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FULL PAPER

Unusual pathways for the reaction between $[MCl_2(Me_2SO)_4]$ (M = Os, Ru) and hydrazine dihydrochloride: deoxygenation of sulfoxides *vs*. coordination of hydrazinium

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Reaction of *trans*-$[OsCl_2(Me_2SO)_4]$ **1** with excess $N_2H_4\cdot 2HCl$ leads to the osmium(III) compound *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2** in the course of concerted reactions, *i.e.* oxidation of the metal, deoxygenation of the sulfoxide, disproportionation of hydrazine and substitution by NH_3. In contrast, interaction of *cis*-$[RuCl_2(Me_2SO)_4]$ *cis*-**3** with hydrazine dihydrochloride brings about easy substitution (without redox conversion) leading to *mer*-$[RuCl_3(N_2H_5)(Me_2SO)_2]$ **4** which is a rare example of a hydrazinium complex. X-Ray single-crystal diffraction analyses were performed on **1**, **2** and **4**. In **4**, one Ru–S bond is unusually short due to the enhanced π bonding contribution as a result of an intramolecular H-bond between the Me_2SO and the *cis* $N_2H_5^+$ group. The complexes show anodic oxidations and **4**, that in aqueous medium undergoes spontaneous dehydrochlorination, exhibits by controlled potential electrolysis a multi-electron oxidation process with anodically-induced H^+ loss, oxidation of the hydrazine ligand to N_2 and N-oxides, and of Me_2SO to SO_2. The anodic waves of Me_2SO or H_2O solutions of *cis*-**3** were assigned to *trans*-$[RuCl_2(Me_2SO\text{-}S)_4]$ *trans*-**3** and $[RuCl(H_2O)_2(Me_2SO\text{-}S)_3]^+$, respectively. The oxidation potential values were interpreted on the basis of redox potential–structure relationships and the Lever electrochemical parameter E_L was tentatively estimated for both S- and O-coordinated Me_2SO and for the hydrazinium ligand, showing that Me_2SO-*S* in our complexes behaves as a significant π-electron acceptor and $N_2H_5^+$ as a rather weak net electron donor, and applied to predict the oxidation potential of some Ru and Os complexes.

Introduction

Dialkyl sulfoxides in general and dimethyl sulfoxide in particular are among the most studied solvents and reagents in organic chemistry.[1–3] Despite the fact that their coordination chemistry started only in the early sixties[4] and has a much poorer history, various reactions of sulfoxides with a variety of metal ions and complexes,[5] including the versatile coordination modes of R_2SO,[6–8] the application of sulfoxide metal compounds as useful synthons in preparative coordination chemistry,[9] their homogeneous catalytic properties[10] and the potential of sulfoxide complexes in medicine,[11,12] have been extensively investigated.

One of the most fundamental chemical properties of sulfoxides is their ability to undergo deoxygenation of the sulfinyl group to give the corresponding sulfides, a reaction that has been studied in depth in organic chemistry,[1–3] while the deoxygenation of sulfoxide ligands has received much less attention and only one review on the subject has been written.[13] Besides the data analysed in the article,[13] new interesting examples of the deoxygenation have been reported in the last five years.[14–23]

Inspection of the massive amount of structural data[6] as well as theoretical calculations[24] indicate that the S=O bonds are stronger in S-bound R_2SO ligands than those in free and O-coordinated sulfoxides and this indirectly implies that it is more difficult to abstract oxygen from S-bound sulfoxides than from both uncoordinated and O-bound ones. Indeed, data on the reduction of S-coordinated sulfoxides (in contrast to O-coordinated ligands) are rather scarce and restricted mainly to complexes of the platinum group metals.[13] Most of the methods known so far for the reduction of the very strong S=O bond in S-coordinated R_2SO ligands are based upon an initial activation of the sulfinyl oxygen by a reagent having a highly reactive electrophilic centre. The activator, E^+, binds to the oxygen atom, increases the partial positive charge on the sulfur atom and thus facilitates the reduction, Scheme 1.

The combination of an electrophilic activator and a reducing agent such as $HX–Pt^{II}$ (X = Cl, Br),[25] $SOCl_2–Pt^{II}$,[26] $HCl–N_2H_4$,[19] $PCl_5–Pr^iOH$[27] proved to be useful in deoxygenations of S-coordinated sulfoxides. However, all these processes were carried out for Pt complexes only, while deoxygenation of other metal compounds that contain S-bound R_2SO ligands is still a very little known area. Thus, only reductive thermolysis studies[28] and deoxygenations involving HCl,[29,30] CO[21] and PCl_3[22,23] were reported for both Os and Ru S-bound complexes.

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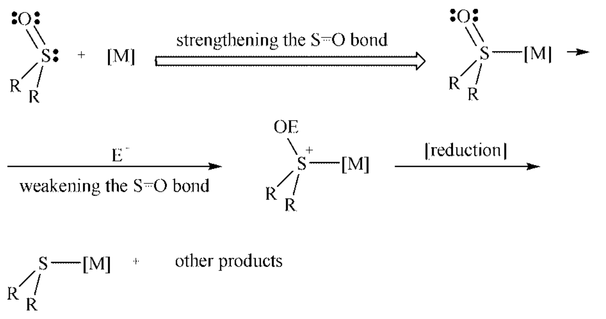

Scheme 1

In view of our interest in the chemistry of metal sulfoxide complexes,[6,7,9,11,13] we focused our efforts on deoxygenation of sulfoxide ligands in the Os^{II} and Ru^{II} compounds $[MCl_2(Me_2SO)_4]$. For this study we selected $N_2H_4{\cdot}2HCl$ as a deoxygenating reagent which was known to be efficient for the reduction of dimethyl sulfoxide ligands in $[PtCl_n(Me_2SO)_2]$ ($n = 2$ or 4) to afford $[PtCl_2(Me_2S)_2]$.[19] In the case of the Os complex, we observed metal oxidation with concomitant reduction of Me_2SO to Me_2S and N_2H_4 to NH_3, while for the Ru^{II} compound the reaction proceeds in the unexpected direction giving a rare hydrazinium complex *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ without oxidation of the metal. In view of the different redox/substitution behaviours exhibited in these reactions by the Os^{II} and Ru^{II} sites, an electrochemical study was also performed, (i) indicating a higher lability of the latter towards ligand displacement but its higher stability towards oxidation, (ii) providing a distinction between the S- and O-coordination modes of Me_2SO and (iii) allowing us to tentatively estimate the corresponding values of the Lever E_L ligand parameter[31] which was used for assignment of the binding mode of Me_2SO and the identification of new products. All these results along with structural data are reported below.

Experimental

Materials and instrumentation (chemical studies)

Hydrazine dihydrochloride (Reakhim) was used as received. *cis*-$[RuCl_2(Me_2SO)_4]$ was prepared in accord with the published method.[32] All other chemicals and solvents were obtained from commercial sources and were used as received. Decomposition points were determined on a Kofler table. For TLC, Silufol UV254 SiO_2-plates were used. Elemental analyses were carried out by the Microanalytical Service, St. Petersburg State Technological Institute. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrices of samples with 8 keV (*ca.* 1.28×10^{-15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–220 cm^{-1}) were recorded on a Perkin-Elmer 983G spectrometer in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra (δ values relative to $SiMe_4$ as an internal reference) were measured on a Varian UNITY 300 spectrometer at ambient temperature.

Synthetic work and characterisation

***trans*-$[OsCl_2(Me_2SO)_4]$ 1.** This was obtained by a slightly modified version of a literature method[33] using $K_2[OsCl_6]$ instead of $H_2[OsCl_6]$. Found: C, 16.7; H, 4.0; Cl, 12.5; Os, 33.3. $C_8H_{24}Cl_2O_4OsS_4$ requires C, 16.8; H, 4.2; Cl, 12.4; Os, 33.2%. FAB^+-MS, *m/z*: 574 $[M]^+$. IR spectrum, cm^{-1}: 3041 m, 3014 m and 2929 w ν(C–H); 1081 vs and 1027 s ν(S=O). ^1H NMR spectrum in $CDCl_3$, δ: 3.47. $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 42.0. Crystals suitable for X-ray analysis were grown on slow evaporation of a chloroform solution.

***mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ 2.** A mixture of *trans*-$[OsCl_2(Me_2SO)_4]$ **1** (0.20 g, 0.35 mmol) and $N_2H_4{\cdot}2HCl$ (0.40 g, 3.81 mmol) in water (2 ml) was heated at 90–95 °C for 5 h, cooled to room temperature and left to stand for 1 d. A crystalline precipitate was filtered off, washed on a filter with water (10 ml), ethanol (5 ml) and chloroform (5 ml) and dried in air at 20–25 °C. Yield of *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ was 0.06 g, 43% based on Os. Found: C, 6.4; N, 6.8; Os, 48.7. $C_2H_{12}N_2Cl_3OsS$ requires C, 6.1; N, 7.1; Os, 48.4%. FAB^+-MS, *m/z*: 393 $[M]^+$. This complex has no characteristic melting point, it decomposes above 225 °C. IR spectrum, cm^{-1}: 3291 m-s, 3233 m-s and 3180 m-s ν(N–H); 2998 w and 2929 w ν(C–H); 1618 m, br δ_{as}(HNH); 1333 vs and 1309 vs δ_s(HNH); 1028 m and 967 m $\rho(SCH_3)$; 788 m, br $\rho(NH_3)$. Solubility of the compound in the most common deuterated solvents is insufficient to measure NMR spectra even at high acquisition time. In dimethylformamide-d_7, where the complex exhibits a rather moderate solubility, signals due to the methyl groups overlap with solvent peaks and cannot be reliably attributed. Crystals suitable for X-ray analysis were grown on slow evaporation of DMF solution at room temperature.

***mer*-$[RuCl_3(N_2H_5)(Me_2SO)_2]$ 4.** *cis*-$[RuCl_2(Me_2SO)_4]$ *cis*-**3** (0.20 g, 0.41 mmol) and $N_2H_4{\cdot}2HCl$ (0.45 g, 4.29 mmol) in water (2 ml) were heated at 90–95 °C for 30 min, cooled to room temperature and left to stand for 1 h. A crystalline precipitate was filtered off, washed on a filter with water (1–2 ml), ethanol (5 ml) and chloroform (5 ml) and dried in air at 20–25 °C. Yield of *mer*-$[RuCl_3(N_2H_5)(Me_2SO)_2]$ was 0.07 g, 50% based on Ru. Concentration of the filtrate on evaporation of the solvent at room temperature to *ca.* 1 ml led to the precipitation of a further crop (*ca.* 20–30%) of less pure complex. Found: C, 12.3; N, 7.2; Ru, 25.3. $C_4H_{17}N_2Cl_3O_2RuS_2$ requires C, 12.1; N, 7.1; Ru, 25.5%. FAB^+-MS, *m/z*: 397 $[M - H]^+$. This complex decomposes above 215 °C. IR spectrum, cm^{-1}: intense absorption in the range 3200–2900 cm^{-1} due to C–H and N^+–H stretches; 1084 and 1044 vs ν(S=O); the band at 1011 (vs), in accord with the data reported by Gajapathy *et al.*[34] can be attributed to the ν(N–N) stretch in coordinated hydrazinium ligand. ^1H NMR spectrum in D_2O/HCl, δ: 3.13 and 3.18 (Me). Crystals suitable for X-ray analysis were obtained directly from the reaction mixture.

Heating of *cis*-$[RuCl_2(Me_2SO)_4]$ *cis*-**3** (0.20 g, 0.41 mmol) and $N_2H_4{\cdot}2HCl$ (0.45 g, 4.29 mmol) in water (2 ml) at 90–95 °C for 5 h (the reaction time for the osmium complex) resulted in the formation of $[RuCl_2(NH_3)_4]Cl$ (35% yield) among other unidentified sulfur- and carbon-free products. Found: H, 5.0; N, 19.8; Ru, 36.4. $H_{12}N_4Cl_3Ru$ requires H, 4.4; N, 20.3; Ru, 36.7%. FAB^+-MS, *m/z*: 240 $[M]^+$. IR spectrum, cm^{-1}: 3295 m-s, 3237 m-s and 3171 m-s ν(N–H); 1611 m, br δ_{as}(HNH); 1285 vs δ_s(HNH); 798 m, br $\rho(NH_3)$.

Electrochemical studies

The electrochemical experiments were performed on an EG & G PARC 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG & G PAR 173 potentiostat/galvanostat and an EG & G PARC 175 Universal programmer. Cyclic voltammetry (CV), chronoamperometry (CA) and steady-state voltammetry (SSV) were undertaken in a two-compartment three-electrode cell, at platinum-disc working electrodes with a diameter of 0.5 mm (CV and CA) or 0.25 µm (SSV), probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolyses (CPE) were carried out in a two-compartment three-electrode cell with platinum gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The electrochemical experiments were performed in a N_2 or argon atmosphere at room temperature. The potentials were measured in 0.2 mol dm^{-3} KCl (or KNO_3)/H_2O or Me_2SO (Ru complexes) or in

Table 1 Crystal data and structure refinement of compounds *mer*-$[OsCl_3(NH_3)_2(SMe_2)]$ **2** and *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ **4**

	2	**4**
Formula	$C_2H_{12}N_2Cl_3OsS$	$C_4H_{17}N_2Cl_3O_2RuS_2$
M	392.75	396.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	9.5765(10)	26.202(4)
b/Å	8.9186(8)	8.455(1)
c/Å	11.8001(9)	12.918(2)
Volume/Å^3	994.2(2)	2743.3(7)
Z	4	8
μ/mm^{-1}	13.774	2.012
Reflections collected	3205	4407
Independent reflections	2896	3985
Reflections [$I > 2\sigma(I)$]	2594	3781
R(int)	0.0443	0.0349
R1	0.0291	0.0247
wR2	0.0771	0.0703

Table 2 Bond lengths (Å) and angles (°) for *mer*-$[OsCl_3(NH_3)_2(SMe_2)]$ **2**

Os–Cl(1)	2.363(1)	Os–N(1)	2.131(4)
Os–Cl(2)	2.358(1)	Os–N(2)	2.099(4)
Os–Cl(3)	2.384(1)	S(1)–C(1)	1.802(7)
Os–S(1)	2.345(1)	S(1)–C(2)	1.791(6)
Cl(1)–Os–Cl(2)	174.26(5)	Cl(3)–Os–N(2)	174.1(2)
Cl(1)–Os–Cl(3)	91.66(5)	Cl(3)–Os–N(1)	88.1(1)
Cl(1)–Os–S(1)	86.63(5)	Cl(3)–Os–S(1)	89.65(5)
Cl(1)–Os–N(1)	90.5(1)	S(1)–Os–N(1)	176.3(1)
Cl(1)–Os–N(2)	88.5(2)	S(1)–Os–N(2)	96.3(2)
Cl(2)–Os–Cl(3)	94.08(5)	N(1)–Os–N(2)	86.0(2)
Cl(2)–Os–S(1)	93.54(4)	Os–S(1)–C(1)	110.8(3)
Cl(2)–Os–N(1)	89.5(1)	Os–S(1)–C(2)	110.5(2)
Cl(2)–Os–N(2)	85.8(1)	C(1)–S(1)–C(2)	99.7(4)

Table 3 Bond lengths (Å) and angles (°) for *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ **4**

Ru–Cl(1)	2.4377(5)	S(1)–C(1)	1.776(2)
Ru–Cl(2)	2.4139(6)	S(1)–C(2)	1.771(2)
Ru–Cl(3)	2.3970(6)	S(2)–O(2)	1.494(2)
Ru–S(1)	2.2420(5)	S(2)–C(3)	1.781(2)
Ru–S(2)	2.2187(5)	S(2)–C(4)	1.782(2)
Ru–N(1)	2.157(2)	N(1)–N(2)	1.443(2)
S(1)–O(1)	1.483(2)		
Cl(1)–Ru–Cl(2)	89.71(2)	S(2)–Ru–N(1)	92.02(5)
Cl(1)–Ru–Cl(3)	88.57(2)	Ru–S(1)–O(1)	119.27(7)
Cl(2)–Ru–Cl(3)	174.13(2)	Ru–S(1)–C(1)	112.02(8)
Cl(1)–Ru–S(1)	89.68(2)	Ru–S(1)–C(2)	112.33(9)
Cl(1)–Ru–S(2)	175.60(2)	Ru–S(2)–O(2)	115.02(7)
Cl(2)–Ru–S(1)	92.31(2)	Ru–S(2)–C(3)	115.12(8)
Cl(2)–Ru–S(2)	91.03(2)	Ru–S(2)–C(4)	114.94(8)
Cl(3)–Ru–S(1)	93.29(2)	Ru–N(1)–N(2)	119.4(1)
Cl(3)–Ru–S(2)	90.27(2)	O(1)–S(1)–C(1)	106.4(1)
Cl(1)–Ru–N(1)	83.71(5)	O(1)–S(1)–C(2)	106.0(1)
Cl(2)–Ru–N(1)	86.31(5)	C(1)–S(1)–C(2)	98.8(2)
Cl(3)–Ru–N(1)	87.93(5)	O(2)–S(2)–C(3)	104.7(1)
S(1)–Ru–S(2)	94.62(2)	O(2)–S(2)–C(4)	105.0(1)
S(1)–Ru–N(1)	173.25(5)	C(3)–S(2)–C(4)	100.5(1)

0.2 mol dm^{-3} $[NBu_4][BF_4]$/Me_2SO, DMF or CH_2Cl_2 (Os complexes) and are quoted relative to the saturated calomel electrode (SCE) by using as internal reference methylviologen ($E° = -0.68$ V *vs.* SCE) for the aqueous medium, or $[Fe(\eta^5\text{-}C_5H_4COCl)(\eta^5\text{-}C_5H_5)]$ ($E° = 0.67$ or 0.53 V *vs.* SCE, in Me_2SO or CH_2Cl_2, respectively). The acid–base potentiometric titrations were carried out by using an aqueous solution of KOH. The results presented were corrected for background effects by performing also the titration of a blank aqueous solution of the electrolyte (0.2 mol dm^{-3} KCl) which had been electrolysed under identical conditions to those used for the corresponding complex solution.

The gaseous atmosphere of the electrochemically oxidised solution of the ruthenium complex and the solution itself were analysed by EI and FAB mass spectrometric measurements, respectively, performed on a Trio 2000 spectrometer. For the EI experiment, the sample was injected *via* an empty glass capillary column (temperatures of the injector, oven, interface and source were, respectively: 120, 50, 120 and 200 °C). Positive-ion FAB mass spectra were obtained by bombarding 3-nitrobenzyl alcohol matrices of the liquid electrolysed solution with 8 keV Xe atoms.

X-Ray crystallography of *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ 1, *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ 2 and *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ 4

Diffraction measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer, equipped with graphite monochromator and Mo-Kα radiation ($\lambda = 0.71069$ Å). All the three structures were solved by conventional Patterson[35] and Fourier techniques[36] and refined by full-matrix anisotropic least-squares on F^2. In the final cycles the contribution of hydrogen atoms was held fixed at calculated positions. The structure of **1** presents the Me_2SO ligands disordered as already reported.[37] However, the set of diffraction data collected by us (39% larger) allowed a higher resolution and consequently a better refinement, avoiding the unreliable S–O bond distance of 1.77(1) Å previously found for the minor component (18%).[37] Crystal data and refinement parameters of the new structures **2** and **4** are reported in Table 1. Bond lengths and angles are given in Tables 2 and 3.

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See http://www.rsc.org/suppdata/dt/a9/a908170d/ for crystallographic files in .cif format.

Results and discussion

Deoxygenation of Me_2SO in the osmium complex

The starting material for the deoxygenation study, *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ **1**, was prepared by reacting $K_2[OsCl_6]$ with dimethyl sulfoxide in the presence of $SnCl_2{\cdot}2H_2O$. On treatment of the dimethyl sulfoxide osmium(II) complex **1** with excess $N_2H_4{\cdot}2HCl$ in an aqueous solution at 90–95 °C for 5 h the osmium(III) complex *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2** was formed and isolated as a solid in *ca.* 40% yield. IR monitoring of the residue (after isolation of **2** and evaporation of the solvent to dryness) shows no characteristic bands due to ν(N–N) stretch in the coordinated hydrazinium ligand.[34] The dimethyl sulfide complex **2** was characterised by elemental analyses, FAB-MS, IR and ^1H NMR spectroscopies (see Experimental section) and also by X-ray single-crystal diffraction analysis (see below).

Deoxygenations of osmium(II) sulfoxide complexes are known although scarce. Thus, it has been reported[28] that heating of the isomeric osmium(II) compounds $[OsCl_2(Me_2SO\text{-}S)_4]$ and $[OsCl_2(Me_2SO\text{-}O)(Me_2SO\text{-}S)_3]$ at 150 °C *in vacuo* causes the disproportionation of dimethyl sulfoxide to dimethyl sulfone and the osmium(III) thioether complexes $[Os_2Cl_4(\mu\text{-}SMe)_2(Me_2S)_2]$ and $[Os_2Cl_4(Me_2SO\text{-}O)(\mu\text{-}SMe)_2(Me_2S)]$, respectively. Chakravorty and colleagues[16,17] have deoxygenated both dimethyl and dibenzyl sulfoxides on treatment with $[OsBr_6]^{2-}$ in refluxing 2-methoxyethanol to give the osmium(III) complexes $[OsBr_3(R_2S)_3]$ (R = Me, CH_2Ph) that contain coordinated thioethers. Eventually, one of us performed deoxygenation of *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ with HCl to yield $[OsCl_4(Me_2S)_2]$.[23]

Currently, there is only one reported example indicating that hydrazine hydrochloride can be employed for reduction of both sulfoxide species and also the platinum(IV) centre in $[PtCl_4(Me_2SO)_2]$ to give $[PtCl_2(Me_2S)_2]$;[19] no ammonia containing products were detected in this reaction. Although disproportionation of free hydrazine to NH_3 and N_2 is well-known,[38] and

Table 4 M–S–C and C–S–C bond angles (°) in Ru and Os thioether complexes

Complex	M–S–C	C–S–C	Ref.
$[RuBr_3(NO)(\textit{n}\text{-}Pr_2S)_2]$	109.3(3), 109.8(3), 112.3(3), 106.9(3)	99.4(4), 100.8(5)	77
$[RuBr_3(NO)(Et_2S)_2(Et_2SO)]$	102.3(7)	99.3(9)	77
$[Ru(OEP)(MeSDe)_2]^a$	107.5(1), 111.2(1), 109.0(1), 108.1(1)	98.4(2), 101.0(2)	47
$[Ru(OEP)(Ph_2S)_2]$	115.4(2), 110.9(2)	103.3(2)	47
$[Ru(NH_3)_5(MeSEt)]^{3+}$	112.17(8), 107.86(8)	100.7(1)	48(*a*)
$[Ru(NH_3)_5(MeSEt)]^{2+}$	113.4(2), 112.5(2)	99.5(3)	48(*b*)
$[Ru(NH_3)_5(Me_2S)]^{3+}$	113.8(3)^b	99.5(3)	48(*a*)
$[OsCl_3(NH_3)_2(Me_2S)]$	110.5(2), 110.8(3)	99.7(4)	This work
$[Ru(Cp)(chir)(MeSPh)]^{+c}$	110.2(4), 115.3(5)	99.2(5)	78
$[Ru(Cp)(chir)(\textit{i}\text{-}PrSMe)]^{+c}$	121.2(4), 106.1(3)	101.3(4)	78
	110.8(9)^d	100.2(4)^d	

^{a} De = *n*-decyl. ^{b} Possibly overestimated because of twinning. ^{c} chir = 2(*S*),3(*S*)-bis(diphenylphosphino)butane. ^{d} Unweighted average values with standard deviations in parentheses.

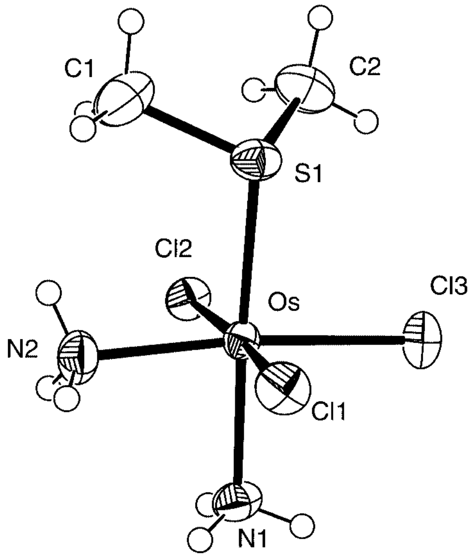


Fig. 1 Perspective view of compound *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2**.

documented even for osmium-mediated processes[39] (coordinated hydrazine is proved to be resistant towards reduction[40]), formation of *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2** from *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ **1** in concerted deoxygenation/oxidation/substitution processes is the first observation of this kind. We believe that deoxygenation proceeds *via* formation of electrophilically activated dimethyl sulfoxide[3,13] (Scheme 1) and its reduction by hydrazine and/or by the osmium(II) centre. Taking into account that it is the high *trans*-effect of S-bound sulfoxides that labilises coordinated Me_2SO,[41] it is perhaps reasonable to assume that the reaction might proceed dissociatively to give free Me_2SO species before deoxygenation. However, a possibility of intramolecular reaction (Scheme 1) should not be ruled out.

Molecular and crystal structures of *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ 1 and *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ 2

The structures of the osmium complexes appear of interest because of the paucity of available crystallographic data of both sulfoxide and sulfide derivatives which can provide some insight into the nature of the Os–S bonds and hence into the metal redox properties.

To the best of our knowledge, the only known crystal structures of S-bonded sulfoxide osmium complexes concern $[(\eta^6\text{-}p\text{-}cym)OsCl_2(Me_2SO\text{-}S)]$ (*p*-cym = *p*-cymene),[42] *trans,cis*, *cis*-$[Os(CN)_2(Me_2SO\text{-}S)_2L]$ (L = diphenylphenanthroline),[43] *trans*-$[OsBr_2(Me_2SO\text{-}S)_4]$,[44] and *cis*- and *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$.[37] The structure of the last complex, **1**, isostructural with the Br derivative,[44] and its ruthenium analogue,[45] have been already reported,[37] but because of static disorder, some bond lengths and angles around the sulfur atoms were affected by large errors. More accurate and reliable data have been obtained now by us. The results are reported in the deposited .cif file. The average Os–S and S–O bond distances are 2.340 and 1.486 Å, respectively, close to the mean values of 2.34(1) and 1.48(1) Å found in the above Os(II)–Me_2SO-*S* complexes.[6]

The molecular structure of *mer,cis*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2** is shown in Fig. 1. Interestingly, the Os^{III}–S distance of 2.345(1) Å is shorter than those found in other Os^{III} thioether complexes, like *trans*-$[Os(OEP)(PMS)_2][PF_6]$ (PMS = pentamethylene sulfide), 2.382(2) Å,[46] and *mer*-$[OsBr_3\{S(CH_2Ph)_2\}_3]$, 2.387(5) Å (*trans* to Br) and 2.398(3) Å (*trans* to S).[16] It is comparable, within experimental error, to the Os^{II}–S distance of 2.352(2) Å in *trans*-$[Os(OEP)(PMS)_2]$.[46] The trend of the Os–S distances confirms the π accepting ability of the thioether ligands.[46–48] However, thioethers display a lower π accepting ability with respect to sulfoxides, as evidenced by the comparison of the Ru–S distances in complexes containing both ligands, *e.g.* Ru–S(sulfide), 2.359(4) Å and Ru–S(sulfoxide), 2.298(4) Å, in *trans*-$[RuCl_2L_2]$ (L = 1,5-dithiacyclooctane 1-oxide);[49] Ru–S(sulfide), 2.38(1) Å and Ru–S(sulfoxide), 2.26(3) Å, in *cis*-$[RuBr_2(Me_2SO\text{-}S)\{EtS(CH_2)_3S(O)\}_2]$.[50] This is consistent with the higher oxidation potential of **1** with respect to **2** (see Table 5).

As already observed, the coordinated thioether sulfur atom displays a pyramidal geometry with an average C–S–C angle of 100.2(4)° (Table 4). The orientation of the SC_2 group in $(NH_3)_5Ru$–sulfide complexes has been discussed in terms of bonding requirements of the thioether ligand and its steric repulsions with the *cis* amines which provoke a tilting of the SC_2 plane with respect to the RuN_3 plane.[48] This was evaluated by measuring the Ru–S–X angle, X being the midpoint between the two C atoms, which was found to be 130.1°, 132.0° in Ru^{II} complexes and 122.1°, 125.5° in Ru^{III} complexes.[48] In the present Os^{III} complex **2**, the Os–S–X angle is 123.1°, while the Os–S–C angles are 110.5(2)° and 110.8(3)°. These data suggest a tetrahedral hybridization of the sulfur atom, for which a M–S–X angle of 125.3° is expected. In **2**, the orientation of the Me_2S group with respect to the equatorial ligands is determined by van der Waals interactions between the CH_3 and NH_3 groups which lower the molecular potential energy, in spite of a slight repulsion between the two groups, as shown by the widening of the S(1)–Os–N(2) and S(1)–Os–Cl(2) angles with respect to S(1)–Os–Cl(1) and S(1)–Os–Cl(3). In fact, density functional calculations have shown that also in Ru–Me_2SO complexes steric interactions are prevalent over electronic factors.[24]

Substitution of Me_2SO in the ruthenium complex and crystal structure of *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ 4

In contrast to the reaction of *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ **1**, interaction of *cis*-$[RuCl_2(Me_2SO\text{-}O)(Me_2SO\text{-}S)_3]$ *cis*-**3** with excess hydrazine dihydrochloride under the same reaction conditions

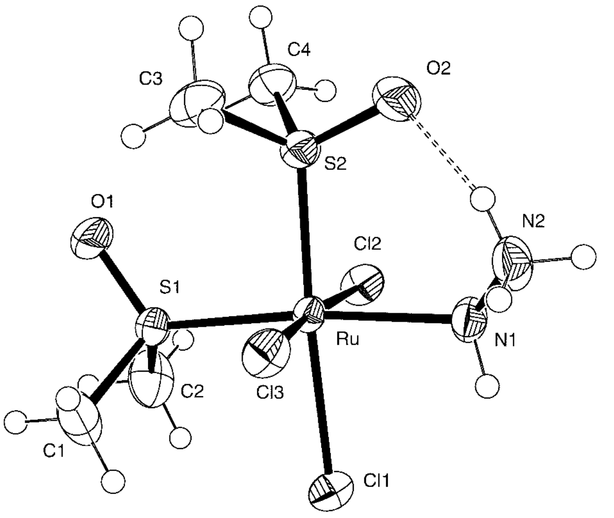


Fig. 2 Perspective view of compound *mer*-[$RuCl_3(N_2H_5)(Me_2SO$-*S*$)_2$] **4**, the dotted line indicating the intramolecular H-bond.

(but shorter reaction time) brings about fast substitution. The reaction is completed after 30 min and subsequent work up led to isolation of the hydrazinium Ru^{II} complex *mer*-[$RuCl_3(N_2H_5)(Me_2SO$-*S*$)_2$] **4** as a solid in good yield. Heating the Ru reaction mixture for 5 h gave the amine complex [$RuCl_2(NH_3)_4$]Cl along with other unidentified products in which we were unable to detect (by IR and NMR methods) either dimethyl sulfoxide or dimethyl sulfide products.

Complex **4** represents a rare example of a η^1 metal hydrazinium complex. In general, the chemistry of transition metal compounds containing hydrazine derivatives and other partially reduced dinitrogen ligands is of particular importance due to the fact that such species are relevant to intermediates in the nitrogen fixation process and that such complexes also display diverse and intriguing reactivity modes.[51] The structure of the hydrazinium complex **4** was determined by X-ray diffractometry.

As shown in Fig. 2, its molecular structure is characterised by the unusual η^1 metal coordination of the hydrazinium ion, *trans* to one Me_2SO-*S* ligand. This arrangement corresponds to the expected minimum molecular energy structure, in view of the presence of Cl and N donor ligands *trans* to the π accepting sulfoxide groups.[6] The structure of this stereoisomer is further stabilised by a strong two-centre hydrogen bond between the terminal NH_3^+ group and the oxygen atom of the *cis* Me_2SO-*S* ligand [N · · · O, 2.665(2) Å]. In fact, the Ru–S(1) bond distance of 2.2420(5) Å is within the range of Ru^{II}–S bond lengths (2.237(1)–2.2576(7) Å) found in *cis,cis,cis*-[$RuCl_2L_2(Me_2SO$-*S*$)_2$] complexes, with L = N-aromatic base, where a stabilising π bond contribution is present.[52] The Ru–S(2) distance of 2.2187(5) Å is significantly shorter, suggesting an enhanced π back-donation from Ru^{II} to the S(2)-sulfoxide empty orbitals. This could be due to the intramolecular N–H · · · O H-bonding which, reducing the bond order over the S(2)–O(2) bond, increases the positive charge on the sulfur atom enhancing the sulfoxide π accepting properties. However, a similar lengthening, due to H-bonding, has been observed in other Ru^{II}–Me_2SO-*S* complexes,[53] as well as in uncoordinated sulfoxides.[6] Besides the N · · · O H-bond, all the other hydrogen atoms of the hydrazinium ion are involved in intermolecular H-bonds with the chloride ligands, with N · · · Cl distances ranging from 3.165 to 3.274 Å.

The N–N bond distance of 1.443(2) Å is comparable, within experimental error, to the value of 1.427(6) Å found in [Pd-(polyether)$(N_2H_5)]^{2+}$, which represents the only other known crystal structure of a η^1 hydrazinium metal complex.[54] It is also close to the values found in the uncoordinated $N_2H_5^+$ cation, *e.g.* 1.443(1),[55] 1.444(2),[56] and 1.450(3) Å,[57] and within the range of values observed for metal η^1- and μ-coordinated hydrazine complexes, 1.439(10)–1.454(2) Å,[58–60] and 1.43(1)–1.48(1) Å,[61–64] respectively.

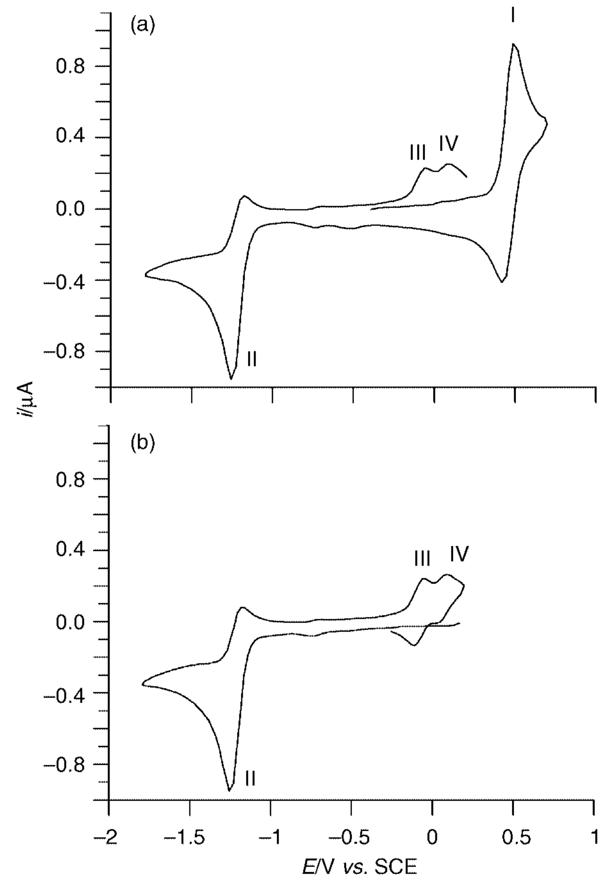


Fig. 3 Cyclic voltammograms of *mer*-[$OsCl_3(NH_3)_2(Me_2S)$] **2** (2.6 mmol dm^{-3} in Me_2SO with 0.2 mol dm^{-3} [NBu_4][BF_4]) at a platinum disc (*d* = 0.5 mm) working electrode: (a) anodic scan; (b) cathodic scan. Scan rate: 0.2 V s^{-1}.

Electrochemical study

Osmium complexes. The cyclic voltammograms of *trans*-[$OsCl_2(Me_2SO$-*S*$)_4$] **1** and *mer*-[$OsCl_3(NH_3)_2(Me_2S)$] **2** (Fig. 3), in aprotic media, exhibit a single-electron (confirmed by CPE) reversible anodic wave (I) at $E_{1/2}^{ox}$ = 1.18 or 0.48 V *vs.* SCE, respectively (Table 5). The lower oxidation potential of the latter complex agrees with the stronger net electron-donor character of its chloride, ammonia and dimethyl sulfide ligands compared with dimethyl sulfoxide in the former compound (see below).

Complex **2** also undergoes, by CV, a single-electron (confirmed by CPE) partially reversible cathodic wave (II, Fig. 3b) at $E_{1/2}^{red} = -1.20$ V. Upon scan reversal, following this wave, two anodic waves (III and IV), with a partial reversible character, are detected at $E_{1/2}^{ox} = -0.07$ and 0.06 V in Me_2SO (but not observed in DMF) due to the oxidation of products formed in the cathodic process in Me_2SO. CPE at the cathodic wave (II) of the starting Os^{III} complex in Me_2SO also generates the same species as shown by monitoring the electrolysis by CV (Fig. 4). Wave IV is due to an intermediate species conceivably the pentacoordinate [$OsCl_2(NH_3)_2(Me_2S)$],[65–67] generated in the cathodic process, that converts into the final product oxidised at wave III (the latter wave is the only one detected upon standing the fully electrolysed solution, Fig. 4d). Attempts to isolate, in a pure form, this final product have failed, but we propose its formulation as [$OsCl_2(NH_3)_2(Me_2S)(Me_2SO$-*S*$)$] (formed by cathodically induced chloride loss with formation of the above intermediate, a type of reaction well documented,[68,69] followed by addition of the Me_2SO molecule: overall Scheme 2), on the

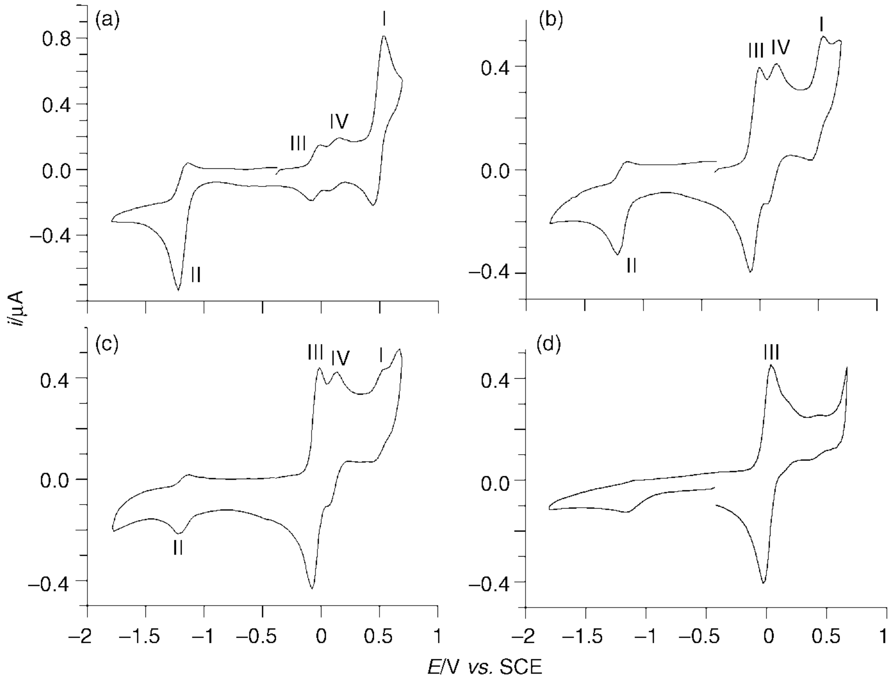
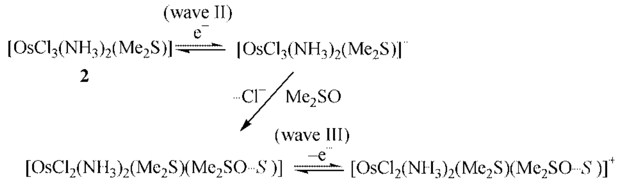


Fig. 4 Cyclic voltammograms run along the cathodic controlled potential electrolysis (at −1.3 V) of a solution of *mer*-$[OsCl_3(NH_3)_2(Me_2S)]$ **2** (2.6 mmol dm^{-3} in Me_2SO with 0.2 mol dm^{-3} $[NBu_4][BF_4]$) at a platinum disc (d = 0.5 mm) working electrode, after the consumption of (a) *ca.* 0.2, (b) *ca.* 0.7 and (c) *ca.* 0.9 F mol^{-1}, and (d) upon standing the solution for 4 hours after completion of the electrolysis. Scan rate: 0.2 V s^{-1}.

Table 5 Cyclic voltammetric data[a] for Os and Ru complexes

Complex	$^{I}E_{\frac{1}{2}}^{ox}$ ($^{I}E_{p/2}^{ox}$)	$E_{\frac{1}{2}}^{red}$ ($E_{p/2}^{red}$)
trans-$[OsCl_2(Me_2SO\text{-}S)_4]$ **1**[b]	1.18	
mer-$[OsCl_3(NH_3)_2(Me_2S)]$ **2**[c]	0.48[d]	−1.20[e]
trans-$[RuCl_2(Me_2SO\text{-}S)_4]$ *trans*-**3**[c,f]	(1.47)[g]	(−1.93)
mer-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ **4**[h]	(0.79)[i]	

[a] Potentials ($E_{\frac{1}{2}}$ for reversible processes, or, in parentheses $E_{p/2}$ for irreversible ones) in V ± 0.02 *vs.* SCE, measured at a Pt disc (d = 0.5 mm) electrode. [b] In 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$. [c] In 0.2 mol dm^{-3} $[NBu_4][BF_4]/Me_2SO$. [d] Upon scan reversal following this anodic wave, cathodic waves are observed at $E_p^{red} = -0.54$ and −0.73 V. [e] Upon scan reversal following this cathodic wave, an anodic wave is observed at $E_{\frac{1}{2}}^{ox} = -0.07$ V which is followed by a less intense one at $E_{\frac{1}{2}}^{ox} = 0.06$ V, assigned (see text) to $[OsCl_2(NH_3)_2(Me_2S)(Me_2SO\text{-}S)]$ and, tentatively, to $[OsCl_2(NH_3)_2(Me_2S)]$, respectively. [f] Generated *in situ* from *cis*-**3** which, in 0.2 mol dm^{-3} KNO_3/H_2O, forms $[RuCl(H_2O)_2(Me_2SO\text{-}S)_3]^+$ ($E_{p/2}^{ox} = 1.28$ V). [g] Upon scan reversal following this anodic wave, a cathodic wave is observed at $E_{p/2}^{red} = -0.39$ V. [h] In 0.2 mol dm^{-3} KCl/H_2O. [i] This wave is progressively replaced, with time, by a second one (which initially has a very weak current intensity) at $^{II}E_{1/2}^{ox} = 0.90$ V, assigned to $[RuCl_2(N_2H_4)(Me_2SO\text{-}S)_2(H_2O)]$, due to the conversion of the starting complex into the latter (see text); in 0.2 mol dm^{-3} KNO_3/H_2O, the conversion is faster and in addition the formation of a third wave at $^{III}E_p^{ox} = 1.16$ V, involving the oxidation of liberated chloride ligand, is detected.



Scheme 2

basis of the agreement (within the experimental error, ±0.02 V) between the measured (−0.07 V *vs.* SCE) value of its oxidation potential and the predicted one (0.15 V *vs.* NHE = −0.09 V *vs.* SCE) by applying Lever's[31] empirical expression (1) which

$$E = S_M\,(\Sigma E_L) + I_M \qquad (1)$$

relates the redox potential of a complex (E, expressed in V *vs.* NHE) with the sum of the electrochemical E_L ligand parameter for all the ligands, and with the S_M and I_M metal centre parameters which depend upon the metal and redox couple, the spin state and stereochemistry.

For this purpose, we had to start with the estimate of E_L for S-coordinated Me_2SO, since for this ligand no reliable value was known.[31] Hence, application of eqn. (1) to *trans*-$[OsCl_2(Me_2SO\text{-}S)_4]$ **1**, considering our measured value of its oxidation potential (1.43 V *vs.* NHE) and the known[31] values of E_L (−0.24 V for the chloride ligand) and of S_M (1.01) and I_M (−0.40 V *vs.* NHE) for the Os$^{II/III}$ redox couple, led to $E_L = 0.57$ V. This value is identical to those (0.55–0.58 V) we have estimated in a similar way for $[RuCl_2(EtSCH_2CH_2SEt)(Me_2SO\text{-}S)_2]$,[70a] $[RuX_2(SMe_2)_3(Me_2SO\text{-}S)]$ (X = Cl or Br)[70a] and $[Ru(NH_3)_5(Me_2SO\text{-}S)]^{2+}$,[70b] which present clearly defined reversible anodic waves. Although this value is not unambiguously established,[31] it is clearly high showing that Me_2SO-S behaves as a significant net electron π-acceptor/σ-donor ligand in agreement with its expected (on the basis of X-ray data[6,24]) significant π-electron acceptor ability. It is comparable to benzyl isocyanide ($E_L = 0.56$ V),[31] being a weaker net electron donor than *e.g.* Me_2S ($E_L = 0.31$).[31]

$[RuCl_2(Me_2SO)_4]$. The cyclic voltammogram of a Me_2SO or an aqueous solution of *cis*-$[RuCl_2(Me_2SO\text{-}O)(Me_2SO\text{-}S)_3]$ *cis*-**3** exhibits a single-electron irreversible anodic wave at $E_{p/2}^{ox}$ = 1.47 or 1.28 V *vs.* SCE, respectively. These values are remarkably higher (by *ca.* 0.9 V) than those expected for this complex in these media (0.62 or 0.39 V, correspondingly) on the basis of eqn. (1) and the known[31] values of S_M (0.97 or 1.14, in organic or aqueous medium, respectively) and I_M (0.04 V or −0.35 V *vs.* NHE, in such media) for the Ru$^{II/III}$ redox couple, and of E_L for the various ligands. Incidentally, the use of eqn. (1) required the previous estimate of E_L for O-coordinated Me_2SO by applying this expression to $[Ru(NH_3)_5(Me_2SO\text{-}O)]^{2+}$ ($E^{ox} = 0.02$ V *vs.* NHE,[71] $E_L(NH_3) = 0.07$ V[31]). Although one should be cautious about this estimated value ($E_L = -0.37$ V) since it is based on the oxidation potential of a single complex, it is drastically lower (by 0.94 V) than that of Me_2SO-S (see above), being intermediate between those of Cl$^-$ (−0.24 V)[31] and F$^-$ (−0.42 V),[31] showing that O-coordination results in a remarkable enhancement of the net electron-donor ability of Me_2SO which then should not behave as an appreciable π-electron acceptor, in contrast to the S-bonded ligand.

However, the measured oxidation potentials of the anodic waves of the above solutions of *cis*-**3** are in close agreement with those estimated using eqn. (1), for the known[45] products of its spontaneous conversion in those media, *i.e.* *trans*-$[RuCl_2(Me_2SO\text{-}S)_4]$ *trans*-**3** in Me_2SO and $[RuCl(H_2O)_2(Me_2SO\text{-}S)_3]^+$ in H_2O (1.48 and 1.2 V *vs.* SCE, respectively). *trans*-**3** is oxidised at a more anodic potential (by *ca.* 0.3 V) than the analogous Os^{II} compound **1** (see above), thus accounting for the stronger resistance to oxidation of the Ru^{II} centre, in comparison with the Os^{II} site, in the above reactions with $N_2H_4 \cdot 2HCl$.

$[RuCl_3(N_2H_5)(Me_2SO)_2]$. The cyclic voltammogram of an aqueous solution of *mer*-$[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]$ **4** also indicates its lability in solution, presenting one irreversible anodic wave (wave I) at ${}^{I}E_{p/2}^{ox} = 0.79$ V *vs.* SCE that, with time, is progressively replaced by another one (wave II), at a slightly higher potential (${}^{II}E_{p/2}^{ox} = 0.90$ V), with the occurrence of an isopotential point (at 0.87 V). Hence, in solution, the starting complex **4** (oxidised at wave I) converts into another species **5** (oxidised at wave II). This conversion conceivably involves dehydrochlorination (eqn. (2)) *via* $[RuCl_3(N_2H_4)(Me_2SO\text{-}S)_2]^-$

$$\underset{\mathbf{4}}{[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]} + 2H_2O \rightleftharpoons \underset{\mathbf{5}}{[RuCl_2(N_2H_4)(Me_2SO\text{-}S)_2(H_2O)]} + H_3O^+ + Cl^- \quad (2)$$

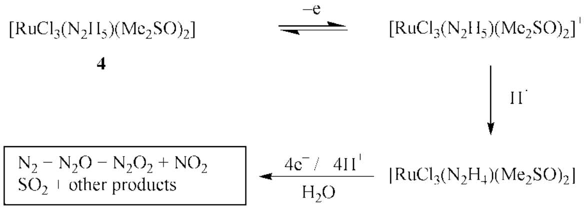
to give $[RuCl_2(N_2H_4)(Me_2SO\text{-}S)_2(H_2O)]$ **5**, on the basis of the following evidence: (i) acidic character, pH = 4.2, of a solution of **4** and titration (by a KOH solution) of $1H^+$/molecule; (ii) promotion of the conversion of **4** into **5** by addition of that base and on replacement of the KCl electrolyte by another one without Cl^-, such as KNO_3, when a third anodic wave (III) then forms at ${}^{III}E_p^{ox} = 1.2$ V, a value identical to that measured for the oxidation of Cl^- under a solution of $[NEt_4]Cl$ under the same experimental conditions (0.2 mol dm^{-3} KNO_3/H_2O).

The anodic waves correspond to single-electron processes at relatively short time scales, as measured by chronoamperometry and steady-state voltammetry at an ultramicroelectrode[72] (using methylviologen as the reference compound), but over the longer time scale of CPE (see below) a multi-electron process is involved. The oxidation potentials of our Ru^{II} complexes are comparable to (or even higher than) those reported, *ca.* 0.8 V, for $[Ru(NH_3)_5(Me_2SO\text{-}S)]^{2+}$ and related complexes,[70b,71,73] in which Me_2SO-*S* is behaving also as a significant π-electron acceptor. O-coordination would result in a dramatic cathodic shift (by *ca.* 0.6–1.0 V)[70b,71,73] of the redox potential that would also occur if an S-bonded Me_2SO did not act as a π-electron acceptor as observed[73] for *mer*-$[RuCl_3(Me_2SO\text{-}S)(tmen)]$ (tmen = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) with $E_{1/2}$ ($Ru^{III/II}$) = −0.14 V *vs.* SCE.

The coordination electronic properties of the hydrazinium ligand can also be investigated in complex **4** by attempting to estimate its as yet unknown E_L value through the application of eqn. (1), considering our measured ${}^{I}E_{p/2}^{ox} = 1.04$ V *vs.* NHE and our estimated E_L (Me_2SO-*S*) = 0.57 V. The obtained value, E_L ($N_2H_5^+$) = 0.80 V, is one of the highest so far reported, suggesting that hydrazinium behaves as a rather weak overall electron-donor ligand, being comparable to *N*-methylpyrazinium (E_L = 0.79 V)[31] and weaker than *e.g.* pyrimidinium (E_L = 0.43 V)[31] or ammonia (0.07 V),[31] but not so weak as the strong π-electron acceptors CO (0.99 V)[31] or carbynes (*ca.* 1.2 V).[74] However, the estimated E_L value for $N_2H_5^+$ should be taken cautiously since it is based on the oxidation potential of a single complex which, moreover, presents a ligand (Me_2SO) whose E_L value has not yet been fully established.

Exhaustive CPE at 0.90 V of a solution of **4** led to the consumption of *ca.* 5 F mol^{-1}, but the trend of the variation of current *vs.* charge indicates the initial involvement of a single electron process (see above). CV of the electrolysed solution showed the presence of a partially reversible cathodic wave at $E_p^{red} = -0.44$ V, due to H^+ reduction, as corroborated (i) by its high cathodic shift upon replacement of the Pt by a vitreous C working electrode and (ii) by acid–base potentiometric titration, with a KOH solution, of the electrochemically oxidised solution of the complex ($5H^+$/molecule of complex in a titration curve with only one very well defined end-point).

The acidity character of the hydrazinium or hydrazine ligand is enhanced upon oxidation of the complex, and the oxidised forms $[RuCl_3(N_2H_5)(Me_2SO\text{-}S)_2]^+$ or $[RuCl_2(N_2H_4)(Me_2SO\text{-}S)_2(H_2O)]^+$ (see above) generated at waves I or II, respectively, are expected to undergo ready H^+ loss (Scheme 3 for the former case). The promotion of acidity upon further oxidation steps would account for the observed multi-deprotonation in the overall multi-electron anodic process. Related behaviour was reported by us[75] for aminocarbene ligands in some complexes of Pd^{II} or Pt^{II}, whereas the aminocarbyne CNH_2 ligating a Re phosphinic site is anodically converted into the corresponding isocyanide (CNH) and cyano complexes.[76]



Scheme 3

In order to try to identify the products formed during the CPE, this was also performed in a closed system, under argon, and the atmosphere in the electrochemical cell was then analysed by EI-MS that showed the presence of several volatile N- and S-containing species such as N_2, N_2O, N_2O_2, NO_2 and SO_2, therefore indicating an oxidative conversion of the hydrazine and the Me_2SO ligands into N_2 and N-oxides or SO_2, respectively. The oxidation of Me_2SO was only partial, and the analysis of the electrolysed solution, by FAB-MS, detected *e.g.* $\{RuCl_2O(Me_2SO)_2\}^+$ (*m*/*z* 345), $\{Ru_2Cl_6(Me_2SO)\}^+$ (*m*/*z* 498) and $\{Ru_2Cl_6O(Me_2SO)\}^+$ (*m*/*z* 514).

Acknowledgements

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