

Stereochemistry of Ruthenium Bis-chelate Disulfoxide Complexes. A Molecular Mechanics Investigation

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A topological analysis of bis-chelate disulfoxide metal complexes is presented together with the results of molecular mechanics calculations on dichloro-1,2-bis(methylsulfinyl)ethane Ru(II) complexes. The goal of the work is to study the influence of the nonbonded atom interactions arising from linkage and cis–trans isomerism, combined with different arrangements of the sulfur chiral centers, on the strain energy of the compounds. The calculated strain energies show that the van der Waals and electrostatic interactions largely favor the S-bonding with respect to a mixed S,O-bonding and the cis isomers with respect to the trans isomers. Different arrangements of the chiral sulfur centers yield markedly different molecular energies; in general, meso ligands produce strain energies lower than racemic ligands. A “conformation discriminator” ΔC has been introduced for the description of the ring conformations in the case of cycles characterized by marked inequalities of bond lengths and angles.

Introduction

Ruthenium sulfoxide complexes have been widely studied for their use in homogeneous catalytic processes¹ and for their potential in medicinal chemistry.² Related stereochemical and conformational properties have been investigated through X-ray diffraction,³ NMR,⁴ and molecular mechanics (MM) techniques.⁵ Surprisingly, the coordination chemistry of analogous disulfoxide complexes has received much less attention, despite their implication in catalytic asymmetric reactions⁶ and of their antitumor properties.⁷ Furthermore, disulfoxide metal complexes present many intriguing stereochemical features, because of the ambidentate nature of the ligands and the inherent chiral properties of the sulfur atoms. In fact, disulfoxides are configur-

ationally rather inert, and meso forms are easily separated from racemates.^{8,9} As to ruthenium, to our knowledge, the only compounds to have been structurally characterized by X-ray analyses are *trans*-RuCl₂[MeS(O)(CH₂)₂S(O)Me]₂ (*trans*-RuCl₂(BMSE)₂, **1**), *cis*-RuCl₂[EtS(O)(CH₂)₂S(O)Et]₂ (*cis*-RuCl₂(BESE)₂, **2**), *trans*-RuCl₂[ⁿPrS(O)(CH₂)₂S(O)ⁿPr]₂ (*trans*-RuCl₂(BPSE)₂, **3**), and *cis*-RuCl₂(MeS(O)(CH₂)₃S(O)Me)₂ (*cis*-RuCl₂(BMSP)₂).⁷ In all these compounds, disulfoxides are S-bonded. A *trans*-RuCl₂[(*p*-tolyl)S(O)(C₆H₄)S(O)(*p*-tolyl)]₂ complex has been also synthesized and spectroscopically characterized, again showing S-bonding.¹⁰ Similar bonding modes have been found for the few examined platinum and palladium compounds,^{9,10} while O-bonding has been proposed, from IR spectroscopic data, for disulfoxide complexes of the first series transition metals.¹¹

As a contribution to the study of the coordination chemistry of disulfoxide metal complexes we have started a stereochemical investigation of bis-chelate ruthenium(II) complexes of the type RuCl₂(BMSE)₂, using the force field previously derived for dimethyl sulfoxide (DMSO) complexes.^{5a}

Octahedral bis(disulfoxide) metal complexes containing ancillary monodentate ligands, like RuCl₂(BMSE)₂, can give rise to bis- and tris-heteroleptic complexes, as sketched in Chart 1 (methyl groups are omitted for sake of clarity), according to S- and/or O-bonding. Chelate ligands are symbolized as (S^S), (S^O), and (O^O), depending on the ligating atoms, *i.e.* sulfur and/or oxygen.

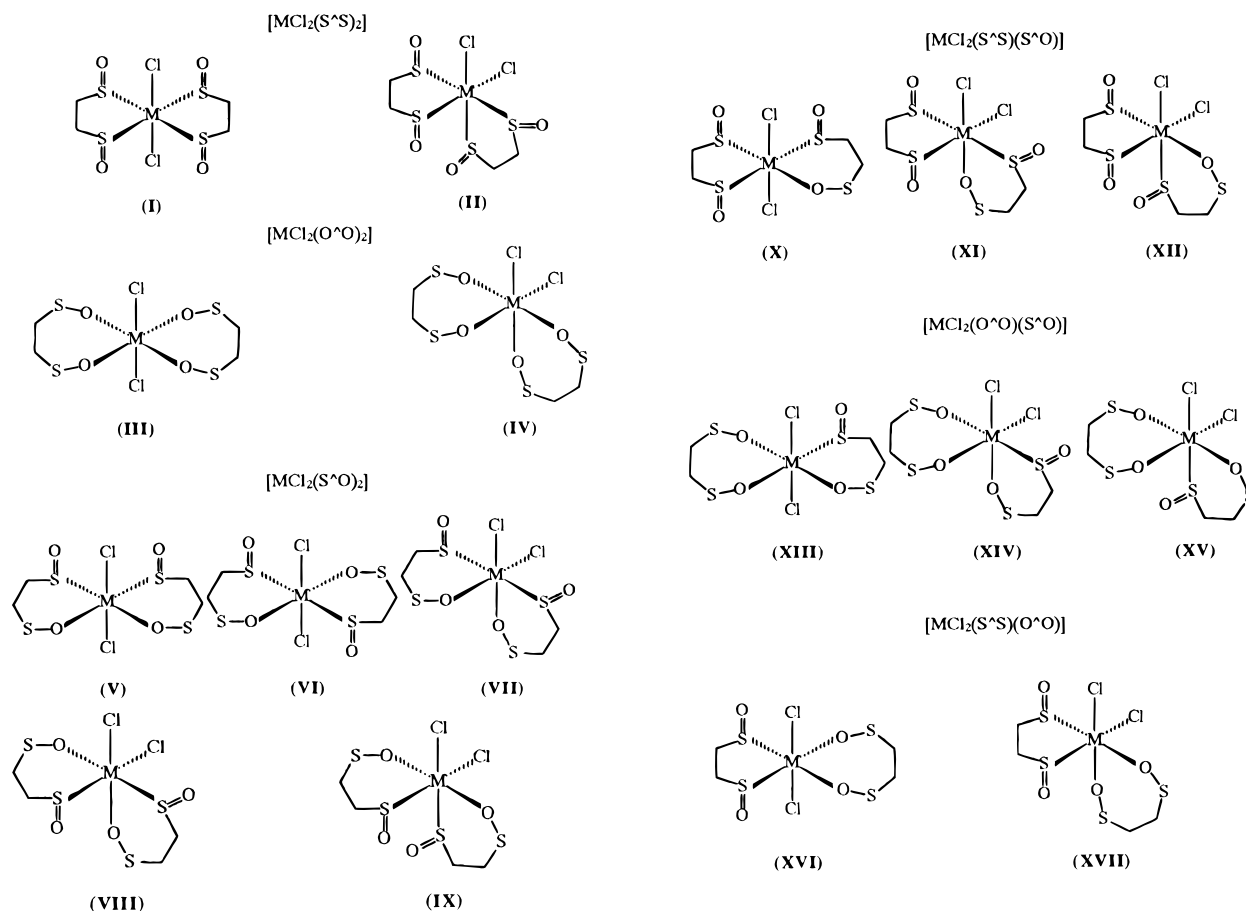
In the case of the bis-heteroleptic complexes, [MCl₂(S^S)₂] and [MCl₂(O^O)₂], two stereoisomers are possible for each type: [*trans*-MCl₂(S^S)₂] (**I**) and [*cis*-MCl₂(S^S)₂] (**II**), and [*trans*-MCl₂(O^O)₂] (**III**) and [*cis*-MCl₂(O^O)₂] (**IV**). Fur-

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Chart 1. Possible Stereoisomers for Octahedral (OC-6) $[MCl_2(chel)_2]$ Complexes with $chel = (S^{\wedge}S)$, $(O^{\wedge}O)$, and $(S^{\wedge}O)$ Ligands

thermore, **II** and **IV** consist of enantiomeric pairs, identified by the Δ and Λ chirality descriptors.

Tris-heteroleptic compounds can be of four types, $[MCl_2(S^{\wedge}O)_2]$, $[MCl_2(S^{\wedge}S)(S^{\wedge}O)]$, $[MCl_2(O^{\wedge}O)(S^{\wedge}O)]$, and $[MCl_2(S^{\wedge}S)(O^{\wedge}O)]$. The first one gives rise to five isomers (**V–IX**), with three chiral pairs Δ/Λ (**VII–IX**), while, for both the second and the third types, three isomers are possible (**X–XII** and **XIII–XV**), each with two chiral pairs Δ/Λ (**XI, XII** and **XIV, XV**). Finally, for the last type of complexes two isomers can be formed (**XVI, XVII**), with one chiral pair (**XVII**).

As mentioned above, disulfoxide ligands can be present as racemates (so far, enantiomerically pure ligands seem not to have been isolated) or in the meso form, because of the chirotopic nature of the trigonal pyramidal sulfur atoms. The absolute configuration of the sulfur atoms can be either *R* or *S*, and accordingly, symbols [*R*] or [*S*] will be added to define the ligand chirality. For oxygen donors, the chirality descriptor refers to the chirality of the adjacently bonded sulfur atom. It must be remembered that upon *S*-coordination, the chirality descriptor of the ligated sulfur atom changes from *R* to *S*, and *vice versa* if the original configuration was *S* (pseudo-inversion). Thus for example, $(S^{\wedge}S[R,R])$ and $(O^{\wedge}O[R,R])$ will describe *S*- and *O*-coordinated ligands, in complexes obtained from enantiomerically pure ligands having sulfur atoms originally in the *S* and *R* configuration, respectively. Similarly, $(S^{\wedge}O[R,S])$ means that the mixed *S,O*-bonded complex has been obtained from an enantiomerically pure ligand containing sulfur atoms originally both in the *S* configuration, while $(S^{\wedge}S[R,S])$, $(O^{\wedge}O[R,S])$, and $(S^{\wedge}O[R,R])$ indicate the use of meso ligands. In the case of a racemic ligand mixture, it is possible to obtain

bis-chelate complexes containing different combinations of the enantiomerically pure ligands. Thus for example, in the case of complexes of type **I** and **II**, we may have: $RuCl_2(S^{\wedge}S[R,R])_2$, $RuCl_2(S^{\wedge}S[S,S])_2$, and $RuCl_2(S^{\wedge}S[R,R])(S^{\wedge}S[S,S])$. The structures of a few examples are shown in Figure 1.

The various diastereomers are represented by their IUPAC stereochemical descriptors,¹² which consist of the polyhedral symbol (OC-6, for octahedrons), the configuration index (based on the priority numbers, according to the Cahn, Ingold, and Prelog rules¹³), and the chirality symbols (*R* and *S* for sulfur atoms, Δ and Λ for the molecules as a whole). Remembering that, according to the Sequence Rule (5),¹³ *R* precedes *S*, the priority sequence for ligands is $Cl > S[R](S^{\wedge}S) > S[S](S^{\wedge}S) > S[R](S^{\wedge}O) > S[S](S^{\wedge}O) > O[R](S^{\wedge}O) > O[S](S^{\wedge}O) > O[R](O^{\wedge}O) > O[S](O^{\wedge}O)$.

It is well-known that in Ru(II) complexes *S*-bonding is preferred as long as the metal electron density charge is high enough to ensure a π back-donation from Ru to sulfoxide antibonding orbitals.³ Furthermore, sulfur atoms tend to be trans to Cl or to O atoms, when no Cl is available, to avoid π back-bonding competition between trans *S* ligands. In fact, a trans arrangement of the sulfur atoms, even if possible, yields a thermodynamically less stable form. For example, for $RuCl_2(DMSO)_4$ the most stable isomer is $[cis-RuCl_2(DMSO)_3(DMSO)]$ (*S* = *S*-bonded sulfoxide, *O* = *O*-bonded sulfoxide), while the isomer $[trans-RuCl_2(DMSO)_4]$ is unstable and isomer-

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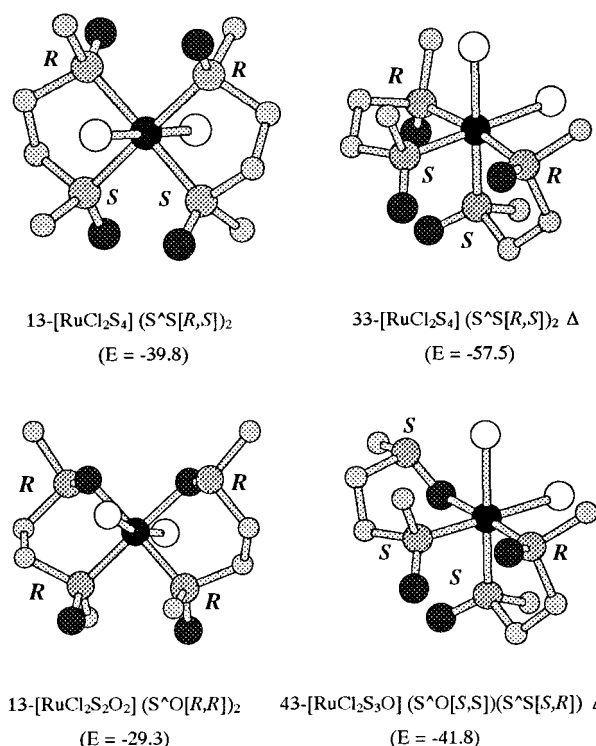


Figure 1. Molecular structures of the minimum energy diastereomers, containing *meso*-BMSE ligands, of type **I**, 13-[RuCl₂S₄](S^S[R,R,S])₂; **II**, 33-[RuCl₂S₄](S^S[R,S,S])₂ Δ; **V**, 13-[RuCl₂S₂O₂](S^O[R,R,R])₂; and **XII**, 43-[RuCl₂S₃O](S^O[S,S,S])(S^S[S,R,R]) Δ. Total strain energies *E* (kcal mol⁻¹) are also reported.

izes to the cis complex.¹⁴ From this point of view, it should be expected that the most stable isomer would be **XII**, approximately followed by **II**, **I**, and **V**.

In the case of disulfoxides, however, other factors can affect the linkage isomerism, such as the chelate ring size, owing to the decreasing magnitude of the chelate effect with the increasing ring size.¹⁵ For 1,2-bis(sulfinyl)ethane derivatives, passing from (S^S) to (S^O) and (O^O) ligands, where the ring size increases from 5 to 6 and 7, respectively, the first bonding mode should be kinetically favored.

In this paper we will describe the results of a MM investigation of topological effects upon the strain energy of [RuCl₂-(MeS(O)(CH₂)₂S(O)Me)₂] complexes of type **I**, **II**, **V**, and **XII**, considering both the meso and the racemic ligands, providing an indication of the thermodynamic stability of the different diastereomers. This, of course, will be fully reliable only when strain energy differences are either consistent with the trend expected from electronic contributions or large enough to overwhelm opposite thermodynamic contributions deriving from different bond energies in topologically dissimilar molecules.

Particular attention will be also devoted to the description of the ring conformations, suggesting a new criterion, valid for every kind of ring. In fact, as already pointed out,¹⁶ the Cremer and Pople (CP) formalism¹⁷ can give ambiguous results in the case of marked inequalities of bond lengths and angles, just as in disulfoxide chelate cycles. Furthermore, the conformational study of unsymmetric six-membered rings appears of interest

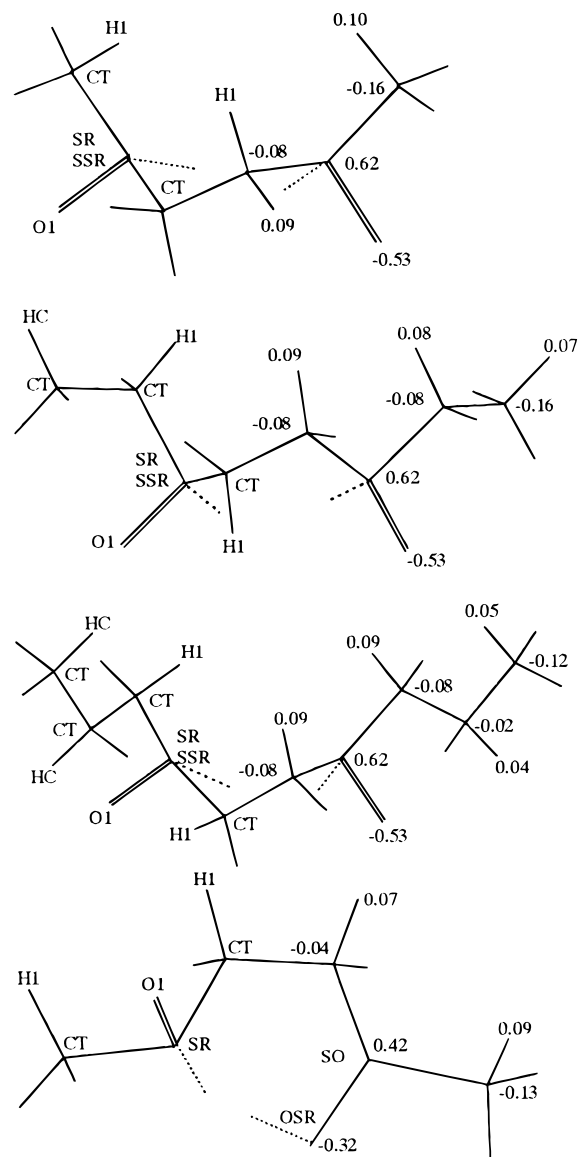


Figure 2. Atom types and average atom charges for (S^S) and (S^O) BMSE ligands in RuCl₂(BMSE)₂ complexes.

since, to our knowledge, the inorganic MM publications have only analyzed the geometry of symmetric chelate complexes, such as those derived from diamine ligands.¹⁸

Experimental Section

MM Computational Details. As for the DMSO compounds,^{5a} calculations have been performed on a Pentium 200 PC using the HyperChem molecular modeling package,¹⁹ and the Amber force field.²⁰ Atomic charges have been assigned as in ref 5a. For S-bonded disulfoxides, atom charges of the bis-sulfinyl ethane group, S(O)-(CH₂)₂S(O), have been obtained averaging all the chemically equivalent atom charges calculated by the ZINDO/1 method,¹⁹ assuming the X-ray structure geometries of **1**, **2**, and **3**.⁷ For O-bonded disulfoxides, because of the lack of X-ray structures, charges have been calculated

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Table 1. Average Differences between Observed and Calculated Bond Distances (Å) and Angles (deg) with Rms Values in Parentheses (Ranges of the Rms Values in Ru-DMSO Complexes (Ref 5a) Are Reported in Footnotes; X, Y, and Z Represent Generic Nonmetal Atoms)

complex	Ru-X ^a	X-Y ^b	X-Ru-Y ^c	Ru-X-Y ^d	X-Y-Z ^e
<i>trans</i> -RuCl ₂ (BMSE) ₂ (1)	-0.018 (0.017)	0.002 (0.027)	-0.5 (1.6)	-0.1 (1.4)	0.2 (1.7)
<i>cis</i> -RuCl ₂ (BESE) ₂ (2)	-0.001 (0.021)	0.000 (0.016)	-0.5 (2.0)	0.3 (1.5)	0.4 (1.3)
<i>trans</i> -RuCl ₂ (BPSE) ₂ (3)	-0.013 (0.017)	-0.025 (0.087)	0.1 (1.0)	0.7 (2.8)	0.7 (6.2)

^a 0.009–0.013. ^b 0.008–0.029. ^c 0.5–1.9. ^d 1.0–3.6. ^e 0.4–2.3.

from the model structures of *trans*-RuCl₂(MeS(O)(CH₂)₂S(O)Me)₂ and *cis*-RuCl₂(MeS(O)(CH₂)₂S(O)Me)(MeS(O)(CH₂)₂S(O)Me). The structures were obtained from strain energy minimizations without the electrostatic terms. Final refinements with the electrostatic contributions showed no significant changes in the molecular geometries. Average charges for the different atom types are reported in Figure 2. Force field parameters were taken from ref 5a, with the addition of the S–C–C bending parameters, $k = 74.9 \text{ kcal mol}^{-1} \text{ rad}^{-2}$ and $\theta = 109.5^\circ$.

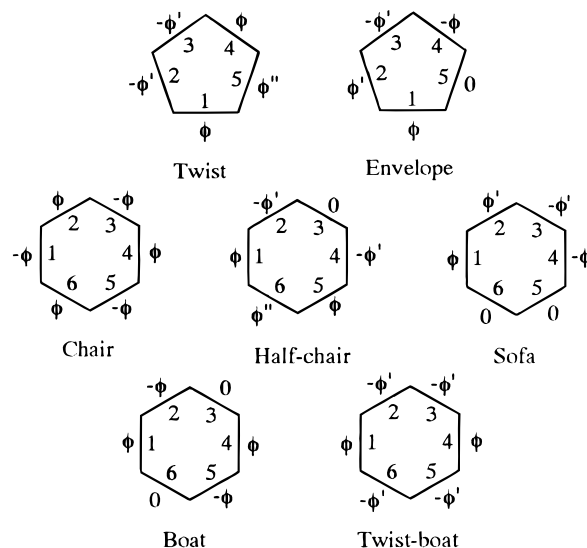
When comparing solid-state structures with the energy minimized ones, we introduced energy barriers of 16 kcal mol^{-1} for the side group conformations, constrained to the experimental values, to simulate packing effects.^{5a}

To explore the conformational space of [RuCl₂(BMSE)₂] stereoisomers as thoroughly as possible, a large number of different starting geometries were built through HyperChem, considering possible combinations of sulfur atom chiralities and chelate ring geometries. Starting from 16 structures for complexes of type **I**, 28 of type **II**, 244 of type **V**, and 128 of type **XII**, we have obtained 10, 18, 40, and 55 nonequivalent minimum energy structures, respectively. In the energy minimization, the Polak–Ribiere version of the conjugate gradient method was employed, with a convergence criterion of $0.001 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. As for the investigation of the rotamer distribution of Ru-DMSO complexes in solution,^{5a} a distance-dependent dielectric constant was used. In fact, it has been shown that, with the same force field parameters, the passage from $D = \text{constant}$ to $D = r_{ij}$ helps to compensate for the lack of explicit solvation by implicitly damping long-range charge interactions more than shorter-range ones.²⁰

Ring Conformations. A local program was used for the calculation of the ring puckering parameters defined by Cremer and Pople.¹⁷ However, since the pseudorotational parameter Φ does not always allow a straightforward description of the ring conformation in case of nonregular polygons (see Results and Discussion), we have calculated a “conformation discriminator”, ΔC , extending the concept proposed for the assessment of single symmetry elements.²¹ This is based on the definition of ideal geometries, uniquely on the basis of the symmetry of the torsion angles (Figure 3), regardless of the ring symmetry, which involves also atom types and bond lengths and angles.

A ΔC value is calculated for each of the possible conformations (5 twist and 5 envelope conformations for the five-membered rings; 1 chair, 6 half-chair, 6 sofa, 3 boat, and 3 twist-boat conformations for the six-membered rings) as the root-mean-square (rms) value of the differences, Δ_j , between the actual torsion angles φ_i and the ideal values φ ; $\Delta C = [\sum_{j=1,n} \Delta_j^2/n]^{1/2}$, where Δ_j , φ , and n are defined in Table 4. The best description of the ring conformation is identified by the lowest value of ΔC , which then gives a quantitative measure of the ring deformation from “ideality”.

To identify the various envelope, half-chair, sofa, and boat conformations, the symbols of the noncoplanar atoms, “flag atoms”, are added to the conformation label (e.g., envelope-Ru indicates that Ru is the flag atom; boat-OC indicates that the O atom and its opposite C atom are the flag atoms). For the twist and the twist-boat conformations, the symbols of the atoms through which a 2-fold axis passes are indicated (e.g., twist-Ru, implies that the C₂ axis passes through the metal atom; twist-boat-SS means that the vertical C₂ axis passes through the two S atoms).

**Figure 3.** Definition of symmetric conformations for five- and six-membered rings. Numbers inside the rings refer to the index i of the torsion angles φ_i in Table 4.

To define the ring helicity,¹¹ δ and λ descriptors have been used for both five- and six-membered chelate rings, doubling the number of ring conformations. For the sofa-Ru and envelope-Ru conformations, where δ and λ cannot be used, the new descriptors “folded” (f) and “unfolded” (u) have been introduced (see Ring Conformations). Tables 5 and 6 report the ring geometries for the minimum-energy stereoisomers of complexes in Tables 2 and 3, together with the CP puckering parameters (polar coordinates for six-membered rings) and the corresponding ΔC values.

Results and Discussion

Force Field Validation. To check the transferability of the Ru-DMSO force field parameters^{5a} to disulfoxide complexes, we have taken into account the following complexes whose X-ray structures have been reported: *trans*-RuCl₂(BMSE)₂ (**1**), *cis*-RuCl₂(BESE)₂ (**2**), and *trans*-RuCl₂(BPSE)₂ (**3**).⁷ Deviations (Δ_j) of the calculated bond lengths and angles, after energy minimization, from the experimental data (see Table 1) are measured by the average differences, over the m observables ($\sum \Delta_j/m$), and by their root-mean-square values ($\text{rms} = [\sum \Delta_j^2/m]^{1/2}$).^{5a} In **1** and **2**, where two crystallographically independent molecules are present, the experimental values have been taken as the average between the chemically equivalent parameters. The agreement appears quite satisfactory for the first two compounds, specially when experimental errors are considered. In fact, in **1**, the average differences between the two crystallographically independent molecules are as large as 0.025 \AA and 1.9° for bond lengths and angles, respectively. It is also interesting to observe that the rms values are comparable with those of the Ru-DMSO complexes,^{5a} as shown in Table 1. It seems likely that the larger deviations in **3**, between calculated

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Table 2. Strain Energies E (kcal mol⁻¹) for the Most Likely Diastereomers of [RuCl₂(*meso*-BMSE)₂]; Stretching (E_s), Bending (E_b), Torsional (E_t), van der Waals (E_v), and Electrostatic (E_e) Energy Contributions (kcal mol⁻¹) Are Also Reported

type	configuration index	ligand type and chirality	strain energies					
			E	E_s	E_b	E_t	E_v	E_e
I	13-[RuCl ₂ S ₄]	(S [^] S[R,S]) ₂	-39.8	0.4	3.0	0.3	-6.7	-36.7
	12-[RuCl ₂ S ₄]	(S [^] S[R,S]) ₂	-31.6	0.3	3.8	0.4	-6.5	-29.6
II	33-[RuCl ₂ S ₄]	(S [^] S[R,S]) ₂ Δ	-57.5	0.2	2.8	0.4	-7.2	-53.8
	32-[RuCl ₂ S ₄]	(S [^] S[R,S]) ₂ Δ	-43.3	0.2	5.7	0.3	-6.1	-43.5
	22-[RuCl ₂ S ₄]	(S [^] S[R,S]) ₂ Δ	-17.6	0.3	9.3	0.2	-5.9	-21.5
V	13-[RuCl ₂ S ₂ O ₂]	(S [^] O[R,R]) ₂	-29.3	0.6	4.9	0.0	-3.2	-31.7
	15-[RuCl ₂ S ₂ O ₂]	(S [^] O[S])(S [^] O[R])	-25.1	0.5	3.6	0.5	-3.9	-25.7
XII	43-[RuCl ₂ S ₃ O]	(S [^] O[S,S])(S [^] S[S,R]) Δ	-41.8	0.4	3.3	0.3	-4.6	-41.0
	43-[RuCl ₂ S ₃ O]	(S [^] O[R,R])(S [^] S[S,R]) Δ	-36.5	0.3	5.5	1.2	-3.3	-40.3
	42-[RuCl ₂ S ₃ O]	(S [^] O[S,S])(S [^] S[R,S]) Δ	-24.3	0.5	5.7	0.3	-3.2	-27.6
	42-[RuCl ₂ S ₃ O]	(S [^] O[R,R])(S [^] S[R,S]) Δ	-12.7	0.6	13.8	2.5	-2.7	-27.0

Table 3. Strain Energies E (kcal mol⁻¹) for the Most Likely Diastereomers of [RuCl₂(*rac*-BMSE)₂]; Stretching (E_s), Bending (E_b), Torsional (E_t), van der Waals (E_v), and Electrostatic (E_e) Energy Contributions (kcal mol⁻¹) Are Also Reported

type	configuration index	ligand type and chirality	strain energies					
			E	E_s	E_b	E_t	E_v	E_e
I	12-[RuCl ₂ S ₄]	(S [^] S[R,R]) ₂	-41.8	0.3	3.0	0.1	-6.5	-38.7
	13-[RuCl ₂ S ₄]	(S [^] S[R,R])(S [^] S[S,S])	-36.0	0.3	5.1	1.1	-5.6	-37.0
II	32-[RuCl ₂ S ₄]	(S [^] S[S,S])(S [^] S[R,R]) Δ	-46.5	0.3	6.5	1.4	-4.3	-50.4
	22-[RuCl ₂ S ₄]	(S [^] S[S,S]) ₂ Δ	-46.0	0.2	5.4	2.0	-5.0	-48.6
	22-[RuCl ₂ S ₄]	(S [^] S[R,R]) ₂ Δ	-40.0	0.4	9.4	4.7	-4.8	-49.7
V	13-[RuCl ₂ S ₂ O ₂]	(S [^] O[R,S]) ₂	-32.9	0.4	2.9	0.3	-2.4	-34.1
	14-[RuCl ₂ S ₂ O ₂]	(S [^] O[R,S])(S [^] O[S,R])	-31.3	0.4	3.0	0.1	-3.3	-31.4
XII	32-[RuCl ₂ S ₃ O]	(S [^] O[S,R])(S [^] S[R,R]) Δ	-35.5	0.3	5.8	1.7	-3.3	-40.0
	32-[RuCl ₂ S ₃ O]	(S [^] O[S,R])(S [^] S[S,S]) Δ	-35.3	0.3	4.2	0.5	-4.7	-35.6
	32-[RuCl ₂ S ₃ O]	(S [^] O[R,S])(S [^] S[S,S]) Δ	-34.2	0.4	5.7	0.5	-2.5	-38.2
	32-[RuCl ₂ S ₃ O]	(S [^] O[R,S])(S [^] S[R,R]) Δ	-29.0	0.5	8.1	2.5	-3.3	-36.8

and experimental values involving the light atoms, reflect the low accuracy of the carbon atom location due to static disorder in two of the ¹³Pr chains and the high thermal factors of the terminal methyl groups, found in the X-ray structure analysis.⁷ As an example, the experimental S-C and C-C bond distances range from 1.748 to 1.911 Å and from 1.336 to 1.649 Å, respectively.⁷ Finally, it is worth noting that the difference between the observed Ru-S-C(endo) (av 104(2)°) and Ru-S-C(exo) (av 115(1)°) bond angles is well reproduced, even using the same unstrained value ($\theta = 110.9^\circ$) for the Ru-S-C angles. In fact, the average calculated values are 106(1) and 114(1)°, respectively. This mimics the ring strain effects induced by chelation well. It is to be emphasized that the force field ability to reproduce the observed structural parameters is also due to the proper weighting of the electrostatic contributions, obtained through optimization of the dielectric constant to an acceptable value. The consistency of the calculated atomic charges was further shown by the ability of the force field to calculate distributions of rotamers in solution, in reasonable agreement with experimental data, when a distance dependent dielectric was assumed.^{5a} This allows us to be confident in the calculation of the electrostatic energy contributions, which are shown to be relevant for the strain energy calculations.

Stereochemistry of RuCl₂(BMSE)₂. Table 2 shows that for the cis type complexes, **II** and **XII**, containing meso-BMSE ligands, the minimum energy structure is found for the diastereomer 33-[RuCl₂S₄] Δ of type **II**. This same kind of stereomer is present in the solid-state structure of *cis*-RuCl₂(BESE)₂ (**2**), which contains the enantiomeric pair 33-[RuCl₂S₄] Δ and 22-[RuCl₂S₄] Λ. These are characterized by trans sulfur atoms with the same chirality (Figure 1). All other isomers, of both types **II** and **XII**, have significantly higher strain energies (> 14 kcal mol⁻¹). For the trans complexes of types **I** and **V**, the

Table 4. Definition of φ and Δ_i for the Calculation of the Conformation Discriminator, $\Delta C = [\sum_{i=1,n}(\Delta_i^2/n)]^{1/2}$, Where n , for Each Conformation, Is the Maximum Value of i in Column 2

conformation	i	Δ_j (deg)	φ (deg)
twist (C_2)	1, 4	$\varphi_i - \varphi$	$(\varphi_1 + \varphi_4)/2$
	2, 3	$\varphi_i - \varphi$	$(\varphi_2 + \varphi_3)/2$
envelope (C_s)	1, 4	$\varphi_i + (-1)^i \varphi$	$(\varphi_1 - \varphi_4)/2$
	2, 3	$\varphi_i - (-1)^i \varphi$	$(\varphi_2 - \varphi_3)/2$
	5	φ_i	0
chair (D_{3d})	1-6	$\varphi_i - (-1)^i \varphi$	$\sum_{i=1-6} (-1)^i \varphi_i / 6$
half-chair (C_2)	1, 5	$\varphi_i - \varphi$	$(\varphi_1 + \varphi_5)/2$
	2, 4	$\varphi_i - \varphi$	$(\varphi_2 + \varphi_4)/2$
	3	φ_i	0
sofa (C_s)	1, 4	$\varphi_i + (-1)^i \varphi$	$(\varphi_1 - \varphi_4)/2$
	2, 3	$\varphi_i - (-1)^i \varphi$	$(\varphi_2 - \varphi_3)/2$
	5, 6	φ_i	0
boat (C_{2v})	1, 4	$\varphi_i - \varphi$	$(\varphi_1 - \varphi_2 + \varphi_4 - \varphi_5)/4$
	2, 5	$\varphi_i + \varphi$	$(\varphi_1 - \varphi_2 + \varphi_4 - \varphi_5)/4$
	3, 6	φ_i	0
twist-boat (D_2)	1, 4	$\varphi_i - \varphi$	$(\varphi_1 + \varphi_4)/2$
	2, 3, 5, 6	$\varphi_i - \varphi$	$(\varphi_2 + \varphi_3 + \varphi_5 + \varphi_6)/4$

lowest energy is found for the isomer 13-[RuCl₂S₄] of type **I** (Figure 1), that is, for the isomer with sulfur atoms of opposite chirality trans to each other. Analogous stereomers have been observed in the crystal structures of both *trans*-RuCl₂(BMSE)₂ (**1**) and *trans*-RuCl₂(BPSE)₂ (**3**).

Using a racemic mixture of BMSE, we found the most stable cis isomer to be (Table 3) the isomer 32-[RuCl₂S₄] Δ (type **II**), containing one [R,R] and one [S,S] ligand. The 22-[RuCl₂S₄] isomers, where all the sulfur stereogenic centers have the same chirality, S or R, have an energy 0.5 and 6.5 kcal mol⁻¹ higher. For trans isomers, the most stable one is again of type **I**, 12-[RuCl₂S₄], with a strain energy 5.8 kcal mol⁻¹ lower than that of 13-[RuCl₂S₄].

Table 5. Ring Geometries, with ΔC Values and CP Puckering Parameters for the Minimum Energy Diastereomers of $[\text{RuCl}_2(\text{meso-BMSE})_2]$;^a The Most Significant Conformers Are Also Reported

type	configuration index	ligand type and chirality	<i>E</i>	ring geometries	ΔC (deg)	<i>Q</i> (Å)	Φ (deg)	θ (deg)		
I	13- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2$	-39.8	δ twist-Ru	3.0	0.462	263.0			
				δ twist-Ru	3.0	0.462	263.0			
			-39.7	δ twist-Ru	1.2	0.460	267.1			
				λ twist-Ru	5.8	0.477	103.1			
				δ envelope-C	3.5	0.501	235.7			
	12- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2$	-31.6	δ twist-Ru	5.9	0.495	257.1			
				λ twist-S	4.5	0.511	132.3			
			-31.0	δ envelope-C	1.2	0.524	242.0			
				δ envelope-C	4.9	0.457	285.1			
				δ envelope-C	4.9	0.457	254.8			
II	33- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2 \Delta$	-56.5	δ twist-Ru	5.0	0.470	282.0			
				λ twist-Ru	1.6	0.415	93.1			
			-53.9	λ twist-Ru	3.6	0.404	100.0			
				λ twist-Ru	3.6	0.404	80.0			
				δ envelope-C	1.2	0.525	244.9			
				λ envelope-C	2.9	0.486				
	32- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2 \Delta$	-43.0	δ twist-Ru	1.1	0.483	271.7			
				δ envelope-C	2.0	0.522	300.4			
			-38.7	λ envelope-C	4.6	0.493	125.9			
				λ envelope-S	5.5	0.664	158.6			
			-38.4	λ envelope-C	2.9	0.457	122.4			
				δ twist-Ru	1.0	0.504	272.8			
			22- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2 \Delta$	-17.6	λ twist-Ru	4.7	0.484	101.0	
						λ twist-Ru	4.8	0.484	78.8	
					-15.3	λ twist-Ru	7.7	0.468	87.2	
						δ twist-Ru	0.5	0.463	268.3	
					-12.0	δ twist-Ru	5.0	0.447	282.3	
						δ twist-Ru	5.0	0.447	257.6	
V	13- $[\text{RuCl}_2\text{S}_2\text{O}_2]$	$(S^{\wedge}O[R])_2$	-29.3	λ boat-OC	9.6	0.911	109.5	91.2		
				λ boat-OC	9.5	0.911	109.5	91.2		
			-28.9	δ twist-boat-SS	17.3	0.835	329.0	97.4		
				δ twist-boat-SS	17.3	0.835	329.0	97.4		
			-28.6	δ half-chair-CS	13.9	0.708	28.6	160.0		
				λ boat-OC	6.8	0.914	131.4	94.2		
			-28.6	δ half-chair-CS	12.6	0.703	30.0	157.0		
				δ half-chair-CS	12.6	0.703	30.0	157.0		
			-28.6	λ boat-OC	9.9	0.907	108.8	91.0		
				δ twist-boat-SS	17.4	0.827	330.6	97.8		
			-28.2	δ boat-OC	20.9	0.798	313.8	102.0		
				δ half-chair-CS	14.7	0.710	27.2	162.0		
			-25.9	λ sofa-C	8.2	0.596	168.8	173.0		
				λ boat-OC	10.5	0.915	108.3	91.1		
			15- $[\text{RuCl}_2\text{S}_2\text{O}_2]$	$(S^{\wedge}O[R])(S^{\wedge}O[S])$	-25.1	λ twist-boat-RuC	10.5	0.935	96.4	88.6
						λ chair	13.4	0.734	204.8	10.0
					-24.9	δ chair	13.7	0.733	27.0	169.0
						λ twist-boat-SS	9.6	0.886	157.8	89.2
	-24.5	δ boat-OC			19.2	0.818	282.9	105.0		
		δ twist-boat-RuC			10.1	0.934	276.1	91.1		
	XII	43- $[\text{RuCl}_2\text{S}_3\text{O}]$	$(S^{\wedge}O[S])(S^{\wedge}S[S,R]) \Delta$	-23.9	δ chair	11.0	0.644	268.6	162.0	
					δ chair	14.5	0.727	28.2	167.0	
				-23.7	λ half-chair-CS	17.7	0.908	215.8	80.7	
					δ chair	13.8	0.733	28.6	168.0	
43- $[\text{RuCl}_2\text{S}_3\text{O}]$				$(S^{\wedge}O[R])(S^{\wedge}S[S,R]) \Delta$	-41.8	δ boat-OC	5.8	0.911	296.7	87.3
						δ twist-Ru	5.0	0.445	258.5	
					-40.4	δ boat-OC	10.2	0.916	289.5	87.8
						λ twist-Ru	4.1	0.445	100.0	
					-40.0	λ half-chair-CS	3.9	0.720	215.9	50.6
						δ envelope-C	4.7	0.464	255.0	
43- $[\text{RuCl}_2\text{S}_3\text{O}]$				$(S^{\wedge}O[R])(S^{\wedge}S[S,R]) \Delta$	-39.6	λ half-chair-CS	6.8	0.693	207.0	38.4
						δ twist-Ru	5.2	0.463	258.4	
		-38.3	λ half-chair-CS		7.5	0.766	218.3	60.5		
			λ twist-Ru		4.4	0.419	100.6			
		-38.1	λ half-chair-CC		17.8	0.740	139.5	72.3		
			δ twist-Ru		4.9	0.468	259.2			
43- $[\text{RuCl}_2\text{S}_3\text{O}]$		$(S^{\wedge}O[R])(S^{\wedge}S[S,R]) \Delta$	-36.5	δ boat-OC	20.8	0.816	316.6	101.0		
				δ twist-S	5.3	0.538	230.8			
	-34.4		δ half-chair-CS	11.6	0.683	19.5	152.0			
			δ envelope-C	5.7	0.523	232.5				
	-34.3		δ boat-OC	17.7	0.818	284.5	104.0			
			λ twist-S	3.5	0.517	132.3				

Table 5 (Continued)

type	configuration index	ligand type and chirality	E	ring geometries	ΔC (deg)	Q (Å)	Φ (deg)	θ (deg)
			-33.0	λ boat-OC	3.1	0.878	124.4	91.8
				δ envelope-C	5.6	0.543	233.3	
			-32.1	δ half-chair-CS	15.4	0.685	4.5	160.0
				λ envelope-C	5.3	0.483	127.6	
			-31.3	λ sofa-C	4.8	0.624	187.0	54.8
				δ twist-S	5.4	0.544	230.7	
	42-[RuCl ₂ S ₃ O]	(S [^] O[S])(S [^] S[R,S]) Δ	-24.3	δ boat-OC	5.7	0.934	308.3	85.7
				δ envelope-C	3.9	0.475	287.0	
			-24.0	δ boat-OC	9.6	0.921	292.1	87.0
				λ envelope-C	4.8	0.483	74.8	
			-22.1	λ half-chair-CS	14.9	0.723	225.6	17.7
				λ envelope-S	4.9	0.649	22.6	
			-21.6	λ half-chair-CS	13.6	0.712	216.2	20.1
				δ twist-S	2.6	0.571	223.2	
			-20.6	λ sofa-S	8.4	0.790	225.0	63.9
				λ twist-Ru	3.1	0.480	83.4	
			-18.9	λ twist-boat-SS	18.6	0.815	164.0	82.0
				λ twist-S	2.6	0.555	137.3	
	42-[RuCl ₂ S ₃ O]	(S [^] O[R])(S [^] S[R,S]) Δ	-12.7	λ chair	10.3	0.774	38.7	26.7
				δ twist-C	3.9	0.684	348.8	
			-12.6	λ chair	10.7	0.775	39.2	27.4
				δ envelope-S	5.3	0.655	338.1	
			-11.6	λ twist-boat-OC	11.1	1.03	35.9	85.0
				λ twist-S	2.7	0.578	135.7	
			-11.1	λ twist-boat-SS	5.1	0.932	341.9	84.5
				λ envelope-S	4.1	0.643	24.5	
			-10.0	λ twist-boat-OC	8.0	1.03	33.3	83.3
				δ envelope-S	6.4	0.657	340.1	
			-9.9	λ twist-boat-OC	7.8	1.04	32.9	83.5
				δ twist-C	3.6	0.676	346.4	
			-9.4	δ boat-RuC	17.2	1.01	11.5	72.9
				δ envelope-S	6.0	0.660	339.4	
			-8.6	δ twist-boat-SS	13.3	0.886	328.1	92.5
				δ twist-S	3.4	0.484	311.9	
			-8.4	λ twist-boat-RuC	1.0	0.958	80.5	84.9
				λ twist-S	3.2	0.599	139.9	

^a For five-membered rings, $Q \equiv q_2$ and $\Phi = \phi_2$.

Careful analysis of Tables 2 and 3 shows that for each type of diastereomer (**I**, **II**, **V**, and **XII**) the strain energy is markedly changed with the change of the chiral center environment. In fact, the change of chirality of the sulfur atoms implies a different orientation of the negatively charged oxygen atoms and correspondingly of the positively charged methyl groups. This gives a variation of the electrostatic energy contributions, besides to smaller changes in the van der Waals and bending energy terms. Thus, for complexes of type **I**, considering together meso and rac ligands, the strain energy increases from -41.8 kcal mol⁻¹ for 12-[RuCl₂S₄](S[^]S[R,R])₂, where the oxygen atoms are alternatively up and down with respect to the Ru-S₄ coordination plane, to -31.6 kcal mol⁻¹ for 12-[RuCl₂S₄](S[^]S[R,S])₂, where all the oxygen atoms lie on the same side of the Ru-S₄ plane. For the other two diastereomers at -39.8 and -36.0 kcal mol⁻¹, two adjacent oxygen atoms are up and two are down with respect to the coordination plane. In all these cases, the electrostatic interaction with the chlorine atoms is essentially constant because all the S atoms are in cis positions with respect to the Cl ligands. On the contrary, for the cis complexes of type **II**, the electrostatic oxygen-chlorine interactions appear to be prevalent over the oxygen-oxygen interactions. In fact, we can observe an increase of about 30 kcal mol⁻¹ in the E_c term, paralleled by the total strain energies, going from 33-[RuCl₂S₄](S[^]S[R,S])₂ Δ , where the sulfur atom configurations allow an oxygen atom arrangement away from the chlorine atoms, to 22-[RuCl₂S₄](S[^]S[R,S])₂ Δ , in which the sulfur atom configurations are reversed with respect to the

previous case, leading to a geometry with all the oxygen atoms directed toward the chlorine ligands. The other four diastereomers, which have only two oxygen atoms pointing toward the chlorine atoms, have similar energies (-40.0 to -46.5 kcal mol⁻¹), the smaller energy differences being due to oxygen-oxygen interactions.

It is interesting to observe (Tables 2 and 3) that the trans isomers of type **I** have lower strain energies than those of type **V** and that the cis isomers of type **II** have lower energies than those of type **XII**. This suggests that formation of six-membered S[^]O rings is unfavored, from the steric point of view, with respect to formation of five-membered S[^]S rings. Therefore, it seems likely that the S,O-bonding, even if expected from an electronic point of view (see Introduction), is not achieved, because of unfavorable thermodynamic (higher strain energies) and kinetic (chelate effect) factors.

Ring Conformations. Tables 5 and 6 report the ring conformations for the lowest energy conformers of the diastereomers given in Tables 2 and 3, respectively, together with the ΔC and CP puckering parameters. We can see that the puckering amplitude, Q , for five-membered rings ranges from 0.404 to 0.749 Å, while for the six-membered rings Q ranges from 0.569 to 1.04 Å. Q values for the five-membered rings in complexes **1-3** are in the range 0.489-0.548 Å, in fairly good agreement with the calculated values.

Inspection of Tables 5 and 6 shows that the distinction between twist and envelope conformations of five-membered rings is not always easy from the CP pseudorotational Φ angles.

Table 6. Ring Geometries, with ΔC Values and CP Puckering Parameters for the Minimum Energy Diastereomers of $[\text{RuCl}_2(\text{rac-BMSE})_2]$;^a The Most Significant Conformers Are Also Reported

type	configuration index	ligand type and chirality	E	ring geometries	ΔC (deg)	Q (Å)	Φ (deg)	θ (deg)
I	12- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R])_2$	-41.8	δ twist-Ru	0.0	0.493	269.9	
				δ twist-Ru	0.0	0.490	270.0	
			-40.9	δ twist-Ru	0.0	0.493	269.9	
				λ twist-Ru	0.0	0.432	90.0	
			-40.1	λ twist-Ru	0.0	0.430	90.0	
	13- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R])(S^{\wedge}S[S])$	-36.0	δ twist-S	2.8	0.578	221.9	
				λ twist-S	2.8	0.578	138.0	
			-35.3	λ twist-S	3.2	0.525	135.7	
				λ twist-S	2.9	0.581	137.5	
			-34.6	λ twist-S	3.7	0.552	142.3	
	δ twist-S	3.7	0.552	217.6				
II	32- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R])(S^{\wedge}S[S]) \Delta$	-46.5	λ envelope-C	5.4	0.566	53.0	
				λ envelope-S	4.3	0.624	28.0	
			-43.3	δ envelope-S	5.6	0.664	200.8	
				λ envelope-S	5.2	0.667	21.8	
			-42.0	δ envelope-C	1.1	0.437	244.5	
	22- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[S])_2 \Delta$		δ envelope-C	3.0	0.515	290.8	
			-46.0	λ envelope-C	2.9	0.465	110.1	
				λ envelope-S	3.4	0.552	28.0	
	22- $[\text{RuCl}_2\text{S}_4]$	$(S^{\wedge}S[R,S])_2 \Delta$	-45.3	f envelope-Ru	4.2	0.524	185.6	
				f envelope-Ru	4.2	0.524	354.4	
			-40.0	λ twist-C	4.4	0.734	9.9	
				λ twist-C	4.4	0.734	170.0	
			-39.9	δ envelope-C	1.3	0.540	295.3	
		δ envelope-C	1.3	0.540	244.7			
		λ twist-C	5.8	0.701	16.6			
	δ twist-S	2.5	0.609	318.0				
V	13- $[\text{RuCl}_2\text{S}_2\text{O}_2]$	$(S^{\wedge}O[R,S])_2$	-32.9	δ boat-OC	3.1	0.932	302.6	89.2
				δ boat-OC	3.1	0.932	302.6	89.2
			-32.1	λ chair	13.7	0.730	235.3	11.8
				δ boat-OC	3.8	0.936	305.5	88.7
			-30.4	λ half-chair-CS	11.1	0.700	219.5	27.4
				λ half-chair-CS	11.1	0.700	219.5	27.4
			-28.5	δ boat-OC	3.6	0.928	304.5	89.3
				λ twist-boat-SS	17.9	0.801	148.6	81.3
			-28.2	λ twist-boat-SS	18.0	0.802	149.2	81.2
	14- $[\text{RuCl}_2\text{S}_2\text{O}_2]$	$(S^{\wedge}O[R,S])(S^{\wedge}O[S,R])$	-31.3	δ boat-OC	4.1	0.928	305.8	89.1
				δ boat-OC	10.3	0.951	288.1	90.9
				δ chair	10.7	0.757	91.1	173.0
			-27.9	λ twist-boat-RuC	12.3	0.974	99.0	87.8
				δ boat-OC	12.0	0.952	319.8	85.0
			-27.6	λ chair	10.9	0.759	271.9	6.8
				δ chair	10.9	0.758	91.3	173.0
			-26.8	δ chair	9.7	0.773	117.0	173.0
				λ twist-boat-SS	15.7	0.820	151.5	83.5
	δ half-chair-CC	4.0	0.636	320.3	133.0			
	δ chair	10.1	0.774	114.0	172.0			
XII	32- $[\text{RuCl}_2\text{S}_3\text{O}]$	$(S^{\wedge}O[S,R])(S^{\wedge}S[R]) \Delta$	-35.5	λ boat-OC	13.6	0.953	103.0	87.7
				λ twist-C	6.8	0.674	160.8	
			-35.2	δ twist-boat-SS	13.5	0.854	330.2	93.7
				δ twist-Ru	1.8	0.491	273.8	
			-32.5	δ twist-boat-SS	11.6	0.861	332.2	92.1
				λ envelope-S	4.4	0.647	156.3	
			-32.3	δ half-chair-CS	8.4	0.702	15.8	123.0
				δ twist-Ru	2.7	0.494	264.4	
			-31.5	λ chair	14.2	0.652	109.3	20.0
		λ twist-C	5.3	0.679	162.9			
	-31.3	λ chair	13.7	0.641	113.8	18.7		
		δ envelope-C	2.5	0.532	300.2			
	-31.0	δ half-chair-CS	4.5	0.694	30.7	136.0		
		λ twist-S	4.5	0.506	130.6			
	32- $[\text{RuCl}_2\text{S}_3\text{O}]$	$(S^{\wedge}O[S,R])(S^{\wedge}S[S]) \Delta$	-35.3	δ half-chair-CS	12.2	0.692	42.5	154.0
			λ envelope-C	2.9	0.447	71.0		
-33.0			λ boat-OC	3.4	0.907	121.6	89.9	
			λ envelope-S	5.2	0.561	33.0		
-32.2			δ boat-OC	15.0	0.755	306.2	101.0	
			λ twist-Ru	5.5	0.456	77.5		
	λ boat-OC	3.4	0.903	122.0	89.9			
	δ envelope-C	1.0	0.475	245.0				

Table 6 (Continued)

type	configuration index	ligand type and chirality	E	ring geometries	ΔC (deg)	Q (Å)	Φ (deg)	θ (deg)
			-30.0	δ twist-boat-SS	18.8	0.806	323.6	98.8
				δ twist-Ru	0.5	0.414	268.5	
	32-[RuCl ₂ S ₃ O]	(S [^] O[R,S])(S [^] S[S]) Δ	-34.2	λ chair	8.9	0.813	326.8	9.7
				λ twist-S	4.4	0.543	49.5	
			-30.0	λ chair	8.7	0.822	331.0	10.2
				δ envelope-S	5.4	0.658	201.5	
			-29.0	δ boat-OC	3.6	0.953	305.3	87.5
				λ twist-Ru	0.1	0.457	90.2	
	32-[RuCl ₂ S ₃ O]	(S [^] O[R,S])(S [^] S[R]) Δ	-29.0	λ chair	8.7	0.832	337.0	11.8
				λ twist-C	6.0	0.749	171.9	
			-23.5	λ chair	8.1	0.861	348.1	15.1
				δ twist-S	4.9	0.606	323.0	

^a For five-membered rings, $Q \equiv q_2$ and $\Phi = \phi_2$.

So, for example, the Φ value of 263.0° for isomer 13-[RuCl₂S₄] (**I**) at -39.8 kcal mol⁻¹ in Table 5, is nearly intermediate between the value of 252°, expected for an envelope conformation, and 270°, expected for a twist conformation.¹⁷ On the contrary, the ΔC value of 3.0° shows a good agreement between observed and ideal torsion angles for the twist geometry (the best ΔC value calculated for an envelope conformation is 8.2°). On the other hand, in the case of the conformer at -31.6 kcal mol⁻¹, the Φ value is 235.7°, very close to the value of 234°, correct for a twist conformation, but the torsion angle symmetry clearly indicates an envelope conformation, because of the markedly lower ΔC value (3.5° vs 8.4°).

The agreement between conformations deduced from Φ and ΔC values is much better for six-membered rings Ru(S[^]O). On the other hand, θ values do not always give the best description of the ring conformation. For example, the conformer at -25.9 kcal mol⁻¹ of isomer 13-[RuCl₂S₂O₂] (**V**) in Table 5 has a θ value of 173.0°, which would indicate a chair conformation ($\theta = 0$ or 180°). This is not consistent with the marked departure from the ideal chair conformation, as shown by the ΔC value of 25.3°, while the reported sofa-C conformation gives $\Delta C = 8.2^\circ$. This is not surprising since θ values have been deduced for regular polygons and small Q values.¹⁷

In the case of twist and envelope-C conformations of chelate five-membered rings, δ and λ descriptors are used to describe the ring helicity.¹² The same definition can also be used for six-membered chelate rings, when the two donor atoms are not identical.¹² However, if we assume, as suggested by IUPAC,¹² that the two skew lines are given by the line joining the donor atoms and the line joining the two ring atoms which are neighbors to each of the ligating atoms, the definition fails for all the geometries where the torsion angles are related by a mirror plane perpendicular to the "bite" axis (*i.e.*, chair, sofa-Ru, and boat-Ru conformations) since the two lines are parallel. On the contrary, if we take as the second line, the bond involving the donor atom of highest priority (C-C, in our case, C being linked to S), we avoid most of the singularities (see Tables 5 and 6). The only undefined geometry remains the sofa conformation with the metal as a flag atom, sofa-Ru (*e.g.*, conformers at -25.9 kcal mol⁻¹ (**V**) and at -31.3 kcal mol⁻¹ (**XII**) in Table 5), as well as the envelope-Ru conformation, in the case of five-membered rings (*e.g.*, conformer at -45.3 kcal mol⁻¹ (**II**)). In these cases, reference to an external axis must be considered, as proposed for tris-chelate complexes.^{18d} In the case of bis-chelate complexes, like RuCl₂(BMSE)₂, this direction is given by the 2-fold axis passing through the chlorine atoms in the trans isomers, or between the chlorine atoms and the metal atom in the cis isomers. The plane of the ring is either bent

toward the 2-fold axis or is pushed away from it, giving rise to "folded" (*f*) or "unfolded" (*u*) arrangements of the chelate rings.

It is worth noting that the trans complexes **1** and **3**, 13-[RuCl₂S₄](S[^]S[R,S])₂ (**I**), display a twist-Ru conformation for both the five-membered rings, with mixed δ - λ helicities in **1** and δ - δ helicities in **3**. For the two rings of the two crystallographically independent molecules of **1**, $\Delta C = 1.8^\circ$ (λ), 0.5° (δ) and $\Delta C = 0.8^\circ$ (δ), 0.5° (λ) for molecules 1 and 2, respectively. For the symmetry equivalent rings of **3**, $\Delta C = 3.4^\circ$ (δ), 3.4° (δ). This is in agreement with the calculated minimum energy structures, which also show that these conformers have practically identical strain energies ($\Delta E = 0.1$ kcal mol⁻¹, Table 5). The crystal structure of the cis complex **2**, containing the meso BESE ligand, is constituted from the racemic mixture of 33-[RuCl₂S₄](S[^]S[R,S])₂ Δ and 22-[RuCl₂S₄](S[^]S[S,R])₂ Λ (**II**), each with a pair of crystallographically independent molecules (1-2 Δ ; 1-2 Λ). In molecule 1 Δ , the chelate rings have both a λ twist-Ru conformation ($\Delta C = 1.8$ and 2.8°), while in molecule 2 Δ , one has a λ envelope-C ($\Delta C = 6.0^\circ$) and the other a λ twist-Ru ($\Delta C = 0.7^\circ$) conformation. On the other hand, the calculated minimum energy structure for the meso BMSE complex 33-[RuCl₂S₄](S[^]S[R,S])₂ Δ has a pair of δ envelope-C rings. Higher energy conformers have only twist-Ru conformations (Table 5). This suggests that side groups, as well as packing, can affect the ring conformations.

Conclusions

The results of the present MM analysis show the transferability of the force field previously obtained for Ru-monosulfide complexes^{5a} to Ru-disulfide chelates, finding good agreement between observed and calculated structural parameters. Moreover, the experimental molecular structures of complexes **1-3** correspond to the calculated lowest strain energy diastereoisomers.

MM results show that for each type of diastereomer (**I**, **II**, **V**, and **XII**) the strain energy is markedly changed with the change of the chiral center environment, essentially because of the increase in the electrostatic energy terms. In fact, the change of chirality of the sulfur atoms means a different orientation of the negatively charged oxygen atoms and correspondingly of the positively charged methyl groups.

The comparison between the examined trans isomers **I** and **V**, and the cis isomers **II** and **XII**, shows that the passage from S,S to S,O bonding, that is, from five- to six-membered rings, implies a significant increase of the strain energies.

Finally, it is interesting to observe that the lowest energy isomer of type **I**, has a strain energy 17.7 kcal mol⁻¹ higher

than that of type **II**, in the case of meso ligands. The difference is reduced to 3.7 kcal mol⁻¹ in the case of a rac mixture. Therefore, it might be expected that the trans isomers were thermodynamically unstable both for electronic (σ, π trans influence) and steric factors and should isomerize to the cis forms. Unfortunately, no stereochemical investigations in solution have yet been carried out, and only few structural characterizations have been so far reported for disulfoxide ruthenium complexes,⁷ so that no experimental information is available about the thermodynamic stability of the various

isomers. In any case, only S-bonding is found in the five complexes quoted in the Introduction, consistent with the MM findings that formation of five-membered chelate rings is sterically favored with respect to that of larger rings.

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