ethanol (100 cm^3), at reflux,

TABLE I. Infrared Spectroscopic Data for Pyridinium Zirconates (cm^{-1})[a]

$ZrCl_5(OR_1)^{2-}$	$ZrCl_4(OR_1)_2^{2-}$	$ZrCl_2(OR_1)_4^{2-}$	$Zr(OR_1)_4$	$ZrCl_5(OR_2)^{2-}$	$ZrCl_4(OR_2)_2^{2-}$	$ZrCl_4(OR_3)_2^{2-}$	$ZrCl_2(OR_1)_2(OR_2)_2^{2-}$	Assignments
3257(m)	3260(m)	3260(m)		3260(m)	3260(m)	3265(m)	3260(m)	N–H str
3182(s)	3182(s)	3180(s)		3180(s)	3180(s)	3180(s)	3180(s)	aryl C–H str
2905(m)	2905(m)	2910(s)	2910(s)					C–H str
2855(w)	2850(m)	2850(m)	2850(s)					C–H str
1530(w)	1530(w)	1525(w)		1530(w)	1530(w)	1530(w)	1535(w)	N–H bend
			1152(s)	1145(m)	1145(s)	1140(s)	1152(s)	C–O
							1145(m)	C–O
			1075(m)	1070(m)	1070(m)	1075(m)	1065(m)	C–O
636(w)	740(w)	740(w)				1005(s)		
				740(m)	745(s)		745(s)	C–Cl str
					740(m)		740(m)	C–Cl str
735(w)	725(w)	725(w)	722(w)	715(w)	710(w)		725(m)	
520(m)	510(m)	520(m)	530(m)	520(w)	520(m)	520(m)	540(m)	Zr–O str
							530(w)	Zr–O str
245(w)	230(w)	235(m)			240(w)	245(w)		Zr–Cl str
235(m)	225(m)			226(m)	225(m)	225(m)	230(m)	Zr–Cl str

[a] $OR_1 = OC_2H_5$, $OR_2 = OCH_2CCl_3$ and $OR_3 = OCH_2CF_3$.

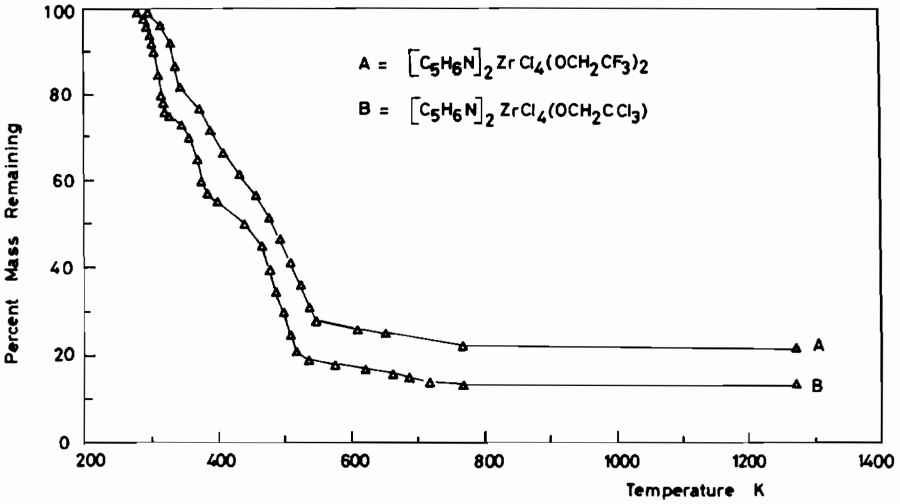

Fig. 1. Thermal breakdown profiles for $[C_5H_6N]_2ZrCl_4(OCH_2CF_3)_2$ (A) and $[C_5H_6N]_2ZrCl_4(OCH_2CCl_3)_2$ (B).

under nitrogen. The zirconate was slowly consumed and replaced by a finely divided precipitate during an 8 h period of reflux. The precipitate was removed by filtration and the filtrate evaporated to dryness to give a white solid (1.9 g). *Anal.* Found: Zr, 13.0; Cl^-, 10.1. Calc. for $(C_5H_6N)_2[ZrCl_2(OCH_2CH_3)_2(OCH_2CCl_3)_2]$: Zr, 12.86; Cl^-, 10.0%.

The infrared spectra of all the compounds described were measured and the data are summarized, together with some assignments, in Table I. In most cases the thermal gravimetric analysis profiles of these compounds showed very few features of particular interest, a typical profile is shown in Fig. 1. Exceptionally, pyridinium bistrichloroethoxotetrachlorozirconate shows a stepwise thermal breakdown pattern, the profile for which is also given in Fig. 1.

Discussion

The preparation of alkoxochlorozirconates may be approached in two ways; direct substitution on hexachlorozirconates or indirectly from zirconium tetralkoxides or zirconium tetrachloride.

Direct substitution takes place readily when sodium ethoxide or sodium trichloroethoxide is refluxed in the corresponding alcohol solution with pyridinium hexachlorozirconate. Yields of 75% and 16% respectively have been obtained. This disparity in yield is not attributable to steric effects since it is possible to prepare a bis(trichloroethoxy)-tetrachlorozirconate species. Therefore the lower yield of the trichloroethoxy derivative is probably due to the lower nucleophilic reactivity of the trichloroethoxy anion relative to that of the ethoxide ion, attributable to the electron withdrawing effect of the chlorine atoms. It is interesting to note that when a substitution reaction was carried out in the presence of both ethanol and trichloroethanol only the trichloroethoxo substituted product was obtained. This reflects the higher acidity of trichloroethanol which reacts preferentially with the sodium to give the trichloroethoxy anion exclusively.

Bis(trifluoroethoxy)- and bis(trichloroethoxy)-tetrachlorozirconates are readily prepared from zirconium tetrachloride in 90% yield or better by treating zirconium tetrachloride with the corresponding alcohol and pyridine. By contrast the bis(ethoxy) derivative is only obtained in low yield (19%). This reaction is expected to proceed via protonation of the pyridine by the alcohol, followed by attack of the alkoxide ion so produced on zirconium tetrachloride, resulting finally in the formation of

$$C_5H_5N + ROH \longrightarrow C_5H_5\overset{+}{N}H + RO^-$$

$$RO^- + ZrCl_4 \longrightarrow ZrCl_4(OR)^- \text{ etc.}$$

pyridinium dialkoxotetrachlorozirconate. The yields are consistent with the high acidity of trichloroethanol ($pK_A = 12.24$) [11] and trifluoroethanol ($pK_A = 12.4$) [11] compared with ethanol ($pK_A = 15.9$) [12]. The more acidic alcohols, trichloroethanol and trifluoroethanol, protonate the pyridine more readily than ethanol hence giving high yields of the disubstituted halozirconate.

The preparation of mixed alkoxochlorozirconates is also possible by further substitution of chloride ligands. Thus pyridinium bistrichloroethoxotetrachlorozirconate when treated with sodium ethoxide in boiling ethanol gives a 36% yield of pyridinium bistrichloroethoxodiethoxodichlorozirconate. No displacement of the trichloroethoxo ligands is observed which may be attributed to the strength of the zirconium oxygen bond. However under conditions of high acidity the ethoxo group is readily displaced by chloride ion from the ion $[ZrCl_5(OC_2H_5)]^{2-}$.

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