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Synthesis and Crystal Structure of a Neodymium Isopropoxide Chloride, $Nd_6[OCH(CH_3)_2]_{17}Cl$[1]

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Neodymium(III) chloride reacts with sodium isopropoxide in isopropyl alcohol to produce a complex which has been characterized by an X-ray crystal structure determination to be hexaisopropoxynona-μ-isopropoxy-di-μ_3-isopropoxy-μ_6-chloro-hexaneodymium, $Nd_6[OCH(CH_3)_2]_{17}Cl$. The pale blue crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a = 24.52$ (2) Å, $b = 22.60$ (2) Å, $c = 14.22$ (1) Å, and $\beta = 101.05$ (5)°; for four molecules in the unit cell the calculated density is 1.636 g/cm^3. The structure was refined by full-matrix least squares to a conventional R factor of 0.076 for 2327 data with $I > 2\sigma$. The six neodymium atoms form a trigonal prism centered about the chlorine atom. Six isopropoxide groups are terminal, nine are edge bridging, and two are bridging a trigonal face of the prism yielding six two-coordinate, nine three-coordinate, and two four-coordinate oyxgen atoms, respectively. The average Nd–Cl distance is 3.05 (1) Å. The average Nd–O distances for oxygen atoms which are bonded to one, two, and three Nd atoms are 2.05 (2), 2.36 (4), and 2.45 (5) Å, respectively.

Introduction

Neodymium triisopropoxide, prepared from neodymium trichloride and sodium isopropoxide in refluxing isopropyl alcohol, is said to be monomeric in benzene solution (ebullioscopically) as is the praseodymium analogue.[2,3] In contrast, gadolinium and erbium isopropoxides are tetrameric in benzene.[4] The samarium[5] and ytterbium[6] compounds are also known though their solution molecular weights have not been reported. Mass spectrometric examination of $M(O\text{-}i\text{-}Pr)_3$ [M = Nd, Er, Tb, Lu], prepared from the metal and alcohol, shows tetrameric ions in the gas phase.[7]

It has been said that preparation of isopropoxides of the lanthanide elements from sodium isopropoxide and metal chloride results in materials that are contaminated by chloride though nothing was known about their constitution.[7,8] We have carried out a single-crystal X-ray analysis of the chloride-containing material and have shown it to be $Nd_6(O\text{-}i\text{-}Pr)_{17}Cl$.

Experimental Section

Microanalysis was performed by Analytical Laboratories, University of California, Berkeley, Calif. Isopropyl alcohol was dried by refluxing over and distilling from magnesium isopropoxide. Neodymium trichloride was dried by refluxing with thionyl chloride. The magnetic susceptibility was measured with a PAR Model 155 vibrating-sample magnetometer and was calibrated with $HgCo(CNS)_4$.[9] Temperature was measured with a calibrated GaAs diode.

Heptadecaisopropoxychlorohexaneodymium(III). Sodium isopropoxide was prepared from sodium (1.3 g, 0.055 mol), isopropyl alcohol (20 mL), and benzene (40 mL); it was then added to a gently refluxing solution of neodymium trichloride (4.6 g, 0.018 mol) in isopropyl alcohol (40 mL). The suspension was refluxed for 12 h and then centrifuged. The light blue mother liquor was filtered, and the residue was washed with benzene (2 × 25 mL). The combined extracts were evaporated to dryness in vacuo. The blue solid was crystallized from toluene (−15 °C) as light blue needles. The yield was 6.2 g. The compound did not melt nor decompose when heated in a sealed capillary to 300 °C. Anal. Calcd. for $C_{51}H_{119}ClNd_6O_{17}$: C, 32.2; H, 6.25; Cl, 1.86. Found: C, 31.8; H, 6.04; Cl, 1.80.

X-ray Diffraction. The pale blue crystals were transferred to quartz capillaries inside an argon-filled drybox and sealed with vacuum grease. The capillaries were fire-sealed immediately upon removal from the box. Weissenberg photography showed the material to be monoclinic, and rough cell dimensions were obtained. A crystal was mounted on a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. The cell dimensions were obtained by a least-squares procedure from the angular settings of 12 manually centered reflections for which the 2θ values were between 29 and 32°. The space group and cell dimensions are given in Table I with some other details of the experiment. ω scans of several low-angle reflections showed widths at half-peak height of about 0.25°. Using the θ–2θ scan technique, a total of 10 397 scans, including standards, were measured and later averaged to give a set of 4920 unique data of which 2137 had $F^2 > 2\sigma$. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. A decay of about 15% was observed in the intensities of all three standard reflections, and the data were adjusted accordingly.

No absorption correction was made because the crystal faces were too indistinct to measure. Azimuthal scans of a few reflections indicated variations in intensities of about 10% from the average. The data were processed, averaged, and given estimated standard deviations using formulas available as supplementary material. The factor $p = 0.06$ was used in the calculation of $\sigma(F^2)$.

The full-matrix least-squares program used minimizes the function $\sum w(\Delta F)^2/\sum wF_o^2$. Scattering factors for Nd were taken from Cromer and Waber[10] and those for Cl, C, and O from Doyle and Turner;[11] dispersion corrections used were from Cromer and Liberman.[12]

Structure Determination. The positions of the six Nd atoms, at the corners of a regular trigonal prism, were deduced from a three-dimensional Patterson function calculation. A least-squares

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Table I. Summary of Crystal Data and Intensity Collection

Compd	$Nd_6[OCH(CH_3)_2]_{17}Cl$
Formula wt	1905.4
a, Å	24.52 (2)
b, Å	22.60 (2)
c, Å	14.22 (1)
β, deg	101.05 (5)
V, Å^3	7736
Z	4
Density, calcd, g/cm^3	1.636
Space group^a	$P2_1/n$ (alternate setting of $P2_1/c$)
Cryst shape and size, mm	Roundish fragment; 0.25 × 0.15 × 0.20
Temp, °C	21
Radiation	Mo Kα (λ 0.709 26 and 0.713 54 Å), monochromated from (002) face of mosaic graphite
μ, cm^{-1}	40.5
Data collection method	θ-2θ scan (1°/min along 2θ)
Scan range, deg 2θ	0.9° below Kα_1 to 0.9° above Kα_2
Bgd counts	8-s bgd offset from scan limits by 0.12° 2θ
2θ limits, deg	3.5-40
Final no. of variables	314
Unique data used for $F_o^2 > 2\sigma$; $0.127 < (\sin\theta)/\lambda < 0.428$	2327
No. distance restraints	102
R_w^{b}	0.074
R^{c} (2327 data used in R_w)	0.076
R (all 4920 data)	0.239
Goodness of fit	1.36

[a] The general positions are $\pm(x, y, z)$ and $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

refinement of the Nd atoms followed by a difference-Fourier calculation revealed the positions of 18 additional atoms which were presumed to be oxygen atoms. One of these atoms occupied the center of the trigonal prism and was equidistant from all six Nd atoms. Refinement of the 6 Nd atoms and the 18 oxygen atoms yielded a negative temperature parameter for the atom at the prism center. When this atom was assumed to be a chlorine atom, derived from the $NdCl_3$ in the synthesis, further refinement resulted in comparable thermal parameters for all the atoms. The presence of chlorine was confirmed by a chemical test using silver nitrate and by the analysis reported above. Least-squares calculations and difference-Fourier maps were used to determine the locations of the 51 carbon atoms. The carbon atoms were not well resolved, due to the paucity of high-angle data; and although most of the carbon atoms refined to reasonable positions, some did not. To handle this poor resolution problem, restraints were imposed on the interatomic distances as suggested by Waser.[13] In this method, interatomic distances between selected atoms are introduced into the least-squares calculations and treated as observations; estimated standard deviations of these distances are also introduced and used to calculate the weights. Except that the derivatives are calculated by a special patch and these "observations" are not included in the R values reported here, these terms are included in the least-squares calculation in the same manner as observed structure factors. This procedure allows the structure to adjust to the electron density with a flexibility governed by the weighting. The isopropoxide carbon atoms were restrained by the following distances: O–C (nearest neighbor) to 1.44 ± 0.66 Å, O–C (second neighbor) to 2.42 ± 0.1 Å, C–C (nearest neighbor) to 1.52 ± 0.03 Å, and C–C (second neighbor) to 2.48 ± 0.1 Å. These distances impose tetrahedral bond angles on this isopropoxide group but permit rotation about the O–C bond. To promote faster convergence of the structure, the isotropic thermal parameters of the two terminal carbon atoms from each isopropoxide group were constrained to a single value. No extinction was indicated, and no correction for it was made. Because of some large weighted residuals at low angles, all 87 data for $(\sin\theta)/\lambda < 0.127$ were zero weighted.

The final structure with R indices as given in Table I and parameters as shown in Table II is partially shown in Figure 1. In the last cycle the largest shift of a parameter was 0.19σ. The largest peak in the final difference Fourier was 1.5 e/Å^3. Hydrogen atoms were not observed and not included in the calculations. A list of distances is given in Table III, with atoms numbered as in Figure 1.

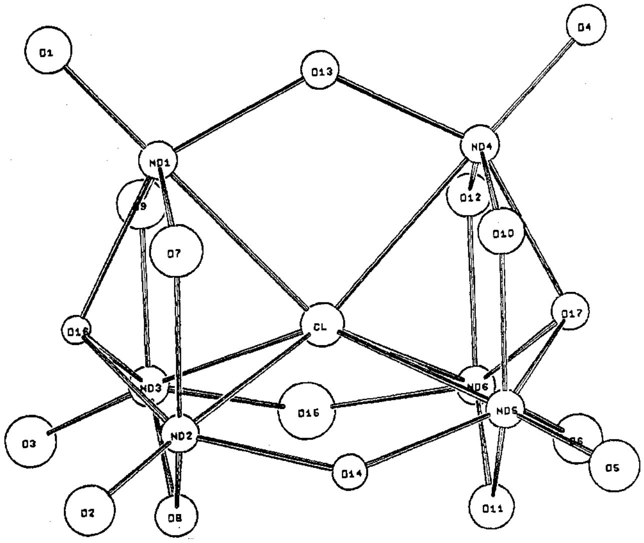

Figure 1. ORTEP drawing of the Nd, Cl, and O framework in $Nd_6[OCH(CH_3)_2]_{17}Cl$.

Discussion

The neodymium atoms are at the corners of a very nearly regular trigonal prism in which the triangular edges average 3.808 ± 0.006 Å and the axial edges average 4.230 ± 0.010 Å. All of the angles in the triangular faces are within 0.1° of 60°. Because of a slight twist of the triangular faces with respect to each other about the prism axis, the angles are about 1° from 90° for the three quadrilateral faces. The cause of this minor distortion is unknown; perhaps it is a result of some steric effects of the isopropoxide ligands. The chloride ion is equidistant from the six Nd atoms at a distance of 3.05 ± 0.01 Å and is perhaps the stabilizing factor for this remarkable cluster of atoms. This distance is about what would be expected from ionic radii, or a little less, considering the high coordination number. It may be compared with 3.11 Å for Nd–Cl in NdOCl,[14] where Cl has five Nd neighbors, and with 2.94 Å for $NdCl_3$, where Cl has three neighbors.[15]

There are three types of O–Nd bonds. Each Nd atom is bonded singly to an isopropoxide ligand with an average Nd–O distance of 2.05 ± 0.02 Å. A bridging isopropoxide ligand bonds two Nd atoms at each edge of the prism to give 18 Nd–O bond lengths that average 2.36 ± 0.04 Å. The isopropoxide ligands which are centered on the triangular faces bond to three Nd atoms with an average bond length of 2.45 ± 0.05 Å. If each oxygen atom is regarded as having a total of two bonds, one to carbon and one to its neodymium neighbor(s), then the three types of O–Nd distances can be designated as a single bond (2.05 Å), a half-bond (2.36 Å), and a one-third bond (2.45 Å). The half-bond value is like the distance 2.38 Å observed in Nd_2O_3[16,17] and 2.36 Å in NdOCl,[14] where the Nd–O contacts are half-bonds by a similar formal count. The 0.31 and 0.09 Å differences between the single-bond, half-bond, and one-third-bond distances are similar to differences which average about 0.27 and 0.06 Å for U–N contacts with corresponding bond orders which we observed in several uranium(IV) amide structures.[18-20]

The molecular packing resembles the hexagonal closest packing of spheres. The globular complexes with centers near $y = {}^1/_4$ form a layer in which each cluster has six neighbors, and a similar layer occurs at $y = {}^3/_4$. The stacking of these layers is according to the ABAB sequence of hexagonal closest packing. This description is imperfect because the molecules are not spherical, and Cl–Cl distances for the 12 nearest

Table II. Parameters for $Nd_6[OCH(CH_3)_2]_{17}Cl$

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nd(1)	0.3206 (1)	0.1954 (2)	0.2153 (2)	4.8 (2)	8.4 (2)	4.1 (2)	−1.3 (2)	0.4 (1)	−0.5 (2)
Nd(2)	0.4709 (1)	0.1944 (1)	0.3476 (2)	4.2 (2)	6.9 (2)	5.3 (2)	0.5 (1)	1.3 (1)	−0.1 (2)
Nd(3)	0.3963 (1)	0.3410 (1)	0.2799 (2)	6.2 (2)	6.0 (2)	5.3 (2)	−0.5 (1)	1.6 (1)	0.8 (1)
Nd(4)	0.2624 (1)	0.2044 (1)	0.4756 (2)	4.1 (2)	7.2 (2)	5.3 (2)	−0.8 (1)	1.4 (1)	0.6 (1)
Nd(5)	0.4121 (1)	0.1893 (1)	0.6084 (2)	5.1 (2)	7.1 (2)	4.2 (2)	0.7 (2)	0.2 (1)	0.5 (1)
Nd(6)	0.3487 (1)	0.3422 (2)	0.5512 (2)	5.7 (2)	6.2 (2)	5.5 (2)	0.3 (1)	1.7 (1)	−1.0 (1)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O(1)	0.286 (1)	0.164 (2)	0.083 (2)	7.4 (9)	C(18)	0.282 (5)	0.460 (6)	0.74 (1)	26.7
O(2)	0.540 (2)	0.159 (2)	0.303 (3)	10.0 (11)	C(19)	0.397 (3)	0.067 (2)	0.288 (4)	10.4 (19)
O(3)	0.415 (1)	0.405 (2)	0.189 (3)	7.8 (9)	C(20)	0.339 (3)	0.039 (3)	0.256 (5)	11.7 (14)
O(4)	0.190 (1)	0.176 (2)	0.518 (2)	7.7 (9)	C(21)	0.435 (2)	0.042 (3)	0.227 (5)	11.7
O(5)	0.443 (2)	0.146 (2)	0.732 (3)	10.2 (11)	C(22)	0.522 (3)	0.343 (3)	0.403 (5)	12.6 (23)
O(6)	0.338 (1)	0.405 (2)	0.649 (3)	8.9 (10)	C(23)	0.563 (4)	0.302 (4)	0.467 (7)	19.7 (25)
O(7)	0.394 (1)	0.130 (2)	0.282 (2)	6.0 (8)	C(24)	0.551 (4)	0.365 (4)	0.326 (7)	19.7
O(8)	0.479 (1)	0.301 (1)	0.360 (2)	6.3 (8)	C(25)	0.260 (3)	0.333 (3)	0.164 (5)	13.4 (24)
O(9)	0.311 (1)	0.300 (1)	0.201 (2)	6.5 (8)	C(26)	0.265 (5)	0.399 (4)	0.163 (8)	22.0 (31)
O(10)	0.334 (1)	0.136 (2)	0.542 (2)	7.2 (10)	C(27)	0.231 (5)	0.302 (5)	0.074 (7)	22.0
O(11)	0.430 (1)	0.292 (1)	0.619 (2)	6.2 (8)	C(28)	0.319 (3)	0.074 (2)	0.534 (5)	12.3 (22)
O(12)	0.258 (1)	0.305 (1)	0.474 (2)	5.2 (7)	C(29)	0.376 (3)	0.043 (4)	0.560 (7)	18.0 (22)
O(13)	0.253 (1)	0.180 (1)	0.311 (2)	5.7 (7)	C(30)	0.297 (4)	0.062 (4)	0.626 (6)	18.0
O(14)	0.476 (1)	0.166 (1)	0.508 (2)	4.7 (7)	C(31)	0.481 (2)	0.320 (3)	0.663 (5)	14.3 (25)
O(15)	0.371 (2)	0.387 (1)	0.415 (3)	6.4 (7)	C(32)	0.484 (4)	0.385 (4)	0.638 (7)	18.0 (23)
O(16)	0.410 (1)	0.247 (1)	0.212 (2)	4.3 (7)	C(33)	0.501 (4)	0.302 (4)	0.764 (6)	18.0
O(17)	0.327 (1)	0.246 (1)	0.611 (2)	6.0 (8)	C(34)	0.217 (2)	0.342 (3)	0.420 (4)	11.7 (22)
Cl	0.3681 (5)	0.2449 (4)	0.4132 (9)	4.0 (2)	C(35)	0.170 (3)	0.305 (3)	0.361 (5)	13.4 (17)
C(1)	0.270 (3)	0.122 (3)	0.006 (5)	17.2 (32)	C(36)	0.196 (3)	0.386 (3)	0.484 (5)	13.4
C(2)	0.305 (4)	0.088 (4)	−0.049 (6)	17.3 (21)	C(37)	0.207 (3)	0.148 (3)	0.252 (6)	20.5 (39)
C(3)	0.216 (3)	0.148 (4)	−0.047 (6)	17.3	C(38)	0.198 (3)	0.094 (3)	0.305 (6)	14.4 (18)
C(4)	0.586 (3)	0.124 (3)	0.281 (6)	14.9 (26)	C(39)	0.164 (3)	0.193 (3)	0.212 (5)	14.4
C(5)	0.576 (4)	0.127 (5)	0.172 (6)	21.4 (27)	C(40)	0.519 (3)	0.129 (3)	0.565 (6)	20.1 (38)
C(6)	0.642 (3)	0.145 (5)	0.328 (7)	21.4	C(41)	0.568 (3)	0.166 (4)	0.612 (6)	17.3 (22)
C(7)	0.431 (5)	0.443 (4)	0.116 (7)	22.0 (43)	C(42)	0.531 (4)	0.076 (4)	0.507 (7)	17.3
C(8)	0.472 (6)	0.488 (6)	0.16 (1)	31.6 (51)	C(43)	0.370 (3)	0.450 (2)	0.404 (6)	12.8 (20)
C(9)	0.377 (6)	0.468 (7)	0.06 (1)	31.6	C(44)	0.421 (3)	0.483 (3)	0.448 (6)	14.2 (17)
C(10)	0.143 (3)	0.144 (4)	0.544 (7)	18.6 (34)	C(45)	0.315 (3)	0.477 (3)	0.410 (6)	14.2
C(11)	0.092 (4)	0.166 (6)	0.476 (8)	23.0 (29)	C(46)	0.436 (3)	0.238 (3)	0.126 (4)	12.9 (23)
C(12)	0.142 (5)	0.169 (6)	0.645 (7)	23.0	C(47)	0.424 (4)	0.172 (3)	0.106 (6)	17.7 (22)
C(13)	0.459 (3)	0.129 (4)	0.831 (4)	19.1 (36)	C(48)	0.394 (4)	0.262 (4)	0.040 (5)	17.7
C(14)	0.441 (3)	0.066 (3)	0.843 (6)	14.7 (18)	C(49)	0.309 (3)	0.246 (4)	0.702 (4)	18.7 (34)
C(15)	0.519 (3)	0.141 (4)	0.872 (5)	14.7	C(50)	0.254 (3)	0.278 (3)	0.696 (5)	12.8 (15)
C(16)	0.339 (5)	0.440 (4)	0.735 (6)	22.4 (42)	C(51)	0.349 (3)	0.275 (3)	0.782 (5)	12.8
C(17)	0.379 (5)	0.490 (5)	0.73 (1)	26.7 (39)					

[a] The form of the anisotropic temperature factor is $\exp[-0.25(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \dots)]$.

Table III. Interatomic Distances (Å)[a]

Cl–Nd(1)	3.05 (2)	O(12)–Nd(6)	2.43 (3)
–Nd(2)	3.07 (2)	–Nd(4)	2.27 (3)
–Nd(3)	3.05 (2)	O(13)–Nd(1)	2.36 (3)
–Nd(4)	3.04 (2)	–Nd(4)	2.37 (3)
–Nd(5)	3.05 (2)	O(14)–Nd(2)	2.34 (3)
–Nd(6)	3.05 (2)	–Nd(5)	2.38 (3)
O(1)–Nd(1)	2.03 (4)	O(15)–Nd(3)	2.36 (4)
O(2)–Nd(2)	2.07 (4)	–Nd(6)	2.34 (4)
O(3)–Nd(3)	2.04 (4)	O(16)–Nd(1)	2.49 (3)
O(4)–Nd(4)	2.07 (4)	–Nd(2)	2.51 (3)
O(5)–Nd(5)	2.02 (4)	–Nd(3)	2.38 (3)
O(6)–Nd(6)	2.05 (4)	O(17)–Nd(4)	2.44 (3)
O(7)–Nd(1)	2.38 (4)	–Nd(5)	2.44 (3)
–Nd(2)	2.42 (4)	–Nd(6)	2.43 (3)
O(8)–Nd(2)	2.43 (4)	Nd(1)–Nd(2)	3.81 (1)
–Nd(3)	2.31 (4)	–Nd(3)	3.80 (1)
O(9)–Nd(3)	2.38 (3)	Nd(2)–Nd(3)	3.82 (1)
–Nd(1)	2.37 (4)	Nd(4)–Nd(5)	3.81 (1)
O(10)–Nd(4)	2.39 (4)	–Nd(6)	3.80 (1)
–Nd(5)	2.30 (4)	Nd(5)–Nd(6)	3.81 (1)
O(11)–Nd(5)	2.36 (4)	Nd(1)–Nd(4)	4.22 (1)
–Nd(6)	2.33 (3)	Nd(2)–Nd(5)	4.23 (1)
		Nd(3)–Nd(6)	4.24 (1)

[a] O–C and C–C distances were restrained in the least-squares refinements and averaged to the values reported in the text.

neighbors range from 12.94 to 16.34 Å.

The magnetic susceptibility of the complex followed the Curie–Weiss equation $\chi = C_M/(T + \Theta)$ in the temperature range 7.5–100 K. The magnetic moment, μ_{eff}, was 3.22 μ_B per neodymium atom with $\Theta = -2.8$ K and $C_M = 1.293$.

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Registry No. $Nd_6[OCH(CH_3)_2]_{17}Cl$, 66373-84-0; neodymium trichloride, 10024-93-8; sodium isopropoxide, 683-60-3.

Supplementary Material Available: A list of selected angles, data processing formulas, and a listing of observed structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and X-ray Structural Characterization of the Hexakis(dimethyl sulfoxide)ruthenium(II) Cation

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The compound $[Ru(Me_2SO)_6][BF_4]_2$, Me_2SO = dimethyl sulfoxide, crystallizes in the monoclinic space group $P2_1/c$, with cell dimensions a = 17.833 (4) Å, b = 10.486 (3) Å, c = 33.800 (8) Å, β = 109.68 (1)°, and Z = 8. Of the 5569 reflections measured by counter methods (Mo Kα radiation, λ_{α_1} = 0.709 26 Å), 3961 $\geq 2.3\sigma$ were used for the structural determination. Full-matrix, least-squares refinement gave a final R value of 0.051. Two crystallographically distinct $Ru(Me_2SO)_6{}^{2+}$ cations occur in the asymmetric units which are chemically identical. The ruthenium(II) atom is coordinated to three Me_2SO molecules via the oxygen atom and to three via the sulfur atom to give the facial isomer of irregular octahedral geometry. Selected mean bond lengths (corrected for thermal motion, assuming the light atom to ride on the ruthenium) are Ru–S = 2.259 Å and Ru–O = 2.133 Å (the corresponding uncorrected values are 2.250 and 2.127 Å). The mean S–O bonds are 1.482 Å for S-bonded and 1.536 Å for O-bonded ligands. Infrared and proton magnetic resonance data are also given.

Introduction

This work stems from an interest in the use of ruthenium(II) sulfoxide complexes as homogeneous hydrogenation catalysts,[2] including ones containing chiral sulfoxides.[3] An appreciation of the electronic and steric properties of sulfoxide derivatives (e.g., O vs. S bonding) is essential for an evaluation of such compounds as potential catalysts, an S-bonded ligand (a weak π acceptor) being more likely to stabilize an intermediate hydrido species than an O-bonded ligand.[4] Following characterization of the *fac*-$[RuCl_3(Me_2SO)_3]^-$ anion, which has all S-bonding sulfoxides,[2] and the *cis*-$RuCl_2(Me_2SO)_4$ complex,[5,6] which has three S-bonded ligands, and one O-bonded Me_2SO (trans to a S-bonded one), we have now characterized the $[Ru(Me_2SO)_6][BF_4]_2$ complex by X-ray crystallography; infrared and proton magnetic resonance data are also reported. The cation was first prepared by Evans et al.[7] as the perchlorate salt.

Experimental Section

Preparation of Hexakis(dimethyl sulfoxide)ruthenium(II) Tetrafluoroborate(III). A solution of $AgBF_4$ (1.2 g) in acetone (10 mL) was added under argon to the *cis*-$RuCl_2(Me_2SO)_4$ complex[6,7] (1.5 g) dissolved in warm Me_2SO (25 mL). The $AgCl(Me_2SO)_n$ precipitate was filtered off after cooling to room temperature. Addition of acetone (30 mL) precipitated the product as a white powder which was recrystallized from Me_2SO–acetone, washed with acetone, and vacuum dried (1.8 g, 70%), mp 240 °C (decomposition in vacuo). The fully deuterated complex was made using Me_2SO-d_6.

Physical Measurements. Infrared spectra (4000–250 cm^{-1}) were recorded on a Perkin-Elmer 457. Proton magnetic resonance spectra were recorded on Varian T60 and XL100 spectrometers at 30 °C, the sample solutions being kept under argon. The procedure for following H_2 uptake at constant pressure has been described previously.[8]

X-ray Intensity Data. A $[Ru(Me_2SO)_6][BF_4]_2$ crystal of approximate dimensions 0.11 × 0.27 × 0.09 mm was mounted along the needle axis for the purpose of data collection. Using copper radiation (λ 1.5418 Å), Weissenberg photographs of the reciprocal lattice layers $h0l$ and $h1l$ and precession photographs of the $hk0$ and $0kl$ zones were taken which established monoclinic Laue symmetry, with systematic absences consistent with the space group $P2_1/c$. Accurate cell parameters were determined from counter measurement of 12 of the strongest reflections having $2\theta > 30°$, using a Picker FACS-1 computer-controlled, four-circle diffractometer, and Mo Kα radiation (λ_{α_1} 0.709 26 Å).

The crystal was mounted with the b axis (corresponding to the needle direction) slightly offset from the ϕ axis of the diffractometer. The crystal has a formula weight of 743.5, space group $P2_1/c$: a = 17.833 (4) Å, b = 10.486 (3) Å, c = 33.800 (8) Å, β = 109.68 (1)°, V = 5952.0 Å^3, d_M = 1.62 (2) g cm^{-3} (flotation), Z = 8, d_x = 1.66 g cm^{-3}, μ(Mo Kα) = 9.83 cm^{-1}, T = 21 (±1) °C. Reflections for the unique set of data were measured in two sets using a scintillation detector with pulse height analysis and monochromatized radiation (graphite monochromator, λ(Mo Kα) = 0.709 26 Å). Those reflections for which $\sin\theta < 0.1737$ were measured with a symmetrical θ–2θ scan of 1.2° base width with 10-s background counts made at both scan limits. For reflections where $0.1737 < \sin\theta < 0.3420$, a scan of 0.8° base width was used, with 4-s background counts. Two standard reflections were measured after each 100 reflections; their variation was ±3% over the entire data collection. The intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to introduce an extreme error of ±8.0% in F. A total of 5569 reflections were measured, of which 3961 were considered to be observed (i.e., greater than $2.3\sigma_{I(\mathrm{net})}$, where $\sigma_{I(\mathrm{net})} = [\mathrm{TC} + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$, where TC is the total count, B_1 and B_2 are the background counts, t_s is the scan time, t_b is the total background count time, k is a constant set to 0.03, and I is the net count).

Structure Determination and Refinement. Examination of the three-dimensional Patterson function based on data for which $\sin\theta < 0.1737$ gave the positions of the two ruthenium atoms of the asymmetric unit and ten sulfur atoms. Refinement of the scale and these atomic coordinates gave R = 0.456, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. Several cycles of refinement and subsequent electron density difference maps based on the complete set of observed data gave the positions of all nonhydrogen atoms. A difference Fourier synthesis based on an inner set of data revealed the positions of at least one of the hydrogen atoms of each methyl group. The remaining hydrogen atom positions were then calculated, with a C–H bond length of 0.96 Å, and assigned isotropic temperature factors of 0.076 Å^2. Anisotropic thermal parameters were assigned to all nonhydrogen atoms save the boron atoms, and full-matrix, least-squares refinement reduced the R factor to a final value of 0.051. At this stage comparison of the interatomic distances and angles within each cation showed that they adopted very similar configurations and that the pattern of bond lengths and angles in one cation was followed very closely in the other. An inspection of the ruthenium atomic coordinates and thermal motion parameters revealed (i) that the ruthenium atoms are roughly related by the transformation $^1/_2 + x, y, {}^1/_2 - z$ and (ii) that U_{22} is the highest thermal motion parameter for one ruthenium and the lowest for the other. The possibility existed that the refinement had been "locked" by this false symmetry, relating the two cations, in particular with respect to the y coordinates of the ruthenium atoms.

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