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Geometrical isomers of $ScCl_3(THF)_x(H_2O)_{3-x}$: isolation and crystal structure of the compound where $x = 2$

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Abstract—Controlled hydrolysis of $ScCl_3(THF)_3$ results in the replacement of one tetrahydrofuran molecule to provide colourless crystals of $ScCl_3(THF)_2(H_2O)$. An X-ray structure determination of this 'mixed' solvate shows discrete six co-ordinate scandium atoms bonded to three chlorine atoms and three O-donor solvent molecules in a *mer*-octahedral arrangement. Sc—Cl 2.399(3), 2.477(3), 2.478(3) Å, Sc—O(H_2O) 2.197(3) Å and Sc—O(THF) 2.170(4), 2.172(4) Å. © 1997 Elsevier Science Ltd

Keywords: structure; scandium(III); tetrahydrofuran; water; adduct; octahedral.

The *tris*-tetrahydrofuran adduct, $ScCl_3(THF)_3$ is a convenient precursor for the synthesis of scandium(III) compounds. It can be obtained from the oxide, i.e. treatment of Sc_2O_3 with hydrochloric acid provides $ScCl_3 \cdot 6H_2O$ which can then be dehydrated using thionyl chloride in the presence of an excess of tetrahydrofuran or, more directly, by recrystallisation of the anhydrous metal chloride [1]. An X-ray crystallographic study shows individual six co-ordinate scandium atoms with a *mer*-octahedral geometry [2]. Recently we have reported the structure of the *tris*-aqua adduct $ScCl_3(H_2O)_3$ which, similarly, features a near-idealised *mer*-octahedral metal geometry; the latter was obtained as an unexpected inclusion adduct in the cryptate compound $[H_2L]Cl_2 \cdot ScCl_3(H_2O)_3 \cdot 3H_2O$ [3] where L = cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). Both these compounds belong to the generic series $ScCl_3(THF)_x(H_2O)_{3-x}$ where $x = 0$, 1, 2 and 3.

In this report we describe the isolation and structural characterisation of $ScCl_3(THF)_2(H_2O)$ as another member ($x = 2$) of the series.

EXPERIMENTAL

Manipulations were carried out using standard Schlenk techniques and a dinitrogen metal gloved box. Solvents were dried over CaH_2–P_4O_{10} and benzophenone ketyl and distilled under dinitrogen prior to use. The compound $ScCl_3(THF)_3$ was prepared as described in the literature [1]. Microanalytical data were obtained using a Leeman Labs Inc. PS1000 sequential inductively coupled plasma (ICP) spectrometer and a Leeman Labs Inc. CE440 elemental (C, H, N) analyser.

Preparation of $ScCl_3(THF)_2(H_2O)$

A standard H_2O–THF solution (0.02 g cm^{-3}) was prepared by careful addition of H_2O (1 cm^3) to tetrahydrofuran in a calibrated 50 cm^3 volume flask.

A solution of $ScCl_3(THF)_3$ (0.50 g, 0.136 mmol) in tetrahydrofuran (25 cm^3) was added dropwise to a stirred, chilled (0°C) solution containing tetrahydrofuran (15 cm^3) and the standard H_2O–THF solution (0.125 cm^3, 0.136 mmol). After stirring the mixture for 2 h and heating at reflux for 6 h the resulting colourless solution was concentrated (*ca* 15 cm^3) and placed in the refrigerator to provide a crop of clear, block crystals. Yield 0.35 g, 83%. Found: C, 30.33; H, 5.72; Cl, 33.81. $C_8H_{18}Cl_3O_3Sc$ requires C, 30.65; H, 5.79; Cl, 33.92%. IR ν/cm^{-1} (Nujol) 3315(s), 1615(s) (H_2O), 1007(vs) 856(s) (THF), 310(br)vs, 297(br) ν(Sc—Cl).

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Table 1. Crystallographic data

Identification code	$ScCl_3(H_2O)(THF)_2$
Empirical formula	C(8)H(18)C(13)O(3)Sc
Formula weight	313.53
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 9.245(9)$ Å
	$b = 13.413(13)$ Å
	$c = 12.441(13)$ Å
	$\beta = 103.76(1)°$
Volume (Å^3)	1499(3)
Z	4
Density (calculated) (Mg/m^3)	1.390
Absorption coefficient (mm^{-1})	1.013
F(000)	648
Crystal size (mm)	0.25 × 0.35 × 0.15
θ range for data collection (°)	2.27–24.99
Index ranges	$0 < h < 10$,
	$-15 < k < 15$,
	$-14 < l < 13$
Reflections collected	4486
Independent reflections	2410 [R(int) = 0.0325]
Weighting Scheme (a, b)[a]	0.136, 1.114
Data/restraints/parameters	2410/0/137
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0671$,
	$wR2 = 0.1817$
R indices (all data)	$R1 = 0.0801$,
	$wR2 = 0.1998$
Extinction coefficient	0.052(5)
Largest diff. peak and hole	1.104 and −0.835 e Å^{-3}

[a] Weighting scheme $w = 1/(\sigma^2(F_o^2)+(aP)^2+bP)$, where $P = (F_o^2+2F_c^2)/3$.

X-ray crystallography

Crystal data are given in Table 1, together with refinement details. Data were collected with Mo–Kα radiation using the MAR research Image Plate System. The crystal was positioned at 75 mm from the Image Plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [4]. The structure was solved using direct methods with the SHELX86 program [5]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms on the water molecule bonded to the metal could not be located. The structure was then refined on F^2 using SHELXL [6]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Supplementary material including atomic co-ordinates, tables of thermal parameters, hydrogen atom co-ordinates and observed/calculated structure factors has been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The controlled hydrolysis reaction of $ScCl_3(THF)_3$ was carried out in tetrahydrofuran solution using a 1 : 1 stoichiometry of metal : water. The identity of the product, obtained as colourless block crystals in good yield (83%), was established by X-ray crystallography.

Of the three geometrical isomers possible for $ScCl_3(THF)_2(H_2O)$, the one adopted here has a *mer*-octahedral metal geometry with the two tetrahydrofuran molecules mutually *trans* (C_{2v}). The structure is shown in Fig. 1 with the atom numbering scheme. The metal–chlorine bond distances are non-equivalent; it is noteworthy that the chlorine atom directly opposite to the water molecule (Sc—Cl 2.399(3) Å) is much more tightly bound than the other two which are mutually *trans* (Sc—Cl, 2.477(3), 2.478(3) Å, Cl—Sc—Cl 167.72(5)°). The two tetrahydrofuran molecules are equidistant from the metal Sc—O 2.170(4), 2.172(4) Å and exhibit the familiar propeller-blade configuration as witnessed in $ScCl_3(THF)_3$ [2]; the O—Sc—O linkage (174.24(12)°) is essentially linear. For the co-ordinated water molecule the Sc—O bond distance is perceptibly larger at 2.197(3) Å. These bond dimensions compare favourably with those observed in the related isomers: viz., *mer*-$ScCl_3(THF)_3$ [2] Sc—Cl 2.406(4), 2.420(4), 2.415(4) Å, Sc—O 2.236(8), 2.147(7), 2.164(7) Å; *mer*-$ScCl_3(H_2O)_3$ [3] Sc—Cl 2.413(6), 2.419(4), 2.419(5) Å, Sc—O 2.078(10), 2.132(9), 2.155(9) Å. As gauged by the *cis*-interbond angles (Table 2), O—Sc—O 86.86(11), 87.49(10)°, O—Sc—Cl 88.12(9)–93.08(9), mean 90.74(9)° there is some

Table 2. Bond lengths (Å) and angles (°) in the metal coordination sphere of **1**

Sc—O(20)	2.170(4)
Sc—O(10)	2.172(4)
Sc—O(100)	2.197(3)
Sc—Cl(2)	2.399(3)
Sc—Cl(4)	2.477(3)
Sc—Cl(3)	2.478(3)
O(20)—Sc—O(10)	174.24(12)
O(20)—Sc—O(100)	86.86(11)
O(10)—Sc—O(100)	87.49(10)
O(20)—Sc—Cl(2)	92.59(9)
O(10)—Sc—Cl(2)	93.08(9)
O(100)—Sc—Cl(2)	178.93(7)
O(20)—Sc—Cl(4)	90.57(10)
O(10)—Sc—Cl(4)	89.90(9)
O(100)—Sc—Cl(4)	83.36(7)
Cl(2)—Sc—Cl(4)	95.73(5)
O(20)—Sc—Cl(3)	90.20(9)
O(10)—Sc—Cl(3)	88.12(9)
O(100)—Sc—Cl(3)	84.44(7)
Cl(2)—Sc—Cl(3)	96.48(4)
Cl(4)—Sc—Cl(3)	167.72(5)

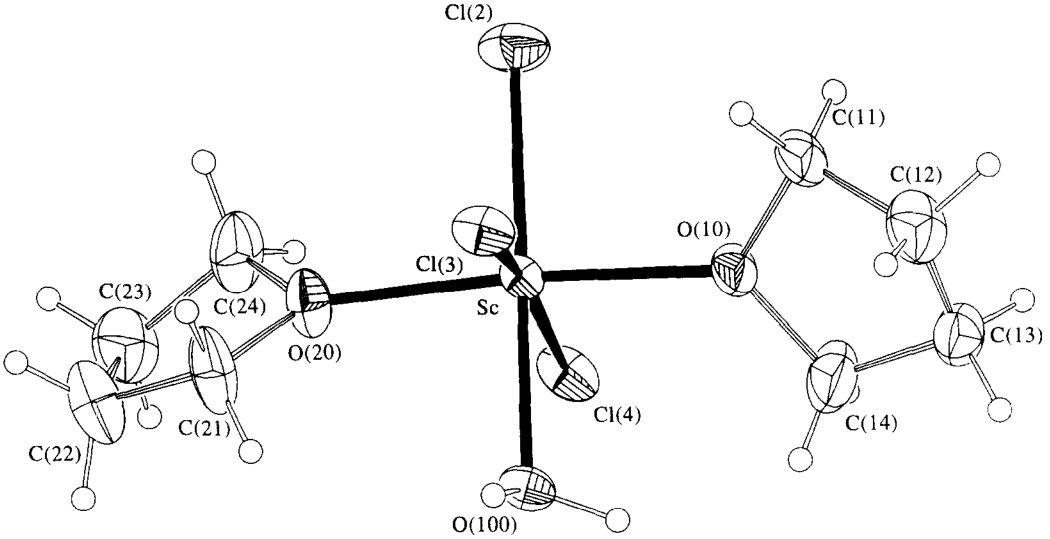

Fig. 1. The structure of $ScCl_3(THF)_2(H_2O)$ with ellipsoids drawn at 30% probability. The hydrogen atoms are included with small arbitrary radii. The hydrogen atoms in the water molecule are located in arbitrary tetrahedral positions.

deformity from the ideal (90°) but not in a significant sense. Interestingly, the six co-ordinate analogues $MCl_3(THF)_3$ where M = Ti [7], V [8] and Cr [9] also exhibit a *mer*-octahedral (C_{3v}) stereochemistry. A conspicuous 'propeller-like' orientation of the tetrahydrofuran solvent molecule(s) about the M—O bond direction is a key-note and the subtle structural variations within these first row early transition metal complexes have been noted and discussed by Cotton *et al.* [9]. Our search for $ScCl_3(THF)(H_2O)_2$ as the final member of the series ($x = 1$) continues.

Corollary—Bearing in mind the structural rearrangement reported by Sobota *et al.* [10] for the yttrium (Group 3) analogue

$$viz: YCl_3(THF)_{3.5} \xrightarrow{\text{Dichloromethane}} [YCl_3(THF)_2]_n$$

we were interested in establishing a similar re-organisation from mononuclear $ScCl_3(THF)_3$ (CN = 6) into polymeric $[ScCl_3(THF)_2]n$ involving double halogen bridging units (CN = 7). However, attempted recrystallisations of *mer*-$ScCl_3(THF)_3$ in boiling dichloromethane provided unchanged starting material.

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