Steric Properties of Sulfoxide Ligands. Synthesis and Crystal Structure of *mer*-$[RuCl_3(Ph_2SO)_3]$†

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Solid and circular cone angles and ligand profiles have been calculated for some sulfoxides, showing that S-bonded ligands are markedly bulkier than O-bonded ligands. An application of the cone angles to complexes of Ru^{II} and Ru^{III} showed that the bonding mode of sulfoxides appears to be the result of a balance between electronic and steric effects. The complex *mer*-$[RuCl_3(dpso)_3]$ (dpso = Ph_2SO) has been synthesized and structurally characterized: triclinic, space group $P\bar{1}$, $Z = 2$ with a = 10.315(3), b = 13.093(4), c = 15.692(5) Å, α = 102.98(2), β = 106.79(1), γ = 102.17(2)°. Two of the three sulfoxides are O- and one is S-bonded. One dpso-*O* is *trans* to dpso-*S*, while the other is *trans* to Cl. The co-ordination bond distances are consistent with the *trans*-influence order O < Cl < S. Strain-energy and conformational-entropy terms of three isomers of *mer*-$[RuCl_3(dpso)_3]$ have been evaluated through molecular mechanics calculations. The energy difference of 7.6 kcal mol^{-1} between the characterized complex and the linkage isomer with two *trans* dpso-*S* ligands indicates that the isomer isolated is probably favoured thermodynamically and suggests that the interligand steric interactions play an important role in the isomer stability.

The relative importance of electronic and steric factors in determining the bonding of sulfoxides through O or S to soft or borderline metal centres, such as Ru^{II}, Ru^{III} and Rh^{III}, is still an open question. Many examples of isomers, differing in the geometry and/or the binding mode of the sulfoxides, can be found in the literature.[1–4] This suggests that the difference in stability between the isomers is often rather small and that their geometry can be the result of a delicate balance between electronic and steric factors. As a general rule, in second- and third-row platinum-group metals, bonding through S is largely prevalent.[5] This has been rationalized in terms of the soft character of the co-ordinated atoms and a partial double-bond contribution in the metal-to-sulfur bond. Sulfur-bonded sulfoxides are generally found *trans* to oxygen-bonded ligands or halide ions. It has been suggested that this arrangement avoids the competition between *trans* π-accepting ligands for back donation from the metal centre.[1,3,5] Therefore, from an electronic point of view, a *cis* arrangement of two S-bonded sulfoxides is generally preferred over a *trans* one, even though this latter is sterically favoured.[6] However, there has been no systematic investigation of the role played by steric interactions among the ligands in determining the stability of the sulfoxide complexes.

In order to gain an insight into this topic we have tried to quantify the steric properties of sulfoxides through the calculation of 'cone angles'. The cone-angle concept, originally defined by Tolman for phosphine ligands,[7] has been developed and applied to other ligands, allowing a rationalization of kinetic, spectroscopic and thermodynamic data in terms of the ligand bulkiness.[8,9] Many different mathematical methods have been proposed for estimating cone angles from crystal structures.[9] We have adopted that described by Immirzi and Musco,[10] which gives rise to a generalized non-circular cone, defined by a solid angle Ω, from which an angular parameter $\Theta = 2\cos^{-1}[1 - (\Omega/2\pi)]$ is derived. This represents the Tolman ligand cone angle.[10] This method also allows the calculation of 'ligand profiles', which are useful in depicting the 'cog-like' nature of the ligands and the gaps between the ligand moieties.[11] It has been suggested that, for bulky ligands differing greatly from conic symmetry, the best cone angle is obtained by doubling the maximum semicone angle, $\theta/2$.[11] By applying Immirzi's algorithm, we have calculated the cone angle and the ligand profile for several sulfoxides, with parameters derived either from molecular models or from crystal structures.

Further information was obtained from the structure analysis of complexes containing bulky sulfoxides. According to literature data, both Ru^{III} and Rh^{III} give neutral complexes of general formula *mer*-MCl_3(sulfoxide-*S*)$_2$(sulfoxide-*O*),[2,12] with sulfoxide = dmso, tmso, mpso and dnpso.‡ However, the James' group reported that an anomaly in this series occurred with diphenyl sulfoxide (dpso), both Rh^{III}[12] and Ru^{III}[13] replacing one S-bonded sulfoxide with one molecule of alcoholic solvent to yield *mer*-$[RhCl_3$(dpso-*S*)(dpso-*O*)$(Pr^iOH)]$ and *mer*-$[RuCl_3$(dpso-*S*)(dpso-*O*)$(MeOH)]$, respectively. This result suggested that the arrangement of one dpso-*O* and two dpso-*S* molecules might be prevented by the increased steric demand of the ligand, the electronic properties being presumably not very different from those of the other sulfoxides examined. In order to test this hypothesis and establish which isomer is eventually formed with three sulfoxide molecules, we have synthesized in non-co-ordinating solvents the complex *mer*-$[RuCl_3(dpso)_3]$ and determined its crystal structure.

Finally, the role of the interligand steric interactions in the isomer stability has been investigated using molecular mechanics calculations. Strain energies and conformational entropies of three isomers of *mer*-$[RuCl_3(dpso)_3]$ have been evaluated.

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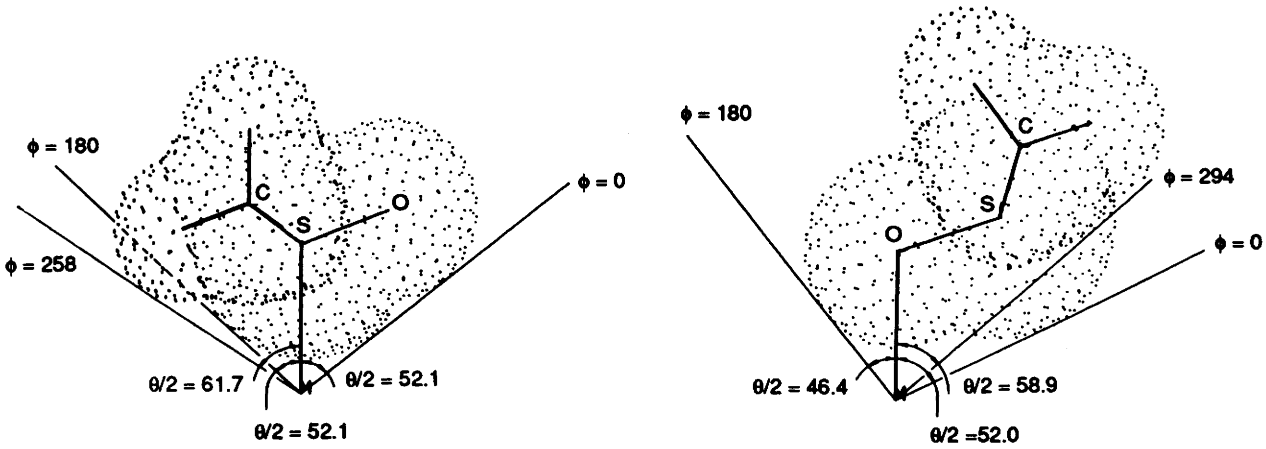
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: cal = 4.184 J.

‡ The following abbreviations are employed: dmso = Me_2SO, deso = Et_2SO, dpso = Ph_2SO, dipso = $Pr^i{}_2SO$, dnpso = $Pr^n{}_2SO$, ipmso = Pr^iMeSO, enpso = $EtPr^nSO$, pnpso = $PhPr^nSO$, eipso = $EtPr^iSO$, ippso = Pr^iPhSO, ipnpso = Pr^iPr^nSO, epso = EtPhSO, emso = EtMeSO, mpso = MePhSO, tmso = $(CH_2)_4SO$.



S-Bonded Me$_2$SO O-Bonded Me$_2$SO

Fig. 1 Definition of semicone (θ/2) and rotation (Φ) angles for S- and O-bonded dmso

Experimental

Materials.—Solvents (Baker) and diphenyl sulfoxide (Aldrich) were used as received.

Synthesis.—[RuCl$_3$(dpso)$_3$]. Hydrated RuCl$_3$ (1 g, 3.8 mmol) was dissolved in absolute ethanol (30 cm^3) and refluxed for 3 h. After concentration of the deep green solution to *ca.* 3 cm^3, 37% HCl (1 cm^3) and dpso (4.0 g, 20 mmol) were added. The mixture was warmed for 45 min until it turned bright red and clear. It was evaporated to an oil, which was then redissolved in acetone (10 cm^3). Addition of diethyl ether (5 cm^3) to the clear deep red solution induced precipitation of the product as red microcrystals upon standing overnight at room temperature. They were filtered off, washed rapidly with cold acetone and diethyl ether and vacuum dried at room temperature (r.t.). Yield 1.65 g (55%). The complex was recrystallized from dichloromethane upon addition of diethyl ether (Found: C, 52.50; H, 3.55; Cl, 12.90; S, 11.45. Calc. for $C_{36}H_{30}Cl_3O_3RuS_3$: C, 53.10; H, 3.70; Cl, 13.05; S, 11.80%). Selected IR absorption bands: ν_{SO} 1128m (dpso-*S*), 919vs (br) (dpso-*O*); ν(Ru–S) 440w; ν(Ru–O) 463m; ν(Ru–Cl) 341s cm^{-1}. Visible spectrum in CHCl$_3$ solution [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 455 (1338) and 388 (3185).

Physical Measurements.—Electronic absorption spectra were recorded in stoppered quartz cells with a Perkin-Elmer Lambda5 UV/VIS spectrophotometer, solid-state infrared spectra (KBr) on a Perkin-Elmer 983G spectrometer.

Cone-angle Calculations.—In order to obtain the Tolman cone angles, models were 'computer built', using the following bond lengths and angles: S-bonded sulfoxides, M–S 2.28, S–O 1.48, S–C 1.79, C–C (sp^3) 1.54, C–C (Ph) 1.395, C–H 1.10 Å; M–S–O 117, M–S–C 113, O–S–C 106, C–S–C 99, angles around C(sp^3) 109.5, around C(sp^2) 120°; O-bonded sulfoxides (where different), M–O 2.10, S–O 1.54 Å; M–O–S 123, O–S–C 103°. The van der Waals radii used were: S, 1.80; O, 1.52; C, 1.70; H, 1.20 Å.[14]

The atom coordinates for each model corresponded to the geometry of minimum potential energy. Conformational analysis was performed on the basis of the non-bonded atom interactions, using the TRIPOS 5.2 force-field parameters.[15] Solid angles, Ω, and the apertures of the related circular cones, Θ, were calculated by rotating around the M–X (X = S or O) bond by an angle Φ, in the range 0–360°, with a step of 2° (Fig. 1). The angular parameter Θ was taken as a measure of the Tolman cone angle.[10] Ligand profiles have also been calculated by Immirzi's procedure, deriving the maximum semicone angles, θ/2, as suggested by Ferguson and co-workers.[11] The 'minimum' semicone angles, θ/2, for S- and O-bonded sulfoxides, were 52.1 (Φ = 0) and 46.4° (Φ = 180°), respectively.

Calculated values for some models are reported in Tables 1 and 2. Selected ligand profiles are shown in Fig. 2, together with a sketch of the metal–ligand fragments, viewed down the X–M bond (X = S or O), and the atomic van der Waals contours.

Values calculated for actual crystal structures are given in Tables 3 and 4 for S- and O-bonded ligands, respectively. Calculations were performed by adopting either fixed metal–ligand distances of 2.28 and 2.10 Å for M–S and M–O, respectively (figures in italics) or the actual X-ray-determined co-ordination distances (figures in bold). The positions of the hydrogen atoms were calculated assuming staggered conformations. The complexes presented in Tables 3 and 4 have been selected from the available data to represent different co-ordination and conformational environments.[1,2,16–29]

Local programs in QuickBasic 4.5 were used for model building, conformational analysis and cone-angle calculations.

Molecular Mechanics Calculations.—Calculations were performed on an Evans-Sutherland PS 390 graphic station, on line with a MicroVAX 2000 computer by using the program SYBYL[30] and the TRIPOS 5.2 force field.[15] The total strain energy, E_{st} was taken as the sum of the deformation terms for bond lengths (E_{str}), valence angles (E_{bend}), torsion angles (E_{tor}), and out-of-plane displacements (E_{oop}), besides the non-bonded (E_{vdw}) interactions [equations (1)–(6)]. Here k^d_i, k^θ_i and k^δ_i are

$$E_{st} = \Sigma(E_{str} + E_{bend} + E_{tor} + E_{oop} + E_{vdw}) \quad (1)$$

$$E_{str} = \tfrac{1}{2}k^d_i(d_i - d^0_i)^2 \quad (2)$$

$$E_{bend} = \tfrac{1}{2}k^\theta_i(\theta_i - \theta^0_i)^2 \quad (3)$$

$$E_{tor} = \tfrac{1}{2}V_i[1 + s_i \cos(|n_i|\varphi_i)] \quad (4)$$

$$E_{oop} = \tfrac{1}{2}k^\delta_i\delta_i^2 \quad (5)$$

$$E_{vdw} = E_{ij}(a_{ij}^{-12} - 2a_{ij}^{-6}),\ a_{ij} = r_{ij}/(R_i + R_j) \quad (6)$$

the force constants for bond length, valence angle and out-of-plane deformations, respectively, d^0_i, θ^0_i are the respective strain-free values, δ_i is the distance of atom *i* from the plane of its substituents, V_i and n_i represent the torsional barrier and the periodicity of the rotation, respectively with $s_i = +1$ when the minimum energy corresponds to staggered or -1 for eclipsed conformations, E_{ij} terms are given by the geometrical mean of the k_i^{vdw} constants[15] associated with each atom type, r_{ij} is the distance between the non-bonded atoms, while R_i and R_j are their van der Waals radii.

Since TRIPOS 5.2 does not contain the force-field parameters for ruthenium, the strain-free values around the metal, d^0 and θ^0 (Table 5), were estimated by averaging the available literature data for ruthenium(III) sulfoxide complexes [31] and assuming an idealized octahedral geometry. The corresponding stretching, k^d, and bending, k^θ, values were calculated for *i–j* bonds and *i–j–k* angles by using the parameters proposed by Herschbach and Laurie [32] for Badger's rule [33] $k^d{}_{ij} = [(A_{ij} - D_{ij})/(d^0{}_{ij} - D_{ij})]^3$ and the Halgren equation [34] $k^\theta{}_{ijk} = 1.75Z_iC_jZ_k(d_{ij} + d_{jk})^{-1}(\theta^0)^{-2}\cdot\exp[-2(d_{ij} - d_{jk})^2/(d_{ij} + d_{jk})^2]$. For bonds between third-period (X′) and second-transition-series elements (M′), for which the *A* and *D* parameters were not available, the constants were evaluated from known structural and spectroscopic data,[31,35] combining the previous expressions with the usual relationship between force constants and stretching frequencies:[36] $k^0{}_{ij} = 5.1 \times 10^{19}(\mu_{ij}\nu^2)$ kcal mol^{-1} Å^{-2}, where μ_{ij} is the reduced mass (g) of the *i–j* system and ν is the harmonic stretching frequency (cm^{-1}), obtained by IR spectroscopy. By using the above equations we derived the constants $A_{M'-X'} = 2.73$ and $D_{M'-X'} = 1.05$. Constants *C* and *Z* for Ru were obtained from known structural data and spectroscopic data [37] $C = 0.11$ and $Z = 2.47$.

As is usual in transition-metal complex force fields,[38] non-bonded interactions involving the metal centre were neglected, as were the torsional contributions around the metal–ligand bonds. Parameters for the TRIPOS 5.2 force field with the 'metal dependent' values are given in Table 5.

Three isomers of the *mer*-[RuCl$_3$(dpso)$_3$] system, *mer,cis*-[RuCl$_3$(dpso-*S*)(dpso-*O*)$_2$] **1**, *mer,trans*-[RuCl$_3$(dpso-*S*)$_2$(dpso-*O*)] **2** and *mer,cis*-[RuCl$_3$(dpso-*S*)$_2$(dpso-*O*)] **3** have been analysed. The potential-energy surfaces for these compounds were explored using the SEARCH routine of SYBYL.[30] This routine allows calculation of the strain energy as the conformation of the molecule is varied through torsional angle rotations. There are 11 degrees of torsional freedom for the [RuCl$_3$(dpso-*S*)(dpso-*O*)$_2$] isomer and 10 for the *cis* and *trans* isomers of [RuCl$_3$(dpso-*S*)$_2$(dpso-*O*)]. The rotation step used for the torsional angles was 30°. Conformers with negative energy were used as starting geometries for the energy minimization. Owing to the high number of conformers, only those differing more than 30° in one torsional angle were taken into account. The conjugate-gradient method was used to perform the energy minimization, till the convergence criterion of 0.01 cal mol^{-1} was reached. The consistency of the force field is shown by the acceptably low standard deviations of the differences between observed and calculated bond lengths (σ_b) and angles (σ_a) for isomer **1**. The values are $\sigma_b = 0.013$ Å (0.015 Å considering only distances involving Ru) and $\sigma_a = 2.56°$ (3.23° considering only angles involving Ru).

The dramatic difference in the number of possible low-energy conformers among the three isomers shown by SEARCH suggested the opportunity to evaluate an entropy term related to the conformational freedom of the complexes. The entropy associated with internal rotation, which is the rotation about a single bond of one group against another, depends upon the moment of inertia and symmetry of the rotating group, the temperature, and the shape of the energy barrier to rotation. Such conformational entropies for restricted internal rotation, S_{co}, were derived from the entropy terms due to free internal rotations, S_{fr}, and strain-energy terms, obtained from the analysis of the conformational space, as explored by means of SEARCH. The parameter S_{fr} can be calculated, for high values of reduced moments of inertia, by using the relation [39] $S_{fr} = R(\ln Q_{fr} + 0.5)$ where *R* is the gas constant and Q_{fr} is the partition function of free rotation. The classical expression [40] for Q_{fr} is $Q_{fr} = 0.363\ (IT)^{\frac{1}{2}}/n$ where *T* is the temperature in K, *n* the symmetry number of the internal rotation and *I* the reduced moment of inertia. The latter was calculated by the approximate method of Pitzer and co-workers,[41] being expressed in g Å^2 mol^{-1}. The S_{co} terms were then evaluated by using the expression $S_{co} = -(S_{fr}/\ln N)\ \Sigma^N_{i=1}p_i\ln p_i$ derived from Boltzmann's well known entropy relation,[42] where *N* is the number of rotamers examined in the conformer space and p_i is the Boltzmann probability of conformer *i*, calculated as $\exp(-E_{st_i}/RT)/\Sigma^N_{i=1}\exp(-E_{st_i}/RT)$, E_{st_i} being the strain energy of the *i*th conformer. The pseudo-Boltzmann function of S_{co} assumes the value S_{fr} when all *N* rotamers have the same energy (free internal rotation) and 0 when the conformational freedom is lost (complete freezing of the internal rotations).

Crystallography for mer-[RuCl$_3$(dpso)$_3$].—*Crystal data.* $C_{36}H_{30}Cl_3O_3RuS_3$, $M = 814.26$, triclinic, space group $P\bar{1}$, $a = 10.315(3)$, $b = 13.093(4)$, $c = 15.692(5)$ Å, $\alpha = 102.98(2)$, $\beta = 106.79(1)$, $\gamma = 102.17(2)°$, $U = 1889(1)$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\ 69$ Å), $Z = 2$, $D_c = 1.43$ g cm^{-3}, $F(000) = 826$. Crystal dimensions 0.3 × 0.3 × 0.4 mm, μ(Mo-Kα) = 8.12 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω-scan width = 0.85 + 0.35 tan θ, ω-scan speed 1–7° min^{-1}, graphite-monochromated Mo-Kα radiation, 9419 reflections measured ($2.0 \leqslant \theta \leqslant 28.0°$, $\pm h$, $\pm k$, l), 5992 unique with $I > 3\sigma(I)$ after empirical (ψ scans) absorption correction (maximum, minimum transmission factors = 0.950, 0.999).

Structure analysis and refinement. Heavy-atom method. Electron-density maps showed that one phenyl group was disordered, essentially occupying two positions. Owing to the difficulties in refining some atoms of this group, these were held fixed and only their thermal parameters were isotropically refined. Hydrogen atoms were located at calculated positions and not refined, with thermal parameters = $1.3B_{eq}$ of the bonded carbon atom. Hydrogen atoms of the disordered phenyl group were not included. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, with the exception of the disordered phenyl group. The weighting scheme $w = 1/[1 + \sigma(|F_o|)^2 + (0.02|F_o|)^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ were 0.058 and 0.083, goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(m - n)] = 0.66$, with m = number of observables and n = number of variables (397). Atomic scattering factors and anomalous dispersion terms were those of the program package MOLEN.[43] The positional parameters are listed in Table 8. Selected bond lengths and angles in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Steric Parameters.—Inspection of the calculated cone angles for S-bonded sulfoxides (Table 1) shows that they increase with substitution of the methyl groups by bulkier groups, such as ethyl, phenyl and propyl. Maximum semicone angles, θ/2, do not show the same trend as Ω and Θ. This is to be expected, since they are determined by the most protruding atom, while Ω and Θ derive from a contribution of all the outermost atoms. Therefore, cone angles calculated from the maximum semicone angles, 2θ/2, are markedly larger than the Θ values. In our opinion they do not appear appropriate for a measure of the overall sulfoxide bulkiness, unless the metal centre environment is such as to allow free rotation around the metal–ligand bond. In actual compounds the other ligands will hinder free rotation, so that the overall ligand encumbrance is reduced and better measured by Θ.

Comparison of data in Tables 1 and 2 shows that cone angles for S-bonded sulfoxides are markedly larger than those of the corresponding O-bonded sulfoxides, in spite of the

Table 1 Solid cone angles (Ω/sr), circular cone apertures (Θ/°), and 'maximum' ($\frac{\theta}{2}$/°) semicone angles, at Φ/° for metal S-bonded sulfoxide molecular models (M–S 2.28 Å)

RR'SO ligand	R	R'	Ω	Θ	$\theta/2$	Φ
tmso	CH_2	CH_2	2.68	110.1	63.2	144
dmso	Me	Me	2.75	111.6	61.7	258
emso	Et	Me	3.11	119.3	85.9	264
mnpso	Me	Pr^n	3.13	119.8	85.6	98
mpso	Me	Ph	3.15	120.1	90.7	140
dpso	Ph	Ph	3.35	124.4	93.4	236
ipmso	Pr^i	Me	3.41	125.6	92.8	134
deso	Et	Et	3.46	126.6	85.8	264
enpso	Et	Pr^n	3.48	127.1	85.7	98
dnpso	Pr^n	Pr^n	3.51	127.6	85.8	264
epso	Et	Ph	3.64	130.2	91.7	224
pnpso	Ph	Pr^n	3.64	130.2	91.7	224
eipso	Et	Pr^i	3.70	131.5	93.4	124
ippso	Pr^i	Ph	3.88	135.0	92.7	134
ipnpso	Pr^i	Pr^n	3.90	135.4	93.2	128
dipso	Pr^i	Pr^i	4.16	140.6	93.2	232

Table 2 Solid cone angles (Ω/sr), circular cone apertures (Θ/°), and 'maximum' ($\frac{\theta}{2}$/°) semicone angles, at Φ/° for metal O-bonded sulfoxide molecular models (M–O 2.10 Å)

RR'SO ligand	R	R'	Ω	Θ	$\theta/2$	Φ
tmso	CH_2	CH_2	2.18	98.4	55.4	284
mpso	Me	Ph	2.23	99.6	59.0	298
dmso	Me	Me	2.26	100.4	58.9	296
pnpso	Ph	Pr^n	2.28	100.8	58.5	292
dpso	Ph	Ph	2.53	106.7	70.4	94
epso	Et	Ph	2.55	107.1	78.8	304
emso	Et	Me	2.66	109.5	75.4	76
mnpso	Me	Pr^n	2.66	109.5	75.7	76
ipmso	Pr^i	Me	2.74	111.3	75.9	74
ippso	Pr^i	Ph	2.76	111.8	74.8	302
deso	Et	Et	3.12	119.4	77.1	76
enpso	Et	Pr^n	3.12	119.5	75.8	82
ipnpso	Pr^i	Pr^n	3.14	119.9	76.1	56
dnpso	Pr^n	Pr^n	3.20	121.2	78.0	80
eipso	Et	Pr^i	3.20	121.3	77.5	66
dipso	Pr^i	Pr^i	3.25	122.3	76.1	290

reduction of the metal co-ordination bond distance in the second case.

Another interesting feature is the marked difference between $\theta^0/2$ (the minimum semicone angle, given by the sulfur or oxygen atom) and $\theta/2$ (the maximum semicone angle due to a hydrogen atom of a side group), due to the lack of conic symmetry in sulfoxides. Figs. 2 and 3 show that the 'distorted' ligand profiles are the consequence of the 'non-regular' shape of the ligands.

It is worthy of note that the cone angles reported in Tables 3 and 4 for 'real' structures with the fixed metal–ligand distances (in italics) differ only by a few degrees in Θ from those calculated for the models (Tables 1 and 2). Larger differences can be observed when 'real' co-ordination distances are taken into account (figures in bold in Tables 3 and 4), especially when complexes with different metal atoms are compared. Therefore, the data of Tables 1 and 2 provide a scale of cone angles for the sulfoxide ligands within a series of complexes of the same metal atom and oxidation state.

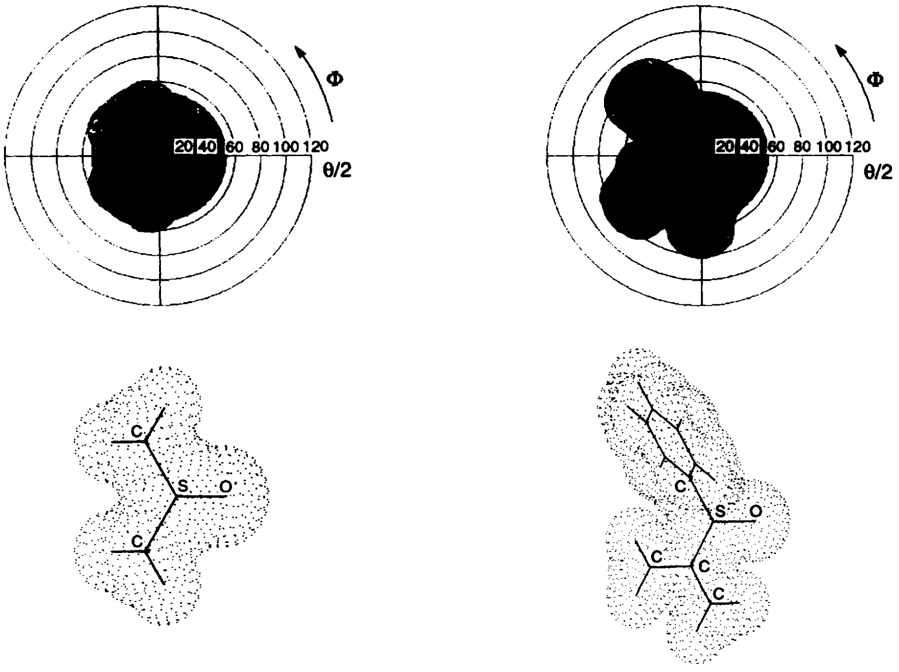
An interesting application of the sulfoxide cone angles is shown in Fig. 4, a plot of the sums of the solid angles Ω of the six ligands around the metal atom ($\Sigma\Omega$) calculated for several octahedral ruthenium sulfoxide complexes reported in the literature. For each compound the $\Sigma\Omega$ values were calculated for all possible linkage isomers, namely compounds differing only in the manner in which the sulfoxide ligands are bonded to Ru. Solid circles represent the isomers isolated to date. The value of $\Sigma\Omega$, which can be assumed as a measure of the overall steric crowding around the metal centre, increases with the number of S-bonded sulfoxides. It is apparent that points representative of known isomers for the complexes of Ru^{II} and Ru^{III} lie approximately on two different horizontal lines. These lines represent the 'experimental' mean $\Sigma\Omega$ values, 15.0(1) and 14.2(2) for Ru^{II} and Ru^{III}, respectively. The higher mean $\Sigma\Omega$ value for Ru^{II} compared to Ru^{III} can be attributed both to the larger ionic radius of Ru^{II} and to the 'softer' nature of Ru^{II}, favouring S-bonded sulfoxides and allowing more crowded geometries. The remaining points, denoted by open circles, can be divided into two groups: points above the line, and points below the line. Those above represent potential isomers which are probably destabilized by steric factors, since the $\Sigma\Omega$ are higher than the 'experimental' mean $\Sigma\Omega$ values. Points below the line correspond to linkage isomers with a high number of O-bonded sulfoxides. These complexes, although sterically not strained, are not observed, presumably because the Ru–O bond is electronically less favoured than is the Ru–S. This suggests that the formation of the stable linkage isomer can be the result of a delicate balance between electronic and steric factors. In Fig. 4 it is possible to recognize two outliers, within the isolated isomers, corresponding to *cis,cis,trans*-[$Ru^{II}Cl_2(CO)_2$(dmso-*S*$)_2$] and *trans*-[$Ru^{III}Cl_4$(dnpso-*S*$)_2$]. These are characterized by the presence of only two sulfoxide ligands in *trans* position. This probably permits a partial relief of steric interactions and consequently a higher $\Sigma\Omega$ value.

Molecular Mechanics Calculations.—The number of conformers with negative energy obtained by SEARCH analysis for the three isomers of *mer*-[$RuCl_3$(dpso$)_3$], *i.e. mer,cis*-[$RuCl_3$(dpso-*S*)(dpso-*O*$)_2$] **1**, *mer,trans*-[$RuCl_3$(dpso-*S*$)_2$(dpso-*O*)] **2** and *mer,cis*-[$RuCl_3$(dpso-*S*$)_2$(dpso-*O*)] **3**, are reported in Table 6. It is worthwhile to note that the number of conformers obtained for **1** (the isolated compound) is considerably larger than that found for the other two isomers. This is due both to the larger number of free torsional angles (11 in **1** *vs.* 10 in **2** and **3**) and to the less-crowded co-ordination of ligands in **1** compared to **2** and **3** (**1** < **2** < **3**). The conformational freedom of **1** suggests that this system has a higher conformational entropy with respect to **2** and **3**. Considering only free internal rotations, the difference of one degree of freedom between **1** and the other two isomers leads to an increase of the $-TS_{fr}$ term of about 3.4 kcal mol^{-1} at 300 K. The calculated conformational entropy S_{co} (Table 6), which takes into account also the conformational restrictions due to steric interactions by the Boltzmann distribution of the rotamers, shows a difference in $-TS_{fr}$ at 300 K of 5.5 and 6.4 kcal mol^{-1} between the isomers **1** and **2**, and **1** and **3**, respectively. The total strain energy E_{st}, for the minimum-energy conformers obtained by the minimization procedure, is lower in **1** than in **2** and in **3** by 2.1 and 6.5 kcal mol^{-1}, respectively.

Even if the absolute energies in Table 6 have no physical meaning, energy differences among closely related molecules can give important information. Inspection of the data shows that isomer **1** is probably the thermodynamically stable one, as is also suggested by the synthetic preparation of the complex which involves rather high temperatures. The differences in energies $E_{st} - TS_{co}$ between **1** and **2** and **3** are 7.6 and 12.8 kcal mol^{-1}, respectively. These differences give a measure of the interligand steric interactions.

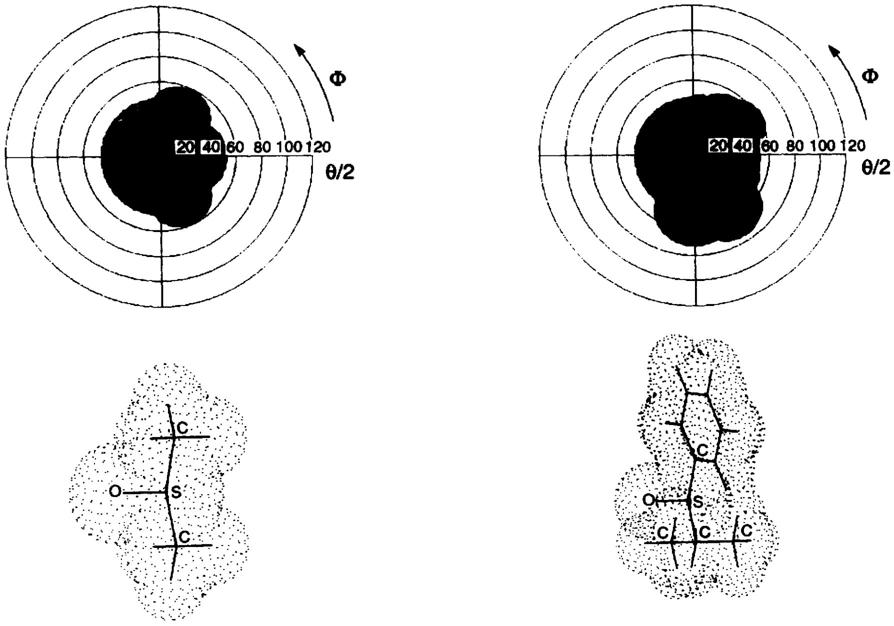
According to what is observed with less bulky sulfoxides,[2,12] either isomer **2** or **3** should be favoured by electronic considerations. On the contrary, in the dpso derivative, steric factors are responsible for the bonding mode of the ligands in the thermodynamically stable isomer.

Crystal Structure.—The X-ray analysis results confirmed the spectroscopic evidence of a *mer* arrangement of the three chlorides and the presence of both S- and O-bonded diphenyl sulfoxides, showing that two are O- and one is S-bonded. One dpso-*O* is *trans* to dpso-*S*, the other is *trans* to Cl (Fig. 5). This is



(a) (b)

Fig. 2 Ligand profiles for S-bonded sulfoxides: (*a*) Me_2SO and (*b*) Pr^iPhSO. A sketch of the ligand (some of the H and C atoms overlap), viewed down the metal–sulfur bond, with the atomic van der Waals contours, is also shown



(a) (b)

Fig. 3 Ligand profiles for O-bonded sulfoxides: (*a*) Me_2SO and (*b*) Pr^iPhSO. A sketch of the ligand, viewed down the metal–oxygen bond, with the atomic van der Waals contours, is also shown

the first example of a ruthenium complex showing an excess of O- over S-bonded sulfoxides, the analogous dmso derivative being *mer,trans*-$[RuCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$.

The arrangement of dpso-*S* is such that its oxygen atom, O(1), is nearly eclipsed with O(2), while the corresponding dpso-*O* ligand is rotated so as to move away the two phenyl groups, the O(2)–S(2) bond nearly bisecting the O(3)–Ru–Cl(3) angle. The orientation of the second dpso-*O* is such that O(3)–S(3) bisects the Cl(1)–Ru–Cl(2) bond angle.

Interestingly, the Ru–Cl bond distance *trans* to O [2.307(2) Å] is significantly shorter than that *trans* to Cl [average 2.331(9) Å]. The same trend [2.301(1) *vs.* 2.328(16) Å] has been observed in *mer*-$[RuCl_3(dpso\text{-}S)(dpso\text{-}O)(MeOH)]$[13] showing that dpso-*O* and MeOH have a similar *trans* influence and supporting the suggestion that this is weaker than that of Cl.[3,13] On the other hand, the Ru–O distance *trans* to S [2.114(5) Å] is longer than that *trans* to Cl [2.091(6) Å]. A similar situation [2.122(2) *vs.* 2.094(3) Å] was found in $[RuCl_3(dpso\text{-}S)(dpso\text{-}O)(MeOH)]$.[13]

Table 3 Solid cone angles (Ω/sr), circular cone apertures (Θ/°) and 'minimum' ($\frac{\theta^0}{2}$/° at $\Phi = 0°$) and 'maximum' ($\frac{\theta}{2}$/° at Φ/°) semicone angles for metal S-bonded sulfoxide complexes (calculated values, with M–S 2.28 Å in italic; with crystallographic M–S distances in bold)

Ligand	Complex *	Ω	Θ	θ⁰/2	θ/2	Φ	Ref.
tmso	*cis*-[RuCl$_2$(tmso-*S*)$_4$]	*2.68*	*110.1*	*52.6*	*65.1*	*222*	2
		2.69	*110.3*	*52.5*	*65.5*	*222*	
		2.75	*111.5*	*52.4*	*70.1*	*230*	
		2.77	*112.0*	*52.5*	*70.4*	*234*	
		2.70	**110.4**	**52.7**	**65.2**	**222**	
		2.71	**110.7**	**52.6**	**65.6**	**222**	
		2.60	**108.2**	**51.3**	**68.9**	**230**	
		2.61	**108.5**	**51.3**	**69.0**	**234**	
	cis-[PtCl$_2$(tmso-*S*)$_2$]	*2.80*	*112.6*	*53.3*	*68.7*	*126*	16
		2.81	*112.9*	*52.6*	*68.6*	*128*	
		2.87	**114.2**	**53.8**	**69.3**	**126**	
		2.93	**115.5**	**53.9**	**69.5**	**128**	
dmso	*trans,cis*-[RhCl$_2$(dmso-*S*)$_2$(dmso-*O*)$_2$]	*2.81*	*113.0*	*52.4*	*65.1*	*216*	17
		2.77	*112.0*	*54.2*	*63.3*	*144*	
		2.87	**114.2**	**53.0**	**65.5**	**216**	
		2.80	**112.7**	**54.5**	**63.5**	**144**	
	trans-[RuCl$_2$(dmso-*S*)$_4$]	*2.70*	*110.5*	*54.5*	*61.2*	*142*	1
		2.57	**107.6**	**53.3**	**60.2**	**142**	
	cis,fac-[RuCl$_2$(dmso-*S*)$_3$(dmso-*O*)]	*2.75*	*111.7*	*52.1*	*65.1*	*142*	1
		2.76	*111.8*	*52.1*	*65.5*	*218*	
		2.71	*110.6*	*53.0*	*62.3*	*216*	
		2.83	**113.3**	**53.3**	**65.7**	**142**	
		2.78	**112.1**	**52.3**	**65.6**	**218**	
		2.70	**110.4**	**52.9**	**62.3**	**216**	
	fac-[Ru(dmso-*S*)$_3$(dmso-*O*)$_3$]$^{2+}$	*2.73*	*111.0*	*54.2*	*63.5*	*144*	18
		2.79	*112.5*	*52.1*	*65.2*	*216*	
		2.70	*110.5*	*54.4*	*63.4*	*142*	
		2.77	**112.0**	**54.5**	**63.8**	**144**	
		2.89	**114.6**	**53.6**	**65.9**	**216**	
		2.74	**111.4**	**54.8**	**63.8**	**142**	
	cis-[PtCl$_2$(dmso-*S*)(py)]	*2.84*	*113.6*	*52.3*	*66.0*	*144*	19
		3.00	**117.1**	**54.6**	**67.2**	**144**	
	cis-[Pt(dmso-*S*)$_2$(dmso-*O*)$_2$]$^{2+}$	*2.87*	*114.3*	*52.1*	*66.6*	*218*	20
		2.79	*112.6*	*54.5*	*63.4*	*216*	
		3.04	**117.9**	**54.6**	**67.8**	**218**	
		2.96	**116.1**	**55.8**	**64.7**	**216**	
	trans-[Pd(O$_2$CCF$_3$)$_2$(dmso-*S*)(dmso-*O*)]	*2.84*	*113.6*	*53.0*	*65.4*	*142*	21
		2.83	*113.4*	*53.1*	*65.7*	*218*	
		3.01	**117.3**	**54.8**	**66.7**	**142**	
		2.99	**116.8**	**54.6**	**66.9**	**218**	
emso	*cis*-[PtCl$_2$(emso-*S*)$_2$]	*3.23*	*121.9*	*52.1*	*88.0*	*100*	22
		3.17	*120.7*	*52.2*	*86.6*	*264*	
		3.31	**123.4**	**53.2**	**88.7**	**100**	
		3.21	**121.5**	**52.7**	**86.9**	**264**	
mpso	*cis*-[PtCl$_2$(mpso-*S*)$_2$]	*3.16*	*120.4*	*53.1*	*89.0*	*148*	23
		3.19	*121.1*	*53.8*	*91.7*	*144*	
		3.24	**122.1**	**53.7**	**89.7**	**148**	
		3.29	**123.0**	**54.5**	**92.6**	**144**	
dpso	*mer,cis*-[RuCl$_3$(dpso-*S*)(dpso-*O*)$_2$]	*3.15*	*120.2*	*54.1*	*79.0*	*208*	This work
		3.22	**121.6**	**54.6**	**79.5**	**208**	
	mer-[RuCl$_3$(dpso-*S*)(dpso-*O*)(MeOH)]	*3.18*	*120.8*	*56.1*	*82.7*	*142*	13
		3.27	**122.6**	**56.8**	**83.5**	**142**	
	[PtCl$_3$(dpso-*S*)]$^-$	*3.33*	*124.0*	*52.1*	*91.9*	*140*	24
		3.50	**127.4**	**54.6**	**93.5**	**140**	
		3.41	*125.5*	*52.1*	*90.5*	*212*	23
		3.55	**128.5**	**54.4**	**91.9**	**212**	
deso	[PtCl$_3$(deso-*S*)]$^-$	*3.22*	*121.7*	*52.1*	*87.9*	*98*	25
		3.38	**125.0**	**54.6**	**89.4**	**98**	
	[PtBr$_3$(deso-*S*)]$^-$	*3.23*	*121.9*	*52.1*	*89.0*	*98*	26
		3.37	**124.8**	**54.3**	**90.3**	**98**	
dnpso	*cis*-[PtCl$_2$(dnpso-*S*)$_2$]	*3.56*	*128.6*	*52.7*	*85.6*	*268*	22
		3.60	**129.4**	**52.7**	**86.0**	**268**	
		3.39	*125.2*	*53.2*	*84.0*	*260*	
		3.46	**126.6**	**53.2**	**84.6**	**260**	
	trans-[PtCl$_2$(dnpso-*S*)$_2$]	*3.49*	*127.1*	*52.2*	*85.0*	*94*	27
		3.46	**126.6**	**52.0**	**84.7**	**94**	
	trans-[RuCl$_4$(dnpso-*S*)$_2$]$^-$	*3.35*	*124.4*	*52.1*	*80.6*	*92*	13
		3.15	**120.5**	**50.0**	**78.6**	**92**	

* py = Pyridine.

Table 4 Solid cone angles (Ω/sr), circular cone apertures (Θ/°) and 'minimum' ($\frac{\theta^0}{2}$/° at Φ = 180°) and 'maximum' ($\frac{\theta}{2}$/°) semicone angles for metal O-bonded sulfoxide complexes (calculated values, with M–O 2.10 Å in italic; with crystallographic M–O distances in bold)

Ligand	Complex*	Ω	Θ	$\theta^0/2$	$\theta/2$	Φ	Ref.
tmso	*trans*-$[Fe(tpp)(tmso\text{-}O)_2]^+$	*2.35*	*102.6*	*49.3*	*71.7*	*62*	28
		2.37	*103.0*	*52.3*	*71.2*	*300*	
		2.38	**103.2**	**49.5**	**71.9**	**62**	
		2.43	**104.4**	**52.8**	**71.8**	**300**	
	$[Cu(tmso\text{-}O)_4][Cu_2Br_6]$	*2.41*	*104.0*	*53.6*	*72.5*	*62*	29
		2.15	*97.7*	*51.5*	*55.7*	*284*	
		2.76	**111.9**	**56.3**	**75.1**	**62**	
		2.47	**105.3**	**54.2**	**57.7**	**284**	
dmso	*trans,cis*-$[RhCl_2(dmso\text{-}S)_2(dmso\text{-}O)_2]$	*2.27*	*100.6*	*46.4*	*66.0*	*300*	17
		2.34	*102.2*	*46.4*	*60.8*	*66*	
		2.30	**101.4**	**46.9**	**66.3**	**300**	
		2.37	**103.0**	**47.0**	**61.1**	**66**	
	cis,fac-$[RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)]$	*2.32*	*101.9*	*46.4*	*64.6*	*64*	11
		2.27	**100.5**	**45.4**	**64.1**	**64**	
	fac-$[Ru(dmso\text{-}S)_3(dmso\text{-}O)_3]^{2+}$	*2.29*	*101.1*	*46.4*	*61.7*	*294*	18
		2.16	*97.9*	*46.4*	*59.5*	*68*	
		2.37	*103.0*	*46.4*	*72.7*	*56*	
		2.26	**100.4**	**45.9**	**61.4**	**294**	
		2.09	**96.4**	**45.3**	**59.1**	**68**	
		2.33	**102.0**	**45.8**	**72.4**	**56**	
	cis-$[Pt(dmso\text{-}S)_2(dmso\text{-}O)_2]^{2+}$	*2.28*	*100.8*	*46.4*	*62.0*	*66*	20
		2.28	*100.8*	*46.4*	*66.6*	*298*	
		2.36	**102.8**	**47.8**	**62.7**	**66**	
		2.39	**103.4**	**48.2**	**67.4**	**300**	
	trans-$[Pd(O_2CCF_3)_2(dmso\text{-}S)(dmso\text{-}O)]$	*2.42*	*104.0*	*46.4*	*71.3*	*300*	21
		2.39	*103.5*	*46.4*	*70.5*	*60*	
		2.46	**105.0**	**47.0**	**71.7**	**300**	
		2.51	**106.1**	**48.2**	**71.4**	**60**	
dpso	*mer,cis*-$[RuCl_3(dpso\text{-}S)(dpso\text{-}O)_2]$	*2.66*	*109.7*	*46.4*	*70.9*	*266*	This work
		2.64	**109.1**	**46.0**	**70.6**	**266**	
	mer-$[RuCl_3(dpso\text{-}S)(dpso\text{-}O)(MeOH)]$	*2.33*	*102.1*	*46.4*	*69.5*	*330*	13
		2.30	**101.3**	**45.7**	**69.2**	**330**	

* H_2tpp = 5,10,15,20-Tetraphenylporphyrin.

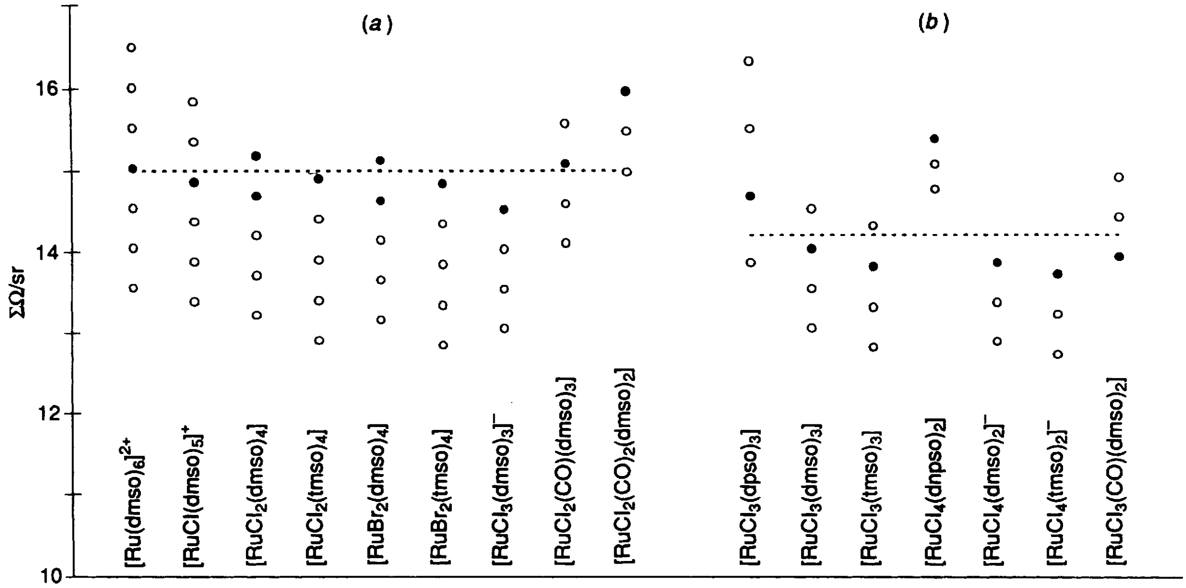


Fig. 4 Sums of Ω for the six co-ordinated ligands, ΣΩ, for several octahedral ruthenium sulfoxide complexes. For a given compound, ΣΩ calculated for all possible linkage isomers lie in the same column. Solid circles represent the so far characterized isomers. The lines of the mean ΣΩ values of the observed isomers for complexes of Ru^{II} (*a*) and Ru^{III} (*b*) are also shown. The Ω values (Cl, 2.09; Br, 2.06; and CO, 3.14 sr) were calculated using the bond lengths Ru–Cl 2.35; Ru–Br 2.50; and Ru–CO 1.84 Å and the van der Waals radii 1.75 (Cl), 1.85 (Br) and 1.70 Å (C)

This is in agreement with the *trans*-influence order O < Cl < S, observed also in rhodium(III) complexes.[3]

The lengthening of the Ru–O bond distance *trans* to Cl with respect to the analogous distances found in *mer,trans*-$[RuCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$[2.077(3) Å][45] and in *mer,cis*-$[RuCl_3(dmso\text{-}S)(dmso\text{-}O)(NH_3)]$ [2.070(2) Å][46] is probably due to steric interactions. The Ru–S(1) bond length of 2.251(2) Å is slightly longer than the analogous distance of 2.239(1) Å in *mer*-[$RuCl_3$(dpso-*S*)(dpso-*O*)(MeOH)].[13]

Conclusion

In spite of all the shortcomings intrinsic in the cone-angle definition for sulfoxides, parameters like Ω and Θ can be used to quantify the steric properties of such ligands, providing a rough measure of their bulkiness. Our results show that S-bonded sulfoxide ligands have cone angles significantly larger than the corresponding O-bonded ones.

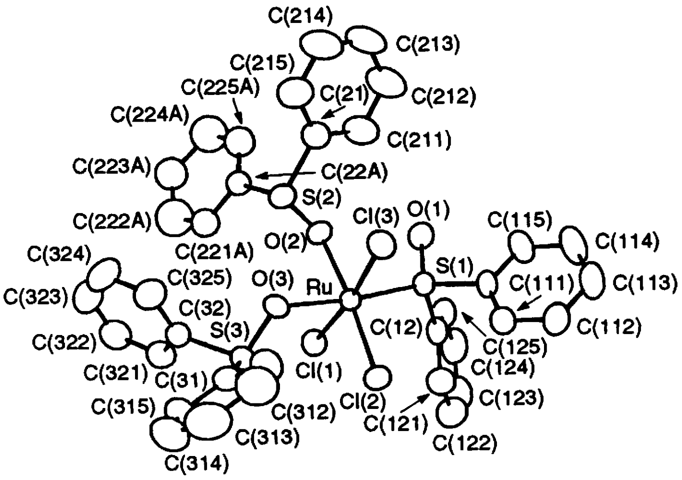


Fig. 5 An ORTEP[44] drawing of *mer,cis*-[$RuCl_3$(dpso-*S*)(dpso-*O*)$_2$], with thermal ellipsoids at the 50% probability level. For the C(22) phenyl group only position A is shown

The graphical representation of $\Sigma\Omega$ for complexes of Ru^{II} and Ru^{III} (Fig. 4) shows that in stable linkage isomers the bonding mode of sulfoxides appears to be the result of a balance between electronic and steric effects. The mean $\Sigma\Omega$ values of the isolated sulfoxide complexes for Ru^{II} and Ru^{III} suggest that in Ru^{II} the electronic factor is more relevant in determining the co-ordination mode of sulfoxides than in Ru^{III}, *cf.* [$Ru^{II}Cl_3$(dmso-*S*)$_3$]$^-$ *vs.* [$Ru^{III}Cl_3$(dmso-*S*)$_2$(dmso-*O*)].

This work shows that significant steric effects appear with ligands with large cone angles, like dpso. The crystal structure of [$RuCl_3$(dpso)$_3$] reveals that, unlike in the analogous *mer,trans*-[$RuCl_3$(dmso-*S*)$_2$(dmso-*O*)][3] of the three sulfoxide ligands two are O- and one is S-bonded. It seems likely that the greater ligand bulkiness of dpso-*S* reduces the number of S-bonded sulfoxides with respect to the dmso derivative. The relevant steric hindrance of dpso-*S* is further shown by the fact that the three chlorine atoms are pushed away from the S(1) ligand towards the less bulky O(3) ligand (see Table 7). The strain energies and conformational entropy of three isomers of the system [$RuCl_3$(dpso)$_3$], evaluated through molecular mechanics calculations, confirm the importance of the interligand steric interactions to the isomer stability.

Therefore, when the ligands are particularly bulky, steric interactions do play a role in determining the stability of the linkage isomer in sulfoxide complexes.

Acknowledgements

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Table 5 Bond-stretching and angle-bending force-field parameters

Bond	d^0/Å	k^d/kcal mol^{-1} Å^{-2}
Ru–O	2.09	296.2
Ru–S	2.25	394.9
Ru–S[a]	2.34	361.0
Ru–Cl	2.35	310.6
Angle	θ^0/°	10^2 k^θ/kcal mol^{-1} deg^{-2}
Ru–O–S	120	4.254
Ru–S–C	109.5	3.809
Ru–S–O	116	4.330
O–Ru–O[b]	90	0.773
Cl–Ru–O[b]	90	0.660
Cl–Ru–S[b]	90	0.635
Cl–Ru–S[a,b]	90	0.646
O–Ru–S[b]	90	0.738
O–Ru–S[a,b]	90	0.720
Cl–Ru–Cl[b]	90	0.570
S–Ru–S[b]	90	0.688
S–Ru–S[c]	180	0.165
Cl–Ru–Cl[c]	180	0.142
Cl–Ru–S[c]	180	0.159
O–Ru–S[c]	180	0.184

[a] S ligand *trans* to S. [b] *cis* Ligands. [c] *trans* Ligands.

Table 7 Selected bond distances (Å) and angles (°)

Ru–Cl(1)	2.324(2)	S(1)–C(12)	1.797(7)
Ru–Cl(2)	2.307(2)	S(2)–O(2)	1.522(6)
Ru–Cl(3)	2.337(2)	S(2)–C(21)	1.78(1)
Ru–S(1)	2.251(2)	S(2)–C(22A)	1.95(2)
Ru–O(2)	2.091(6)	S(2)–C(22B)	1.67(2)
Ru–O(3)	2.114(5)	S(3)–O(3)	1.546(6)
S(1)–O(1)	1.463(7)	S(3)–C(31)	1.783(7)
S(1)–C(11)	1.796(8)	S(3)–C(32)	1.78(1)
Cl(1)–Ru–Cl(2)	93.17(8)	Ru–S(1)–C(11)	117.2(2)
Cl(1)–Ru–Cl(3)	172.54(9)	Ru–S(1)–C(12)	114.7(3)
Cl(1)–Ru–S(1)	91.67(7)	O(1)–S(1)–C(11)	106.0(4)
Cl(1)–Ru–O(2)	86.3(1)	O(1)–S(1)–C(12)	105.7(3)
Cl(1)–Ru–O(3)	89.7(1)	C(11)–S(1)–C(12)	98.8(4)
Cl(2)–Ru–Cl(3)	93.19(8)	O(2)–S(2)–C(21)	104.7(4)
Cl(2)–Ru–S(1)	98.88(8)	O(2)–S(2)–C(22A)	95.1(5)
Cl(2)–Ru–O(2)	174.0(2)	O(2)–S(2)–C(22B)	113.0(6)
Cl(2)–Ru–O(3)	87.4(2)	C(21)–S(2)–C(22A)	97.2(6)
Cl(3)–Ru–O(2)	87.0(1)	C(21)–S(2)–C(22B)	107.3(8)
Cl(3)–Ru–S(1)	91.19(7)	O(3)–S(3)–C(31)	103.3(3)
Cl(3)–Ru–O(3)	86.7(1)	O(3)–S(3)–C(32)	103.3(4)
S(1)–Ru–O(2)	87.1(2)	C(31)–S(3)–C(32)	101.7(4)
S(1)–Ru–O(3)	173.5(2)	Ru–O(2)–S(2)	119.9(3)
O(2)–Ru–O(3)	86.6(2)	Ru–O(3)–S(3)	119.7(3)
Ru–S(1)–O(1)	112.9(3)		

Table 6 Entropy terms S_{fr}/cal K^{-1} mol^{-1}, for free internal rotation at 300 K, number of conformers $N_{est<0}$ with strain energy $E_{st} < 0$, conformational entropy S_{co}/cal K^{-1} mol^{-1}, strain energy E_{st}/kcal mol^{-1}, and sum ($E_{st} - TS_{co}$)/kcal mol^{-1} for some [$RuCl_3$(dpso)$_3$] isomers

Complex	S_{fr}	$N_{est<0}$	S_{co}	E_{st}	$E_{st} - TS_{co}$
1 *mer,cis*-[$RuCl_3$(dpso-*S*)(dpso-*O*)$_2$]	103.5	14 064 448	40.1	−19.4	−31.4
2 *mer,trans*-[$RuCl_3$(dpso-*S*)$_2$(dpso-*O*)]	92.2	29 504	21.7	−17.3	−23.8
3 *mer,cis*-[$RuCl_3$(dpso-*S*)$_2$(dpso-*O*)]	92.0	8 640	18.9	−12.9	−18.6

Table 8 Atomic fractional coordinates with estimated standard deviations in parentheses for *mer*-[$RuCl_3(dpso)_3$]; starred parameters were not refined

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.215 01(6)	0.119 36(5)	0.355 22(4)	C(214)	0.028(1)	0.181(1)	−0.056 9(8)
Cl(1)	0.449 3(2)	0.171 3(2)	0.455 3(1)	C(215)	0.103(1)	0.131 2(9)	−0.002 2(7)
Cl(2)	0.131 9(2)	0.029 0(2)	0.448 0(1)	C(22A)	0.447(2)	0.176(1)	0.161(1)
Cl(3)	−0.008 8(2)	0.066 4(2)	0.238 9(2)	C(221A)	0.556*	0.140*	0.211*
S(1)	0.192 1(2)	0.285 0(1)	0.414 7(1)	C(222A)	0.695*	0.179*	0.213*
S(2)	0.260 3(3)	0.115 9(2)	0.165 2(2)	C(223A)	0.720(2)	0.238(2)	0.157(2)
S(3)	0.326 7(2)	−0.089 9(2)	0.343 9(1)	C(224A)	0.621(3)	0.298(2)	0.115(2)
O(1)	0.225 7(6)	0.362 0(4)	0.364 1(4)	C(225A)	0.480(2)	0.251(2)	0.117(1)
O(2)	0.294 6(6)	0.186 2(4)	0.264 9(4)	C(22B)	0.405(2)	0.111(1)	0.139(1)
O(3)	0.238 8(6)	−0.030 2(4)	0.286 3(4)	C(221B)	0.538*	0.172*	0.204*
C(11)	0.023 1(7)	0.288 9(6)	0.423 2(5)	C(222B)	0.655*	0.167*	0.194*
C(111)	−0.055 6(8)	0.215 5(7)	0.452 5(6)	C(223B)	0.657(3)	0.113(2)	0.111(2)
C(112)	−0.181 5(9)	0.228 5(8)	0.460 7(7)	C(224B)	0.530(3)	0.054(2)	0.037(2)
C(113)	−0.225 8(9)	0.314 8(8)	0.440 3(7)	C(225B)	0.391(3)	0.048(2)	0.049(2)
C(114)	−0.147(1)	0.386 0(8)	0.410 9(9)	C(31)	0.209 2(8)	−0.225 3(6)	0.307 4(5)
C(115)	−0.022 1(9)	0.374 2(7)	0.401 7(7)	C(311)	0.064 8(9)	−0.238 3(8)	0.280 4(7)
C(12)	0.301 4(8)	0.353 5(6)	0.535 2(6)	C(312)	−0.024(1)	−0.341 5(9)	0.259 1(8)
C(121)	0.301(1)	0.303 8(7)	0.603 7(6)	C(313)	0.026(1)	−0.429 0(9)	0.266 6(8)
C(122)	0.385(1)	0.362 0(9)	0.694 0(7)	C(314)	0.170(1)	−0.414 3(8)	0.294 9(8)
C(123)	0.468(1)	0.468 1(9)	0.715 9(8)	C(315)	0.261(1)	−0.313 0(7)	0.316 0(7)
C(124)	0.468(1)	0.516 5(8)	0.648 4(8)	C(32)	0.450 5(8)	−0.110 2(6)	0.288 0(5)
C(125)	0.383 4(9)	0.459 4(7)	0.555 7(6)	C(321)	0.592 2(9)	−0.069 2(7)	0.343 1(6)
C(21)	0.167 4(9)	0.184 3(7)	0.093 7(6)	C(322)	0.693(1)	−0.075 2(8)	0.300 5(7)
C(211)	0.156(1)	0.284 5(9)	0.133 1(8)	C(323)	0.651(1)	−0.120 3(9)	0.207 1(7)
C(212)	0.081(2)	0.333(1)	0.075 3(9)	C(324)	0.508(1)	−0.162 6(9)	0.152 1(7)
C(213)	0.020(1)	0.282(1)	−0.019 4(8)	C(325)	0.407(1)	−0.156 7(9)	0.193 0(7)

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