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The synthesis of $RuBr_2(DMSO)_3$ revisited: a mixture of Li[*fac*-$RuCl_nBr_{3-n}(DMSO)_3$] isomers ($n=0$–3) is the reaction product

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Abstract

In this paper we report the correct formulation of a ruthenium(II)–dimethyl sulfoxide complex previously reported in the literature as $RuBr_2(DMSO)_3$. By repeating the published synthetic procedure we isolated a product that has been unambiguously characterized as a mixture of Li[*fac*-$RuCl_nBr_{3-n}(DMSO)_3$] ($n=0$–3) isomers. Our proposal is supported by detailed ^1H NMR spectroscopic studies, as well as by ^7Li and ^{37}Cl NMR spectra. We also report the crystal structure of $[NEt_4]$[*fac*-$RuBr_3(DMSO)_3$]·0.5MeOH as determined by three dimensional X-ray analysis. Crystal data: $a=10.96(1)$, $b=14.30(1)$, $c=18.25(1)$ Å; $\beta=106.0(1)°$, space group $P2_1/c$, $Z=4$. Least-squares refinement based on 1470 reflections converged to $R=0.113$.

Introduction

In 1988 Poddar and co-workers [1, 2] reported the synthesis of several new halogen–dimethyl sulfoxide–ruthenium(III) and ruthenium(II) complexes formulated as $[Ru_2Cl_6(DMSO)_4]$ (**1**), *fac*- and *mer*-$RuCl_3(DMSO)_3$ (**2**, **3**), $RuBr_3(DMSO)_3$ (**4**) and $RuBr_2(DMSO)_3$ (**5**)†, their characterization being mainly based on elemental analyses and IR spectroscopy. No crystal data were given in Poddar's reports. In a recent publication, James and co-workers [3] repeated the synthetic procedures described by Poddar's group for complexes **1**–**4**, but isolated instead, following the respective recipes, *trans*-$RuCl_2(DMSO)_4$ (**6**) [4], $[(DMSO)_2H]$[*trans*-$RuCl_4(DMSO)_2$] (**7**) [5, 6], *mer*-$RuCl_3(DMS)_3$ (**8**) (DMS = dimethyl sulfide) and *mer*-$RuBr_3(DMS)_3$ (**9**). The characterization of compounds **6**–**8** was supported by X-ray crystallographic analyses.

Despite the apparent contradictions in their former papers [1, 2], and still unaware of some fundamental publications on this subject [3, 4, 7], Poddar and co-workers recently reported that their compounds [8], and in particular $RuBr_2(DMSO)_3$ [9], can be used as versatile precursors in the synthesis of several Ru(III) and Ru(II) derivatives containing the halide ion and other ligands (e.g. phosphines, arsines, pyridine, 2,2′-bipyridine, 1,10-phenanthroline). $RuBr_2(DMSO)_3$ was also found to catalyze the oxidation of PPh_3 by molecular oxygen [9].

At the appearance of Poddar's first report [2], we were rather surprised at the proposal of the pentacoordinated ruthenium(II) complex, $RuBr_2(DMSO)_3$, as in the same period we reported the synthesis and crystal structure of *cis*-$RuBr_2(DMSO)_4$ [4], and the corresponding *trans* isomer was known since 1984 [10]. In our opinion there was in fact no apparent reason for the existence of a 16 electron pentacoordinated compound when no particular steric demand is present and the corresponding 18 electron hexacoordinated derivatives are stable.

In view of our recent results on derivatives of *cis*- and *trans*-$RuCl_2(DMSO)_4$ with nitrogen donor ligands [11], we also found that some derivatives of $RuBr_2(DMSO)_3$ reported by Poddar's group had a rather ambiguous NMR characterization [9]. This ultimately induced us to reinvestigate the synthesis and characterization of **5**. By repeating the synthetic procedure for $RuBr_2(DMSO)_3$, we isolated a product with features (elemental analysis, solid state IR spectrum, visible spectrum) very similar to those reported by Poddar and co-workers for **5**, but that was unambiguously characterized as a mixture of chloro and bromo derivatives of general formula Li[*fac*-$RuCl_n$-$Br_{3-n}(DMSO)_3$] ($n=0$–3). Similar complexes have been known for a long time. In fact, the synthesis and the

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†DMSO = O-bonded dimethyl sulfoxide; DMSO = S-bonded dimethyl sulfoxide.

crystal structure of $[NMe_2H_2][fac\text{-}RuCl_3(DMSO)_3]$ was reported in 1975 [12] and we ourselves recently described the synthesis of the tetraethylammonium salt [5]. The synthesis and NMR characterization in aprotic medium of the corresponding bromo isomer as the tetrabutylammonium salt, $[NBu^n{}_4][fac\text{-}RuBr_3(DMSO)_3]$, was reported in an exhaustive paper by Barnes and Goodfellow [7].

In the effort to assess the nature of the mixture, we also synthesized the lithium salt of the bromo derivative, $Li[fac\text{-}RuBr_3(DMSO)_3]$ (**10**).

In this paper we report its spectroscopic characterization, together with the crystal structure of the corresponding tetraethylammonium derivative, $[NEt_4][fac\text{-}RuBr_3(DMSO)_3]$ (**11**), determined by a single-crystal X-ray analysis.

Experimental

Materials

Samples of commercial hydrated $RuCl_3$ were purchased from Johnson Matthey and from Aldrich. Analytical grade solvents (Merck, C. Erba) were used without further purification for synthetic and spectroscopic purposes. Deuterated solvents (99.9% D) were obtained from MSD isotopes. Deuterated DMSO was purchased in 1 g sealed vials and used immediately after opening.

Physical measurements

Electronic absorption spectra were obtained in stoppered quartz cells with a Perkin-Elmer Lambda 5 UV–Vis spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 983G spectrometer. ^1H NMR spectra were obtained on a Nicolet 360-MHz spectrometer. ^{37}Cl and ^7Li NMR spectra were recorded at 16.32 and 77.77 MHz, respectively, on an IBM WP-200 SY spectrometer. All spectra were recorded at room temperature with tetramethylsilane (TMS) as internal reference for $CDCl_3$ and DMSO-d^6 solutions and 3-(trimethylsilyl)tetradeutero sodium propionate (TSP) for D_2O solutions. No internal references were used for ^7Li and ^{37}Cl NMR spectra since these measurements were used to ascertain the presence of Li and Cl in the reaction product.

Conductivity measurements were carried out on a Beckman RC-18A conductivity bridge equipped with a fill-type cell and thermostated with a Julabo F40 thermostatic bath.

Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA, USA).

Synthesis of the complexes

cis-$RuBr_2(DMSO)_4$ and $[NEt_4][fac\text{-}RuCl_3(DMSO)_3]$ were synthesized according to the procedures reported in refs. 4 and 5, respectively.

Lithium fac-tris(dimethyl sulfoxide)tribromo ruthenate(II) $Li[fac\text{-}RuBr_3(DMSO)_3]$ (10)

The complex was synthesized from *cis*-$RuBr_2(DMSO)_4$ according to the following procedure. 600 mg of *cis*-$RuBr_2(DMSO)_4$ were partially dissolved in 30 ml of CH_3OH containing 2 g of LiBr. The mixture was refluxed for 15 min, during which time it turned from yellow to orange and all the remaining *cis*-$RuBr_2(DMSO)_4$ dissolved. The volume of the cool solution was reduced under vacuum and diethyl ether (1 ml) added dropwise. Deep-yellow microcrystals of the product precipitated from the solution within 24 h at r.t. They were filtered, washed with acetone and then with diethyl ether and vacuum dried. Yield 60%. *Anal.* Calc. for $Li[RuBr_3(DMSO)_3]$ (M_r 582.12): C, 12.37; H, 3.11; S, 16.52; Br, 41.18. Found: C, 12.33; H, 3.32; S, 16.42; Br, 41.90%.

The complex could be also obtained upon recrystallization of the reaction mixture obtained according to Poddar's procedure from methanol/LiBr solution (see text).

Tetraethylammonium fac-tris(dimethyl sulfoxide)-tribromo ruthenate(II) $[NEt_4][fac\text{-}RuBr_3(DMSO)_3]\cdot 0.5MeOH$ (11)

The complex was synthesized from *cis*-$RuBr_2(DMSO)_4$, with a procedure that closely followed that reported by us for the synthesis of the chloro analogue [5], using NEt_4Br instead of NEt_4Cl. Yield 50%. *Anal.* Calc. for $[NEt_4][RuBr_3(DMSO)_3]\cdot 0.5MeOH$ (M_r 721.43): C, 24.1; H, 5.59; N, 1.94; S, 13.33; Br, 33.22. Found: C, 23.88; H, 5.30; N, 1.88; S, 13.10; Br, 33.08%.

Crystal structure

Crystals of **10** were of inadequate quality for X-ray analysis. Crystals of the tetraethylammonium derivative, **11**, appeared of better quality, even if they also, quickly, lose crystallinity in the solid state. Covering with epoxy slows down the crystal decay, but does not prevent it. The crystal decay is probably due to partial hydrolysis of superficial Ru–Br bonds by atmospheric moisture (see 'Results and discussion'), and not to a decomposition or isomerization reaction, as freshly prepared or aged crystals give identical NMR spectra.

A crystal well covered with epoxy cement was mounted on a CAD4 diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$ Å). Unit cell parameters were determined by least-squares refinement of the setting angles of 25 automatically centered reflections.

Crystal data: space group $P2_1/c$; $a=10.96(1)$, $b=14.30(1)$, $c=18.25(1)$ Å, $\beta=106.0(1)°$, $V=2750(4)$ Å^3, $D(\text{calc.})=1.74$ g cm^{-3}, for $Z=4$ of [NEt$_4$][*fac*-RuBr$_3$(DM*S*O)$_3$]·0.5MeOH; $\mu=51.1$ cm^{-1}. Intensities of the $\pm h+k+l$ reflections were measured in the $3\leqslant\theta\leqslant26°$ range, with the $\omega/2\theta$ scan mode, at room temperature. The three standard reflections showed a dramatic decay of the crystal with a reduction of their intensity of *c.* 100% when $l=8$ (against the maximum expected value, for a complete reflection sphere, of 22). A total of 1470 unique data, with $I>3\sigma(I)$, was obtained and corrected for Lorentz–polarization and decay effects.

In spite of the serious truncation effects, direct methods (MULTAN) [13] easily gave the positions of the ruthenium and coordinated Br and S atoms. All the other non-hydrogen atoms were located in subsequent Fourier maps. After a few cycles of isotropic least-squares refinement the semi-empirical method of Walker and Stuart [14] was applied for absorption correction (ABSORB) [15]. Scattering factors, anomalous dispersion terms and programs were taken from the Enraf-Nonius SDP library [16].

TABLE 1. Fractional atomic coordinates[a] and B_{eq} of [NEt$_4$][*fac*-RuBr$_3$(DM*S*O)$_3$]·0.5MeOH

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Ru	0.6141(2)	0.2673(2)	0.8884(2)	2.59(9)
Br1	0.6526(4)	0.3213(3)	1.0271(3)	5.7(2)
Br2	0.7664(4)	0.1317(3)	0.9398(3)	8.3(2)
Br3	0.8084(4)	0.3615(3)	0.8829(4)	8.7(2)
S1	0.5963(7)	0.2286(5)	0.7673(6)	3.0(2)
S2	0.4833(7)	0.3938(5)	0.8553(6)	3.0(2)
S3	0.4512(8)	0.1708(5)	0.8937(7)	3.5(2)
O1	0.472(2)	0.185(1)	0.726(1)	3.7(5)
O2	0.407(2)	0.404(1)	0.777(2)	5.4(6)
O3	0.319(2)	0.205(1)	0.862(1)	4.4(5)
O4	0.816(4)	0.038(3)	0.106(3)	6(1)
N	1.093(2)	0.283(2)	1.134(2)	3.5(6)
C1	0.726(3)	0.155(2)	0.756(2)	5.0(9)
C2	0.621(3)	0.323(2)	0.706(2)	4.7(8)
C3	0.373(3)	0.407(2)	0.909(2)	4.6(8)
C4	0.573(2)	0.500(2)	0.884(2)	3.0(7)
C5	0.458(3)	0.137(2)	0.989(2)	5.0(9)
C6	0.459(3)	0.057(2)	0.855(2)	4.3(8)
C7	0.991(3)	0.229(2)	1.160(2)	5.2(9)
C8	1.041(4)	0.194(3)	1.244(3)	9(1)
C9	1.121(5)	0.369(3)	1.189(3)	10(1)
C10	0.999(4)	0.435(3)	1.174(3)	9(1)
C11	1.028(4)	0.307(3)	1.062(3)	9(1)
C12	1.133(5)	0.364(3)	1.018(3)	11(2)
C13	1.209(4)	0.225(3)	1.152(3)	9(1)
C14	1.214(4)	0.135(3)	1.106(3)	9(1)
C15	0.908(6)	−0.050(5)	0.101(5)	6(2)

[a] O, N, C atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3[a^2\beta_{1,1}+b^2\beta_{2,2}+c^2\beta_{3,3}+ab(\cos\gamma)\beta_{1,2}+ac(\cos\beta)\beta_{1,3}+bc(\cos\alpha)\beta_{2,3}]$.

TABLE 2. Bond distances (Å) and angles (°) for [NEt$_4$][*fac*-RuBr$_3$(DM*S*O)$_3$]·0.5MeOH

Distances			
(a) [RuBr$_3$(DM*S*O)$_3$]$^-$			
Ru–Br1	2.569(6)	S1–C1	1.83(4)
Ru–Br2	2.562(5)	S1–C2	1.82(4)
Ru–Br3	2.546(5)	S2–C3	1.76(4)
Ru–S1	2.23(1)	S2–C4	1.81(3)
Ru–S2	2.283(7)	S3–C5	1.78(5)
Ru–S3	2.279(9)	S3–C6	1.79(3)
S1–O1	1.50(2)		
S2–O2	1.45(3)		
S3–O3	1.48(2)		
(b) [NEt$_4$]$^+$, MeOH			
N–C (av.)	1.49(8)		
C–C (av.)	1.62(9)		
O4–C15	1.63(9)		
Angles			
(a) [RuBr$_3$(DM*S*O)$_3$]$^-$			
Br1–Ru–Br2	87.3(2)	Ru–S1–O1	115(1)
Br1–Ru–Br3	88.1(2)	Ru–S1–C1	113(1)
Br1–Ru–S1	174.6(3)	Ru–S1–C2	116(1)
Br1–Ru–S2	86.7(3)	Ru–S2–O2	119(1)
Br1–Ru–S3	93.3(3)	Ru–S2–C3	115(1)
Br2–Ru–Br3	86.9(2)	Ru–S2–C4	110(1)
Br2–Ru–S1	92.6(3)	Ru–S3–O3	119(1)
Br2–Ru–S2	174.0(3)	Ru–S3–C5	113(1)
Br2–Ru–S3	88.0(3)	Ru–S3–C6	114(1)
Br3–Ru–S1	86.5(3)	O1–S1–C1	109(1)
Br3–Ru–S2	92.4(3)	O1–S1–C2	105(1)
Br3–Ru–S3	174.7(3)	O2–S2–C3	104(2)
S1–Ru–S2	93.3(4)	O2–S2–C4	109(1)
S1–Ru–S3	92.1(4)	O3–S3–C5	104(2)
S2–Ru–S3	92.8(3)	O3–S3–C6	107(1)
		C1–S1–C2	96(2)
		C3–S2–C4	99(2)
		C5–S3–C6	98(2)
(b) [NEt$_4$]$^+$			
C–N–C (av.)	109(7)		
N–C–C (av.)	113(4)		

After anisotropic refinement of Ru, Br and S atoms the *R* factor was 0.129. The final Fourier maps, as well as the difference Fourier maps, showed the presence of two low electron density peaks, nearly 1.5 Å apart, which were interpreted as crystallization solvent (methanol) with a half occupancy factor. Final full-matrix least-squares refinement ($w=1/[\sigma^2(F)+(0.02F)^2+1]$), including extinction correction ($g=1.7(5)\times10^{-7}$), and the fixed contribution of the hydrogen atoms in idealized positions, gave the final residual indexes, $R=0.113$, and $R_w=0.135$, with a goodness of fit of 3.77. The hydrogen atoms of methanol were not included in view of its fractional occupancy factors. The highest peaks in the final difference Fourier map were of ±1.8 e/Å^3, close to the heavy metal atom.

The final atom parameters for non-hydrogen atoms are listed in Table 1. Selected bond lengths and angles are given in Table 2. See also 'Supplementary material'.

Results and discussion

We followed as closely as possible the rather simple preparation given by Poddar and co-workers for $RuBr_2(DMSO)_3$ [2], which requires refluxing commercially available $RuCl_3 \cdot 3H_2O$ in ethanol in the presence of excess LiBr and DMSO. As described by Poddar's group, we obtained a yellow precipitate with spectroscopic features closely similar to those reported for $RuBr_2(DMSO)_3$: S=O stretching band for exclusively S-bonded sulfoxides at 1088 cm^{-1} versus the reported 1097 cm^{-1}, and electronic absorption bands in CH_3CN at 374 and 219 nm versus the reported 365 and 220 nm. The synthesis was repeated several times and with different commercial sources of hydrated ruthenium trichloride. The results were fairly well reproducible. The elemental analysis gave results similar to those reported by Poddar for **5**, but with generally higher bromine values (average 39% versus 32% required by $RuBr_2(DMSO)_3$). Variable amounts of crystallization solvent (see below) partially affected the reproducibility of the analysis in different preparations.

Despite this partial agreement with Poddar's findings, other experimental evidence convinced us that the formulation reported for the reaction product [2] was not correct. First of all, the product was perfectly and instantly soluble in water, suggesting an ionic nature. Its molar conductivity fell well in the range of 1:1 electrolytes ($\Lambda = 121\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 25 °C). On the contrary, it was almost insoluble in chloroform (a rather unusual feature for a presumed neutral DMSO complex). In agreement with Poddar's report, it showed a rather low conductivity in CH_3CN ($\Lambda = 24\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 25 °C).

The electronic absorption spectrum of the product in aqueous solution was very similar to that of *cis*-$RuBr_2(DMSO)_4$, initially leading us to believe that the compound might be formulated as Li[*fac*-$RuBr_3(DMSO)_3$] (**10**). In fact, in agreement with the chemical behavior of its chloro analogue [12], **10** would be expected to dissociate readily one bromide in aqueous solution. Therefore, both Li[*fac*-$RuBr_3(DMSO)_3$] and *cis*-$RuBr_2(DMSO)_4$ [4] would produce the same species, namely *cis,fac*-$RuBr_2(DMSO)_3(H_2O)$, upon dissolution in water.

However, the ^1H NMR spectra of the product in D_2O was not in agreement with such simple interpretation, consisting of a rather complicated time-dependent pattern of signals in the region of S-bonded DMSOs (Fig. 1). At least 12 main peaks could be resolved between 3.37 and 3.63 ppm in freshly prepared solutions. Spectra of different samples showed always the same pattern but could be slightly different in the relative intensity of the peaks. Moreover, the peak of free DMSO of crystallization could be present and, to our experience, this is a rather common feature for anionic sulfoxide complexes [3, 5, 17].

This complicated NMR pattern could not be attributed to a single DMSO–bromo complex, even upon consideration that new species with inequivalent sulfoxides might be generated in solution upon bromide dissociation. As elemental analysis and stoichiometric considerations did not allow for polynuclear species, a mixture of complexes was hypothesized and the following experiments were performed to figure out the intriguing nature of the reaction product. Recrystallization of the product from *N,N*-dimethylacetamide (DMA)/diethyl ether left it unchanged (unless for the presence of variable amounts of DMA of crystallization) as proved by ^1H NMR spectra.

The strong signal observed in the ^7Li NMR spectrum of a recrystallized sample proved the product to be a lithium salt.

As in the case of *fac*-$RuCl_3(DMSO)_3^-$ [12], the D_2O ^1H NMR spectrum of the product was extremely simplified by the presence of excess halogen ion, added as LiBr. In fact, in 6 M Br^- solutions, the pattern for S-bonded sulfoxides became a singlet (3.66 ppm) attributable to the eighteen equivalent methyl protons of the three S-bonded DMSOs in *fac*-$RuBr_3(DMSO)_3^-$. In agreement with this finding, recrystallization of the product from methanol in the presence of excess LiBr (2 M) yielded, upon addition of ether, a complex that could be unambiguously characterized by elemental analysis and spectroscopic techniques as Li[*fac*-$RuBr_3(DMSO)_3$] (**10**). Indeed, the solid state IR spectrum of **10** is very similar to that of the product from Poddar's synthesis, but its ^1H NMR spectrum in D_2O is much simpler and, as expected (*vide supra*), equal to that of *cis*-$RuBr_2(DMSO)_4$. The spectrum of a fresh solution of **10** consists of three peaks of equal intensity at 3.63, 3.61 and 3.43 ppm, attributable to the methyl protons in *cis,fac*-$RuBr_2(DMSO)_3(H_2O)$ (the two *cis* DMSOs *trans* to Br are chemically equivalent but bear magnetically non-equivalent methyl groups [7, 11, 18]). The spectrum changes with time, as a second bromide is released.

In order to be absolutely sure of our assignments, we synthesized **10** also from *cis*-$RuBr_2(DMSO)_4$ (see 'Experimental'). With a similar procedure also the corresponding tetraethylammonium salt, $[NEt_4]$[*fac*-$RuBr_3(DMSO)_3$] (**11**), was synthesized and crystals suitable for X-ray analysis (see last section) could be obtained. The ^1H NMR spectrum of **11** in D_2O is obviously equal to that of **10**, but for the cation peaks. As expected, its ^1H NMR spectrum in $CDCl_3$ consists of a single signal at 3.69 ppm. This is in good agreement with the value reported by Barnes and Goodfellow (3.61 ppm) for the tetrabutylammonium salt in CD_2Cl_2 [7].

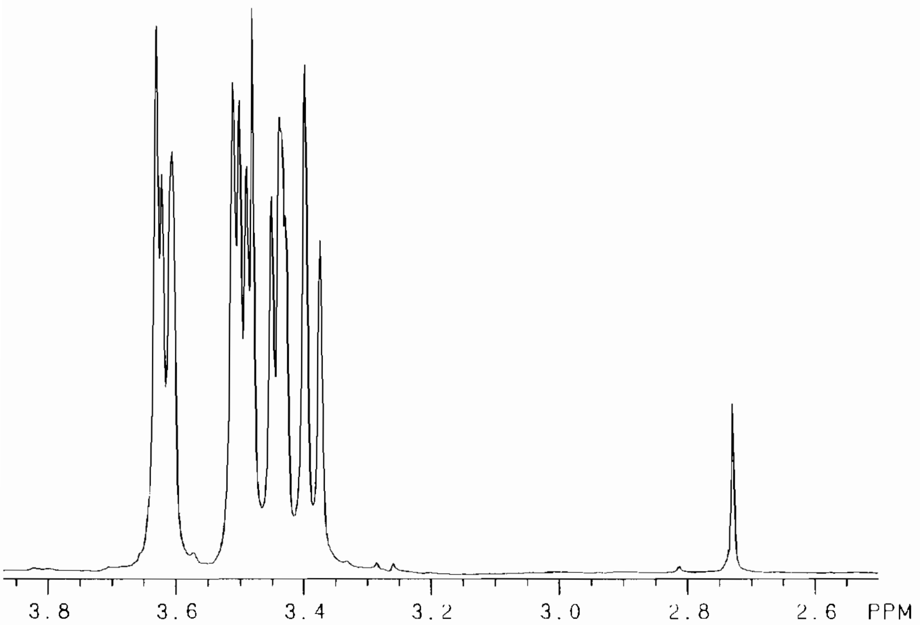

Fig. 1. ^{1}H NMR spectrum (D_2O, 360 MHz) of the reaction product in the S-bonded sulfoxide region.

A careful comparison of the ^{1}H NMR spectra showed that three peaks in the pattern of the reaction product (3.63, 3.61 and 3.43 ppm) were coincident with those of **10**, clearly stating that Li[*fac*-$RuBr_3(DMSO)_3$] was a component of the mixture. Similarly, three other peaks (3.50, 3.48 and 3.40 ppm) could be identified as belonging to *fac*-$RuCl_3(DMSO)_3^-$, by comparison with the D_2O ^{1}H NMR spectrum of a sample of [NEt_4][*fac*-$RuCl_3(DMSO)_3$]. The remaining peaks could be attributed to mixed chloro–bromo species. No attempts were made to isolate or synthesize such mixed species. However, the presence of chlorine in the sample was unambiguously established by running a ^{37}Cl NMR spectrum.

Finally, we were able to reproduce exactly the ^{1}H NMR pattern of the reaction product by adding a small excess of LiBr to a D_2O solution of [NEt_4][*fac*-$RuCl_3(DMSO)_3$]. As the chloride substitution reaction proceeded, the three initial peaks decreased in intensity and all the other features of the complicated pattern appeared. This experiment provided conclusive evidence that the product of Poddar's reaction is actually a mixture of Li[*fac*-$RuCl_nBr_{3-n}(DMSO)_3$] complexes ($n = 0$–3). In view of this finding, also the other intriguing experimental results find an explanation, such as the high values for bromine analysis, due to chlorine being analyzed as bromine.

The behavior of this mixture in deuterated DMSO deserves a final comment, since Poddar and co-workers largely based upon it their formulation of the reaction product as $RuBr_2(DMSO)_3$ [2]. Contrary to a suggestion by Poddar's group, but in agreement with previous observations on Ru(II)–DMSO complexes [12, 19], the reaction product, when dissolved in deuterated DMSO at 20 °C, does exchange the coordinated DMSO molecules. A spectrum recorded soon after dissolution (5 min) revealed the presence of at least 8 peaks in the region of S-bonded DMSOs, between 3.51 and 3.71 ppm. The intensity of such peaks decreased with time at different rates and the signal of free DMSO (2.54 ppm) correspondingly increased. The exchange process was almost complete in two hours and no other peak beside that of free DMSO appeared, confirming that no other neutral ligand (e.g. dimethyl sulfide) is bound to ruthenium.

These results support our believe that the interpretation of ^{1}H NMR spectra of DMSO derivatives in deuterated dimethyl sulfoxide should be done cautiously, as it can easily give misleading results. First of all, fast exchange reactions between coordinated DMSOs and the solvent might prevent the observation of some signals and not allow recognition of the presence of DMSO molecules of crystallization. Moreover, while the multiplet of residual, partially deuterated, DMSO (2.50 ppm) can be easily distinguished from the sharp signal of free, undeuterated, DMSO (2.54 ppm), the water signal falls in the region of S-bonded DMSOs. Due to the hygroscopic nature of dimethyl sulfoxide, the intensity of this latter signal can be very high compared to those of S-bonded DMSOs, especially in samples prepared with not high quality solvents. The water peak at 3.41 ppm is the only signal that remained unchanged in this region of the spectrum of the reaction product. In our opinion, in Poddar's report it was erroneously attributed to the signal of equivalent non-exchanging S-bonded DMSOs.

Crystal structure of [NEt$_4$][fac-RuBr$_3$(DMSO)$_3$]·0.5MeOH

In spite of the limited number of available reflections (see 'Experimental'), the molecular structure of [NEt$_4$][RuBr$_3$(DMSO)$_3$] is unambiguously determined (Fig. 2), and definitely confirms the spectroscopically determined structures of both the NEt$_4^+$ and Li$^+$ derivatives of *fac*-[RuBr$_3$(DMSO)$_3$]$^-$. It is interesting to compare this structure with that of {[Li(TMSO)][*fac*-RuBr$_3$(TMSO)$_3$]}$_2$ obtained by James, which consists of centrosymmetric dimeric units, where each lithium ion is tetrahedrically coordinated by the TMSO oxygen atoms [20].

The crystal structure of the tetraethylammonium derivative consists of one crystallographically independent cation and anion held together by van der Waals forces. The latter also interacts with MeOH. The shortest contact occurs between O4 and Br2 (3.24(7) Å), suggesting the existence of a weak hydrogen bonding.

The average Ru–Br (*trans* to S) and Ru–S (*trans* to Br) bond distances of 2.56(1) and 2.26(2) Å, respectively, compare well with those of 2.562(1) and 2.295(6) Å found in *cis*-RuBr$_2$(DMSO)$_3$(DMSO) [4]. The Ru–S bond lengths are also very close to the average value of 2.262(8) Å found in the analogous chloro derivative *fac*-[RuCl$_3$(DMSO)$_3$]$^-$ [12]. It is also interesting to observe that, as in the chloro derivative [12], the S–Ru–S bond angles (av. 92.7(5)°) are significantly larger than the Br–Ru–Br angles (av. 87.4(5)°), because of the steric interactions among the DMSO molecules.

Structural parameters of the dimethyl sulfoxide molecules are in excellent agreement with those found in other DMSO complexes. In fact, the average S–O (1.48(2) Å) and S–C (1.80(2) Å) distances, as well as the O–S–C (106(2)°) and C–S–C (98(1)°) bond angles are equal, within experimental error, with those reported (1.48(1), 1.79(2) Å, 106(1) and 99(2)°, respectively) for Ru(II)–DMSO complexes [5].

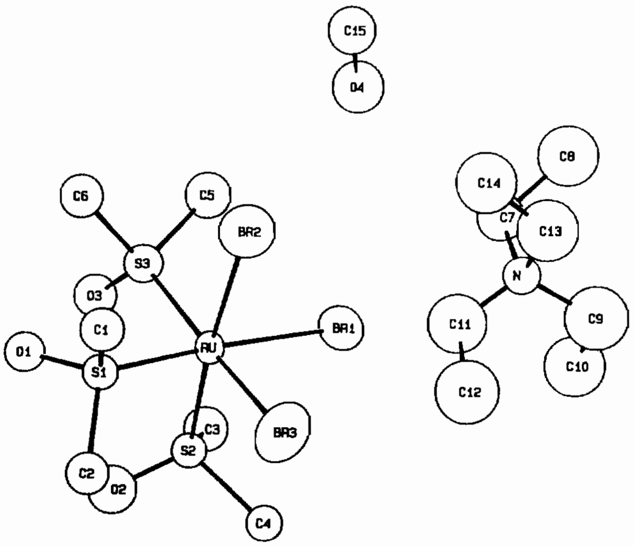

Fig. 2. ORTEP drawing of [NEt$_4$][*fac*-RuBr$_3$(DMSO)$_3$]·0.5MeOH, showing the atom numbering scheme (thermal ellipsoids at 50% probability level).

Conclusions

According to the above results and to available literature data on Ru(II)–DMSO complexes [4, 9, 11, 12], we believe that the compound reported by Poddar's group as RuBr$_2$(DMSO)$_3$ must be reformulated as a mixture of Li[*fac*-RuCl$_n$Br$_{3-n}$(DMSO)$_3$] isomers ($n = 0$–3). Even when complete chloride substitution should take place, complex **10** and not RuBr$_2$(DMSO)$_3$ would be the final product. In view of our findings, the results concerning the synthesis of the RuBr$_2$(DMSO)$_3$ derivatives [8] should also be critically revised.

The crystal structure of **11** completes the series of halogen–dimethyl sulfoxide–ruthenium(II) complexes of general formula [RuX$_n$(DMSO)$_{6-n}$]$^{-(n-2)}$ (X = Cl, Br; $n = 2$, 3) [4, 10, 12, 21, 22].

Supplementary material

Anisotropic thermal parameters, hydrogen atom parameters and tables of observed and calculated structure factors are available from the authors on request.

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References

1 U. C. Sarma, K. P. Sarma and R. K. Poddar, *Polyhedron, 7* (1988) 1727.
2 U. C. Sarma and R. K. Poddar, *Polyhedron, 7* (1988) 1737.
3 J. S. Jaswal, S. J. Rettig and B. R. James, *Can. J. Chem., 68* (1990) 1808.
4 E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava and S. Zorzet, *Inorg. Chem., 27* (1988) 4099.
5 E. Alessio, G. Balducci, M. Calligaris, G. Costa, W. M. Attia and G. Mestroni, *Inorg. Chem., 30* (1991) 609.
6 G. Costa, G. Balducci, E. Alessio, C. Tavagnacco and G. Mestroni, *J. Electroanal. Chem., 296* (1990) 57.

7 J. A. Barnes and R. J. Goodfellow, *J. Chem. Res. Miniprint,* (1979) 4301.

8 U. C. Sarma, S. C. Sarker, B. C. Paul and R. K. Poddar, *Inorg. Chim. Acta, 173* (1990) 195.

9 B. C. Paul, U. C. Sarma and R. K. Poddar, *Inorg. Chim. Acta, 179* (1991) 17.

10 J. D. Oliver and D. P. Riley, *Inorg. Chem., 23* (1984) 156.

11 M. Henn, E. Alessio, G. Mestroni, M. Calligaris and W. M. Attia, *Inorg. Chim. Acta, 187* (1991) 39.

12 R. S. McMillan, A. Mercer, B. R. James and J. Trotter, *J. Chem. Soc., Dalton Trans.,* (1975) 1006.

13 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, *MULTAN82,* a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, UK, and Louvain, Belgium, 1982.

14 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

15 F. Ugozzoli, *Comput. Chem., 11* (1987) 109 (adapted to SDP, on a MicroVAX 2000 computer, by Dr S. Geremia).

16 *Enraf-Nonius Structure Determination Package,* B. A. Frenz & Associates, Enraf-Nonius, Delft, Netherlands, 1985.

17 E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P. Faleschini and W. M. Attia, *Inorg. Chim. Acta, 177* (1990) 255.

18 G. Mestroni, E. Alessio, G. Zassinovich and L. G. Marzilli, *Comments Inorg. Chem., 12* (1991) 67.

19 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1973) 204.

20 B. R. James, personal communication.

21 A. Mercer and J. Trotter, *J. Chem. Soc., Dalton Trans.,* (1975) 2480.

22 W. M. Attia and M. Calligaris, *Acta Crystallogr., Sect. C, 43* (1987) 1426.