The Structural Reformulation of $[Ru_2Cl_4(Me_2SO)_5]$ †

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New i.r. and n.m.r. (^1H and $^{13}C-\{^1H\}$) studies establish that $[Ru_2Cl_4(Me_2SO)_5]$, which forms on heating wet solutions of $[RuCl_2(Me_2SO)_4]$, contains exclusively *S*-bonded terminal sulphoxide ligands and should be reformulated as a triple chloro-bridged diruthenium(II) complex, *i.e.* $[(Me_2SO)_3RuCl_3RuCl(Me_2SO)_2]$. The ^{13}C resonances for *O*-bonded and *S*-bonded Me_2SO ligands are well separated. Analogous $[Ru_2Cl_4L_5]$ complexes, with L = NCMe, pyridine, or 4-methylpyridine (4Me-py), are not formed due to the relative non-lability of $[RuCl_2(NCMe)_4]$, *etc.* Both $[RuCl_2(Me_2SO)_4]^+$ and mixed-valence $[Ru_2Cl_4(Me_2SO)_5]^+$ can be generated electrochemically, though the former is thermally unstable in contrast to $[RuCl_2(4Me\text{-}py)_4]^+$.

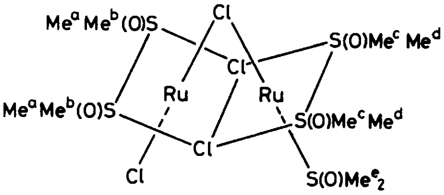
Following the original characterisation of compounds of the type $[(PR_3)_3RuCl_3Ru(PR_3)_3]Cl$ by Chatt and Hayter,[1] many other examples of triple chloro-bridged diruthenium(II) complexes have been reported. Apart from the expanded sandwich compounds $[(arene)RuX_3Ru(arene)]PF_6$ (X = Cl, Br, or I),[2] these are dominated by phosphorus-based ligands, and include complexes of the types $[Ru_2Cl_3L_6]^+$,[1,3] $[Ru_2Cl_4(PR_3)_5]$,[4] $[Ru_2Cl_4(PPh_3)_4Y]$,[5,6] and $[Ru_2Cl_4(PPh_3)_3Y_2]$,[5,6] where L = PR_3 or $P(OR)Ph_2$ and Y = CO, CS, or PF_3. The phosphine-containing systems are remarkable for their ability to undergo reversible step-wise oxidation to the corresponding mixed-valence Ru^{II}–Ru^{III} and diruthenium(III) triply chloro-bridged complexes.[7–9]

Accordingly, we noted with great interest that a recent communication by Hudali *et al.*[10] briefly reported a new compound $[Ru_2Cl_4(Me_2SO)_5]$ (1) which was obtained from solutions of $[RuCl_2(Me_2SO)_4]$ (2) in boiling toluene. Inspection of the i.r. spectrum led Hudali *et al.* to formulate the binuclear complex with two bridging chlorides and a bridging Me_2SO group, together with terminal chloride ligands and both *O*- and *S*-co-ordinated terminal Me_2SO ligands. The envisaged mode of bridging in (1) (*i.e.* Ru–O–Ru or Ru–S–O–Ru) was not specified, however we note that Ru–O–Ru linkages are known in triply alkoxide-bridged Ru^{II} complexes.[11] Simultaneous co-ordination of two metal centres by dialkyl sulphoxide ligands is evidently uncommon, and has not been widely discussed;[12] nevertheless, exclusively *O*-bridged Me_2SO has been established by *X*-ray analysis in binuclear Hg^{II} and infinitely linked Ag^I complexes[13,14] despite their relatively 'soft-acid' character; we have found no examples of the alternative *S,O*-bridged mode.

In view of our interest in structure/redox activity correlations in binuclear ruthenium systems,[9,15] and the proposed disparity between (1) and more familiar $[Ru_2Cl_4L_5]$ complexes, such as $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$, we decided to investigate its nature more fully. The observations described below show that the original suggestion is incorrect and establish that (1) almost certainly has the triple chloro-bridged structure, I, with exclusively terminal *S*-bonded Me_2SO ligands.

Results and Discussion

Formation of $[Ru_2Cl_4(Me_2SO)_5]$.—The analytically pure orange complex (1) is formed in high yield as a microcrystalline, diamagnetic non-electrolyte upon boiling $[RuCl_2(Me_2SO)_4]$ in moist toluene under air or N_2. We find that use of rigorously dry toluene leads only to recovery of the starting material, whereas addition of water (2 drops/0.1 mmol Ru) ensures complete reaction. The product is rather insoluble in common solvents other than CH_2Cl_2; however, like its precursor it is very soluble in water in which it fairly soon rearranges *via* presumed aquation reactions.



I

Infrared Spectral Studies.—I.r. data are recognised as a valuable guide to the bonding of dialkyl sulphoxide ligands, with ν(S=O) found characteristically in the ranges 1 050—1 200 cm^{-1} for *S*-co-ordination and 890—1 050 cm^{-1} for *O*-co-ordination.[12] This is well documented for the divalent ruthenium complexes $[RuX_2(Me_2SO)_4]$ (X = Cl or Br) themselves, which contain both *O*- and *S*-bonded ligands.[16–18] In the spectrum of (1), Hudali *et al.*[10] reported bands at 1 110 and 1 090 cm^{-1} assigned to *S*-bound Me_2SO, as well as bands at 928 and 910 cm^{-1} attributed to *O*-bound Me_2SO and, in particular, a band at 965 cm^{-1} attributed to ν(S=O) of bridging Me_2SO.

Since the region *ca.* 1 030—900 cm^{-1} is well known to be complicated by CH_3 vibrations,[16,19] we have carefully compared the i.r. spectra of (1) and its $(CD_3)_2SO$ analogue. As shown in Figure 1 and Table 1, the isotopic substitution makes clear that only bands near 1 135 (doublet), 1 115 (doublet), and 1 095 cm^{-1} can be attributed to ν(S=O), whereas the bands hitherto attributed to bridging and *O*-bound Me_2SO shift by *ca.* 200 cm^{-1}, consistent with their assignment as methyl rocking vibrations. Furthermore, careful examination of the complete spectrum of (1), and detailed comparisons with (2) and its deuteriated form $[RuCl_2\{(CD_3)_2SO\}_4]$, make clear that complex (1) *shows no i.r. bands except those expected for the exclusively* S-*bonded complex.*‡ Thus the proposed bridging

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† *def*-Tri-μ-chloro-*a*-chloro-*bcghi*-pentakis(dimethyl sulphoxide)-diruthenium(II).

‡ Note that the broad band near 1 020 cm^{-1} in deuteriated (1) and (2) is due to CD_3 deformations. In (2) (and in several other Ru^{II} complexes[18]) *O*-bonded ν(S=O) is clearly identified as a strong band near 930 cm^{-1}, with further CH_3 vibrations at 1 020—980 cm^{-1} descending to 820—770 cm^{-1} upon deuteriation. In exclusively M–O–M bridged complexes of Hg^{II}, ν(S=O) has been tentatively assigned in the range 995—950 cm^{-1}.[13]

Table 1. I.r. spectral data * (4 000—600 cm^{-1}) for (1) and its deuteriated analogue

[$Ru_2Cl_4(Me_2SO)_5$] $\tilde{\nu}$/cm^{-1}	Assignment	[$Ru_2Cl_4\{(CD_3)_2SO\}_5$] $\tilde{\nu}$/cm^{-1}	Assignment
3 005m	$(C-H)_{asym}$ stretch	2 260m	$(C-D)_{asym}$ stretch
2 920m	$(C-H)_{sym}$ stretch	2 130	$(C-D)_{sym}$ stretch
1 425m	$(CH_3)_{asym}$ deformation	1 035m	$(CD_3)_{asym}$ and $(CD_3)_{sym}$ deformations
1 410m		1 030m	
1 322m	$(CH_3)_{sym}$ deformation	1 020m	
1 295m		1 007s	
1 135vs d	S–O stretch	1 137vs d	S–O stretch
1 115vs d		1 110vs d	
1 095vs		1 100vs	
1 028s	CH_3 rock	830m	CD_3 rock
1 020s		815m	
970m		780m	
930w		765m	
914w			
720m	$(C-S)_{sym}$ and $(C-S)_{asym}$ stretches		
675m		620m	C–S stretch

* See Experimental section for data 600—250 cm^{-1}. Data are from pressed KCl discs, fully consistent with Nujol mull spectra. Assignments following the reasoning of Cotton *et al.*[19] v = Very, s = strong, m = medium, w = weak, d = doublet.

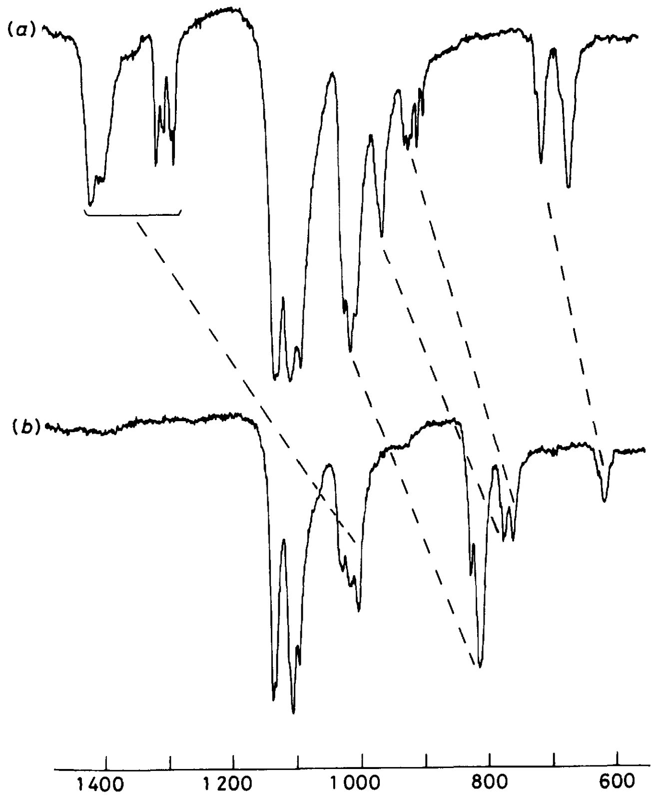
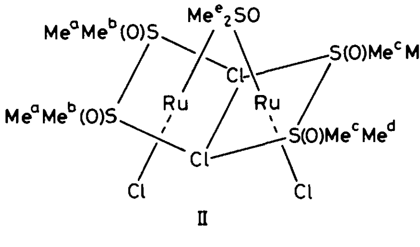


Figure 1. I.r. spectra (1 200—600 cm^{-1}) of (*a*) [$Ru_2Cl_4(Me_2SO)_5$] and (*b*) [$Ru_2Cl_4\{(CD_3)_2SO\}_5$]

Me_2SO moiety is effectively disproved, except in the improbable circumstance of it having ν(S=O) fall within the normal *S*-bonded region or under the 1 020 cm^{-1} band, or being i.r. ' silent ' (*i.e.* very weakly absorbing).

N.M.R. Studies.—High resolution n.m.r. measurements are remarkably helpful in this instance since as well as defining all the sulphoxide ligands as *S*-bonded, they unequivocally establish that the molecule has a mirror plane. Thus in both ^1H and ^{13}C-{^1H} spectra (Figure 2 and Table 2) five equally intense and closely spaced methyl resonances appear, arising from two pairs of symmetry-related ligands and a unique ligand lying on the mirror plane, *i.e.* 2 × Me^aMe^bSO, 2 × Me^cMe^dSO, and Me^e_2SO, as in I. Proton–proton coupling is observed between non-equivalent methyl groups attached to the same sulphur atom, giving rise to quartet signals in the ^1H n.m.r. spectrum that are resolved by line-narrowing techniques (the four-bond coupling is about 0.7 Hz in both cases). A homonuclear decoupling experiment indicates that it is the alternate rather than adjacent quartets which are coupled in this way. This emphasizes that, within the narrow spread of only 0.15 p.p.m. over five resonances (or 2.3 p.p.m. for ^{13}C), the orientation of the individual methyl group exerts a greater influence on the chemical shift than does the particular choice among similar ligand binding sites. Accordingly, only the singlet resonance in the ^1H spectrum is uniquely assigned, and one-to-one correlation of ^{13}C and ^1H resonance signals has not been attempted. The value of ^1H chemical shift information in distinguishing *O*- and *S*-bonded Me_2SO ligands is well recognised,[12,18] and it seems likely from the present observations that similar criteria will emerge for ^{13}C n.m.r. data. In (2) the ^{13}C resonances for the *S*-bonded ligands are well separated from that of their *O*-bonded counterpart, which actually moves in the opposite sense with respect to free Me_2SO. We find that [$RuCl(SOMe_2)_3(OSMe_2)_2$]$^+$ and *fac*-[$Ru(SOMe_2)_3(OSMe_2)_3$]$^{2+}$ also reveal this striking feature with, for example, shifts of +5.14 p.p.m. and −2.73 p.p.m. observed for the latter complex. For (1) all the ligand resonances in both ^1H and ^{13}C spectra fall in the range appropriate to *S*-bonded Me_2SO, in accord with structure I.

The particular formulation proposed by Hudali *et al.*[10] is obviously wrong since it includes *O*-bonded terminal ligands; nonetheless, the rigorous C_s symmetry established by n.m.r. studies does not eliminate the possibility of a bridging Me_2SO ligand lying in the mirror plane, as in structure II.



II

Fortunately, Ru–O–Ru sulphoxide bridging, for which some structural analogy exists,[11,13] may be definitely eliminated since the chemical shift data establish that the unique ligand is *S*-bound, whether or not it engages in further co-ordination. Regarding the hypothetical *S*,*O*-bridged mode, which is apparently less favourable even for ' soft ' metal centres [13,14] the data are not conclusive.* However, the *spread* observed for both the ^{13}C resonances and the ^1H resonances of (1) is less than the corresponding spread delimited by the three normal *S*-bonded ligands of (2) (0.15 *versus* 0.18 p.p.m. for ^1H and

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* Simple addition of the cumulative chemical shifts from free Me_2SO due to *S*- and *O*-bonding would suggest median bridged-ligand δ values in (1) of *ca.* 3.6 p.p.m. (^1H) and 45.4 p.p.m. (^{13}C).

Table 2. N.m.r. parameters for $[RuCl_2(Me_2SO)_4]$ and $[Ru_2Cl_4(Me_2SO)_5]$ [a]

	S-Bound Me_2SO					*O*-Bound Me_2SO	Free Me_2SO
(*a*) ^1H data [b]							
$[RuCl_2(Me_2SO)_4]$ [c]	3.416 (s)	3.364 (q)	3.237 (q)			2.690 (s)	2.550
$[Ru_2Cl_4(Me_2SO)_5]$	3.498 (s)	3.468 (q)	3.439 (q)	3.379 (q)	3.338 (q)		
(*b*) ^{13}C-$\{^1H\}$ data							
$[RuCl_2(Me_2SO)_4]$ [c]	47.709	46.296	44.336			38.958	41.245
$[Ru_2Cl_4(Me_2SO)_5]$	48.995	47.893	47.800	47.684	45.883		

[a] In CD_2Cl_2, δ(p.p.m.) *versus* $SiMe_4$. [b] s = Singlet, q = quartet [^4J(H–H) *ca.* 0.7 Hz in all cases]. [c] Checked in the presence of 10-fold excess of Me_2SO.[18]

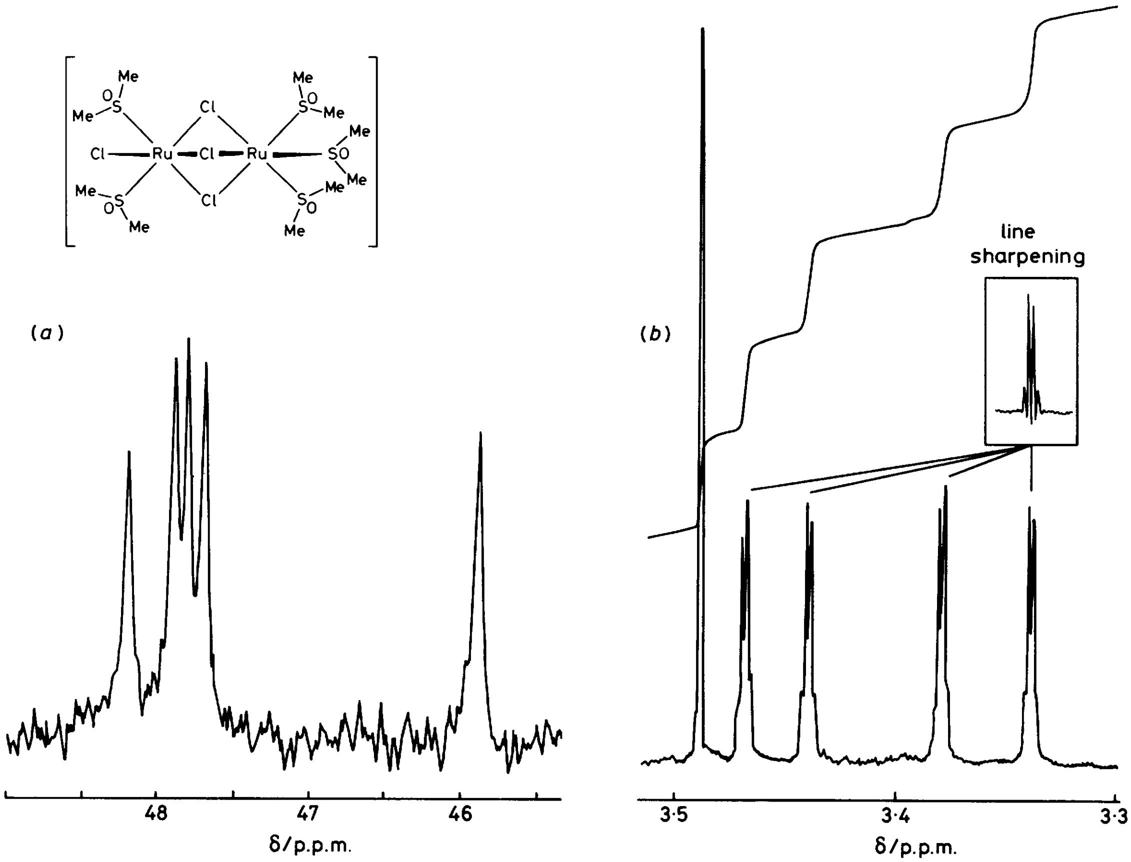

Figure 2. (*a*) ^{13}C-$\{^1H\}$ and (*b*) ^1H n.m.r. spectra of $[Ru_2Cl_4(Me_2SO)_5]$ (structure shown), in CD_2Cl_2 at 303 K

2.37 *versus* 3.34 p.p.m. for ^{13}C), so that there is little internal indication of one ligand in (1) being bound any differently from the rest.

Accordingly, the combined evidence of the i.r. and n.m.r. studies points clearly to structure I as the correct formulation of $[Ru_2Cl_4(Me_2SO)_5]$, which thus provides a most interesting parallel with the redox-active $[Ru_2Cl_4(PR_3)_5]$ complexes mentioned above.

Electrochemical Studies.—Cyclic voltammetry (c.v.) and linear a.c. voltammetry (a.c.v.) in CH_2Cl_2 establish that one-electron oxidation of $[RuCl_2(Me_2SO)_4]$ requires a relatively high potential, *i.e.* +1.64 V *versus* Ag/AgI. The cation is immediately unstable at room temperature (no c.v. return wave) although reversible oxidation is observed at 228 K. In contrast, (1) at room temperature undergoes reversible one-electron oxidation to the mixed-valence complex $[Ru_2Cl_4(Me_2SO)_5]^+$ at +1.40 V. This reflects the general tendency for binuclear complexes to show more facile redox activity in accord with their greater opportunity for charge dispersal.[20] In this case (1), having structure I, may be compared with $[Ru_2Cl_4(PEt_2Ph)_5]$ (oxidations at +0.47 and +1.47 V), so that the second oxidation is not expected until *ca.* 2.4 V, beyond the solvent limit. The separation of the successive $Ru^{II/III}$ couples has been shown to increase systematically with increasing imbalance of terminal chloride co-ordination between the two metal centres, whatever the accompanying neutral ligands,[15] and is in fact diagnostic of structural isomerisation in such complexes.[9]

Synthetic Studies.—It might be thought that the efficient generation of (1) from $[RuCl_2(Me_2SO)_4]$ is a prototype for formation of new binuclear species by condensation of other $[RuCl_2L_4]$ complexes, *e.g.* where L = acetonitrile, 4-methylpyridine (4Me-py), or pyridine. In all these cases no reaction was observed on heating solutions under nitrogen, with or without addition of water. Attempted photolysis of $[RuCl_2(4Me\text{-}py)_4]$ likewise yielded only the starting material, isolated as a CH_2Cl_2 solvate. Interestingly however, it was found that suspensions of $[RuCl_2(4Me\text{-}py)_4]$ in MeOH shaken with excess HBF_4 are readily aerially oxidized to red crystalline $[RuCl_2(4Me\text{-}py)_4]BF_4$, analogous to transient $[RuCl_2(Me_2SO)_4]^+$ referred to above. Voltammagrams for reduction of this product and for oxidation of its precursor $[RuCl_2(4Me\text{-}py)_4]$ coincide ($E_{\frac{1}{2}} = +0.34$ V), as expected for a simple redox process involving no structural change.

We believe that the unique reaction to form the title compound (1) is due to the particular presence of the single *O*-bonded and relatively labile Me_2SO ligand in the precursor. It has been shown previously that in wet $CDCl_3$, $[RuCl_2(SOMe_2)_3(OSMe_2)]$ is hydrolysed to $[RuCl_2(SOMe_2)_3(H_2O)]$.[18] Evidently the aqua-ligand is also readily lost in boiling toluene or ethanol, leading to condensation to (1). It is interesting that this structure is favoured over the hypothetical double-bridged product $[(Me_2SO)_3ClRuCl_2RuCl(Me_2SO)_3]$ which would not require displacement of an *S*-bonded ligand. Similar intermolecular condensation reactions to generate confacial bioctahedral complexes have been observed for other $[RuX_2L_3]$ intermediates,[2] thus emphasising the particular stability of the triple halide-bridged arrangement.

Experimental

Instrumentation.—Microanalyses were performed in the Chemistry Department, University of Edinburgh and by Canadian Microanalytical Services Ltd., Vancouver, B.C. Melting points (uncorrected) were determined with a Köfler hot-stage microscope and conductivity measurements with a Portland Electronics Model 310 conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer 577 grating spectrometer using Nujol mulls on caesium iodide plates (4 000—250 cm^{-1}) and pressed KCl discs (4 000—625 cm^{-1}); ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were measured at 360 and 120 MHz respectively on a Bruker WH360 spectrometer using CD_2Cl_2 solutions at 300 K. Chemical shifts are reported in p.p.m. to high frequency of $SiMe_4$. Electrochemical studies employed a PAR model 170 potentiostat and programmer and $[NBu^t_4][BF_4]$ solutions (0.5 mol dm^{-3}) in CH_2Cl_2 at 298 and 228 K with Pt working and auxiliary electrodes and an Ag/AgI reference electrode (against which ferrocene is oxidized at $E_{\frac{1}{2}} = +0.60$ V). Scan rates were 50—500 mV s^{-1} (c.v.) and 10 mV s^{-1} (a.c.v.) with the frequency of the sinusoidal alternating voltage modulation (a.c.v.) = 205 Hz.

Preparations.—The complexes $[RuCl_2(Me_2SO)_4]$,[16] $[RuCl_2\{(CD_3)_2SO\}_4]$,[16] and *trans*-$[RuCl_2L_4]$ (L = NCMe, pyridine, and 4Me-py)[21] were prepared by literature methods.

def-*Tri*-μ-*chloro*-a-*chloro*-bcghi-*pentakis*(*dimethyl sulphoxide*)*diruthenium*(II) (1). (*i*) Yellow microcrystalline complex (2) (0.20 g) was suspended in dry toluene (20 cm^3), 2 drops of water were added, and the solution was heated to reflux in air or under pure N_2 for 3 h. The orange-brown precipitate of (1) was dried *in vacuo* at 40 °C (typical yield 0.14 g, 95%).

(*ii*) As in method (*i*) above, but in boiling EtOH (20 cm^3, technical grade) for 30 min (yield 95%).

Complex (1) has m.p. 250 °C (decomp.) (Found: C, 16.6; H, 4.2; Cl, 19.4. Calc. for $C_{10}H_{30}Cl_4O_5Ru_2S_5$: C, 16.5; H, 4.1; Cl, 19.4%) and is non-conducting in CH_2Cl_2. I.r. (600—250 cm^{-1}): 450m, 430s, 387m, 350m, 340m (doublet), 310m, and 290w cm^{-1}.

def-*Tri*-μ-*chloro*-a-*chloro*-bcghi-*pentakis*([$^2H_6$]*dimethyl sulphoxide*)*diruthenium*(II). This was synthesised exactly as in method (*i*) above using neat $(CD_3)_2SO$ (Goss, 99.9% D), m.p. 252 °C (decomp.) (Found: C, 16.1; D, 7.90; Cl, 18.8. Calc. for $C_{10}D_{30}Cl_4O_5Ru_2S_5$: C, 15.7; D, 7.85; Cl, 18.6%), non-conducting in CH_2Cl_2. I.r. (600—250 cm^{-1}): 410m, 395s, 360m, 330m (doublet), 305m, and 290w cm^{-1}.

trans-*Dichlorotetrakis*(4-*methylpyridine*)*ruthenium*(III) *tetrafluoroborate*. Orange microcrystalline *trans*-$[RuCl_2(4Me\text{-}py)_4]$ (0.20 g) was suspended in MeOH (20 cm^3) and excess HBF_4 (4 cm^3, 40% aqueous solution) and shaken in air for 2 days. The resulting red crystals were washed with the minimum of EtOH then Et_2O and dried *in vacuo* at 40 °C. Partial filtrate evaporation gave more red crystals which were treated similarly (combined yield 0.20 g, 88%), m.p. 160 °C (decomp.) (Found: C, 45.9; H, 4.5; N, 8.9. Calc. for $C_{24}H_{28}BCl_2F_4N_4Ru$: C, 45.6; H, 4.4; N, 8.9%), Λ (300 K, 1×10^{-3} mol dm^{-3}, in CH_2Cl_2) = 45 Ω^{-1} cm^2 mol^{-1}.

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