Convenient synthesis of hexakis(dimethyl sulfoxide)ruthenium(III) and tetra(halogeno) bis(dimethyl sulfoxide)ruthenate(III)

Uma Charan Sarma, Bipul Chandra Paul & Raj K Poddar*
Department of Chemistry, North-Eastern Hill University
Bijni Complex, Shillong 793 003, India

Received 20 September 1989; revised and accepted 7 December 1989

Cationic and anionic complexes of ruthenium(III), viz., [Ru(Me₂SO)₆]X₃ (X = ClO₄ or BPh₄) and NR₄[RuX₄(Me₂SO)₂] (R = Me, X = Cl; R = Et, X = Br) have been synthesized and characterized by IR, UV-visible and EPR spectroscopy, magnetic susceptibility and molar conductance measurements. [Ru(Me₂SO)₆]³⁺ has three S-bonded and three O-bonded Me₂SO molecules, arranged in a facial octahedral geometry around the metal ion. The anionic complexes possess cis geometry, the coordination of Me₂SO being through the S-atom in the chloro complex and through the O-atom in the bromo analogue.

Hexakis(dimethylsulphoxide)ruthenium(II) cation has been characterized¹−² and is found to have three Me₂SO molecules coordinated to ruthenium(II) via the oxygen atoms and the rest via the sulphur atoms to give the facial isomer of irregular octahedral geometry³. Synthesis of the corresponding ruthenium(III) cation as chloride, bromide or perchlorate salt, starting from RuCl₃ or RuBr₃ has been reported by Bora and Singh⁴–⁵, but it has not been well characterized. Our attempts to repeat the earlier reported preparation⁴–⁵ were unsuccessful. The present work describes the synthesis of [Ru(Me₂SO)₆]X₃ (X = ClO₄ or BPh₄) and NR₄[RuX₄(Me₂SO)₂] (R = Me, X = Cl; R = Et, X = Br).

Experimental
fac- and mer-[RuCl₃(Me₂SO)₃], [Ru₂Cl₆(Me₂SO)₄] and [RuBr₃(Me₂SO)₃] were prepared as reported earlier⁶–⁷. Analytical data and all the physical measurements were obtained as described earlier⁶–⁷. Analytical data, molar conductance values and magnetic moments of the complexes are presented in Table 1. Important IR and electronic absorption bands are given in Table 2.

(a) [Ru(Me₂SO)₆][ClO₄]₃
To a solution/suspension of [Ru₂Cl₆(Me₂SO)₄] or fac or mer-[RuCl₃(Me₂SO)₃] (0.5 g) in ethanol (30 cm³), a solution of AgClO₄ in ethanol (10 cm³) was added. The molar ratio of the complex: AgClO₄ was 1:4 in the case of fac- or mer-[RuCl₃(Me₂SO)₃] and 1:8 in the case of [Ru₂Cl₆(Me₂SO)₄]. The mixture was stirred at room temperature for 10-12 h and then refluxed on a water-bath for 1 hr. The solution was cooled to room temperature and the precipitated AgCl was separated by centrifugation. To the light violet mother liquor, dimethyl sulphoxide (1 cm³) was added and content stirred at room temperature for 2-3 h. The solution was concentrated on a water-bath to a small volume (~ 2 ml). It was cooled in ice and methanol was added to precipitate the violet compound. The compound was recrystallized from acetone and dried in vacuo; yield 0.82g (75%).
(b) \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{BPh}_4]_3\)

\([\text{Ru} (\text{Me}_2\text{SO})_6][\text{ClO}_4]_3\) (0.2g), was dissolved in acetone (10 cm³) and a solution of \(\text{NaBPh}_4\) (0.25g) in acetone (10 cm³) was added to it. The reaction mixture was stirred at room temperature for 1 h, when the colour changed from violet to green. The green solution was concentrated at room temperature, to a small volume (~ 2 cm³). Methanol was added to precipitate the light green compound. The compound was centrifuged, washed with little acetone and dried \textit{in vacuo}.

(c) \([\text{Me}_4\text{N}] [\text{RuCl}_4(\text{Me}_2\text{SO})_2]_2\)

\([\text{Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4]_3\), or fac or mer \([\text{RuCl}_3(\text{Me}_2\text{SO})_3]\) (0.5g) was dissolved in methanol (20 cm³). A solution of tetramethylammonium chloride (0.2 g) in methanol (5 cm³) was added to it and the reaction mixture was refluxed on a water-bath for 1 h. After concentrating and cooling the solution to room temperature, orange crystals separated out. The reaction mixture was stirred at room temperature for 1 h, when the colour changed from violet to green. The green compound was centrifuged, washed with little acetone and dried \textit{in vacuo}. Yield 0.4g (75%).

(d) \([\text{Et}_4\text{N}] [\text{RuBr}_3(\text{Me}_2\text{SO})_3]\)

\([\text{RuBr}_3(\text{Me}_2\text{SO})_3]\) (0.3g) was dissolved in methanol (20 cm³) and a solution of tetraethylammonium bromide (0.15g) in methanol (10 cm³) was added to it. The reaction mixture was refluxed for 10 min, concentrated and cooled to room temperature. Violet crystals separated out which were centrifuged, washed with diethyl ether and dried \textit{in vacuo}. Yield 0.3g (80%).

**Results and discussion**

[\(\text{Ru} (\text{Me}_2\text{SO})_6][\text{ClO}_4]_3\] has been synthesized by the reaction of \([\text{Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4]\) or fac or mer \([\text{RuCl}_3(\text{Me}_2\text{SO})_3]\) with silver perchlorate in presence of excess dimethyl sulphoxide. A metathetic reaction of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{ClO}_4]_3\) with \(\text{NaBPh}_4\) resulted in the formation of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{BPh}_4]_3\) in acetone at 75°C. The molar conductance values for these complexes in acetonitrile were around 350 \(\Omega^{-1} \text{cm}^2\text{mol}^{-1}\), characteristic of 1:1 electrolytic behaviour. The room temperature magnetic moment value of 1.9 B.M. found for the perchlorate complex is characteristic of a low-spin \(d^9\), ruthenium (III) system.

The IR spectra of the complexes were similar to those reported for ruthenium(II) analogues, viz., \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{X}_2]_2 \) (X = BF\(_4\) or BPh\(_4\))\(^{2,3}\). The IR spectrum of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{ClO}_4]_3\) exhibited strong absorptions at 1140, 1120 and 1090 cm\(^{-1}\) assignable to \(\nu_{\text{SO}}\) of S-bonded \(\text{Me}_2\text{SO}\)\(^{2,3}\) and to ionic \(\text{ClO}_4^-\) (ref. 9). The IR spectrum of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{BPh}_4]_3\) showed only one band at 1120 cm\(^{-1}\) in the region 1150-1050 cm\(^{-1}\). The presence of a band at 1120 cm\(^{-1}\) in the IR spectra of both \(\text{ClO}_4^-\) and BPh\(_4^-\) salts confirms its assignment to \(\nu_{\text{SO}}\) of S-bonded \(\text{Me}_2\text{SO}\), and the absorptions at 1140 and 1090 cm\(^{-1}\) in the perchlorate salt can be assigned to ionic perchlorate. Another band of medium intensity observed at 925 cm\(^{-1}\) for the complexes is ascribed to \(\nu_{\text{SO}}\) of the O-bonded \(\text{Me}_2\text{SO}\) groups\(^{2,3}\). In the far IR region, bands of weak to medium intensity at 480 and 429 cm\(^{-1}\) are assigned to \(\nu_{\text{Ru}-\text{O}}\) and \(\nu_{\text{Ru}-\text{S}}\) respectively\(^{10,11}\). The IR spectrum of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{BPh}_4]_3\), showed additional bands at 1570, 1470 and 700 cm\(^{-1}\), which are characteristic of the presence of BPh\(_4^-\) anion\(^2\). As IR spectrum of \([\text{Ru} (\text{Me}_2\text{SO})_6]\)\(^{3+}\) is superimposable on that of \([\text{Ru} (\text{Me}_2\text{SO})_6]\)\(^{2+}\), the former may be suggested to have a structure similar to that of the latter with three S-bonded and three O-bonded \(\text{Me}_2\text{SO}\) molecules, to give the facial isomer of \(C_3\) symmetry\(^1\).

The EPR spectrum of \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{ClO}_4]_3\) in powder form at room temperature showed two signals at \(g = 2.31\) and 1.88, comparable with signals of similar systems with facial geometry\(^{12-13}\). The electronic absorption spectrum of the complex in acetonitrile showed a broad band at 575 nm (\(\epsilon = 320\)), which may be assigned to one of the spin-allowed \(d-d\) transitions\(^{14}\), viz., \(2T_2 \rightarrow 2A_2, 2T_1 \) or \(2T_2\).

The synthesis of the complex ion \([\text{RuCl}_4(\text{Me}_2\text{SO})_2]^-\) reported by Bora and Singh\(^4\) from \([\text{Ru} (\text{Me}_2\text{SO})_6][\text{Cl}]_3\), could not be reproduced. We have synthesised the ion as its \(\text{Me}_4\text{N}^+\) salt (Table 1) using \([\text{RuCl}_4(\text{Me}_2\text{SO})_2]\), fac- or mer- \([\text{RuCl}_3(\text{Me}_2\text{SO})_3]\). The bromo analogue as the \(\text{Et}_4\text{N}^+\) salt has also been synthesized using \([\text{RuBr}_3(\text{Me}_2\text{SO})_3]\). The molar conductance values for the compounds in acetonitrile/methanol were about 120 \(\Omega^{-1} \text{cm}^2\text{mol}^{-1}\), characteristic of 1:1 electrolytic behaviour\(^8\).

The IR spectra of \(\text{Me}_4\text{N}[\text{RuCl}_4(\text{Me}_2\text{SO})_2]\) obtained from different starting materials were superimposable, implying that the mode of coordination of \(\text{Me}_2\text{SO}\) to the metal ion is the same in all the cases. A strong band at 1120 cm\(^{-1}\) due to \(\nu_{\text{SO}}\) of \(\text{S-bonded Me}_2\text{SO}\) and a medium to weak intensity band at 955 cm\(^{-1}\) due to the presence of \(\text{Me}_4\text{N}^+\) cation were observed. The possibility of the latter band being due to \(\nu_{\text{SO}}\) of \(O\)-bonded \(\text{Me}_2\text{SO}\) cannot be ruled out. However, when its intensity (medium to weak) is compared with that of 1120 cm\(^{-1}\) band, it seems unlikely that it is due to \(\nu_{\text{SO}}\) of \(O\)-bonded \(\text{Me}_2\text{SO}\). Further, an absorption at 415 cm\(^{-1}\) could be assigned to \(\nu_{\text{Ru}-\text{Cl}}\)\(^8\). Four bands in the far IR region (Table 2), assignable to \(\nu_{\text{Ru}-\text{Cl}}\) of \textit{cis} structure\(^{15}\), were also observed. If one presumes a \textit{trans} geometry for the
complex \( (D_{4h} \text{ symmetry}) \), only one band due to \( \nu_{\text{Ru-Cl}} \) is expected. The bands at 997 and 977 cm\(^{-1}\) (Table 2) observed for \( \text{Et}_4\text{N}[\text{RuBr}_4(\text{Me}_2\text{SO})_2] \) may be assigned to \( \nu_{\text{SO}} \) of O-bonded \( \text{Me}_2\text{SO} \) molecules. Thus, \( \text{Me}_2\text{SO} \) coordination to ruthenium remains O-bonded only, as in the case of parent compound\(^7\), \([\text{RuBr}_3(\text{Me}_2\text{SO})_3] \). The four bands in the region 350-180 cm\(^{-1}\) (Table 2) may be assigned to \( \nu_{\text{Ru-Br}} \) and a \( \text{cis} \) geometry may be assigned to the complex anion.

The magnetic moment values, \( \mu_{\text{eff}} \), for the two anionic complexes are 1.8 and 1.9 BM, corresponding to low-spin, \( d^5 \) ruthenium. The EPR spectrum of \( \text{Et}_4\text{N}[\text{RuBr}_4(\text{Me}_2\text{SO})_2] \) in powder form at room temperature showed a broad signal at \( g = 2.17 \). However, for a \text{cis} geometry of the complex (vide supra) one expects three \( g \) values. It is likely that the symmetry around ruthenium(III) is close to cubic due to the presence of O-bonded \( \text{Me}_2\text{SO} \) groups and the bromides of comparable ligand field. Similar observations have been made for \([\text{RuBr}_3(\text{Me}_2\text{SO})_3] \). A band at 475 nm (\( \epsilon = 350 \)) in the electronic absorption spectrum of \([\text{RuCl}_4(\text{Me}_2\text{SO})_2] \) may be assigned to one of the \( d-d \) transitions, \( 2T_2 \rightarrow 2T_1 \) or \( 2T_2 \). The other bands of high intensity and also those of the bromo analogue may be assigned to ligand-metal charge transfer transitions.

Acknowledgements

One of the authors (UCS) thanks the UGC, New Delhi for the award of a teacher fellowship under the faculty improvement programme. The authors thank the CSIR, New Delhi for the financial grant. They thank RSIC, NEHU, Shillong for the recording of infrared spectra and UV-visible spectra. They also thank RSIC, CDRI, Lucknow for recording analytical data of the compounds and IACS, Calcutta for recording the magnetic moment. The authors thank Prof. J. Subramanian for the recording of EPR spectra and also for helpful discussion on it.

References