

A trinuclear ruthenium(II) complex with rare S,O-bridging sulfoxide ligands

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Received 19th February 1999, Accepted 1st March 1999

The trimetallic compound $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ (mpso = $\text{C}_7\text{H}_8\text{OS}$, methyl phenyl sulfoxide) **1** was prepared from hydrated RuCl_3 and methyl phenyl sulfoxide. A crystal structure determination revealed a linearly arranged molecule with three ruthenium atoms in distorted octahedral configurations with bridging chloro and S,O-mpso ligands. For the ruthenium metals with triply bridged chloro ligands, the Ru–Cl–Ru angles are 81.8(4), 82.7(1) and 83.2(1)°, and the Ru···Ru non-bonded distance is 3.218 Å. In contrast, the Ru–Cl–Ru angle on the bridging mpso part of the molecule is 100.7(1)°, and the Ru···Ru non-bonded distance is 3.686 Å. The configuration at sulfur on S2, S4 and S5 is opposite to that at S1, S3 and S6. In solution, the methyl resonances in the ^1H and ^{13}C NMR spectra of **1** are found in the δ ranges 3.81–2.70 and 49.7–44.9, respectively. The methyl resonances of the S,O-bridging mpso ligands are shifted upfield in the ^1H NMR spectrum, but furthest downfield in the ^{13}C NMR spectrum.

Introduction

The chemistry of ruthenium(II) sulfoxide complexes has been extensively studied and many investigations focussed on their potential application, especially in the areas of catalysis^{1–3} and antitumour properties.^{4,5} For instance, *cis*- $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ (dmsO = dimethyl sulfoxide) displays strong antitumour activities,^{6,7} and is also an effective catalyst for the selective autoxidation of thioethers to their sulfoxides.^{8,9} In earlier work, James and co-workers^{1,10,11} showed that trinuclear ruthenium(II) complexes of the type $[\text{RuCl}_2(\text{sulfoxide})_2]_3$, with sulfoxide ligands containing chiral centres, exhibit asymmetric hydrogenation properties under homogeneous conditions.

The characterization of the novel dinuclear complex $[\text{Ru}_2(\mu\text{-Cl})_3(\text{dmsO})_5\text{Cl}]$ **A** was important for correlating spectral data and bonding properties of S-bonded sulfoxide ligands.¹² Recently the first structurally characterized examples of S,O-bridging bidentate dimethyl sulfoxide diruthenium complexes $[\text{Ru}_2(\mu\text{-dmsO-S,O})(\mu\text{-Cl})(\mu\text{-H})(\text{dmsO-S})_4\text{Cl}_2]$ ¹³ **B** and $[\text{Ru}_2(\mu\text{-dmsO-S,O})(\mu\text{-Cl})(\text{dmsO-S})_3(\text{CO})_2\text{Cl}_3]$ ¹⁴ **C** have been reported. In the literature, incorrect structural assignments for complexes of Ru^{II} and Ru^{III} were often the result of either limited spectroscopic data and incomplete characterization or the formation of oligomers or polymeric materials.^{1,15,16} The relative importance of electronic and steric factors in determining the bonding modes of sulfoxides to soft or borderline centres, such as Ru^{II} , Ru^{III} and Rh^{III} in multinuclear compounds, is still very relevant, especially after recognizing the ability of sulfoxide ligands to utilize both the softer S and harder O donor atoms simultaneously in bonding.^{17–19} This paper reports the structure of a ruthenium complex which is representative of a trinuclear compound with sulfoxide ligands of intermediate size. We regard this compound as important in revealing additional information about bonding patterns operative in the construction of small oligomeric molecules of ruthenium with sulfoxide ligands. The novel trimetallic compound $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ (mpso = $\text{C}_7\text{H}_8\text{OS}$, methyl phenyl sulfoxide) **1** was prepared and the structure determination revealed only the third example of a compound which contains S,O-bridging sulfoxide ligands. It is also the first example where this mode of bonding is illustrated with sulfoxides other than dmsO and where two such bridges are found between two Ru atoms.

Experimental

Analytical grade chemicals were used and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (38–40% Ru) was purchased from Fluka AG. Methyl phenyl sulfoxide was synthesized according to the literature.²⁰ The method for the preparation of $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ ²¹ from commercial $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was modified for the preparation of $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$.

The infrared spectrum was recorded as a KBr pellet on a Bomem Michelson-100 FTIR spectrometer, and ^1H and ^{13}C -{H} NMR spectra were recorded on a Bruker AC300 spectrometer operating at 300.13 and 75.47 MHz, respectively. Deuterated chloroform obtained from Merck was used for spectra. Elemental analysis for C and H was performed by the Division of Energy Technology, CSIR, Pretoria, South Africa, and for S and Cl from titrations with $\text{Ba}(\text{ClO}_4)_2$ (indicator, thorin) and $\text{Hg}(\text{NO}_3)_2$ (indicator, 1,5-diphenylcarbazole), respectively.

Synthesis of $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ **1**

Hydrated RuCl_3 (1.0 g, 3.8 mmol) was dissolved in absolute ethanol (40 cm^3) and refluxed for 3 h. Addition of 1.68 g (12.0 mmol) of methyl phenyl sulfoxide caused the solution to change from blue to red and on further refluxing an orange precipitate formed. The orange precipitate proved to be insoluble in most common solvents except dichloromethane. The complex $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ **1** (0.82 g, 48% based on Ru) was recrystallized from a mixture of dichloromethane and diethyl ether. (Found: C, 37.59; H, 3.84; Cl, 15.98; S, 13.68. Calc. for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{O}_2\text{RuS}_2$: C, 37.17; H, 3.56; Cl, 15.67; S, 14.18%) IR(KBr, cm^{-1}) 1124, 1088 (S-bound mpso), 1004, 980 (S,O-bound mpso and CH_3 rock), 327, 313 (Ru–Cl terminal), 275, 261 (Ru–Cl bridging). NMR: $^1\text{H}(\text{CDCl}_3)$, relative to TMS, δ 7.90–6.90 (series of multiplet signals, 30 H, Ph), six singlets (18H, CH_3); 3.67, 3.69, 3.72 and 3.81 (S-bound, Me), 2.70 and 2.81 (S,O-bound Me); $^{13}\text{C}(\text{CDCl}_3)$, δ 48.4, 47.1, 45.6, 44.6 (S-bound, Me); 49.9, 49.1 (S,O-bound Me), signals over 4 regions 148.0, 145.3, 145.2, 145.3, 141.4 and 139.0 (*ipso*-C Ph); 131.8 (d), 131.3(d), 130.5 and 130.0 (*p*-C Ph); 128.5, 128.4 and 128.1 (very strong, *m*-C Ph); 126.3, 126.0, 125.8 (d) and 125.6 (strong, *o*-C Ph).

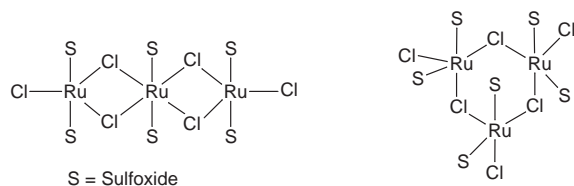


Fig. 1 Proposed structures for the trinuclear complexes $[\text{Ru}_3(\text{sulfoxide})_6\text{Cl}_6]$.

X-Ray crystallographic analysis

Crystallographic data for complex **1**, measured at 296 K with an Enraf-Nonius CAD4 diffractometer, are listed in Table 1. There was no significant crystal decay. The data were corrected for absorption (empirical, based on the azimuthal scans for nine reflections of the crystal), as well as for Lorentz-polarization effects. The structure was solved by conventional Patterson and Fourier techniques using SHELXS 86.²² All the non-hydrogen atoms were refined anisotropically,²³ and the hydrogen atoms were placed in calculated positions and refined (using a riding model) with a common isotropic thermal parameter that converged to $U_{\text{iso}} = 0.074(6) \text{ \AA}^2$. A perspective drawing of the molecule, illustrating the crystallographic numbering scheme, was prepared with ORTEP.²⁴ Atomic scattering factors were taken from ref. 25.

CCDC reference number 186/1366.

Results and discussion

The method used for the preparation of $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ was based on the procedure described for the synthesis of $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ from commercial $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.²¹ The initial reaction was done in pure mpso, as was the case in the literature for dmsO, but this presented practical problems in removing excess of mpso. Also, reactions of mpso and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in high boiling solvents such as toluene and dodecane (it was perceived that higher temperatures may be required for the reactions) were unsuccessful. Therefore, it was decided to utilize the more reactive ruthenium blue, as this alcoholic ruthenium mixture has been known as a reactive starting material for a long time.²⁶ With this starting material, an orange trinuclear complex with the composition $[\text{Ru}_3(\mu\text{-mpso-S,O})_2(\mu\text{-Cl})_4(\text{mpso-S})_4\text{Cl}_2]$ **1** was obtained in reasonable yield (48%). A similar reaction performed by James *et al.*¹ entailed adding two to four equivalents of mpso to a methanolic blue solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and refluxing under H_2 overnight. A golden product of poor solubility was isolated and the polymeric formula $[\text{Ru}(\text{mpso})_2\text{Cl}_2]_x$ assigned to it. This formulation represents a polymerization isomer of the orange complex **1** ($x = 3$). Interestingly, the preparation and characterization of analogous trimetallic complexes, $[\text{Ru}_3(\text{sulfoxide})_6\text{Cl}_6]$ (sulfoxide = mptso or mbmsO; mptso = methyl *p*-tolyl sulfoxide, mbmsO = 2-methylbutyl methyl sulfoxide) described in the same paper, were isolated from two equivalents of sulfoxide for each equivalent ruthenium. The well known bimetallic compound **A**¹² was formed by boiling *cis*- $[\text{Ru}(\text{dmsO})_4\text{Cl}_2]$ in wet toluene or in ethanol.

Earlier predictions concerning the structure of $[\text{Ru}_3(\text{sulfoxide})_6\text{Cl}_6]$ favoured five-co-ordinated ruthenium(II) species with either a linear structure containing four bridging chloro ligands or a triangular structure with three bridging chloro ligands (Fig. 1). The methyl resonances in the ^{13}C NMR spectra of complex **1** consist of six equally intense well resolved singlets spread over the range δ 3.81–2.70 for the ^1H NMR spectrum and δ 49.9–44.6 for the ^{13}C NMR spectrum, respectively. Chemical shifts of the methyl substituents in the ^1H and ^{13}C NMR are observed in characteristic regions for S- and O-bonded dmsO ligands which allows for an easy discrimination between the two bonding modes.^{27–29} Heath *et al.*¹² used

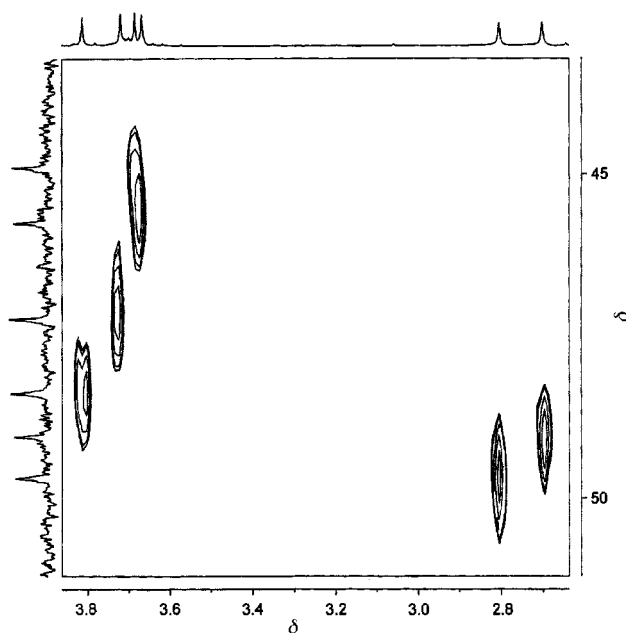


Fig. 2 2-D $\{^1\text{H}, ^{13}\text{C}\}$ one-bond HETCOR spectrum of complex **1**: methyl region.

the position of the shifts and the narrow spread of only 0.15 and 2.3 ppm in the ^1H and ^{13}C NMR spectra of **A**, respectively, as argument that all the dmsO ligands were S-co-ordinated sulfoxides. In fact, this was one of the main arguments used in disputing a proposed structure containing a bridging sulfoxide by Hudali *et al.*³⁰ for **A** in solution and was substantiated by a solid state structure determination, which revealed S-bonded dmsO ligands only.³¹ Analysing the ^1H NMR spectrum of **1**, four signals in the range δ 3.8–3.6, which are typical for S-bonded sulfoxides, and two unprecedented upfield signals at δ 2.70 and 2.81, which are typical for O-bonded sulfoxides, were observed. The shift to higher field of the two signals is even more conspicuous since Alessio and co-workers¹⁴ found chemical shifts for S,O-bonded bridging dmsO in the downfield region adjacent to the region normally allocated for S-bonded sulfoxides. Possible explanations for the unexpected shift to higher field of the two methyl resonances of the mpso ligands in **1** are either that two methyls could, due to restricted rotation in the crowded trinuclear complex, be affected by ring currents of phenyl substituents which could cause a strong localized shielding effect or that the trinuclear complex disintegrates in solution to give two O-bonded sulfoxides. We favour the first explanation as no physical or spectral evidence for the latter was observed. In fact, O-bonded sulfoxides in the ^{13}C NMR spectra are shifted upfield compared to free sulfoxides; for **1** all methyl resonances are below δ 40, suggesting that no O-bonded sulfoxides are present in the solution. Furthermore, the results of a 2-D $\{^1\text{H}, ^{13}\text{C}\}$ one-bond HETCOR experiment (Fig. 2) in the methyl region of mpso ligands of **1**, which assisted in the assignment of chemical shifts to the two different modes of coordination, indicated that the two upfield chemical shifts in the ^1H NMR spectrum correlate with the two resonances furthest downfield of the six signals observed in the ^{13}C NMR spectrum of **1**. These were intuitively assigned to the methyl groups of the S,O-bridging sulfoxide. Support for such an assignment came from Alessio and co-workers¹⁴ who observed a correlation between the furthest downfield resonances in the ^1H and ^{13}C NMR spectra of **C** and assigned these to the S,O-bridging dmsO ligand.

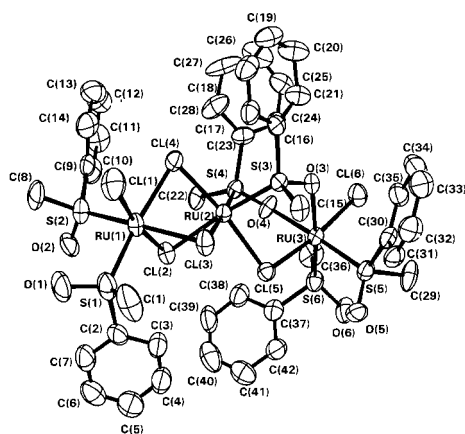
Although structural analogies for Ru–O–Ru sulfoxide bridging exist,^{32–34} the formation of di- and tri-nuclear compounds with S,O-bridging sulfoxides affects the composition of the final products as S is the “softer” and O the “harder” side of the sulfoxide ligands. Steric properties of sulfoxide ligands have

Table 1 Crystallographic data for complex **1**

Empirical formula	C ₄₂ H ₄₈ Cl ₆ O ₆ Ru ₃ S ₆
<i>M</i>	1357.2
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	15.007(2)
<i>b</i> /Å	20.644(2)
<i>c</i> /Å	17.106(2)
β /°	105.51(1)
<i>V</i> /Å ³	5107(1)
<i>Z</i>	4
<i>F</i> (000)	2712
<i>D</i> _c /g cm ⁻³	1.77
μ (Mo-K α)/cm ⁻¹	13.47
No. reflections measured	12695
No. unique reflections [<i>I</i> > 3 σ (<i>I</i>)]	7662
Parameters refined	589
Residuals: <i>R</i> , <i>R</i> '	0.056, 0.041

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Ru(1)–S(1)	2.220(3)	Ru(1)–S(2)	2.227(2)
Ru(1)–Cl(1)	2.379(3)	Ru(1)–Cl(2)	2.422(2)
Ru(1)–Cl(3)	2.484(2)	Ru(1)–Cl(4)	2.463(2)
Ru(2)–S(3)	2.204(2)	Ru(2)–S(4)	2.214(2)
Ru(2)–Cl(2)	2.446(2)	Ru(2)–Cl(3)	2.429(2)
Ru(2)–Cl(4)	2.384(2)	Ru(2)–Cl(5)	2.390(2)
Ru(3)–S(5)	2.241(2)	Ru(3)–S(6)	2.192(2)
Ru(3)–Cl(5)	2.396(2)	Ru(3)–Cl(6)	2.378(2)
Ru(3)–O(3)	2.191(5)	Ru(3)–O(4)	2.199(4)
S(1)–O(1)	1.466(6)	S(1)–C(1)	1.784(7)
S(1)–C(2)	1.804(10)	S(2)–O(2)	1.486(6)
S(3)–O(3)	1.518(5)	S(4)–O(4)	1.507(5)
S(5)–O(5)	1.448(6)	S(6)–O(6)	1.458(6)
Ru(1)–S(1)–O(1)	117.8(3)	Ru(1)–S(2)–O(2)	115.8(2)
Ru(2)–S(3)–O(3)	112.9(2)	Ru(2)–S(4)–O(4)	116.3(2)
Ru(3)–S(5)–O(5)	116.5(2)	Ru(3)–S(6)–O(6)	121.4(2)
Ru(1)–Cl(2)–Ru(2)	82.7(1)	Ru(1)–Cl(3)–Ru(2)	81.8(1)
Ru(1)–Cl(2)–Ru(2)	83.2(1)	Ru(2)–Cl(5)–Ru(3)	100.7(1)
Ru(3)–O(3)–S(3)	121.2(3)	Ru(3)–O(4)–S(4)	120.6(3)

**Fig. 3** Perspective view of complex **1** (ORTEP plot,²⁴ probability level 40%) showing the numbering scheme.

been reported and solid and circular cone angles calculated.¹⁷ Calculations showed that S-bonded sulfoxides are markedly bulkier than O-bonded ligands. This was supported by structural studies which revealed that two of the three bulky diphenyl sulfoxides in *mer*-[RuCl₃(Ph₂SO)₃] were co-ordinated through the oxygen atom. The fact that in this example two O-bonded sulfoxide ligands are found *cis* to each other underlines the importance of steric crowding and violates the normal trend set by the *trans* influence order (O < Cl < S), which affords S-bonded sulfoxides *trans* to Cl and O-bonded sulfoxide ligands.³⁵

The crystal structure of complex **1** (Fig. 3, Table 2) supports the interpretation of the spectroscopic data and displays a linearly arranged molecule with three ruthenium atoms

Table 3 Comparison of important spectral and structural data involving S,O- and S-bridging sulfoxides in ruthenium(II) complexes

Parameter	Compound		
	B ^a	C ^b	1
Bond distances/Å			
S,O-sulfoxides:			
Ru–S	2.188(2)	2.275(2)	2.209(2)
Ru–O	2.160(4)	2.122(5)	2.195(4)
S–O	1.532(4)	1.508(5)	1.513(6)
S-sulfoxides:			
Ru–S	2.256(2)	2.285(2)	2.220(3)
Ru···Ru	2.844(1)	2.979(1)	3.686(1)
NMR (δ): ^c			
CH ₃	3.37, 3.43, 3.46, 3.47, 3.49, 3.50	3.26, 3.42, 3.43, 3.44, 3.45, 3.50, 3.89, 3.92	2.70, 2.81, 3.67, 3.69, 3.72, 3.81
CH ₃	Not recorded	43.9, 44.8, 45.2, 45.9, 48.3, 48.6, 49.2, 51.8	44.6, 45.6, 47.1, 48.4, 49.1, 49.9
Infrared ($\tilde{\nu}$ /cm ⁻¹): ^d			
S=O ^e	1093, 1017, 966	1141, 1107, 1010	1124, 1088, 1004, 980

^a Ref. 13. ^b Ref. 14. ^c In CDCl₃ for **B** and **1**, CD₃NO₂ for **C**. ^d In KBr for **C** and **1**, Nujol for **B**. ^e For lower S,O-bridging sulfoxides overlap with methyl group vibrations is possible.

in distorted octahedral configurations with bridging chloro and mpso ligands. The one end, labelled Ru1, has three bridging chlorides, two terminal S-bonded sulfoxides and one terminal chloride. The central ruthenium atom, labelled Ru2, has four bridging chlorides attached to it and two bridging S-bonded mpso ligands. At the other end, labelled Ru3, two O-bonded bridging mpso, a bridging and terminal chloro and two S-bonded mpso ligand are found. Significantly, the S-bonded mpso ligands are found *trans* to the O-bonded mpso or chloro ligands which are the poorer π -acceptor ligands in the complex. Owing to the intermediate bulkiness of mpso ligand, the atoms are arranged in order to relieve steric hindrance, but still preserve the best possible electronic configuration. The arrangement is such that a neutral complex with all ruthenium atoms in formal oxidation states of II is found. The most significant features of **1** are the two S,O-bridging sulfoxide ligands. Although two structural studies of dinuclear complexes of ruthenium with S,O-bridging dmsoligands appeared recently,^{13,14} **1** is the first structure displaying two mpso bridges in ruthenium-sulfoxide chemistry. In all three examples **1**, **B** and **C** all other terminal sulfoxide ligands are S-bonded. Even though the complexes are very different, and for **1** the sulfoxide ligands are not dmsoligands, spectral and structural features relating to the S,O-bridging ligands are listed in Table 3. The three ruthenium-chloro bridges in complex **1** display Ru1–Cl–Ru2 angles of 81.8(1), 82.7(1) and 83.2(1)°, which are in keeping with other known triple halide bridged dinuclear complexes of ruthenium such as **A**³¹ and [Ru₂(PR₃)₆(μ -Cl)₃]Cl.³⁶ The Ru2–Cl5–Ru3 angle on the bridging mpso side of the molecule is 100.7(1)°, creating space for the S–O bridges and resulting in a long Ru2···Ru3 non-bonded distance of 3.686 Å, which is much larger than the values below 3 Å found in the two dinuclear complexes **B** and **C** or the observed value of 3.218 Å for Ru1···Ru2 in **1**. Although the Ru–O distances of the bridging mpso ligands [2.20(1) Å] are longer than the average values for O-bonded sulfoxides [2.13(2) Å] found in literature, the Ru–S distances [2.21(1) Å] are significantly shorter than the average values [2.27(1) Å] for S-bonded sulfoxides.^{37,38} However, this is also true for the terminal S-bonded mpso ligands [2.22(1)

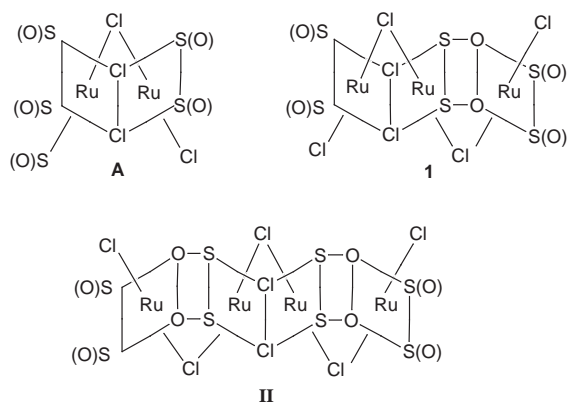


Fig. 4 Possible chain growth via S,O-bridging mpso ligands.

Å] in **1**. The terminal Ru–Cl bond distances are shorter than the Ru–Cl distances of the chloro bridge sharing the mpso bridges which in turn are shorter than the Ru–Cl distances of the three common chloride bridges. The six membered ring formed by Ru₂–S₄–O₄–Ru₃–O₃–S₃ is in a twist-boat conformation, and the relative orientation of the two pseudo axial phenyl groups on the mpso ligands is *cis*. The S–O bond lengths of the S,O-bridging mpso's of 1.518(5) and 1.507(5) Å are intermediate between the distance (average) found for the S–O bond in S- [1.478(1) Å] and O-bonded [1.538(3) Å] sulfoxide complexes of Ru^{II} and slightly longer than the distance [average, 1.492(1) Å] found in free sulfoxides.³⁸ The Ru₂–S–O angles (113, 116°) are smaller than those of Ru₃–O–S (121, 121°) in **1**, but not nearly as distorted as the Ru–O–S angle of 130.4(3)° recorded for **C**.¹⁴ The magnitude of both these types of angles corresponds well with literature values³⁸ and the smaller Ru–S–O angles should rather be ascribed to the size and position of the R substituents on the sulfur atoms. It is interesting that the configurations at sulfur atoms S₂, S₄ and S₅ are opposite to those at S₁, S₃ and S₆. Also, the S-bonded mpso ligands are always *trans* to Cl and O-bonded mpso ligands, minimizing π competition and adhering to the *trans* influence order.

Electronic effects of ligands and steric crowding will determine the composition of small, neutral oligomers containing only sulfoxide and chloride ligands. Starting from the structure of **A**, one can speculate about adding ruthenium fragments to extend the chain on progressing to a trinuclear compound by face-sharing octahedral fragments (Fig. 4). Extending the chain to the right-hand side of **A** and by making use of S,O-bridging sulfoxide ligands, structure **I** is generated when a rule of S-bonded sulfoxides *trans* to O-bonded sulfoxides or chloro ligands only is implemented. The left-hand side of **A** displays three terminal S-bonded dmsoligands which is probably not possible with the more bulky mpso ligands unless S-bonded coordination modes are converted into O-bonded sulfoxides. One is tempted to predict that for a dinuclear complex with mpso ligands the formulation [Ru₂(mpso-S)₄(μ -Cl)₃(L)Cl] (L = small neutral, π -acceptor ligand) may be favourable. Extension to the left-hand side of **A** with S,O-bridging dmsoligands is unlikely due to steric congestion. In **1** both open ends are the same and chain growth by two S,O-bridging mpso ligands and one chloro ligand (as was the case in moving from **A** to **1**) is a possibility, as depicted by **II**. However, any chain growth beyond **1** making use of S,O-bridging mpso ligands seems unlikely as a result of the distortion (see structural data of **1**) caused in the trinuclear compound on accommodating two such bridging ligands. By comparison, complex **C** represents the sharing of one side of an octahedron and belongs to a different class of compounds, whereas **B** contains a bridging hydrogen atom and is the most distorted of the three examples. To obtain a better understanding of size and electronic effects in ruthenium sulfoxide chemistry more research with ligands other than dmsoligands is needed, especially with the objective to generate small oligomers.

Surprisingly, the integrity of the dinuclear complexes **A** and **B** and the trinuclear complex **1** is retained in solution.

Acknowledgements

We are grateful to Impala Platinum for a generous donation of ruthenium trichloride.

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