Dichlorotetrakis(dimethyl sulphoxide)ruthenium(II) and its Use as a Source Material for Some New Ruthenium(II) Complexes †

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A simple preparation of dichlorotetrakis(dimethyl sulphoxide)ruthenium(II) is given. The i.r. and ^1H n.m.r. spectra of the complex suggest there are mixed sulphur and oxygen co-ordination sites. The complex is a useful starting material for other ruthenium(II) complexes.

DURING the course of our studies on ruthenium complexes containing co-ordinated dimethyl sulphoxide, Rempel *et al.*[1] reported the preparation of dichlorotetrakis(dimethyl sulphoxide)ruthenium(II), $RuCl_2(Me_2SO)_4$, by the prolonged interaction of ruthenium trichloride in dimethyl sulphoxide under hydrogen at 80°; they assigned to it a *trans*-configuration. Such conditions are unnecessary and the compound is formed essentially quantitatively when ruthenium trichloride trihydrate is merely refluxed in dimethyl sulphoxide for a few minutes. The solution rapidly turns orange-brown and the complex can be precipitated from the Me_2SO solution as a yellow powder with acetone. This powder is analytically pure but recrystallisation from hot Me_2SO yields bright yellow crystals. The corresponding fully deuteriated complex, $RuCl_2[(CD_3)_2SO]_4$, can be prepared in an essentially similar way using $RuCl_3,3H_2O$ and $(CD_3)_2SO$.

The complex is monomeric in chloroform at 25 °C and is a non-conductor in both acetonitrile and nitromethane. However, in water, the conductivity slowly increases over *ca.* 36 h to that for a 2 : 1 electrolyte ($\Lambda = 161$ Ω^{-1} cm^2 mol^{-1}; 10^{-3}M). Further, when the complex is dissolved in an aqueous solution of silver nitrate, slow precipitation of silver chloride occurs. After 36 h the amount of silver chloride precipitated is *ca.* 85% of the theoretical based on the equation:

$$RuCl_2(Me_2SO)_4 + 2H_2O + 2AgNO_3 \longrightarrow [Ru(Me_2SO)_4(H_2O)_2]^{2+} + 2NO_3^- + 2AgCl$$

By treating an ethanolic solution of $RuCl_2(Me_2SO)_4$ with silver perchlorate we have obtained a chloride-free solution which will react with various ligands. For example, Me_2SO itself gives $[Ru(Me_2SO)_6]^{2+}$. These species are being further investigated.

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† No reprints available.

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

Spectroscopic Data.—Infrared. A complete assignment of all bands in the i.r. spectra of both $RuCl_2(Me_2SO)_4$ and the deuteriated complex in the range 4000—600 cm^{-1} can be made utilising known data on dimethyl sulphoxide complexes (Table 1).[2-4] The SO stretch in neat Me_2SO occurs at 1055 cm^{-1} and is very strong and broad. It is generally accepted that Me_2SO bonded to a metal through the sulphur atom has a higher frequency SO stretch because of an increase in the SO bond order. Conversely, co-ordination through the oxygen atom is considered to lower the SO bond order and hence lower the frequency of the SO stretch. If the spectra of $RuCl_2(Me_2SO)_4$ and $RuCl_2[(CD_3)_2SO]_4$ are compared, there is a strong band with splitting at 1090—1120 cm^{-1} common to both; from both its strength and position it can be unambiguously assigned as an SO stretch of *S*-bonded Me_2SO. The only other band which does not shift on deuteriation significantly is a strong band at 915 cm^{-1} in $RuCl_2(Me_2SO)_4$ and at 928 cm^{-1} in $RuCl_2[(CD_3)_2SO]_4$. This is assigned as the SO stretch of *O*-bonded Me_2SO. It thus appears that in $RuCl_2(Me_2SO)_4$ both *S*- and *O*-bonding of Me_2SO occurs.

Reasonably well resolved far-i.r. spectra of both deuteriated and non-deuteriated complexes were obtained (Table 1). The Ru–Cl stretches may be assigned by comparison with previous work.[5] As expected, they do not shift on deuteriation of the complex. The origin of the weak band at 295 cm^{-1} is uncertain; it is possibly due to a methyl torsion mode. It is not due to a chlorine bridge as the compound is monomeric in solution.

TABLE 1

Infra-red spectra[a] of $RuCl_2(Me_2SO)_4$ and $RuCl_2[CD_3)_2SO]_4$

$RuCl_2(Me_2SO)_4$		$RuCl_2[CD_3)_2SO]_4$		
Frequency	Assignment[b]	Frequency	Assignment[b]	ν_{CH}/ν_{CD}
3000m	ν_{CH}	2250m	ν_{CD}	1·33
2908m	ν_{CH}	2190m	ν_{CD}	1·33
1430s	δ_d CH	Hidden by ν_{SO}		
1400s	δ_d CH	1077sh	δ_d CD	1·33
1303s	δ_d CH	1010s	δ_d CD	1·29
1282m	δ_d CH	Hidden		
1120s	ν_{SO} *S*-bonded	1120s	ν_{SO} *S*-bonded	
1090s	ν_{SO} *S*-bonded	1095	ν_{SO} *S*-bonded	
1024s	ρ_r CH	810	ρ_r CD	1·26
980m	ρ_r CH	770	ρ_r CD	1·27
970m	ρ_r CH	760	ρ_r CD	1·28
915s	ν_{SO} *O*-bonded	928s	ν_{SO} *O*-bonded	
705m	ν_a CS	628m	ν_a CS	1·12
670w	ν_s CS	Not observed		
479s	ν_{Ru}–Ligand	450	ν_{Ru} Ligand	
420m	δ_s CSO	340s	δ_s CSO	1·08
380m	δ_{as} CSO	355m	δ_{as} CSO	1·07
345m	ν_{Ru-Cl}	330s	νRu–Cl	
330m	ν_{Ru-Cl}	325sh	νRu–Cl	
295w		295w		

[a] In cm^{-1}; 3000—600 cm^{-1}, NaCl or KBr plates, Nujol or hexachlorobutadiene mulls; 500—250 cm^{-1}, Vaseline mulls, Polythene plates. [b] ν, stretching; ν_a, asymmetric stretching; ν_s, symmetric stretching; δ, deformation; δ_d, degenerate deformation; δ_s, symmetric deformation; δ_{as}, asymmetric deformation; ρ_r, rocking.

Little is known about Ru–S or Ru–O stretching frequencies. It seems from available data that these come in the region 500—400 cm^{-1}.[6,7] The band at 480 cm^{-1} in the undeuteriated complex cannot therefore be assigned with certainty to either ν_{Ru-S} or ν_{Ru-O}. It is, however, definitely some sort of metal–ligand vibration, probably containing a great deal of ligand character. There is little difference in the far-i.r. of the complex recrystallised from Me_2SO and the powder obtained directly from the reaction mixture, except that in the latter ν_{Ru-Cl} appears as a single band with a shoulder (348 cm^{-1}) whereas in the recrystallised complex the band is broad, with two, though overlapping peaks at 345 cm^{-1} and 330 cm^{-1}. It is possible that the complex as first precipitated from the reaction mixture is mainly *trans*-$RuCl_2(Me_2SO)_4$, as suggested,[1] whereas after recrystallisation it is a mixture of *cis*- and *trans*-isomers, each of which may have both *S*- and *O*-bonded Me_2SO.

N.m.r. Spectra.—The ^1H n.m.r. spectrum of the complex as obtained direct from the reaction mixture without recrystallisation is very complex, with some 11 lines, the exact intensities of which vary from sample to sample. In contrast, the spectra obtained from the recrystallised material are reproducible and consist of six lines. These are singlets due to six sets of chemically distinct protons at τ 6·50, 6·52, 6·57, 6·68, 7·28, and 7·40, confirmed by the identity of spectra at 60 and 100 MHz. On running the spectrum at −60 °C, considerable broadening of the lines can be observed. This indicates that some sort of exchange mechanism is taking place and that the slow exchange limit is being approached. It has not proved possible to reach this limit due to the physical properties of the various useful solvents.

The complex spectrum could arise from ligands being both *S*- and *O*-bonded, as the methyl proton resonance of *S*-bonded Me_2SO is *ca.* 1 p.p.m. downfield from the methyl resonance of *O*-bonded Me_2SO.[8-10] This criterion has proved useful in determining the mode of bonding of various sulphoxides in complexes of Pd^{II} and Pt^{II}.[11]

The resonance at τ 7·40 can be attributed to free Me_2SO since if Me_2SO is added to the solution of the complex in chloroform this peak grows in intensity in the n.m.r. spectrum. The peak at τ 7·28 can be attributed to *O*-bonded Me_2SO since the methyl resonance is close to that of free Me_2SO. The group of peaks about 1 p.p.m. downfield from the free Me_2SO resonance can all be attributed to *S*-bonded Me_2SO. On the addition of *ca.* 5% by volume of $(CD_3)_2SO$, the resonance attributed to *O*-bonded Me_2SO rapidly disappears; the

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

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

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

[5] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, 1967, p. 72.

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

[7] T. Tanaka, *Inorg. Chim. Acta*, 1967, **1**, 217.

[8] W. Kitching, C. J. Moore, and D. Doddrell, *Inorg. Chem.*, 1970, **9**, 541.

[9] W. Kitching and C. J. Moore, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 691.

[10] S. Thomas and W. L. Reynolds, *Inorg. Chem.*, 1969, **8**, 1531.

[11] J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.

resonances attributed to *S*-bonded Me_2SO disappear somewhat more slowly and at varying rates. After 4 h the only signal observed is that due to free Me_2SO indicating that complete exchange has taken place. This exchange occurs similarly with MeCN and pyridine. However in the case of pyridine, two of the four *S*-bonded resonances remain, suggesting the *in situ* formation of $RuCl_2(Me_2SO)_2(C_5H_5N)_2$.

Integrating the original spectrum shows that there are three *S*-bonded Me_2SO molecules to every *O*-bonded one. Integration of the peaks in the *S*-bonded region was not possible owing to their proximity and their sharing the same broad base line. Their intensities were however reproducible if measured in terms of peak height. This seems to rule out the explanation that isomers are responsible for the complexity of the spectrum in this region, as slightly different procedures in recrystallisation would presumably lead to varying quantities of isomers being present in different samples. There is no need to invoke isomers to explain the complexity of the spectrum observed however. In $RuCl_2(Me_2SO)_4$ consisting of three *S*-bonded and one *O*-bonded Me_2SO molecules, the *S*-bonded molecules are *trans* to either *O*-bonded Me_2SO, *S*-bonded Me_2SO or Cl. This could lead to three different chemical shifts for the methyl resonances of these molecules. If some degree of methyl inequivalence is also present, this could lead to the complex spectrum observed. The methyl resonance of *O*-bonded Me_2SO is less affected by the above consideration since the methyl groups are one bond distance further away from influences such as *trans* ligand, for example. The peak at τ 7·40 due to free Me_2SO results from a *ca.* 10% dissociation of the *O*-bonded Me_2SO. This is shown by (i) integration of the peaks due to *S*-bonded ligands against the peak at τ 7·28 gives a ratio $>3:1$; if the peak at τ 7·40 is included, the ratio then becomes exactly $3:1$; (ii) if excess Me_2SO is added to suppress dissociation, integration of the *S*-bonded Me_2SO peak against the peak at τ 7·28 then gives a ratio of $3:1$. The signal due to free Me_2SO increases if the spectrum is recorded at elevated temperatures (60°). This confirms that the free Me_2SO comes from dissociation of the co-ordinated Me_2SO and that the exchange mechanism is a dissociative rather than an associative one.

Studies on the ^1H n.m.r. spectrum of $RhCl_3(Me_2SO)_3$ also indicate bonding of the Me_2SO through both oxygen and sulphur. In this case there are three resonances in the *S*-bonded region, at τ 6·39, 6·51, and 6·57 and one resonance in the *O*-bonded region at τ 7·13. There is essentially no free Me_2SO and as would be expected the spectrum remains virtually unchanged between +40° and −60°. With $(CD_3)_2SO$ exchange is fairly rapid and the peaks at τ 6·39, 6·51, and 7·13 have all disappeared after *ca.* 1 h. The peak at τ 6·57 remains longer (*ca.* 24 h) but after this time complete exchange has taken place, and the only resonance observed is that of free Me_2SO at τ 7·41.

Preparative Uses of the Complex.—The complex $RuCl_2(Me_2SO)_4$, usually in either toluene or ethanol, commonly reacts with other ligands, L, according to the reaction:

$$RuCl_2(Me_2SO)_4 + xL \longrightarrow RuCl_2(Me_2SO)_yL_x$$

In no case did oxidation of the ruthenium(II) to ruthenium(III) occur and no ruthenium(III) complexes were isolated. Indeed, we have been unable to repeat Rose's preparation [12] of the complex $RuCl_3(Me_2SO)_3$ and we assume it must have been a mixture. The complex is thus a useful source of ruthenium(II) complexes which are air-stable. The reactions of the complex are shown in the Scheme.

Nitrogen, Phosphorus, and Sulphur Ligands.—With these ligands, complete replacement of the bound Me_2SO is observed only when the complex is refluxed in the neat ligand. With a ligand dissolved in an inert solvent only two of the Me_2SO molecules are generally displaced. With chelating ligands, displacement of the more weakly held *O*-bonded Me_2SO presumably occurs first, followed by displacement of an Me_2SO molecule *cis* to it.

With triphenyl phosphite the complex $RuCl_2[(PhO)_3P]_3(Me_2SO)$ which is a non-conductor in acetonitrile can be obtained. The molecular weight of this complex is *ca.* 60% of that expected in chloroform suggesting dissociation:

$$RuCl_2[(PhO)_3P]_3(Me_2SO) \rightleftharpoons RuCl_2[(PhO)_3P]_2(Me_2SO) + (PhO)_3P$$

Dissociation of Me_2SO also cannot be excluded as although there is only one Me_2SO signal this is somewhat broadened. Ionisation of chloride does not occur as the complex is a non-conductor.

Using triphenylphosphine, two Me_2SO molecules are lost, but yet the complex $RuCl_2(Ph_3P)(Me_2SO)_2$ is obtained. This has a normal molecular weight in chloroform at room temperature and is hence pseudo-six-co-ordinate, with a ring hydrogen of one of the phosphine groups presumably blocking the vacant octahedral position, as in *e.g.*, $RuCl_2(PPh_3)_3$.[13] The displacement of two Me_2SO groups by one PPh_3 molecule is not surprising as this ligand has a high steric effect as measured by its cone angle of 145 ± 2°.[14] The different behaviour of $(PhO)_3P$ in forming $RuCl_2(PhO)_3P]_3Me_2SO$ may be similarly accounted for, at least in part, by the lesser cone angle of the phosphite, 121 ± 10°.

Sodium diethyl dithiocarbamate yields the complex $Ru(Et_2NCS_2)_2(Me_2SO)_2$ whereas 2-mercaptobenzthiazole (mbth) yields the complex $RuCl_2(mbth)_2(Me_2SO)_2$.

The i.r. of the former complex indicates bidentate $Et_2NCS_2^-$ only.[15]

Both complexes exhibit only one resonance in the n.m.r. for the methyl protons of the co-ordinated Me_2SO. The positions of the resonances, *ca.* 0·8 p.p.m. downfield from free Me_2SO, unambiguously show that bonding is

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[12] J. D. Gilbert, D. Rose, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2765.

[13] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

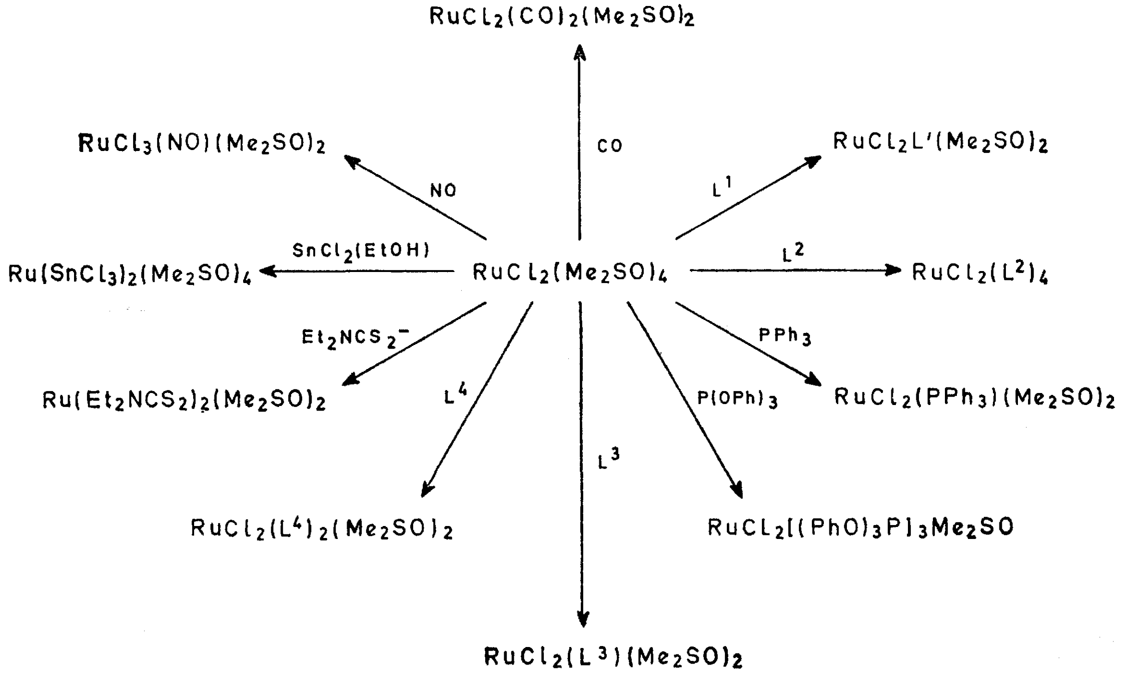
[14] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[15] C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 84.

occurring through the sulphur. The one sharp resonance strongly implies that the Me_2SO ligands are *trans*.

Carbon Monoxide; Nitric Oxide.—The reaction with CO gives best yields of the white product $RuCl_2(CO)_2(Me_2SO)_2$ on refluxing $RuCl_2(Me_2SO)_4$ in toluene in a stream of CO. The complex has ν_{CO} at 2036 and 2082 cm^{-1} indicating *cis* CO groups; a well resolved far-i.r. spectrum could not be obtained, so the structure of the remainder of the molecule is uncertain.

With nitric oxide, only a very low yield of the product $RuNOCl_3(Me_2SO)_2$ can be obtained by direct action of NO on $RuCl_2(Me_2SO)_4$ in refluxing inert solvents. A better synthesis is to employ conditions used for the preparation of $RuCl_2(Me_2SO)_4$, but using an NO atmosphere. The nitrosyl shows a strong N–O stretch at 1880 cm^{-1}. The compound is insoluble in water, ether, benzene, and acetone, but dissolves in acetonitrile and nitromethane in which it is a non-conductor.



SCHEME Reactions of $RuCl_2(Me_2SO)_4$ L^1 = 1,10-phenanthroline or 2,2′-bipyridyl; L^2 = pyridine or 3-methylpyridine; L^3 = 2-aminopyridine; L^4 = 2-mercaptobenzthiazole

EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College.

N.m.r. spectra were measured on a Perkin-Elmer R12B spectrometer equipped with a Variable Temperature Probe Accessory at 60 MHz and a Perkin-Elmer R14 spectrometer at 100 MHz and 35 °C. All spectra were in deuteriochloroform.

I.r. spectra (4000—600 cm^{-1}) were taken on a Perkin-Elmer 257 spectrophotometer and far-i.r. spectra (600—250 cm^{-1}) on a Perkin-Elmer 457 spectrophotometer.

M.p. (uncorrected) were measured on a Kofler hot-stage microscope.

Dried, degassed solvents of reagent grade were used in all reactions, which were carried out under nitrogen, unless otherwise stated. Analytical data are collected in Table 2.

Dichlorotetrakis(dimethyl sulphoxide)ruthenium(II).—Ruthenium trichloride trihydrate (1 g) was refluxed in dimethyl sulphoxide (5 ml) for 5 min. The volume was reduced to half *in vacuo* when addition of acetone (20 ml) gave a yellow precipitate. The yellow *complex* which separated was filtered off, washed with acetone and ether, and vacuum dried.

On standing, the filtrate deposited more of the complex. Recrystallisation from dimethyl sulphoxide by slow evaporation of a hot, concentrated solution yielded *hexagonal plates* (1·33 g, 72%; m.p. 193° decomp.).

Dichlorobis(dimethyl sulphoxide)(triphenylphosphine)ruthenium(II).—$RuCl_2(Me_2SO)_4$ (0·3 g) was suspended in toluene (40 ml) and triphenylphosphine (0·325 g) added. The suspension was refluxed for 40 min to give an orange solution. The toluene was removed, the residue dissolved in the minimum of acetone and the buff complex precipitated by the addition of ether. The complex was washed with acetone (20 ml) and ether (20 ml), vacuum dried and was recrystallised from acetone–ether (0·17 g, 50%; m.p. 200° decomp.).

Bis(diethyl dithiocarbamato)bis(dimethyl sulphoxide)ruthenium(II).—$RuCl_2(Me_2SO)_4$ (0·4 g) was suspended in toluene (50 ml) and sodium diethyl dithiocarbamate trihydrate (0·372 g) added. The suspension was refluxed for 30 min to give a dark coloured solution. The solution was filtered and concentrated to *ca.* 10 ml. Addition of light petroleum (b.p. 80—100°) followed by cooling to −40° produced pale green needles which were recrystallised from acetone–ether (0·3 g, 75%).

Dichlorodicarbonylbis(dimethyl sulphoxide)ruthenium(II).—$RuCl_2(Me_2SO)_4$ (0·5 g) was refluxed in toluene (100 ml) with a slow stream of CO passing through the solution for

24 h. The volume was reduced to *ca.* 10 ml and the white complex precipitated by adding light petroleum (b.p. 40—60°). The complex was washed with ether and vacuum dried (0·14 g, 35%).

Dichlorotetrakis(pyridine)ruthenium(II).—$RuCl_2(Me_2SO)_4$ (0·3 g) was refluxed in pyridine (10 ml) for *ca.* 30 min. Reduction of volume to *ca.* 40% followed by cooling to −40° yielded the orange complex. It was washed with ethanol and dried over silica gel *in vacuo* (0·27 g, 90%).

Dichloro(o-*phenylenediamine*)*bis*(*dimethyl sulphoxide*)-*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·3 g) and *o*-phenylenediamine (0·1 g) were refluxed for 30 min in ethanol (40 ml). The volume was reduced to *ca.* 15 ml when the addition of ether precipitated the pink *complex*. It was recrystallised from ethanol–ether (0·21 g, 70%).

Dichlorotetrakis(3-*methylpyridine*)*ruthenium*(II).—As for dichlorotetrakis(pyridine)ruthenium(II). The red-brown solution obtained after refluxing was stripped and the residue dissolved in chloroform. Addition of ether precipitated the orange *complex* which was washed with ether and vacuum dried (0·24 g, 80%).

TABLE 2

Analytical data for the ruthenium complexes

	Found (%)					Required (%)				
	C	H	N	S	Cl	C	H	N	S	Cl
$RuCl_2(Me_2SO)_4$	19·9	4·9		25·9	14·5	19·8	4·9		26·4	14·7
$RuCl_2(PPh_3)(Me_2SO)_2$	44·5	4·9		8·9	12·2	44·7	4·6		10·8	12·0
$Ru(Et_2NCS_2)_2(Me_2SO)_2$	30·9	6·6	5·6		<0·3	30·4	5·8	5·1	34·7	0·0
$RuCl_2(CO)_2(Me_2SO)_2$	18·9	3·4		19·0	17·7	18·7	3·1		16·7	18·5
$RuCl_2(C_5H_5N)_4$ [a]	49·7	4·1	11·3		14·5	49·2	4·1	11·3		14·5
$RuCl_2(C_6H_7N)_4$	51·8	5·7	9·5		13·5	52·8	5·2	10·2		13·1
$RuCl_2(C_{10}H_8N_2)(Me_2SO)_2$	32·5	4·1	5·2	13·5	14·4	32·5	3·9	5·0	12·4	13·8
$RuCl_2(C_{12}H_8N_2)(Me_2SO)_2$	35·9	4·2	5·1	12·6	14·1	36·7	4·0	5·5	12·3	13·9
$RuCl_2[(PhO)_3P]_3Me_2SO$ [b]	57·9	4·5		2·8	6·3	56·9	4·3		5·2	6·0
$RuCl_2(C_5H_6N_2)(Me_2SO)_2$	25·9	4·5	6·6	15·5		25·6	4·3	6·6	15·2	16·8
$Ru(SnCl_3)_2(Me_2SO)_4$	11·2	3·3		14·5	[c]	11·3	2·8		14·8	24·7
$RuNOCl_3(Me_2SO)_2$	12·9	3·2	3·6	16·1	26·9	12·2	3·1	3·6	16·3	27·1
$Ru(C_4H_6N_2O_3)(Me_2SO)_3$	26·3	5·8	5·7			25·8	5·2	6·0	20·6	
$RuCl_2(C_6H_8N_2)(Me_2SO)$	26·7	5·4	6·1			27·5	4·6	6·4	14·7	16·3
$RuCl_2(C_7H_5NS_2)_2(Me_2SO)_2$	32·8	3·5	4·2		10·6	32·6	3·3	4·2	29·0	10·7
$Ru(Me_2SO)_6(ClO_4)_2$	19·2	4·9		24·6		18·8	4·7		25·0	9·2

[a] Known compound. [b] P Found, 8·6; Required, 7·9%. [c] Sn interferes with Cl analysis.

Dichloro(2,2′-*bipyridyl*)*bis*(*dimethyl sulphoxide*)*ruthenium*-(II).—$RuCl_2(Me_2SO)_4$ (0·5 g) and 2,2′-bipyridyl (0·161 g) were refluxed in chloroform (20 ml) for *ca.* 30 min. The solution was cooled and the solvent removed. The residue was dissolved in acetone. Addition of ether precipitated the yellow complex. This was filtered off, washed with ether, and vacuum dried (0·4 g, 80%).

Dichlorobis(*dimethyl sulphoxide*)(1,10-*phenanthroline*)*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·5 g) and 1,10-phenanthroline (0·2 g) were dissolved in chloroform (20 ml) and the solution refluxed for 30 min. The solution was cooled and the chloroform removed. The residue was dissolved in acetone and ether added. The orange-yellow complex which separated was collected, washed with ether, and dried *in vacuo* over silica gel (0·38 g, 76%).

Dichloro(*dimethyl sulphoxide*)*tris*(*triphenyl phosphite*)-*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·2 g) and triphenyl phosphite (0·26 g) were refluxed in toluene (30 ml) for 40 min to produce an orange solution. The volume was reduced to *ca.* 5 ml and ether was slowly added, with vigorous stirring, to the solution. The yellow precipitate which separated was filtered off. On cooling to −40 °C more precipitate was obtained. Recrystallisation from acetone–ether yielded the white complex (0·29 g, 60%).

Dichloro(2-*aminopyridine*)*bis*(*dimethyl sulphoxide*)*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·2 g) and 2-amino pyridine (0·04 g) were refluxed in toluene (30 ml) for 30 min to yield an orange solution. The solvent was removed and the residue dissolved in the minimum of acetone. Addition of ether followed by cooling to −40 °C caused the separation of the orange-yellow *complex*. It was filtered and dried over silica gel (0·18 g, 50%).

Bis(*trichlorostannyl*)*tetrakis*(*dimethyl sulphoxide*)*ruthenium*(II).—To a refluxing solution of $RuCl_2(Me_2SO)_4$ (0·2 g) in ethanol (20 ml) was added a hot solution of tin(II) chloride (0·16 g) in ethanol (15 ml). The precipitate which formed was filtered hot and washed with acetone (2 × 10 ml) and ether (2 × 10 ml). It was dried *in vacuo*. The yield of the orange *complex* was essentially quantitative.

Nitrosyltrichlorobis(*dimethyl sulphoxide*)*ruthenium*(II).—Nitric oxide was passed rapidly through a refluxing solution of $RuCl_3,3H_2O$ (1 g) in Me_2SO (5 ml). The bulk of the solvent was removed to give a viscous oil. Addition of ethanol (20 ml) and cooling to −78 °C produced the brick-red *complex*. It was filtered, washed with acetone (2 × 10 ml), ether (2 × 10 ml), and vacuum dried (0·63 g, 80%).

N-*Glycylglycinatotris*(*dimethyl sulphoxide*)*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·36 g) and *N*-glycylglycine (0·196 g) were refluxed in ethanol (40 ml) for *ca.* 30 min. The solution was cooled to room temperature and filtered. The bulk of the solution was reduced to *ca.* 15 ml and cooled to −78 °C. The yellow *complex* which separated was filtered off at −78 °C and washed with acetone (3 × 10 ml) and ether (2 × 10 ml). It was dried *in vacuo* over silica gel (0·18 g, 52%).

Dichlorobis(*dimethyl sulphoxide*)*bis*(2-*mercaptobenzthiazole*)*ruthenium*(II).—$RuCl_2(Me_2SO)_4$ (0·2 g) and 2-mercaptobenzthiazole (0·138 g) were refluxed in toluene (40 ml) for 40 min. The wine-red solution was reduced in volume to *ca.* 15 ml and cooled to *ca.* −78 °C. The orange-yellow precipitate which formed was filtered off, washed with cold ethanol (2 × 10 ml) and cold ether (2 × 10 ml), and vacuum dried over silica gel. It was recrystallised from hot acetone–ether (0·12 g, 50%).

Hexakis(*dimethyl sulphoxide*)*ruthenium Perchlorate*.—

$RuCl_2(Me_2SO)_4$ (0·5 g) and $AgClO_4$ (0·435 g) were suspended in ethanol (60 ml). The mixture was gently shaken for 48—72 h. The precipitated $AgCl(Me_2SO)_n$ was filtered off, Me_2SO (0·5 ml) was added, and the solution reduced in volume to *ca.* 15 ml after standing for *ca.* 30 min. On cooling to $-20°$ very pale green microcrystals separated which were filtered off, washed with cold ethanol (2 × 5 ml), and vacuum dried over silica gel. The crystals slowly turn green over a period of days (0·4 g, 50%).

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