(16) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).
(17) G. Brauer and H. Gradinger, *Z. Anorg. Allg. Chem.*, **276**, 209 (1954).
(18) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, **15**, 2498 (1976).
(19) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *Inorg. Chem.*, **16**, 599 (1977).
(20) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *Inorg. Chem.*, **16**, 1090 (1977).

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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, $\beta = 109.68$ (1)°, and $Z = 8$. Of the 5569 reflections measured by counter methods (Mo Kα radiation, $\lambda_{\alpha_1} = 0.709\,26$ 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, $\beta = 109.68$ (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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Table I

Fractional Atomic Coordinates in Crystalline $[Ru(Me_2SO)_6][BF_4]_2$ ($\times 10^4$, $\times 10^5$ for Ru; $\times$ 10^3 for B)[a]

Cations

Atom type	Cation I			Cation II		
	x	*y*	*z*	*x*	*y*	*z*
Ru	222 (5)	24213 (9)	10204 (2)	54688 (4)	24582 (9)	39651 (2)
S1	784 (2)	1739 (3)	647 (1)	5836 (2)	713 (3)	3689 (1)
S2	−953 (2)	1096 (3)	663 (1)	6748 (2)	2974 (3)	4288 (1)
S3	−422 (2)	4182 (3)	625 (1)	5310 (2)	1388 (3)	4510 (1)
S4	1375 (2)	697 (3)	1655 (1)	5084 (2)	3179 (3)	2987 (1)
S5	1072 (2)	4793 (3)	1598 (1)	3486 (2)	2367 (3)	3660 (1)
S6	−301 (2)	2803 (3)	1886 (1)	4541 (2)	5108 (3)	3858 (1)
O1	988 (5)	359 (8)	710 (2)	6304 (4)	1021 (7)	3414 (2)
O2	−1177 (4)	1039 (8)	203 (2)	7287 (4)	1977 (8)	4530 (3)
O3	234 (4)	4961 (7)	577 (2)	4863 (4)	160 (7)	4394 (2)
O4	478 (4)	978 (6)	1476 (2)	5475 (4)	3610 (6)	3452 (2)
O5	1018 (4)	3432 (6)	1435 (2)	4265 (4)	2090 (6)	3590 (2)
O6	−661 (4)	2923 (6)	1403 (2)	5099 (4)	4186 (6)	4180 (2)
C11	1681 (6)	2607 (12)	773 (3)	6379 (7)	−487 (11)	4048 (4)
C12	415 (7)	1984 (12)	97 (3)	4978 (6)	−178 (10)	3395 (4)
C21	−743 (7)	−491 (11)	848 (4)	6863 (7)	4297 (12)	4622 (4)
C22	−1843 (7)	1362 (13)	770 (4)	7196 (6)	3615 (11)	3934 (4)
C31	−956 (7)	5181 (12)	855 (4)	4776 (7)	2320 (11)	4764 (3)
C32	−1151 (7)	4048 (12)	116 (4)	6156 (7)	1035 (11)	4966 (3)
C41	1423 (7)	−993 (11)	1624 (4)	5852 (7)	3310 (11)	2767 (3)
C42	1600 (7)	866 (13)	2199 (4)	4516 (6)	4547 (10)	2743 (3)
C51	1619 (8)	4660 (13)	2140 (4)	2876 (7)	2961 (15)	3174 (5)
C52	1817 (8)	5533 (13)	1449 (4)	3030 (7)	892 (13)	3657 (5)
C61	−842 (9)	3988 (11)	2051 (4)	5142 (8)	643 (12)	3846 (4)
C62	−751 (8)	1433 (11)	2015 (4)	3969 (8)	5736 (12)	4147 (4)

Anion

Atom type	*x*	*y*	*z*	Atom type	*x*	*y*	*z*
F1	2111 (4)	2682 (9)	4883 (2)	F11	336 (12)	3614 (11)	3096 (5)
F2	3422 (5)	2559 (8)	5211 (2)	F12	472 (8)	1919 (15)	3129 (4)
F3	2865 (5)	1488 (8)	4618 (3)	F13	4273 (4)	2206 (8)	2036 (3)
F4	2920 (5)	3566 (8)	4604 (3)	F14	3059 (6)	2998 (9)	1849 (4)
F5	−3648 (7)	2726 (18)	1918 (4)	F15	3228 (6)	1149 (13)	1650 (5)
F6	−2761 (7)	2648 (14)	1658 (4)	F16	3395 (8)	1548 (17)	2254 (5)
F7	−2441 (7)	2717 (13)	2335 (4)	B1	283 (1)	254 (2)	484 (1)
F8	−2980 (10)	1260 (13)	1990 (5)	B2	−292 (1)	246 (3)	201 (1)
F9	897 (5)	2356 (12)	2823 (3)	B3	68 (1)	250 (2)	314 (1)
F10	1205 (6)	2485 (20)	3473 (3)				

Thermal Motion Parameters[b] ($\times 10^3$ Å^2; $\times 10^4$ Å^2 for Ru)

Cations

Atom type	Cation I						Cation II					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	343 (6)	395 (6)	325 (6)	−62 (5)	129 (4)	−33 (5)	300 (5)	291 (6)	344 (6)	−3 (5)	92 (4)	20 (5)
S1	47 (2)	62 (2)	39 (2)	−7 (2)	22 (2)	−6 (2)	52 (2)	30 (2)	59 (2)	7 (2)	26 (2)	4 (2)
S2	49 (2)	57 (2)	47 (2)	−18 (2)	15 (2)	−10 (2)	33 (2)	45 (2)	56 (2)	−4 (2)	5 (2)	10 (2)
S3	47 (2)	57 (2)	45 (2)	−6 (2)	7 (2)	10 (2)	48 (2)	49 (2)	40 (2)	−3 (2)	17 (2)	7 (2)
S4	47 (2)	50 (2)	52 (2)	4 (2)	23 (2)	5 (2)	54 (2)	40 (2)	41 (2)	−3 (2)	14 (2)	3 (2)
S5	49 (2)	48 (2)	77 (2)	−4 (2)	18 (2)	−17 (2)	42 (2)	70 (3)	70 (2)	−8 (2)	16 (2)	−10 (2)
S6	60 (2)	54 (2)	47 (2)	−6 (2)	28 (2)	−8 (2)	54 (2)	39 (2)	50 (2)	8 (2)	12 (2)	−22 (2)
O1	40 (5)	66 (6)	113 (7)	5 (5)	−14 (5)	42 (6)	40 (5)	33 (5)	42 (5)	−2 (4)	10 (4)	−9 (4)
O2	52 (5)	34 (5)	38 (4)	13 (4)	15 (4)	−3 (4)	92 (7)	52 (6)	67 (6)	10 (5)	42 (5)	−5 (5)
O3	83 (6)	53 (6)	59 (5)	−36 (5)	26 (5)	−3 (5)	53 (5)	61 (6)	78 (6)	−25 (5)	20 (5)	18 (5)
O4	52 (5)	27 (4)	34 (4)	−3 (4)	14 (4)	8 (4)	39 (5)	43 (5)	44 (5)	−6 (4)	16 (4)	3 (4)
O5	81 (6)	46 (5)	88 (6)	8 (5)	62 (5)	7 (5)	39 (4)	43 (5)	41 (5)	2 (4)	18 (4)	−4 (4)
O6	32 (4)	52 (5)	53 (5)	−1 (4)	12 (4)	−5 (4)	65 (6)	76 (7)	35 (5)	25 (5)	5 (4)	−8 (5)
C11	67 (4)	67 (9)	72 (9)	−7 (8)	3 (8)	−18 (8)	84 (11)	88 (12)	72 (10)	−14 (9)	18 (9)	−18 (9)
C12	46 (7)	64 (9)	84 (9)	−19 (7)	32 (7)	−5 (8)	101 (11)	75 (11)	108 (12)	−44 (9)	45 (10)	1 (9)
C21	112 (12)	52 (9)	107 (12)	−15 (9)	25 (10)	7 (9)	39 (7)	110 (11)	45 (7)	−11 (8)	25 (6)	−13 (8)
C22	111 (11)	73 (10)	79 (10)	41 (9)	41 (9)	−8 (8)	66 (9)	105 (11)	40 (8)	−6 (8)	25 (7)	−7 (8)
C31	78 (9)	65 (9)	49 (7)	8 (8)	32 (7)	2 (7)	70 (10)	62 (10)	85 (11)	27 (8)	24 (8)	17 (8)
C32	78 (9)	79 (10)	49 (8)	−9 (8)	1 (7)	38 (7)	69 (9)	77 (11)	52 (9)	−10 (8)	−13 (7)	19 (8)
C41	69 (9)	65 (9)	54 (8)	1 (7)	27 (7)	3 (7)	80 (10)	36 (8)	114 (12)	21 (7)	46 (9)	17 (8)
C42	76 (9)	45 (8)	41 (7)	11 (7)	7 (7)	15 (6)	96 (11)	97 (11)	54 (9)	22 (9)	31 (8)	19 (9)
C51	77 (9)	50 (8)	66 (9)	23 (7)	−11 (8)	24 (7)	148 (13)	47 (9)	112 (12)	3 (9)	95 (11)	−6 (8)
C52	49 (8)	43 (8)	75 (9)	−6 (7)	10 (9)	−4 (7)	102 (11)	49 (9)	89 (10)	−5 (8)	64 (9)	7 (8)
C61	41 (8)	150 (15)	127 (12)	16 (9)	20 (7)	36 (11)	87 (10)	41 (9)	82 (11)	−33 (8)	9 (8)	−5 (8)
C62	66 (9)	79 (11)	141 (12)	−25 (9)	12 (7)	0 (10)	47 (8)	111 (12)	86 (10)	−42 (8)	32 (7)	−31 (9)

Table I (*Continued*)

Anion

Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F1	80 (6)	231 (11)	109 (6)	43 (7)	53 (5)	18 (7)	F9	132 (8)	339 (17)	107 (7)	−32 (9)	80 (7)	−85 (9)
F2	109 (6)	127 (7)	68 (5)	20 (6)	−2 (5)	7 (6)	F10	120 (9)	655 (35)	94 (8)	94 (15)	13 (7)	5 (14)
F3	115 (7)	107 (7)	152 (8)	16 (6)	39 (6)	−44 (7)	F11	498 (27)	78 (9)	295 (19)	72 (13)	181 (19)	15 (10)
F4	140 (8)	116 (8)	120 (7)	22 (6)	62 (6)	47 (6)	F12	170 (12)	303 (19)	277 (16)	7 (12)	129 (12)	59 (14)
F5	158 (11)	539 (28)	161 (10)	225 (14)	49 (9)	39 (14)	F13	57 (5)	132 (8)	150 (8)	−9 (5)	32 (5)	−35 (7)
F6	199 (12)	294 (18)	169 (11)	−63 (11)	74 (10)	22 (12)	F14	108 (8)	68 (7)	339 (17)	36 (6)	2 (9)	−15 (9)
F7	162 (10)	326 (19)	158 (10)	−100 (11)	9 (9)	−138 (11)	F15	98 (8)	240 (14)	298 (17)	34 (8)	−45 (9)	−213 (14)
F8	350 (22)	137 (12)	274 (18)	−52 (13)	−40 (15)	47 (12)	F16	193 (13)	356 (22)	274 (17)	−34 (14)	107 (13)	151 (17)

Isotropic Parameters (×10²)

Atom	U, Å²	Atom	U, Å²	Atom	U, Å²	Atom	U, Å²
B1	66 (4)	B2	89 (5)	B3	89 (5)	B4	75 (5)

[a] In this and the following tables, figures in parentheses are the least-squares estimated errors. [b] The anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

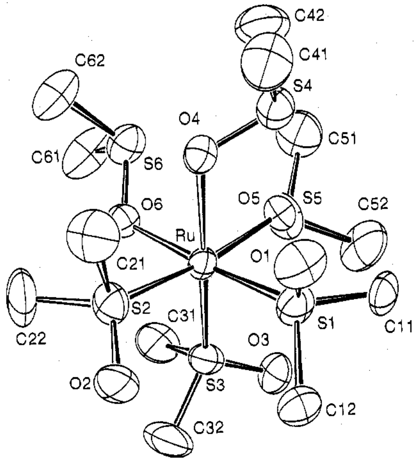

Figure 1. A perspective view of $Ru(Me_2SO)_6^{2+}$ (cation I), showing the labeling and thermal motion ellipsoids (50%). Cation II adopts a very similar configuration (see text) and is labeled to reflect the similarity.

An electron density difference map showing the detail around each metal atom, however, showed no outstanding features, and the refinement was then terminated. The highest peaks in the final difference map (1.0 ± 0.1 electrons/Å³) occurred near the BF_4^- anions. In the early refinement, constant unit weights were used; in the later stages, weights ($=1/\sigma_F^2$) were given in terms of $\sigma_F = \sigma_I/(Lp(2F_o))$. Atomic scattering factors used were taken from ref 9 and included corrections for anomalous dispersion for ruthenium and sulfur atoms. Crystallographic computer programs used in this determination have been cited previously.[10] Tables of the measured and calculated structure factors and the calculated hydrogen atom fractional coordinates are available as supplementary material (see paragraph at the end of this paper). Final atomic parameters and thermal motion parameters are listed in Table I, and interatomic distances and angles are given in Table II.

Results and Discussion

Structural Data. The two crystallographically distinct $Ru(Me_2SO)_6^{2+}$ cations found in the asymmetric unit are very nearly identical with respect to interatomic distances and geometrical configuration, with only small crystallographically (but not chemically) significant differences occurring for several angular parameters (Table II); the labeling of the two cations has been chosen to reflect their close similarity. A perspective view of one of the cations (cation I) is shown in Figure 1.

Each ruthenium atom is coordinated with irregular octahedral geometry to six Me_2SO ligands; three ligands bond via their sulfur atoms and three via their oxygen atoms to give the facial isomer. The choice of linkage and geometric isomers in metal complexes of Me_2SO has been shown to be a balance between steric and electronic effects.[4,5] In the present case, it would appear from the geometry and dimensions of the coordination sphere that steric influences do not determine the choice of isomer. The S–Ru–S angles (for S-bonded ligands) range in value from 90.3 (1) to 97.7 (1)°; the possibility of having six S-bonded ligands cannot be ruled out on steric arguments alone. The facial isomer must therefore be considered to be determined by electronic effects, specifically the desire of an S-bonded ligand (weak π acceptor) to be trans to an O-bonded ligand (strong σ donor, with little competition for metal π electrons). It is also noted that the variation in Ru–S and Ru–O bond lengths in both cations, while not crystallographically significant, is chemically sensible; i.e., the longest Ru–S bond lengths occur trans to the shortest Ru–O bond lengths (Table II). The mean Ru–S bond length corrected for thermal motion (light atom riding on the heavy atom) of 2.259 Å is equal within error to the only other value available for S-bonded Me_2SO trans to oxygen[5] (2.252 (1) Å) and may be compared to values of 2.277 (1) Å (trans to Cl)[5] and 2.188 (3) Å (in $[Ru(NH_3)_5(Me_2SO)]^{2+}$).[11] These distances are consistent with a picture of sulfur as a weak π acceptor in these complexes, and in the absence of large steric influences (as in, for instance, the 2-methylbutyl sulfoxide $[Pd(L_2SO)_4]^{2+}$),[12] the geometrical and linkage isomer is chosen to reduce competition for the π-donor orbitals on the metal.

The average sulfur–oxygen atom distances are 1.482 Å (and 1.506 Å when corrected for the oxygen atom riding on the sulfur) for S-bonded and 1.536 Å for O-bonded ligands, showing the loss of sulfur–oxygen double bond character upon coordination via oxygen. The geometry of the Me_2SO ligands is similar to that found in free Me_2SO.[13] Average O–S–C and C–S–C angles and S–C bond lengths for the S-bonded ligands are 106.7°, 98.8°, and 1.77 Å, respectively. Corresponding values for the O-bonded ligands are 104.0°, 99.1°, and 1.76 Å, and for the free Me_2SO molecule, they are 107°, 98°, and 1.80–1.82 Å.[13]

The packing within the unit cell can be considered to approximate the fluorite structure, each $Ru(Me_2SO)_6^{2+}$ cation being surrounded by eight BF_4^- anions at the corners of an irregular cube and each BF_4^- being surrounded by four $Ru(Me_2SO)_6^{2+}$ cations in an irregular tetrahedral array; no unusually short interatomic contacts are found.

Spectroscopic Data. The infrared spectra of dimethyl sulfoxide complexes are diagnostic of the bonding mode; S bonding usually causes an increase of ν(SO) to about 1100 cm⁻¹ (from the 1055 cm⁻¹ value for free Me_2SO), whereas a shift to the lower range of 1000–900 cm⁻¹ is indicative of donation from oxygen.[2] A strong broad band around 1100 cm⁻¹ for the $[Ru(Me_2SO)_6][BF_4]_2$ complex is attributed to S-bonded ν(SO); a strong, sharp band at 935 cm⁻¹ is assigned

Table II. Interatomic Distances and Angles within the $Ru(Me_2SO)_6{}^{2+}$ Cations

	Cation I	Cation II
	(a) Distances (Å)[a]	
Ru-S1	2.260 (3) [2.268 (3)]	2.250 (3) [2.259 (3)]
Ru-S2	2.237 (3) [2.247 (3)]	2.239 (3) [2.249 (3)]
Ru-S3	2.260 (3) [2.270 (3)]	2.255 (3) [2.264 (3)]
Ru-O4	2.118 (6) [2.123 (6)]	2.117 (6) [2.123 (5)]
Ru-O5	2.138 (6) [2.141 (5)]	2.129 (6) [2.138 (5)]
Ru-O6	2.121 (6) [2.125 (5)]	2.137 (6) [2.150 (5)]
S1-O1	1.492 (7) [1.516 (7)]	1.479 (7) [1.501 (6)]
S2-O2	1.475 (7) [1.489 (6)]	1.469 (7) [1.510 (7)]
S3-O3	1.479 (7) [1.500 (6)]	1.495 (7) [1.521 (7)]
S4-O4	1.536 (6)	1.555 (6)
S5-O5	1.522 (6)	1.515 (6)
S6-O6	1.547 (6)	1.542 (7)
S1-C11	1.76 (1)	1.79 (1)
S1-C12	1.77 (1)	1.78 (1)
S2-C21	1.77 (1)	1.76 (1)
S2-C22	1.77 (1)	1.76 (1)
S3-C31	1.77 (1)	1.77 (1)
S3-C32	1.78 (1)	1.80 (1)
S4-C41	1.75 (1)	1.77 (1)
S4-C42	1.78 (1)	1.79 (1)
S5-C51	1.76 (1)	1.75 (1)
S5-C52	1.75 (1)	1.75 (1)
S6-C61	1.78 (1)	1.76 (1)
S6-C62	1.77 (1)	1.76 (1)
	(b) Angles (Deg)	
S1-Ru-S2	90.3 (1)	90.5 (1)
S1-Ru-S3	94.9 (1)	93.9 (1)
S2-Ru-S3	97.7 (1)	96.3 (1)
S1-Ru-O4	91.3 (2)	92.4 (2)
S1-Ru-O5	90.0 (2)	8.9 (2)
S1-Ru-O6	175.2 (3)	175.5 (2)
S2-Ru-O4	89.2 (2)	88.7 (2)
S2-Ru-O5	170.5 (2)	172.7 (2)
S2-Ru-O6	88.9 (2)	90.6 (2)
S3-Ru-O4	170.7 (2)	171.9 (2)
S3-Ru-O5	91.8 (2)	91.0 (2)
S3-Ru-O6	89.8 (2)	90.4 (2)
O4-Ru-O5	81.2 (2)	84.1 (2)
O4-Ru-O6	83.9 (2)	83.2 (3)
O5-Ru-O6	90.0 (2)	89.5 (2)
Ru-S1-O1	113.0 (3)	112.8 (3)
Ru-S2-O2	118.8 (3)	117.9 (3)
Ru-S3-O3	112.7 (3)	114.6 (3)
Ru-O4-S4	121.2 (4)	122.5 (4)
Ru-O5-S5	129.7 (4)	131.8 (4)
Ru-O6-S6	120.1 (4)	119.5 (4)
Ru-S1-C11	111.8 (4)	110.1 (4)
Ru-C1-C12	117.5 (4)	117.2 (4)
Ru-S2-C21	111.1 (4)	112.5 (4)
Ru-S2-C22	112.3 (4)	112.2 (4)
Ru-S3-C31	111.1 (4)	110.9 (4)
Ru-S3-C32	120.3 (4)	120.2 (4)
O1-S1-C11	107.9 (5)	108.9 (5)
O1-S1-C12	106.1 (5)	106.8 (5)
O2-S2-C21	106.4 (5)	106.9 (5)
O2-S2-C22	106.5 (5)	106.6 (5)
O3-S3-C31	106.5 (5)	106.0 (5)
O3-S3-C32	106.6 (5)	105.5 (5)
O4-S4-C41	103.2 (5)	104.8 (5)
O4-S4-C42	103.5 (5)	103.0 (4)
O5-S5-C51	104.3 (5)	103.5 (5)
O5-S5-C52	105.7 (5)	106.1 (5)
O6-S6-C61	101.3 (5)	101.6 (5)
O6-S6-C62	105.2 (5)	104.9 (5)
C11-S1-C12	99.4 (5)	100.2 (5)
C21-S2-C22	100.0 (6)	98.8 (6)
C31-S3-C32	98.2 (6)	97.6 (5)
C41-S4-C42	99.5 (6)	98.0 (5)
C51-S5-C52	97.3 (6)	99.7 (7)
C61-S6-C62	98.9 (5)	100.9 (6)

[a] Values in square brackets are corrected for thermal motion, the light atom considered to be riding on the heavy atom.

to O-bonded Me_2SO. This latter assignment is somewhat complicated by the presence of other bands in this region; there is a $BF_4{}^-$ stretch[14] at 990 cm^{-1} (and at 525 cm^{-1}), and methyl rocking vibrations in the 950–1000-cm^{-1} region are also present.[2,13] However, the infrared spectrum of the fully deuterated complex which gives a band at 930 cm^{-1} confirms[2,4,7,15] the assignment of ν(SO), O bonded. The assignment at 935 cm^{-1} is further confirmed in that it fits well to an observed correlation[4,16] found between frequency shift of ν(SO), on coordination of O-bonded sulfoxide, and ν(M–O), the ν(Ru–O) stretch[2] being observed at 480 cm^{-1} in the present $Ru(Me_2SO)_6{}^{2+}$ cation. A paper by Singleton et al.,[15] that appeared after completion of our studies, reported on a different synthesis for the cation and the deuterated analogue, and the reported infrared assignments agree with ours.

NMR Spectra. Downfield shifts of up to 1 ppm are usually characteristic of S-bonded Me_2SO methyl protons, while the O-bonded ligands, in which the protons are further removed from the metal, show considerably less variation from the free value (τ 7.40).[2,7] The measured spectra of the $Ru(Me_2SO)_6{}^{2+}$ cation in various solvents at room temperature show singlets in the region τ 6.70–6.90 due to S-bonded Me_2SO, together with singlets in the τ 7.15–7.40 region due to O-bonded or free Me_2SO.

The NMR spectrum in Me_2SO-d_6 at room temperature changes with time. Two minutes after dissolution of the cation, the spectrum shows free Me_2SO (τ 7.40), O-bonded Me_2SO (τ 7.15), and S-bonded Me_2SO (τ 6.80 and 6.64), in the ratios of ca. 1:2:3. This shows that one O-bonded Me_2SO is rapidly displaced; the resulting species should then have two S-bonded ligands (τ 6.64) trans to O-bonded Me_2SO and one S-bonded Me_2SO (τ 6.80) trans to Me_2SO-d_6. Integration of the peaks in the S-bonded region shows about a 2.5:1 ratio which is reasonably consistent considering that the peaks share a somewhat broad baseline and that the spectra are time dependent. After the solution is allowed to stand, the intensity of the free Me_2SO peak increases with concomitant decreasing intensity of the other three peaks; the ratio of the peaks in the S-bonded region remains close to 2:1, while the peak of the O-bonded Me_2SO decreases more rapidly than those of the S-bonded ligands. After 1 h the ratio of free Me_2SO to O bonded to S bonded is about 5:1:3. Slower exchange with S-bonded compared to O-bonded Me_2SO seems typical of ruthenium(II) sulfoxide complexes.[7,17]

The NMR spectrum in D_2O at room temperature is of interest in that it shows the presence of *four* S-bonded, one O-bonded, and one free Me_2SO, a few minutes after dissolution. After the solution is allowed to stand, the O-bonded Me_2SO is displaced while the S-bonded ones are not exchanged and after 30 min the spectrum shows a multiplet in the S-bonded region and a singlet for free Me_2SO with an intensity ratio 2:1, again consistent with four S-bonded Me_2SO ligands. The multiplet is not well resolved but it could presumably result from the presence of a mixture of cis and trans isomers of $Ru(Me_2SO)_4(D_2O)_2{}^{2+}$ (Me_2SO = S-bonded Me_2SO) or a five-coordinate species.

Catalytic Properties. The $Ru(Me_2SO)_6{}^{2+}$ cation was found ineffective as a catalyst for hydrogenation of olefinic substrates under mild conditions in aqueous solutions. However, in *N,N′*-dimethylacetamide solution at 60 °C and 1 atm of H_2 the activated substrate acrylamide was reduced homogeneously to propionamide. A catalyst concentration of 10^{-2} M effected hydrogenation of 0.8 M acrylamide with an initially linear rate of 5×10^{-6} M s^{-1}. The activity is similar to that determined using *cis*-$RuCl_2(Me_2SO)_4$ or *fac*-$[RuCl_3(Me_2SO)_3]^-$ species as catalysts under similar conditions.[2,17]

In the absence of substrate, the $Ru(Me_2SO)_6{}^{2+}$ cation is reduced by H_2 to metal. The catalysis undoubtedly occurs via an unsaturate route[18] in which H_2 interacts with a Ru(II) olefin intermediate, the olefin stabilizing the Ru(II) against reduction to metal.

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Registry No. *cis*-$RuCl_2(Me_2SO)_4$, 59091-96-2; $[Ru(Me_2SO)_6][BF_4]_2$, 66373-94-2.

Supplementary Material Available: Listings of the measured and calculated structure factors and the calculated hydrogen atom fractional coordinates (31 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Simon Fraser University. (b) University of British Columbia.
(2) R. S. McMillan, A. Mercer, B. R. James, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1006 (1975).
(3) B. R. James, R. S. McMillan, and K. J. Reimer, *J. Mol. Catal.*, **1**, 439 (1976); B. R. James and R. S. McMillan, *Can. J. Chem.*, **55**, 3927 (1977); B. R. James, R. S. McMillan, R. H. Morris, and D. K. W. Wang, *Adv. Chem. Ser.*, in press.
(4) B. R. James, R. H. Morris, and K. J. Reimer, *Can. J. Chem.*, **55**, 2353 (1977).
(5) A. Mercer and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2480 (1975).
(6) B. R. James, E. Ochiai, and G. L. Rempel, *Inorg. Nucl. Chem. Lett.*, **7**, 781 (1971).
(7) I. P. Evans, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 204 (1973).
(8) B. R. James and G. L. Rempel, *Discuss. Faraday Soc.*, **46**, 48 (1968).
(9) D. T. Cromer and J. T. Waber in "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(10) F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, **11**, 395 (1972).
(11) F. C. Marah and G. Ferguson, *Can. J. Chem.*, **49**, 3590 (1971).
(12) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, **11**, 1280 (1972); *Chem. Commun.*, 1377 (1970).
(13) W. L. Reynolds, *Prog. Inorg. Chem.*, **12**, 1 (1970).
(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y., 1970, p 110.
(15) T. V. Ashworth, E. Singleton, and J. J. Hough, *J. Chem. Soc., Dalton Trans.*, 1809 (1977).
(16) B. R. James and R. H. Morris, *Spectrochim. Acta, Part A*, in press.
(17) R. S. McMillan, Ph.D. Dissertation, University of British Columbia, 1976.
(18) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973, p 400.

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Unusual Coordination Behavior of Iminoalkyl Ligands. Crystal and Molecular Structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

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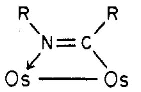
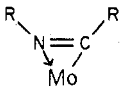
The crystal and molecular structure of the compound $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ has been obtained by single-crystal X-ray diffraction analysis using data collected by counter methods. The compound crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.098$ (2) Å, $b = 16.285$ (2) Å, $c = 15.577$ (4) Å, $\beta = 98.01$ (2)°, $V = 2285.7$ Å^3, $Z = 4$, and $\rho_{\text{calcd}} = 2.818$ g cm^{-3}. The structure was solved by a combination of direct methods and difference Fourier analyses. Least-squares refinement employing 3805 reflections ($F^2 > 3.0\sigma(F^2)$) converged to the final discrepancy indices $R = 0.044$ and $R_w = 0.057$. The molecule contains a triangular arrangement of osmium atoms. Atoms Os(1) and Os(3) each contain three linear carbonyl groups while Os(2) contains four. The most interesting feature is a $\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3$ ligand which is bonded to atoms Os(1) and Os(3). The carbon–nitrogen multiple bond, C(17)–N, is 1.278 (10) Å. The bridging hydride ligand was not located but its position is strongly indicated by geometric considerations and comparisons with related molecules.

Introduction

Recent studies have revealed remarkable abilities of triosmium cluster compounds to produce chemical transformations upon small molecules.[1-10] One of the more fascinating of these is the ability to activate aliphatic C–H bonds positioned α to donor nuclei.[8-10] A recent report on the reaction of $Os_3(CO)_{12}$ with imines and trialkylamines describes the preparation of complexes believed to contain bridging η^2-iminoalkyl ligands, I.[10] The ability of the nitrogen atom of iminoalkyl ligands to engage in supplementary coordination was recently demonstrated through our characterizations of the first examples of η^2-iminoalkyl ligands bonded to single metal atoms, II.[11]



I



II

Muetterties has recently pointed out and emphasized the importance of polynuclear interactions in producing partial bond reductions in unsaturated ligands.[12] It thus seemed likely that comparisons of the type I and type II structures would yet provide another opportunity for testing this important hypothesis. Because of this and our continuing interest in the unusual coordination behavior of iminoalkyl ligands, we have performed a crystal structure analysis of the complex $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ which is reported here.

Experimental Section

A. Data Collection. The compound $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ was prepared by the method of Deeming from $Os_3(CO)_{12}$ and *N*-methylbenzaldimine.[10] Crystals were grown over a period of several days from pentane solutions cooled to −20 °C. A thick crystalline plate of dimensions 0.146 × 0.380 × 0.280 mm was cleaved from a large crystalline cluster. Crystal faces were subsequently identified as $(1\bar{2}5)$, $(\bar{1}2\bar{5})$, $(21\bar{1})$, $(\bar{2}\bar{1}1)$, (141), and $(1\bar{8}1)$ with the last being assigned to the cleavage face. The crystal was mounted and sealed in a thin-walled glass capillary. A preliminary orientation matrix and unit cell parameters were obtained through the search, centering, and indexing of 25 randomly collected reflections obtained using an Enraf-Nonius CAD-4 four-circle automatic diffractometer. ω-Scan peak widths at half-height were generally on the order of 0.1°. Final cell parameters were obtained by the centering and least-squares refinement of 25 high-angle reflections, $2\theta > 40°$. Inspection subsequently revealed the systematic absences $0k0 = 2n + 1$ and $h + l = 2n + 1$ and, thus, identified the space group as $P2_1/n$.[13] Pertinent crystal parameters are listed in Table I.

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