Crystal and Molecular Structure of Dichlorotetrakis(dimethyl sulphoxide)-ruthenium(II)

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Crystals of the title compound are monoclinic, $a = 8.939(3)$, $b = 18.045(7)$, $c = 11.363(3)$ Å, $\beta = 91.52(2)°$, $Z = 4$, space group $P2_1/n$. The structure was determined by Patterson and Fourier syntheses and refined by full-matrix least-squares procedures to a final R of 0.041 for 2 720 independent reflections measured by diffractometer. The co-ordination geometry about the ruthenium atom is essentially octahedral with *cis*-chlorine atoms. Of the four dimethyl sulphoxide ligands three are *S*- and one is *O*-bonded, the *O*-bonded ligand being *trans* to a *S*-bonded ligand. Important mean bond distances are: Ru–Cl 2.435(1), Ru–S 2.277(1) (*trans* to Cl), 2.252(1) (*trans* to O), Ru–O 2.142(3), S–O 1.484(5) (*S*-bonded), and 1.557(4) Å (*O*-bonded).

INFRARED and ^{1}H n.m.r. spectral data on dichlorotetrakis(dimethyl sulphoxide)ruthenium(II) indicated the possibility of a mixture of *S*- and *O*-bonded dimethyl sulphoxide ligands.[1] The *X*-ray crystallographic study of $[(Me_2SO)_4RuCl_2]$ was undertaken to verify this unusual arrangement, and provide additional information [2] for an attempted correlation between structure and the catalytic properties of these molecules.

EXPERIMENTAL

Crystals of $[(Me_2SO)_4RuCl_2]$ from methanol were yellow and approximately cube-shaped. The crystal chosen was mounted with c^* parallel to the goniostat axis and had dimensions *ca.* 0.20 × 0.20 × 0.25 mm. 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 21 reflections measured on a diffractometer with Mo-K_α radiation.

Crystal Data.—$C_8H_{24}Cl_2O_4RuS_4$, $M = 484.54$, Monoclinic, $a = 8.939(3)$, $b = 18.045(7)$, $c = 11.363(3)$ Å, $\beta = 91.52(2)°$, $U = 1\,832(1)$ Å^3, $D_m = 1.74(1)$ g cm^{-3}, $Z = 4$, $D_c = 1.76(1)$ g cm^{-3}, $F(000) = 984$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 15.66$ cm^{-1}. Absent reflections: $h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$ define uniquely space group $P2_1/n$ (C_{2h}^5, No. 14).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Mo-K_α (zirconium filter and pulse-height analyser), and a θ—2θ scan at 2° min^{-1} over a range of $(1.80 + 0.86 \tan\theta)°$ in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to 2θ 45° (minimum interplanar spacing 0.93 Å). Lorentz and polarization corrections were applied, and structure amplitudes derived. No absorption correction was applied owing to the low value of μ, and the fairly uniform shape of the crystal. Of 3 231 independent reflections measured, 511 had $I < 3\sigma(I)$ above background where $\sigma^2(I) = S + B + (0.05S)^2$ with S = scan count and B = time-averaged background count. These reflections were classified as unobserved and given zero weight in the refinement.

Structure Analysis.—The structure was determined by Patterson and Fourier syntheses and was refined by full-matrix least-squares methods with minimization of $\Sigma w(F_o - F_c)^2$. The scattering factors of ref. 3 were used for non-hydrogen atoms, and those of ref. 4 for hydrogen atoms. Anomalous scattering corrections (ref. 5) were applied for the non-hydrogen atoms. The anisotropic temperature factors employed in the refinement are U_{ij} in the expression: $f = f^0\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, where

TABLE 1

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

Atom	x	y	z
Ru	2 484.2(4)	1 217.5(2)	2 654.5(3)
Cl(1)	5 001(1)	701(1)	2 652(1)
Cl(2)	1 570(1)	−28	3 040(1)
S(1)	2 361(2)	1 051(1)	690(1)
S(2)	3 332(1)	2 403(1)	2 507(1)
S(3)	63(1)	1 591(1)	2 791(1)
S(4)	3 528(1)	766(1)	5 290(1)
O(1)	1 036(6)	1 302(3)	−16
O(2)	3 041(6)	2 800(2)	1 379(4)
O(3)	−343	2 378(2)	2 577(4)
O(4)	2 765(4)	1 377(2)	4 515(3)
C(11)	3 980(8)	1 413(4)	−36
C(12)	2 596(9)	96(4)	349(6)
C(21)	5 292(7)	2 486(4)	2 867(8)
C(22)	2 660(7)	2 982(3)	3 649(6)
C(31)	−604	1 365(4)	4 216(6)
C(32)	−1 191	1 047(4)	1 886(6)
C(41)	2 524(8)	843(5)	6 619(6)
C(42)	5 262(8)	1 176(4)	5 778(7)
H(111)	3 600	1 851	10
H(112) *	4 819	1 075	77
H(113) *	3 739	1 460	−887
H(121) *	2 055	−219	896
H(122)	2 488	95	−500
H(123) *	3 686	−39	420
H(211)	6 027	2 329	2 347
H(212)	5 577	3 058	3 184
H(213) *	5 432	2 480	3 753
H(221) *	1 597	2 888	3 775
H(222)	2 950	3 004	4 429
H(223)	3 081	3 456	3 520
H(311)	−47	1 638	4 969
H(312) *	−1 516	1 654	4 370
H(313) *	−869	832	4 241
H(321) *	−754	959	1 111
H(322)	−1 170	490	2 150
H(323) *	−2 150	1 307	1 770
H(411)	2 392	1 321	7 080
H(412)	1 477	1 197	6 664
H(413) *	2 915	490	7 211
H(421)	4 397	1 421	6 023
H(422) *	5 795	829	6 304
H(423) *	5 867	1 287	5 100

* Calculated positions.

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

[2] R. S. McMillan, A. Mercer, B. R. James, and J. Trotter, *J.C.S. Dalton*, 1975, 1006.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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f^0 is the tabulated scattering factor and f is that corrected for thermal motion. The weighting scheme: $\sqrt{w} = |F_o|/12.8$ if $|F_o| \leqslant 12.8$, $\sqrt{w} = 1$ if $22.6 > |F_o| > 12.8$, $\sqrt{w} = 22.6/|F_o|$ if $|F_o| \geqslant 22.6$, and $\sqrt{w} = 0.0$ for unobserved reflections gave constant average values of $w(F_o - F_c)^2$ over ranges of $|F_o|$ and was employed in the final stages of refinement. The conventional R using all non-hydrogen atoms was 0.047; a difference-Fourier performed at this stage indicated the positions of eleven of the twenty-four hydrogen atoms, and the remaining thirteen positions were calculated allowing for minimum intramolecular interactions (see Table 1). The final R for the 2 720 observed reflections was 0.041. Final positional and thermal parameters are given in Tables 1 and 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21445 (31 pp. 1 microfiche).*

TABLE 2

Final anisotropic thermal parameters ($U_{ij} \times 10^2$ Å^2), with estimated standard deviations in parentheses *

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	2.08(2)	2.59(2)	3.21(2)	0.00(1)	0.09(1)	0.10(1)
Cl(1)	2.33(6)	4.38(7)	5.74(8)	0.62(5)	0.20(5)	0.09(5)
Cl(2)	3.72(6)	2.96(6)	5.42(7)	−0.58(5)	−0.01(5)	0.39(5)
S(1)	3.82(7)	5.23(7)	3.34(6)	0.03(6)	−0.03(5)	0.16(5)
S(2)	4.00(7)	2.75(6)	5.49(7)	−0.28(5)	1.06(5)	0.20(5)
S(3)	2.39(6)	3.84(7)	4.92(7)	0.39(5)	0.28(5)	0.19(5)
S(4)	4.00(7)	3.51(6)	3.75(6)	0.19(5)	−0.62(5)	−0.22(5)
O(1)	5.62(29)	12.78(51)	4.73(24)	1.51(26)	−1.56(21)	1.86(26)
O(2)	10.47(39)	4.19(24)	6.45(28)	0.83(25)	2.49(26)	1.74(21)
O(3)	4.18(21)	4.08(22)	9.27(32)	1.78(18)	0.15(20)	0.75(21)
O(4)	4.09(20)	3.95(19)	3.39(16)	0.52(15)	−0.27(14)	−0.11(14)
C(11)	6.89(42)	5.78(36)	4.93(32)	0.76(31)	2.52(29)	1.01(28)
C(12)	9.73(54)	6.32(43)	5.34(35)	−1.56(39)	1.23(34)	−2.07(32)
C(21)	3.82(34)	5.88(41)	13.62(70)	−2.27(31)	1.04(38)	−2.00(43)
C(22)	6.14(38)	3.79(31)	7.86(41)	−1.15(26)	1.54(31)	−1.85(28)
C(31)	4.18(33)	7.34(43)	6.08(36)	0.69(29)	1.93(27)	0.14(31)
C(32)	2.44(26)	7.20(40)	7.31(40)	−0.20(26)	−0.81(24)	−0.78(32)
C(41)	7.67(46)	8.00(48)	4.62(33)	2.60(38)	0.90(31)	1.65(32)
C(42)	4.35(34)	6.22(41)	7.42(42)	0.14(27)	−2.56(30)	−0.10(30)

* All H atoms had isotropic thermal parameters U 6.3 × 10^{-2} Å^2.

DISCUSSION

The co-ordination geometry about the ruthenium atom is essentially octahedral with *cis*-chlorine atoms. Of the four dimethyl sulphoxide (dmso) ligands, three are sulphur- and one is oxygen-bonded, the *O*-bonded ligand being *trans* to one of the *S*-bonded ligands [S(1)]. Figure 1 shows the atom labelling scheme and a general view of the molecule. Individual bond lengths and angles, with standard deviations, are given in Tables 3 and 4.

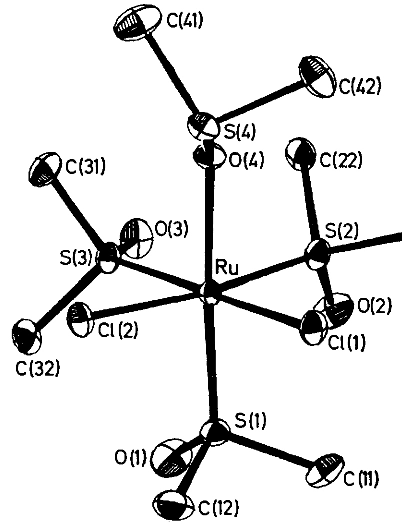

FIGURE 1 General view of the structure showing the crystallographic numbering scheme

Slight distortion does occur, the angles subtended at the central ruthenium atom between the three mutually *cis* *S*-bonded ligands being larger than 90° [92.6—94.9°, mean 94(1)°], while the values for the Cl–Ru–Cl, and the two Cl–Ru–O angles are slightly less than 90° [87.8—88.7°, mean 88.2(5)°]. Equations of selected least-squares mean planes with deviations of the atoms from these planes are given in Table 5. This distortion appears to be governed primarily by steric factors associated with the *S*-bonded dmso groups.

TABLE 3

Bond lengths (Å), with standard deviations in parentheses

Ru–Cl(1)	2.435(1)	S(1)–C(11)	1.808(6)
Ru–Cl(2)	2.435(1)	S(1)–C(12)	1.779(8)
Ru–S(1)	2.252(1)	S(2)–C(21)	1.795(7)
Ru–S(2)	2.277(1)	S(2)–C(22)	1.783(6)
Ru–S(3)	2.276(1)	S(3)–C(31)	1.787(6)
Ru–O(4)	2.142(3)	S(3)–C(32)	1.794(6)
S(1)–O(1)	1.483(5)	O(4)–S(4)	1.557(4)
S(2)–O(2)	1.485(5)	S(4)–C(41)	1.783(6)
S(3)–O(3)	1.485(5)	S(4)–C(42)	1.793(6)

The Ru–Cl bond lengths [2.435(1) Å] are significantly greater than would be expected for a purely σ donor ligand. Typical values of mean Ru–Cl bond lengths in octahedral complexes with *trans* chlorine atoms are 2.390(7) in [$RuCl_3(N_2C_6H_4Me)(PPh_3)_2$]·$Me_2O$ (ref. 6) and 2.398(7) Å in [$RuCl_3(NO)(PMePh_2)_2$].[7] This lengthening

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

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

[7] A. J. Schultz, R. L. Henry, J. Reed, and R. Eisenberg, *Inorg. Chem.*, 1974, **13**, 732.

TABLE 4

Bond angles (°), with standard deviations in parentheses

Cl(1)–Ru–Cl(2)	87.78(5)	Ru–S(3)–C(31)	109.6(2)
Cl(1)–Ru–S(1)	88.22(5)	Ru–S(3)–C(32)	112.3(2)
Cl(1)–Ru–S(2)	92.90(5)	Ru–S(1)–O(1)	120.9(2)
Cl(1)–Ru–S(3)	173.49(5)	Ru–S(2)–O(2)	117.7(2)
Cl(1)–Ru–O(4)	88.2(1)	Ru–S(3)–O(3)	120.1(2)
Cl(2)–Ru–S(1)	92.69(5)	C(11)–S(1)–C(12)	98.6(3)
Cl(2)–Ru–S(2)	173.85(5)	C(21)–S(2)–C(22)	97.5(3)
Cl(2)–Ru–S(3)	86.38(5)	C(31)–S(3)–C(32)	100.1(3)
Cl(2)–Ru–O(4)	88.7(1)	C(11)–S(1)–O(1)	106.3(3)
S(1)–Ru–S(2)	93.44(5)	C(12)–S(1)–O(1)	106.0(4)
S(1)–Ru–S(3)	94.91(5)	C(21)–S(2)–O(2)	107.7(4)
S(1)–Ru–O(4)	176.1(1)	C(22)–S(2)–O(2)	106.9(3)
S(2)–Ru–S(3)	92.61(5)	C(31)–S(3)–O(3)	106.3(3)
S(2)–Ru–O(4)	85.2(1)	C(32)–S(3)–O(3)	106.4(3)
S(3)–Ru–O(4)	88.8(1)	Ru–O(4)–S(4)	120.0(2)
Ru–S(1)–C(11)	112.6(2)	O(4)–S(4)–C(41)	101.6(3)
Ru–S(1)–C(12)	110.0(2)	O(4)–S(4)–C(42)	104.2(3)
Ru–S(2)–C(21)	112.7(2)	C(41)–S(4)–C(42)	99.0(4)
Ru–S(2)–C(22)	112.2(2)		

TABLE 5

Equations of selected weighted least-squares mean planes, with (in square brackets) deviations (Å) of the atoms from the planes

Plane (1): Ru, Cl(2), S(1), S(2), and O(4)

$$0.999X + 0.049Y - 0.013Z = 2.249$$

[Ru −0.042(1), Cl(2) −0.100(1), S(1) −0.079(1), S(2) 0.826(1), O(4) 0.139(4)]

Plane (2): Ru, Cl(1), S(1), S(3), and O(4)

$$0.335X + 0.933Y - 0.129Z = 2.365$$

[Ru 0.013(1), Cl(1) −0.102(1), S(1) 0.003(1), S(3) −0.104(1), O(4) 0.075(4)]

Plane (3): Ru, Cl(1), Cl(2), S(2), and S(3)

$$-0.043X + 0.024Y - 0.999Z = -3.0537$$

[Ru 0.0009(3), Cl(1) −0.166(1), Cl(2) −0.027(1), S(2) 0.186(1), S(3) −0.042(1)]

is an indication of the strong *trans*-effect of *S*-bonded dmso.[8]

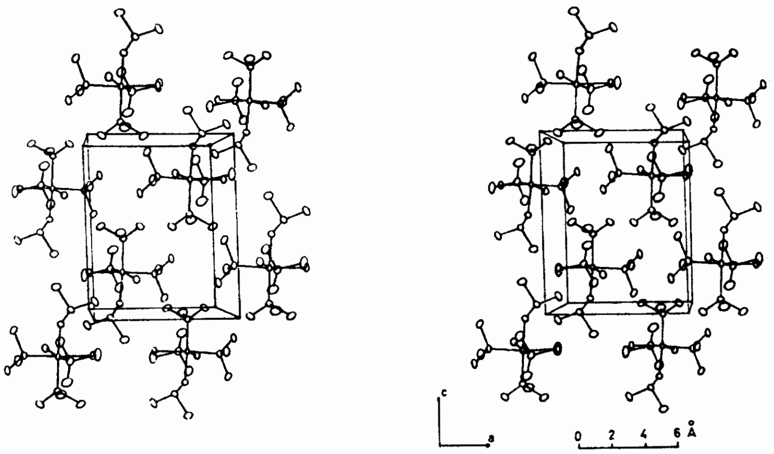

FIGURE 2 Stereodiagram of the unit cell, viewed down *b*

In the interaction between the Ru and S atoms, the sulphur atom appears to be behaving as a weak π acceptor, as a shortening of the bond between a metal atom and a σ donor ligand should be observed if the σ donor is *trans* to a strong π acceptor. For example in $[Ru(NO)Cl_5]^{2-}$ the mean Ru–Cl(eq) distance is 2.376(2) Å, while Ru–Cl for chlorine *trans* to nitrosyl is significantly shorter at 2.357(1) Å.[9]

TABLE 6

Mean bond lengths (Å) and angles (°) for (I) $[RuCl_3(Me_2SO)_3]^-$, (II) $[RuCl_2(Me_2SO)_4]$, (III) $[Ru(NH_3)_5(Me_2SO)]^{2+}$, and (IV) free dimethyl sulphoxide

	(I)	(II)	(III)	(IV)
(*a*) Lengths				
Ru–S	2.261(8)	2.277(1)	2.188(3)	
S–O	1.48(2)	1.485(5)	1.527(7)	1.471—1.531
S–C	1.79(3)	1.790(6)	1.840(8)	1.80—1.82(1)
Ru–Cl	2.43(1)	2.435(1)		
(*b*) Angles				
Ru–S–O	118(1)	119(1)	114.9(3)	
Ru–S–C	112(2)	112(1)	116(1)	
O–S–C	106(2)	106.8(6)	104.2(8)	107
C–S–C	100(2)	99(1)	99.4(6)	98

However evidence supporting some π acceptor nature can be obtained from the Ru–S distances in the *S*-bonded dmso ligands, which are *trans* to the two chlorine atoms. The mean value [2.277(1) Å] indicates the presence of some d_π–p_π back donation from the central metal to the sulphur atom, assuming single-bond covalent radii for ruthenium and sulphur are 1.33 and 1.04 Å.[10] However, this back donation is considerably less than that found [11] in $[Ru(NH_3)_5(Me_2SO)]^{2+}$, where the Ru–S distance is 2.188(3) Å. The increased back donation found in the monosulphoxide is due to the lack of competition for the available π donor orbitals from other π acceptor ligands in the co-ordination sphere. A comparison of similar bond lengths and angles for $[RuCl_3(Me_2SO)_3]^-$,[2] $[Ru(NH_3)_5(Me_2SO)]^{2+}$,[11] and free dmso [12] with those of $[RuCl_2(Me_2SO)_4]$ can be found in Table 6.

Examples of the change in co-ordinating atom with the

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[8] Y. N. Kukushkin, M. A. Kuz'mina, and A. F. U'yugina, *Radiokhimiya*, 1968, **10** (**4**), 470.

[9] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1420.

[10] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, pp. 224, 249.

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

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

variation of the number of dmso ligands attached are somewhat limited. In four-co-ordinate palladium complexes steric influences appear to be of most importance.[13] [Pd(Me$_2$SO)$_2$Cl$_2$] has exclusively sulphur bonding, [Pd(Me$_2$SO)$_4$]$^{2+}$ has both sulphur- and oxygen-bonded ligands in a *cis*-configuration. As the size of the ligand increases mixed *trans*-structures are produced, *i.e.* in the propyl and butyl cationic species, while only oxygen-bonded ligands occur in the 2-methylbutyl sulphoxide complex [Pd(L$_2$SO)$_4$]$^{2+}$. This change in co-ordination is paralleled in these octahedral systems. [RuCl$_3$(Me$_2$SO)$_3$]$^-$ has an all *S*-bonded *cis*-structure, while the inclusion of another dmso ligand approaches the [Pd(Me$_2$SO)$_4$]$^{2+}$ situation, such that steric influences prohibit the formation of an all sulphur-bonded complex, but electronic effects keep the *S*-bonded ligands in a *cis*-configuration. The decrease in central-metal size from ruthenium to iron increases the steric interactions considerably, *i.e.* [FeCl$_2$(Me$_2$SO)$_4$]$^+$ has a *trans*-configuration in which all the dmso ligands are oxygen-bonded.[14]

The Ru–S bond length for the *S*-bonded dimethyl sulphoxide ligand *trans* to the *O*-bonded sulphoxide is 2.252(1) Å. This slight yet significant shortening [*vs.* 2.277(1) Å] is due to the different atoms in the *trans*-positions. Ru–O is 2.142(3) Å, similar to the value [2.007(6) Å] found [14] for Fe–O, considering the difference in covalent radii of the two metals to be *ca.* 0.12 Å.[10]

There is considerable variation in the sulphur–oxygen distances for the two types of differently co-ordinated dmso ligands. In the *S*-bonded ligands the mean is 1.484(5) Å, while in the *O*-bonded ligand the distance is 1.557(4) Å. This represents a considerable decrease in the multiple-bond character of the sulphur–oxygen linkage caused by the differences in co-ordination, though this is still somewhat short of the estimated S–O single-bond length (1.70 Å).[14]

The molecular geometry of the *S*-bonded dmso ligands is very similar to that in free dimethyl sulphoxide.[12] The O–S–C angles [mean 106.6(6)°], C–S–C angles [mean 99(1)°], and the S–C bond lengths [mean 1.79(1) Å] compare with 107°, 98° and 1.80—1.82(1) Å respectively. The corresponding mean values for the *O*-bonded ligand are also similar [103(1)°, 99.0(4)°, and 1.788(5) Å]. The other angles in the distorted tetrahedron have means of 112(2)° for Ru–S–C, 120(2)° for Ru–S–O, and 120.0(2)° for Ru–O–S.

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