Preparation, Characterization, and Crystal and Molecular Structure of Dimethylammonium Trichlorotris(dimethyl sulphoxide)ruthenate(II)

By **Roderick S. McMillan, Anthony Mercer, Brian R. James,*** and **James Trotter,** Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

A simple preparation of the title compound (1) is presented. ^{1}H N.m.r. and i.r. spectra of the *fac*-complex indicate only *S*-bonded sulphoxide ligands, confirmed by *X*-ray crystallographic analysis. Crystals are orthorhombic, a = 27·459(5), b = 9·925(1), c = 14·266(3) Å, Z = 8, space group $Pn2_1a$. The structure was determined by heavy-atom methods and refined by full-matrix least-squares procedures to a final R of 0·045 for 1956 reflexions. The structure consists of two crystallographically nonequivalent anions in the asymmetric unit linked by hydrogen bonding *via* dimethylammonium cations. Some mean bond distances are Ru–Cl 2·426(6), Ru–S 2·261(3), and S–O 1·48(1) Å.

OUR interest[1] in ruthenium(II) halide complexes containing co-ordinated dimethyl sulphoxide (dmso) has led us to the discovery of (1), the first such anionic complex, dimethylammonium trichlorotris(dimethyl sulphoxide)ruthenate(II), $[NH_2Me_2][RuCl_3(Me_2SO)_3]$. The complex effectively catalyses the hydrogenation of acrylamide and ethyl vinyl ketone to propionamide and ethyl methyl ketone, respectively, in *NN*-dimethylacetamide (dma) under mild conditions (60 °C and 1 atm H_2). The catalysis is of interest in that sulphur donors are well known to poison heterogeneous systems.

Complex (1) is easily prepared by reaction of ruthenium trichloride trihydrate with hydrogen at 80 °C in the presence of a stoicheiometric amount of dmso in dma, as a bright yellow powder. Use of deuteriated dmso results in (2), the corresponding deuteriated complex, $[NH_2Me_2][RuCl_3\{(CD_3)_2SO\}_3]$. The hydrogen reduces Ru^{III} to Ru^{II} with the generation of protons,[2] and in the acidic reaction solution formation of the dimethylammonium cation appears to stabilize the $[RuCl_3(Me_2SO)_3]^-$ anion. Gas chromatography of the reaction mixture shows the presence of acetic acid and dimethylamine, the hydrolysis products of dma. Such hydrolysis is known to occur at high temperatures, *ca.* 350 °C,[3] but could be catalysed at 80 °C by the ruthenium.

As expected for a complex of ruthenium(II), (1) is diamagnetic, as determined by the Gouy method.

The conductivity in dma[4] indicates two ions in solution and remains unchanged for 48 h. In aqueous solution, the initial conductivity corresponds to the presence of two ions, but slowly increases over 48 h to that corresponding to the presence of three to four ions. Loss of chloride from the anion would yield a neutral ruthenium species plus two ions in solution (cation plus chloride), and together with visible spectral data (see later) the findings for dissolution in water are consistent with rapid loss of one chloride followed by a much slower loss of the remaining ones. If the complex is dissolved in aqueous silver nitrate, rapid precipitation of silver chloride occurs followed by a much slower precipitation until after 90 h *ca.* 96% of the total chloride present in the complex has been precipitated. The ruthenium species present in solution could then be $[Ru(Me_2SO)_3(H_2O)_3]^{2+}$. Wilkinson *et al.*[5] have reported a corresponding production of cationic species from the $[RuCl_2(Me_2SO)_4]$ complex.

Compound (1) is very soluble in water, dma, and methanol, soluble in chloroform, slightly soluble in acetone and benzene, and insoluble in ether. It is relatively air stable in the solid state, but undergoes air oxidation in dma, slowly in the presence and more slowly in the absence of light, to give a green solution.

I.r. Spectra.—From accepted data for dmso and its transition-metal complexes[1,5-8] the i.r. bands of (1) and of (2) can be assigned (Table 1). The presence of a strong band in the spectra of both complexes at 1100 cm^{-1} is indicative of *S*-bonded dmso. The presence of ν(SO) at a higher frequency than that for dmso alone (1055 cm^{-1}) indicates a larger SO bond-order resulting from co-ordination through sulphur to ruthenium.

---

[1] B. R. James, E. Ochiai, and G. L. Rempel, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 781.

[2] B. C. Hui and B. R. James, *Canad. J. Chem.*, 1974, **52**, 348.

[3] 'Du Pont Product Information Bulletin: DMAC,' E. I. Du Pont de Nemours, Delaware, p. 4.

[4] B. R. James, R. S. McMillan, and E. Ochiai, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 239.

[5] I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.

[6] F. A. Cotton, R. Francis, and W. D. Horrocks, jun., *J. Phys. Chem.*, 1960, **64**, 1534.

[7] W. D. Horrocks, jun., and F. A. Cotton, *Spectrochim. Acta*, 1961, **17**, 134.

[8] C. V. Senoff, E. Maslowsky, jun., and R. G. Goel, *Canad. J. Chem.*, 1971, **49**, 3585.

Co-ordination through oxygen is thought to reduce the SO bond-order[5] and give ν(SO) at *ca.* 915 cm^{-1}. No such band is present in the spectrum of either (1) or (2), indicating that all the dmso ligands are *S*-bonded.

TABLE 1

I.r. spectra (cm^{-1})[a] of $[NH_2Me_2][RuCl_3(Me_2SO)_3]$, (1), and of its deuteriated analogue (2)

(1)		(2)		
Frequency	Assignment[b,c]	Frequency	Assignment	$\frac{\nu(CH)}{\nu(CD)}$
3125br, s	ν(NH)	3125br, s	ν(NH)	
3015s	ν(CH) cation	3015s	ν(CH) cation	
		2975m	ν(CH) cation	
2975s	ν(CH)	2255m	ν(CD)	1·32
2925s	ν(CH)	2125m	ν(CD)	1·38
1605w	δ_d(NH)	1605w	δ_d(NH)	
1570w	δ_d(NH)	1570w	δ_d(NH)	
		1465w	δ_d(CH) cation	
		1430w	δ_d(CH) cation	
1465s	δ_d(CH)	1082m	δ_d(CD)	1·35
1430s	δ_d(CH)	1020m	δ_d(CD)	1·40
1400s	δ_d(CH)	1010sh	δ_d(CD)	1·39
1310s	δ_d(CH)	Not obs.		
1287s	δ_d(CH)	Not obs.		
1250w	ν(CN)	1250w	ν(CN)	
1100br, s	ν(SO) *S*-bond	1100s	ν(SO) *S*-bond	
1025s	ρ_r(CH)	819s	ρ_r(CD)	1·25
975m	ρ_r(CH)	785m	ρ_r(CD)	1·24
930m	ρ_r(CH)	765m	ρ_r(CD)	1·22
		895w	Cation	
843w	Cation	840w	Cation	
820m	Cation			
714m	ν_a(CS)	625m	ν_a(CS)	1·14
675m	ν_s(CS)	Not obs.		
422s	δ_s(CSO)	390s	δ_s(CSO)	1·08
386m	δ_a(CSO)	360m	δ_a(CSO)	1·07
347m	ν(Ru–Cl)	335m	ν(Ru–Cl)	
293m	ν(Ru–Cl)	292m	ν(Ru–Cl)	
266m		Not obs.		

[a] 4000—250 cm^{-1}, CsI plates, Nujol or hexachlorobutadiene mulls. [b] Subscripts: ν_a = asym. str., ν_s = sym. str., δ_d = degenerate def., δ_s = sym. def., δ_a = asym. def., ρ_r = rocking. [c] s = Strong, m = medium, w = weak, sh = shoulder, br = broad.

The Ru–Cl stretches in the far i.r. can be assigned from the strength and position of the bands.[9,10] It was not possible to utilize the bromine shifts in assigning the bands, as attempts to prepare the corresponding tribromo-complex led only to the complex $[RuBr_2(Me_2SO)_4]$.[1,11] Bands at 347 and 293 cm^{-1} in the spectrum of (1) and 335 and 292 cm^{-1} in that of (2) are assigned as the two Ru–Cl stretches of the *fac*-isomers. The *mer*-isomers should have three Ru–Cl bands in the region 360—250 cm^{-1}. The observed spectra are similar to that[12] of *fac*-$[RuCl_3(py)_3]$ which has two Ru–Cl bands at 346 and 301 cm^{-1}.

The initial reaction product, and that recrystallized from dma, both have the same i.r. spectrum, as does the complex in chloroform, indicating that the same isomer is present in each case. The band at 266 cm^{-1} in the spectrum of (1) is unassigned but could be due to a methyl torsion mode.[7,10]

Bands are assigned to the cation by comparison with those for known compounds,[13] although assignment of the exact vibrational mode is not possible in all cases.

The i.r. band at *ca.* 480 cm^{-1} found in the spectrum of $[RuCl_2(Me_2SO)_4]$, which contains both *S*- and *O*-bonded dmso,[1,5] has been previously assigned as either ν(Ru–S) or ν(Ru–O).[5] It is now possible tentatively to assign this band as the latter, since it is not found in the spectrum of either (1) or (2).

Visible Spectra.—Comparison of the solid-state and solution spectra, and use of the i.r. assignment, shows that the *fac*-isomer persists in both chloroform and dma solutions. In water, the initial solution spectrum of the complex is different and also changes slowly with time, with a shift in $\lambda_{max.}$ to shorter wavelengths. On addition of chloride ion, the spectrum rapidly becomes the same as that for the complex in chloroform or dma. These data further indicate loss of chloride to give $[RuCl_2(Me_2SO)_3(H_2O)]$ followed by slow loss of the other chloride ions to give cationic ruthenium species. Addition of chloride regenerates the anion of (1).

TABLE 2

Visible spectra (nm) of (1)

Solvent	Absorbance max (log ε)
Solid state[a]	370, 330sh
dma	369 (2·76), 325 (2·47)sh
$CHCl_3$	368 (2·76), 325 (2·58)sh
H_2O (6M-HCl)[b]	369 (2·76), 325 (2·50)sh
H_2O[c]	346 (2·60), 315 (2·51)sh

[a] Nujol mull. [b] Cl^- added to suppress dissociation. [c] Initial spectrum, taken after dissolution.

N.m.r. Spectra.—In $CDCl_3$ the spectrum of the complex consists (Table 3) of a singlet at τ 6·49 attributed to the eighteen equivalent methyl protons of the *S*-bonded dmso ligands. The position of peaks *ca.* 1 p.p.m. downfield from that for free dmso is indicative that it is *S*-bonded.[5,8] The presence of the singlet and the integration ratio of this peak to that of the six methyl protons of the cation indicate that the solution contains exclusively the *fac*-isomer where all three co-ordinated dmso ligands are equivalent.

TABLE 3

N.m.r. spectra[a] of (1)

Solvent	τ(Me)	Integration ratio	Peak type
$CDCl_3$	6·49	3	s
	7·32	1	t
D_2O (6M-DCl, in D_2O)[b]	6·49	3	s
	7·24	1	s
D_2O[c]	6·52	2	s
	6·61	1	s
	7·29	1	s

[a] Chemical shift relative to 10·0 as tetramethylsilane for $CDCl_3$ and sodium 2,2-dimethyl-2-silapentane-5-sulphonate for D_2O. [b] Cl^- Added to suppress dissociation. [c] Initial spectrum taken after dissolution. s = singlet, t = triplet.

In D_2O the spectrum of the complex is different. In

---

[9] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967, p. 72.

[10] B. F. G. Johnson and R. A. Walton, *Spectrochim. Acta*, 1966, **22**, 1853.

[11] L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770.

[12] J. Lewis, F. E. Mabbs, and R. A. Walton, *J. Chem. Soc.* (*A*), 1967, 1366.

[13] C. R. Johnson and D. J. Pasto, 'Organic Structure Determination,' Prentice-Hall, New York, 1969, p. 121.

the *S*-bonded region there are two singlets at τ 6·52 and 6·61 with an integration ratio of 2 : 1. At τ 7·29 there is a singlet attributed to the methyl protons of the cation. Addition of chloride ion, either as DCl or KCl, causes the appearance in the spectrum of a singlet at τ 6·49, attributed to the eighteen equivalent methyl protons of the three *S*-bonded dmso ligands, and a singlet at τ 7·24, attributed to the six equivalent methyl protons of the cation. These spectral changes are entirely consistent with the visible spectral data. The two singlets observed in D_2O result from a $[RuCl_2(Me_2SO)_3(D_2O)]$ species; added chloride regenerates the *fac*-$[RuCl_3(Me_2SO)_3]^-$ anion.

In $CDCl_3$, addition of *ca.* 10% by volume of $[^2H_6]$-dmso results in the disappearance of the singlet due to the three *S*-bonded dmso ligands. After 8 h, the exchange is complete with the spectrum now consisting of the triplet at τ 7·32 due to the cation and a singlet at τ 7·40 due to free dmso. In D_2O with added chloride ion, addition of *ca.* 10% by volume of $(CD_3)_2SO$ results in the same exchange process; however, the total exchange takes 16 h.

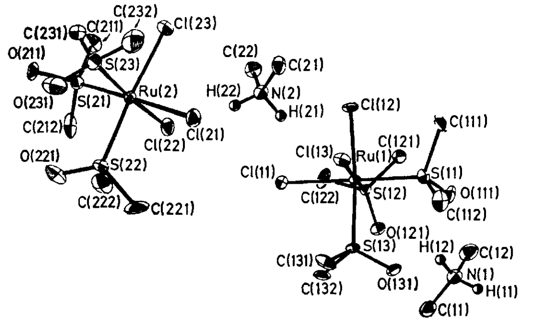

FIGURE 1 A general view of the structure showing the crystallographic atom-numbering scheme

Crystal Structure of (1).—The structure consists of two crystallographically nonequivalent anions in the asymmetric unit, linked by two nonequivalent cations. The atom labelling scheme is illustrated in Figure 1. Most corresponding bond lengths and angles are not significantly different between the two independent formula units (Tables 4 and 5). All three dmso ligands are co-ordinated through the sulphur atoms, the co-ordination geometry about the ruthenium atoms being essentially that of an octahedron, with each dmso mutually *trans* to a chlorine atom. Slight distortion does occur, presumably due to steric interference between the dmso groups, the Cl–Ru–Cl angles being slightly smaller than 90° (mean 87·6°) while those for S–Ru–S are slightly larger (mean 92·6°).

The Ru–S bond lengths (mean 2·261 Å) are significantly longer while the S–O distances (mean 1·48 Å) are shorter than those found [14] in $[Ru(NH_3)_5(dmso)]^{2+}2[PF_6]^-$ [2·188(3) and 1·527(8) Å respectively]. These changes in bond length indicate a decrease in the possible d_π–p_π back-donation from the central metal to the sulphur atom caused by the competition from the other dmso ligands for the available π-donor orbitals. Similar effects are seen for *trans*-$[PdCl_2(dmso)_2]$ (ref. 15) and *cis*-$[Pd(NO_3)_2(dmso)_2]$ (ref. 16). The strong *trans*-effect of *S*-bonded dmso ligands [17] is illustrated in the Ru–Cl bond distance (mean 2·426 Å) which is significantly longer than those for the mutually *trans*-chlorine atoms [mean 2·390(7) Å] in the octahedral complex $[RuCl_3(N_2C_6H_4Me)(PPh_3)_2]$,$Me_2O$.[18]

TABLE 4

Bond lengths (Å) with standard deviations in parentheses

Ru(1)–Cl(11)	2·450(4)	Ru(2)–Cl(21)	2·430(4)
Ru(1)–Cl(12)	2·417(4)	Ru(2)–Cl(22)	2·414(5)
Ru(1)–Cl(13)	2·415(5)	Ru(2)–Cl(23)	2·427(5)
Ru(1)–S(11)	2·256(4)	Ru(2)–S(21)	2·267(4)
Ru(1)–S(12)	2·261(5)	Ru(2)–S(22)	2·273(5)
Ru(1)–S(13)	2·252(4)	Ru(2)–S(23)	2·260(5)
S(11)–O(111)	1·48(1)	S(21)–O(211)	1·47(1)
S(12)–O(121)	1·49(1)	S(22)–O(221)	1·47(2)
S(13)–O(131)	1·50(1)	S(23)–O(231)	1·45(2)
S(11)–C(111)	1·79(2)	S(21)–C(211)	1·77(2)
S(11)–C(112)	1·86(2)	S(21)–C(212)	1·81(2)
S(12)–C(121)	1·80(2)	S(22)–C(221)	1·80(2)
S(12)–C(122)	1·81(2)	S(22)–C(222)	1·75(2)
S(13)–C(131)	1·78(2)	S(23)–C(231)	1·78(3)
S(13)–C(132)	1·80(2)	S(23)–C(232)	1·76(3)
N(1)–C(11)	1·48(3)	N(2)–C(21)	1·48(2)
N(1)–C(12)	1·51(3)	N(2)–C(22)	1·47(3)

TABLE 5

Bond angles (°) with standard deviations in parentheses

Cl(11)–Ru(1)–Cl(12)	87·1(2)	Cl(21)–Ru(2)–Cl(22)	87·7(2)
Cl(11)–Ru(1)–Cl(13)	87·4(2)	Cl(21)–Ru(2)–Cl(23)	87·7(2)
Cl(11)–Ru(1)–S(11)	175·4(2)	Cl(21)–Ru(2)–S(21)	174·7(2)
Cl(11)–Ru(1)–S(12)	92·7(2)	Cl(21)–Ru(2)–S(22)	87·3(2)
Cl(11)–Ru(1)–S(13)	87·4(2)	Cl(21)–Ru(2)–S(23)	92·7(2)
Cl(12)–Ru(1)–Cl(13)	87·4(2)	Cl(22)–Ru(2)–Cl(23)	88·3(2)
Cl(12)–Ru(1)–S(11)	93·4(2)	Cl(22)–Ru(2)–S(21)	86·9(2)
Cl(12)–Ru(1)–S(12)	86·8(2)	Cl(22)–Ru(2)–S(22)	91·2(2)
Cl(12)–Ru(1)–S(13)	174·5(2)	Cl(22)–Ru(2)–S(23)	175·4(2)
Cl(13)–Ru(1)–S(11)	88·0(2)	Cl(23)–Ru(2)–S(21)	92·4(2)
Cl(13)–Ru(1)–S(12)	174·2(2)	Cl(23)–Ru(2)–S(22)	175·0(2)
Cl(13)–Ru(1)–S(13)	92·6(2)	Cl(23)–Ru(2)–S(23)	87·2(2)
S(11)–Ru(1)–S(12)	92·0(2)	S(21)–Ru(2)–S(22)	92·5(2)
S(11)–Ru(1)–S(13)	92·0(2)	S(21)–Ru(2)–S(23)	92·6(2)
S(12)–Ru(1)–S(13)	93·1(2)	S(22)–Ru(2)–S(23)	93·4(2)
Ru(1)–S(11)–O(111)	118·9(6)	Ru(2)–S(21)–O(211)	118·1(6)
Ru(1)–S(12)–O(121)	119·8(5)	Ru(2)–S(22)–O(221)	118 2(7)
Ru(1)–S(13)–O(131)	115·7(5)	Ru(2)–S(23)–O(231)	118·2(7)
Ru(1)–S(11)–C(111)	111·8(8)	Ru(2)–S(21)–C(211)	112·6(6)
Ru(1)–S(11)–C(112)	112·8(7)	Ru(2)–S(21)–C(212)	111·4(7)
Ru(1)–S(12)–C(121)	113·0(7)	Ru(2)–S(22)–C(221)	110(1)
Ru(1)–S(12)–C(122)	111·1(8)	Ru(2)–S(22)–C(222)	114·8(8)
Ru(1)–S(13)–C(131)	112·7(8)	Ru(2)–S(23)–C(231)	115(1)
Ru(1)–S(13)–C(132)	113·8(7)	Ru(2)–S(23)–C(232)	110(1)
O(111)–S(11)–C(111)	104·4(9)	O(211)–S(21)–C(211)	108(1)
O(111)–S(11)–C(112)	104·6(9)	O(211)–S(21)–C(212)	106(1)
O(121)–S(12)–C(121)	105·3(8)	O(221)–S(22)–C(221)	109(1)
O(121)–S(12)–C(122)	105(1)	O(221)–S(22)–C(222)	105(1)
O(131)–S(13)–C(131)	107(1)	O(231)–S(23)–C(231)	104(1)
O(131)–S(13)–C(132)	107·1(9)	O(231)–S(23)–C(232)	110(1)
C(111)–S(11)–C(112)	103(1)	C(211)–S(21)–C(212)	99(1)
C(121)–S(12)–C(122)	101(1)	C(221)–S(22)–C(222)	98(1)
C(131)–S(13)–C(132)	100(1)	C(231)–S(23)–C(232)	98(1)
C(11)–N(1)–C(12)	114(2)	C(21)–N(2)–C(22)	113(2)

---

[14] F. C. March and G. Ferguson, *Canad. J. Chem.*, 1971, **49**, 3590.

[15] M. J. Bennett, F. A. Cotton, B. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Cryst.*, 1967, **23**, 788.

[16] D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Comm.*, 1967, 1080.

[17] Y. N. Kukushkin, M. A. Kuz'mina, and A. F. U'yugina, *Radiokhimiya*, 1968, **10**, 470.

[18] J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 1676.

The geometry about the sulphur atoms is the expected distorted tetrahedron. The O–S–C and C–S–C angles and S–C bond lengths are similar to those found for the free ligand.[19]

The hydrogen atoms attached to nitrogen in the cations are involved in hydrogen bonding to both non-equivalent anions, forming a chain-like structure throughout the crystal lattice. H(11) And H(12) take part in N–H · · · O, and H(21) and H(22) in N–H · · · Cl hydrogen bonding. Although heavy-atom separations do not uniquely define the presence of hydrogen bonding, they can give a reasonable indication, values of typical heavy-atom contact distances being N · · · O 2·9, and N · · · Cl 3·3 Å, representing hydrogen-bonded atoms.[20,21] The overall results (Table 6) would indicate the presence of at least six hydrogen bonds: N(1)–H(12) · · · O(111), N(1)–H(12) · · · O(131), N(1)–H(11) · · · O(211), N(2)–H(21) · · · Cl(11), N(2)–H(21) · · · Cl(12), and N(2)–H(22) · · · Cl(22). Figure 2 shows the contents of the unit cell viewed along *c* with these hydrogen bonds indicated by the dotted lines.

TABLE 6

Intermolecular contacts (Å)

O(111) · · · N(1)	2·99(2)	O(111) · · · H(12)	2·2
O(121) · · · N(1)	3·18(2)	O(121) · · · H(12)	2·8
O(131) · · · N(1)	3·05(3)	O(131) · · · H(12)	2·3
O(211) · · · N(1)	2·89(2)	O(211) · · · H(11)	2·1
O(221) · · · N(1)	3·36(3)	O(221) · · · H(11)	2·9
O(231) · · · N(1)	3·36(3)	O(231) · · · H(11)	2·7
Cl(11) · · · N(2)	3·24(3)	Cl(11) · · · H(21)	2·4
Cl(12) · · · N(2)	3·35(3)	Cl(12) · · · H(21)	2·7
Cl(13) · · · N(2)	3·57(4)	Cl(13) · · · H(21)	2·8
Cl(21) · · · N(2)	3·73(4)	Cl(21) · · · H(22)	3·0
Cl(22) · · · N(2)	3·23(3)	Cl(22) · · · H(22)	2·3
Cl(23) · · · N(2)	3·79(4)	Cl(23) · · · H(22)	3·3

Since the hydrogen positions were calculated, errors in O · · · H and Cl · · · H distances are subject to speculation.

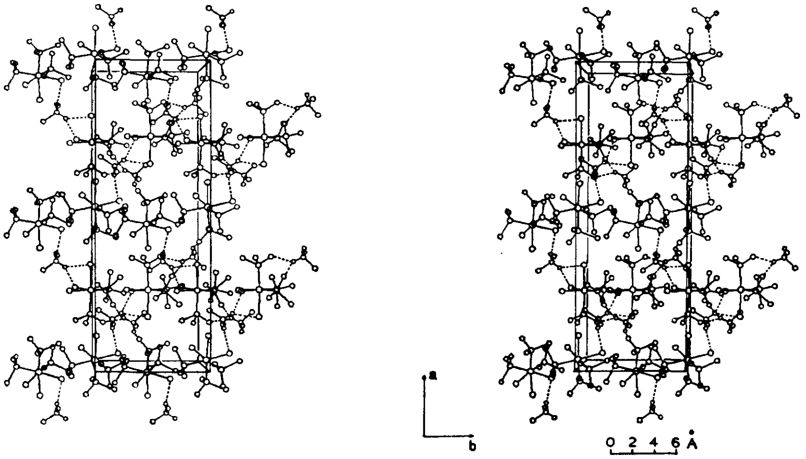

FIGURE 2 A stereoscopic diagram of the unit cell viewed down *c*; hydrogen bonds are indicated by dotted lines

EXPERIMENTAL

Preparation of Dimethylammonium Trichlorotris(dimethyl sulphoxide)ruthenate(II).—Ruthenium trichloride trihydrate (1 g, 39% Ru) and dimethyl sulphoxide (1 ml) were heated at 80 °C in *NN'*-dimethylacetamide (20 ml) under 1 atm hydrogen for 4 h. The resulting red solution was set aside under hydrogen at room temperature (or concentrated to 10 ml and cooled) and gave a bright yellow product which was washed with acetone and ether, and vacuum dried. It was recrystallized from dimethylacetamide as cubes (1·23 g, 66%), m.p. 195 °C (decomp. *in vacuo*) (Found: C, 19·6; H, 5·3; Cl, 21·6; N, 2·8. Calc. for $C_8H_{26}Cl_3NO_3RuS_3$: C, 19·7; H, 5·4; Cl, 21·8; N, 2·9%).

Crystal Data.—$C_8H_{26}Cl_3NO_3RuS_3$, $M = 487{\cdot}9$, Orthorhombic, $a = 27{\cdot}459(5)$, $b = 9{\cdot}925(1)$, $c = 14{\cdot}266(3)$ Å, $U = 3887(1)$ Å^3, $D_m = 1{\cdot}67(1)$, $Z = 8$, $D_c = 1{\cdot}667(5)$, $F(000) = 1984$. Space group *Pnma* (D_{2h}^{16}, No. 62), or $Pn2_1a$ (C_{2v}^{9}, No. 33) from absent reflexions: $0kl$, $k + l \neq 2n$, $hk0$, $h \neq 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 15·036 cm^{-1}.

The crystal chosen (*ca.* 0·3 × 0·25 × 0·25 mm) was mounted with *c* parallel to the goniostat axis. Unit-cell and space-group data were obtained from film and diffractometer measurements. The unit-cell parameters were refined by a least-squares treatment of $\sin^2\theta$ values for 20 reflexions measured on a diffractometer with Mo-K_α radiation.

Intensity data were measured for 2632 independent reflexions ($2\theta < 45°$) of which 676 having intensities $< 3\sigma(I)$ above the background [where $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, and S = scan count and B = background count] were classed as unobserved.

The initial attempt to solve the structure in the space group *Pnma* required a maximum at $0,0{\cdot}5 - 2y,0$ on the Patterson function, but no such peak was revealed other than at the origin. This implies that the *y* co-ordinate for the Ru atom would have to be 0·25, the atom being located on the crystallographic mirror plane. Although the anion could possess mirror symmetry, an attempt was then made to solve the structure in the non-centric space group, $Pn2_1a$. Since this space group has only four equivalent positions, there must be two crystallographically nonequivalent molecules in the asymmetric unit. Both ruthenium positions were found from the Patterson map, and Ru(2) was arbitrarily assigned the *y* co-ordinate zero,

---

[19] W. L. Reynolds, *Progr. Inorg. Chem.*, 1970, **12**, 1.

[20] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968, p. 16.

[21] G. C. Pimental and A. L. McClellan, *Ann. Rev. Phys. Chem.*, 1971, **22**, 347.

which was kept constant throughout later refinements. All nonhydrogen atoms were then found by successive Fourier syntheses. The structure was refined by full-matrix least-squares methods, with minimization of $\Sigma w(F_0 - F_c)^2$. The weighting scheme $\sqrt{w} = 1$ if $|F_0| \leqslant 65$; $\sqrt{w} = 65/|F_0|$ if $|F_0| > 65$, and $\sqrt{w} = 0$ for unobserved reflexions gave constant mean values of $w(F_0 - F_c)^2$ over ranges of $|F_0|$ and was used in the final stages of refinement. The final conventional R factor for 1956 observed reflexions for all nonhydrogen atoms was 0·045. Final positional and thermal parameters are given in Tables 7 * and 8 respectively. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21278 (26 pp., 1 microfiche).†

TABLE 7

Final positional parameters (fractional × 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Ru(1)	2560(0)	4849(2)	3945(1)
Ru(2)	283(0)	0	2858(1)
Cl(11)	1670(1)	4795(6)	3851(3)
Cl(12)	2489(2)	3399(5)	5299(3)
Cl(13)	2563(2)	2834(5)	2997(3)
Cl(21)	1094(2)	10090(8)	2176(3)
Cl(22)	469(2)	2095(6)	3640(4)
Cl(23)	640(2)	8823(7)	4181(4)
S(11)	3381(1)	4766(6)	3943(3)
S(12)	2556(2)	6598(5)	4961(3)
S(13)	2548(2)	6206(5)	2680(3)
S(21)	9543(1)	10104(7)	3556(3)
S(22)	16(2)	1123(6)	1567(3)
S(23)	128(2)	7954(6)	2231(4)
O(111)	3657(5)	5966(14)	4246(11)
O(121)	2672(5)	7981(14)	4620(9)
O(131)	3026(5)	6846(13)	2425(9)
O(211)	9154(4)	9221(15)	3198(10)
O(221)	9487(6)	1271(18)	1434(10)
O(231)	9823(7)	7888(17)	1401(11)
C(111)	3606(8)	3435(22)	4669(18)
C(112)	3638(8)	4336(23)	2772(15)
C(121)	2948(7)	6334(20)	5956(12)
C(122)	1970(8)	6759(27)	5528(16)
C(131)	2335(9)	5372(22)	1655(13)
C(132)	2105(8)	7535(20)	2752(14)
C(211)	9575(7)	125(37)	4788(11)
C(212)	9299(6)	1795(26)	3530(17)
C(221)	293(13)	2769(24)	1510(21)
C(222)	233(9)	491(27)	499(15)
C(231)	9857(9)	6784(28)	3017(20)
C(232)	675(11)	7074(24)	2026(26)
N(1)	3646(6)	8809(18)	3556(13)
N(2)	1569(6)	1629(15)	4378(12)
C(11)	3297(8)	9802(28)	3173(17)
C(12)	3790(10)	9068(28)	4564(17)
C(21)	1870(7)	413(19)	4212(16)
C(22)	1378(9)	1719(22)	5336(14)
H(11)	3944	8818	3163
H(12)	3500	7900	3513
H(21)	1768	2438	4248
H(22)	1292	1624	3934

TABLE 8

Final anisotropic thermal parameters (Å^2 × 10^2) with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	3·28(8)	2·10(6)	1·82(5)	−0·11(8)	−0·07(4)	0·04(6)
Ru(2)	2·82(8)	3·56(7)	2·81(6)	−0·40(6)	−0·12(6)	0·37(9)
Cl(11)	3·5(2)	4·1(3)	4·2(2)	−0·5(3)	−0·2(2)	0·5(3)
Cl(12)	6·5(3)	3·2(3)	2·7(2)	−1·1(2)	−0·9(2)	1·4(2)
Cl(13)	6·5(3)	2·7(2)	3·4(2)	0·1(2)	−1·2(2)	−0·5(2)
Cl(21)	3·4(2)	7·5(3)	5·3(2)	−0·4(3)	0·9(2)	0·5(3)
Cl(22)	4·6(3)	4·5(3)	6·4(3)	−0·8(2)	−1·4(3)	−1·3(3)
Cl(23)	5·5(3)	6·9(4)	4·9(3)	0·1(3)	−1·3(3)	2·0(3)
S(11)	3·2(2)	3·4(3)	3·7(2)	0·8(2)	0·1(3)	−0·9(2)
S(12)	3·0(2)	3·2(2)	1·9(2)	−0·2(2)	0·3(2)	−0·0(2)
S(13)	4·3(3)	2·1(2)	1·9(2)	0·1(2)	0·4(2)	0·1(2)
S(21)	3·4(2)	5·1(3)	3·0(2)	−0·4(3)	0·2(2)	0·5(2)
S(22)	4·7(3)	4·5(3)	3·6(3)	0·3(2)	−0·7(2)	1·3(2)
S(23)	5·7(3)	3·8(3)	5·6(3)	−0·4(2)	−1·3(3)	0·3(3)
O(111)	2·5(7)	4·4(9)	9(1)	−1·0(6)	0·6(7)	−0·8(8)
O(121)	5·5(8)	3·4(7)	4·5(7)	−0·7(6)	0·3(6)	0·0(7)
O(131)	4·8(8)	3·9(8)	4·1(7)	−1·2(7)	0·5(6)	1·0(6)
O(211)	2·1(7)	7·2(9)	6·0(8)	−1·6(7)	0·4(6)	0·4(8)
O(221)	7(1)	9(1)	4·3(8)	3(1)	−1·6(8)	0·0(9)
O(231)	13(1)	5(1)	5·8(9)	−0(1)	−3(1)	−0·2(8)
C(111)	4(1)	5(1)	9(2)	2(1)	−2(1)	1(1)
C(112)	5(1)	6(1)	6(1)	2(1)	−1(1)	−3(1)
C(121)	5(1)	4(1)	3(1)	−1(1)	−1·1(9)	−0·3(9)
C(122)	4(1)	9(2)	5(1)	−3(1)	3(1)	−2(1)
C(131)	9(2)	5(1)	2·5(9)	2(1)	−2(1)	−0·6(9)
C(132)	6(1)	4(1)	5(1)	1(1)	−0(1)	2(1)
C(211)	6(1)	11(2)	2·7(9)	1(2)	1·6(8)	1(2)
C(212)	1·2(9)	9(2)	9(2)	2(1)	1(1)	−4(1)
C(221)	16(3)	4(2)	10(2)	−3(2)	−2(2)	3(1)
C(222)	7(1)	10(2)	3(1)	1(1)	−0(1)	0(1)
C(231)	7(2)	8(2)	10(2)	−3(1)	−3(2)	5(2)
C(232)	9(2)	3(1)	18(3)	0(1)	−2(2)	−0(2)
N(1)	5(1)	3·4(9)	8(1)	1·0(9)	2(1)	0·6(9)
N(2)	3·9(9)	2·4(9)	6(1)	0·7(7)	0·8(8)	−0·6(8)
C(11)	6(1)	6(2)	9(1)	1(1)	3(1)	2(2)
C(21)	3(1)	4(1)	9(2)	0·6(8)	−0(1)	−1(1)
C(12)	10(2)	8(2)	6(1)	−3(2)	−0(1)	0(1)
C(22)	7(2)	6(2)	3(1)	−1(1)	−1(1)	−0(1)

The anisotropic thermal parameters are U_{ij} in the expression: $f = f^0\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

N.m.r. spectra were recorded on Varian T 60 and XL 100 spectrometers at 30 °C. I.r. spectra (4000—250 cm^{-1}) were recorded on a Perkin-Elmer 457, and visible spectra on a Cary 14 spectrophotometer. M.p.s were measured on a Gallenkampt apparatus.

We thank the National Research Council of Canada for financial support, the University of British Columbia Computing Centre for assistance, Peter Borda for microanalyses, and Johnson Matthey for ruthenium.

[4/2080 *Received*, 8*th October*, 1974]

---

* The hydrogen atoms bonded directly to nitrogen in the cations could not be located in the final difference Fourier but their positions were calculated assuming N–H 0·99 Å, and H–N–H 108°. These atoms were not included in the structure refinement.

† For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.