COMMUNICATION

Dalton
www.rsc.org/dalton

The first examples of four and five O-bonded dmso ligands on a ruthenium centre†

Ennio Zangrando,[a] Barbara Serli,[a] Lesley Yellowlees[b] and Enzo Alessio *[a]
[a] *Dipartimento di Scienze Chimiche, University of Trieste, Trieste, Italy.*
E-mail: alessi@univ.trieste.it; Fax: +39 040 5583903; Tel: +39 040 5583961
[b] *Department of Chemistry, University of Edinburgh, Edinburgh, UK EH9 3JJ.*
E-mail: L.J.Yellowlees@ed.ac.uk; Fax: +44 131 650 4743; Tel: +44 131 650 4759

Received 29th August 2003, Accepted 23rd October 2003
First published as an Advance Article on the web 27th October 2003

The synthesis, solution and solid state characterization, and the electrochemical behaviour of $[RuCl(dmso\text{-}O)_4(NO)][OTf]_2$ (2) and $[Ru(dmso\text{-}O)_5(NO)][OTf]_3$ (3), the first examples of Ru complexes having more than three O-bonded dmso ligands, are described.

Dimethyl sulfoxide (dmso) is an ambidentate ligand as it binds to metal centres either through the sulfur (dmso-S) or through the oxygen atom (dmso-O);[1] dmso-S is also a moderate π-acceptor ligand and thus it binds preferentially *trans* to pure σ donor ligands. The chemistry of ruthenium-dmso complexes has been widely investigated over the last 30 years because Ru-dmso species are versatile precursors in inorganic synthesis[2] and some of them have anticancer activity.[3] The wealth of structural and spectroscopic data collected on Ru-dmso species over the years indicated that dmso prefers S-binding to Ru for electronic reasons, and that the facial geometry of three dmso-S ligands seems to be a particularly stable binding motif on Ru(II). However, dmso-S is sterically more demanding compared to dmso-O, and apparently the *fac*-$Ru(dmso\text{-}S)_3$ fragment allows co-ordination of further dmso ligands only through O for steric reasons.[1] In addition, dmso-O co-ordination to Ru(II) is also favoured by a net positive charge of the complex. Until recently, in fact, the only known Ru complex with three dmso-O ligands was the dication [*fac*-$Ru(dmso\text{-}O)_3(dmso\text{-}S)_3]^{2+}$.[4] We described the second example of a *fac*-$Ru(dmso\text{-}O)_3$ fragment in the mono-cationic nitrosyl complex [*cis,fac*-$RuCl_2(dmso\text{-}O)_3(NO)][OTf]$ (**1**), in which coordination of dmso through oxygen is dictated by electronic reasons exclusively.[5]

We find now that further stepwise replacement of chlorides with dmso in **1** leads first to $[RuCl(dmso\text{-}O)_4(NO)][OTf]_2$ (**2**) and eventually to $[Ru(dmso\text{-}O)_5(NO)][OTf]_3$ (**3**).‡ Compounds **2** and **3** are the first examples of Ru complexes having more than three dmso-O ligands and complete the series of $[Ru(dmso\text{-}O)_xCl_{5-x}(NO)]^{(x-2)}$ complexes (x = 1–5) previously described by us.[5]

Perspective drawings of the cations of **2** and **3** are shown in Figs. 1 and 2, respectively.§ In both complexes the metal ion displays a slightly distorted octahedral coordination geometry with a linear Ru–NO fragment. The Ru–N and N–O bond lengths are comparable in the two complexes and agree with values in Ru–NO complexes reported previously.[5] In **2** the Ru–O(1) and Ru–O(3) bond lengths, *trans* to each other, differ by 10σ, probably because of intramolecular steric interactions. A slight shortening is detected for the Ru–O(2) bond length *trans* to NO compared to Ru–O(4) *trans* to Cl. This difference is attributed to the well documented *trans*-shortening effect exerted by NO when coordinated *trans* to a σ-donor ligand.

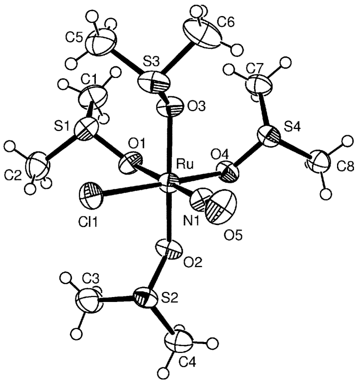

Fig. 1 ORTEP[6] drawing (40% thermal ellipsoids probability) with atom labeling scheme of the molecular cation of **2**. Selected bond lengths (Å) and angles (°): Ru–N(1) 1.733(4), Ru–O(1) 2.029(3), Ru–O(2) 2.025(3), Ru–O(3) 2.056(3), Ru–O(4) 2.050(3), Ru–Cl(1) 2.353(1), N(1)–O(5) 1.149(5), N(1)–Ru–O(1) 177.31(14), O(2)–Ru–O(3) 164.73(12), O(4)–Ru–Cl(1) 172.27(9), O(5)–N(1)–Ru 170.5(4).

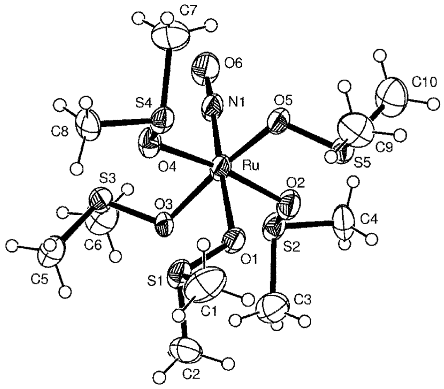

Fig. 2 Molecular cation of **3** (ORTEP[6] drawing, 40% thermal ellipsoids probability). Of the disordered dmso ligands only those at higher occupancy (74%) are shown. Selected bond lengths (Å) and angles (°): Ru–N(1) 1.733(7), Ru–O(1) 2.012(5), Ru–O(2) 2.070(9), Ru–O(3) 2.072(9), Ru–O(4) 2.026(8), Ru–O(5) 1.990(9), N(1)–O(6) 1.158(9), N(1)–Ru–O(1) 177.5(3), O(4)–Ru–O(2) 171.9(5), O(5)–Ru–O(3) 172.5(5), O(6)–N(1)–Ru 177.8(12).

The structural determination of **3** presents a lower accuracy due to the disorder detected for the dmso ligands *cis* to NO (two orientations for each SO group, with occupancy factors of 74 and 26%, with unchanged positions for the methyl carbon atoms). The Ru–O distances involving the disordered ligands vary from 1.986(16) to 2.072(9) Å, while that *trans* to NO compares well with the value found in **2**.

The solution (D_2O) NO stretching frequency, typical for linear nitrosyls, increases slightly but steadily upon going from **1** (1897 cm^{-1}) to **3** (1903 cm^{-1}), as expected for the increase of positive charge. Complexes **2** and **3** are diamagnetic. Four equally intense singlet resonances are found in the dmso-O region of the ^1H NMR (D_2O) spectrum of **2**: the two sharpest

---

† We would like to dedicate this work to the late Prof. Rex Sheperd (Pittsburg University, USA) who was very active in the field of ruthenium-nitrosyls and whose premature and recent death we wish to commemorate.

DOI: 10.1039/b310510e

Table 1 Reduction potentials of $[Ru(dmso\text{-}O)_xCl_{5-x}(NO)]^{(x-2)}$ complexes

Compound	NO^+ based reduction potential
$[$*trans*-$RuCl_4(dmso\text{-}O)(NO)]^-$	−1.25 (irrev)[a]
mer,cis-$RuCl_3(dmso\text{-}O)_2(NO)$	−0.59 (irrev)[a]
$[$*cis,fac*-$RuCl_2(dmso\text{-}O)_3(NO)]^+$	−0.26 (irrev)[a]
$[RuCl(dmso\text{-}O)_4(NO)]^{2+}$	+0.015 (irrev)[b]
$[Ru(dmso\text{-}O)_5(NO)]^{3+}$	+0.14 (irrev)[b]

[a] From ref. 5. [b] This work.

ones ($\delta = 2.97$ and 3.16) belong to the equivalent methyls of the dmso's *trans* to Cl and to NO, while the other two ($\delta = 3.02$ and 3.07) pertain to the diastereotopic methyls of the two equivalent dmso's *trans* to one another and are slightly broadened by the long range coupling (they are connected in the H–H COSY spectrum). Comparison with the spectrum of **3** (see below) suggests that the most downfield singlet belongs to the dmso-O *trans* to NO. The ^1H NMR spectrum of **3** consists of two singlets in 4 : 1 intensity ratio corresponding to the four equivalent dmso-O's in the plane ($\delta = 3.09$) and to the dmso-O *trans* to NO ($\delta = 3.23$), respectively.

At 295 K the cyclic voltammogram of $[RuCl(dmso\text{-}O)_4(NO)][OTf]_2$ (**2**) shows an irreversible one-electron reduction at +0.015 V.¶ As for the other complexes of the series,[5] this process is assigned to reduction of the bound NO^+ to $NO^\bullet$ rapidly followed by its dissociation from the Ru complex. The cyclic voltammogram of **2** also shows an irreversible oxidation wave +0.58 V. This process is only observed if the potential scan is extended to −0.3 V, thus it is due to a daughter product formed following reduction of compound **2**. The cyclic voltammogram of $[Ru(dmso\text{-}O)_5(NO)][OTf]_3$ (**3**) at 295 K shows a quasi-reversible one-electron reduction with a forward peak potential at +0.14 V and an associated return wave at +0.22 V; the one-electron reduction does not become more reversible at low temperature or at scan rates up to 10 V s^{-1} (the highest scan rate employed in this study). There are no other redox processes observed for this complex at room temperature.

Electrochemical data for the $[Ru(dmso\text{-}O)_xCl_{5-x}(NO)]^{(x-2)}$ complexes are summarised in Table 1. Even though the redox potentials do not shift by a constant amount as the number of chlorides varies, replacing four chloride ligands by four dmso-O ligands has resulted in the NO^+ reduction potential moving 1.39 V, that is, adding an electron to **3** is an extremely facile process.

In conclusion, the findings described here are of interest for several reasons: (i) from a synthetic standpoint, complexes **2** and **3** may be investigated, as already done for the other members in the series,[5,7] as new air-stable precursors for the synthesis of ruthenium nitrosyls by substitution of the sulfoxides; (ii) from a more fundamental point of view, complexes **2** and **3** open new perspectives on the coordination chemistry and binding preferences of a widely used ligand such as dmso; it can be stated that the combined effects of the presence of a strong π-acceptor ligand and of the positive charge make the Ru(II) ion in **2** and **3** a quite hard centre, inducing exclusive coordination of dmso through oxygen; (iii) the X-ray characterization of **2** and **3** provides for the first time structural informations on the *trans*-$Ru(dmso\text{-}O)_2$ fragment. Finally, these cationic ruthenium-nitrosyls are very water soluble and might be investigated as NO releasing agents for medicinal applications.[5] In fact, owing to their rather high reduction potentials, they are likely to undergo *in vivo* reduction, which would trigger NO release.

Acknowledgements

We acknowledge financial support by the Fondazione Callerio (Trieste) for a fellowship to B. S. Acknowledgment is also made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research (grant ACS PRF# 38892-AC3). This work is in part a contribution from the Edinburgh Protein Interaction Centre funded by the Wellcome Trust.

Notes and references

‡ $[RuCl(dmso\text{-}O)_4(NO)][OTf]_2$ (**2**). AgOTf (0.50 g, 1.94 mmol) was added to a suspension of *mer*-$RuCl_3(dmso\text{-}O)_2(NO)$ (0.42 g, 1.07 mmol) in 25 mL of toluene. The mixture was refluxed for 20 min; the precipitate was dissolved in 10 mL of acetone. After filtration to remove AgCl, chloroform (10 mL) was added and the solution stored at 4 °C. A small amount of $[Ru(dmso\text{-}O)_5(NO)][OTf]_3$ (**3**) (38 mg, 6%) was filtered after 20 h. Addition of more chloroform to the mother liquor and prolonged storage at 4 °C yielded light-orange crystals of $[RuCl(dmso\text{-}O)_4(NO)][OTf]_2$ (**2**). Yield 0.30 g (40%). Found: C, 15.36; H 3.14; N, 1.72%. $C_{10}H_{24}NClF_6O_{11}RuS_6$ requires C, 15.45; H, 3.11; N, 1.80%. IR (KBr): $\nu(NO)$ 1890 cm^{-1} (vs), $\nu(SO)$ 896, 878 cm^{-1} (vs, dmso-O), ν(Ru–O) 517, 501 cm^{-1} (s), ν(Ru–Cl) 352 cm^{-1} (m). IR (D_2O): $\nu(NO)$ 1900 cm^{-1}. ^1H-NMR (400 MHz, acetone-d_6, *vs.* acetone at δ 2.04): 3.11 (s, 6 H), 3.16 (s, 6 H), 3.21 (s, 6 H), 3.31 (s, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6 *vs.* CO of acetone at 206.0): 37.5, 37.7, 37.9, 38.2. $[Ru(dmso\text{-}O)_5(NO)][OTf]_3$ (**3**). A procedure similar to that reported above for **2** was used: reflux 1 h, 0.82 g (3.20 mmol) of AgOTf for 0.42 g (1.07 mmol) of *mer*-$RuCl_3(dmso\text{-}O)_2(NO)$. Yield 0.72 g (68%). Found: C, 16.50; H 3.22; N, 1.47%. $C_{13}H_{30}NClF_9O_{15}RuS_8$ requires C, 16.11; H, 3.12; N, 1.44%. IR (KBr): $\nu(NO)$ 1898 cm^{-1} (vs), $\nu(SO)$ 870 cm^{-1} (vs, dmso-O), ν(Ru–O) 517 cm^{-1} (s). IR (D_2O): $\nu(NO)$ 1903 cm^{-1}. ^1H-NMR (400 MHz, acetone-d_6, *vs.* acetone at δ 2.04): 3.30 (s, 24 H), 3.44 (s, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6 *vs.* CO of acetone at 206.0): 37.9, 38.1.

§ Diffraction data of both structures carried out at 150 K on a Nonius DIP-1030H system, Mo-Kα radiation ($\lambda = 0.71073$ Å) with graphite monochromator. All the calculations were performed using the WinGX System, Ver 1.64.02.[8] *Crystal data*: (**2**) $C_{10.5}H_{25}Cl_2F_6NO_{11}RuS_6$, $M = 819.65$, triclinic, space group $P{-}1$, $a = 8.540(3)$, $b = 13.012(4)$, $c = 15.407(4)$ Å, $\alpha = 110.87(3)$, $\beta = 89.77(2)$, $\gamma = 104.79(3)°$, $V = 1539.5(8)$ Å^3, $Z = 2$, $D_c = 1.768$ g cm^{-3}, μ(Mo-Kα) = 1.171 mm^{-1}, $F(000) = 822$, $T = 150(2)$ K. Final $R1 = 0.0493$, $wR2 = 0.1396$, $S = 1.043$ for 360 parameters and 10297 reflections, 6219 unique [R(int) = 0.0435], of which 5390 with $I > 2\sigma(I)$. (**3**) $C_{13}H_{30}F_9NO_{15}RuS_8$, $M = 968.93$, orthorhombic, space group $Pna2_1$, $a = 14.206(4)$, $b = 22.620(5)$, $c = 11.196(4)$ Å, $V = 3597.7(18)$ Å^3, $Z = 4$, $D_c = 1.789$ g cm^{-3}, μ(Mo-Kα) = 1.005 mm^{-1}, $F(000) = 1952$. Final $R1 = 0.0665$, $wR2 = 0.1709$, $S = 1.061$ for 458 parameters and 8142 reflections, 7824 unique [R(int) = 0.0330], of which 5602 with $I > 2\sigma(I)$. The choice of the non-centrosymmetric space group was confirmed by the successful final refinement. The value of the Flack parameter 0.58(9) indicates racemic twinning of the crystal. CCDC reference numbers 215684 and 215685. See http://www.rsc.org/suppdata/dt/b3/b310510e/ for crystallographic data in CIF or other electronic format.

¶ The electrochemical behavior of complexes **2** and **3** was studied in dmf/0.1 M $[^nBu_4N]BF_4$ using a Pt working and counter electrodes and a Ag/AgCl reference electrode. All redox potentials quoted are measured against Ag/AgCl. The oxidation potential for ferrocene was measured at +0.49 V *vs.* Ag/AgCl using the experimental set-up described. A voltammetric scan of 0.1 V s^{-1} has been used unless stated otherwise. All redox processes discussed, irreversible and quasi-reversible, show fast electron transfer kinetics as evidenced by the wave profile and a linear peak current to (scan rate)$^{1/2}$ response. The electron transfer processes are followed by chemical reactions thereby resulting in an absent or diminished return peak in the cyclic voltammogram.

1 M. Calligaris and O. Carugo, *Coord. Chem. Rev.*, 1996, **153**, 83.
2 E. Iengo, E. Zangrando, R. Minatel and E. Alessio, *J. Am. Chem. Soc.*, 2002, **124**, 1003; E. Iengo, E. Zangrando and E. Alessio, *Eur. J. Inorg. Chem.*, 2003, 2371 and references therein.
3 G. Sava, E. Alessio, A. Bergamo, G. Mestroni, in *Topics in Biological Inorganic Chemistry*, ed. M. J. Clarke and P. J. Sadler, Springer, Berlin, 1999, vol. 1, pp. 143–169.
4 A. R. Davies, F. W. B. Einstein, N. P. Farrell, B. R. James and R. S. McMillan, *Inorg. Chem.*, 1978, **17**, 1965.
5 B. Serli, E. Zangrando, E. Iengo, G. Mestroni, L. Yellowlees and E. Alessio, *Inorg. Chem.*, 2002, **41**, 4033; B. Serli, E. Zangrando, T. Gianferrara, L. Yellowlees and E. Alessio, *Coord. Chem. Rev.*, 2003, **245**, 75.
6 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976 .
7 B. Serli, E. Zangrando, E. Iengo and E. Alessio, *Inorg. Chim. Acta*, 2002, **339**, 265.
8 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.