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The First Coordination Complexes of Selenones: A Structural Comparison with Complexes of Sulfones[†]

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Reactivity of the two classes of very weak donors R_2XO_2 (X = S, R = Me (**1**) and Ph (**2**); X = Se, R = Me (**3**) and Ph (**4**)) have been studied. Coordination properties of sulfones and selenones in solution and in the gas phase have been compared for the first time using a model bidentate metal complex, $[Rh_2(O_2CCF_3)_4]$. Two coordination modes, bridging μ_2-O,O′ and terminal η^1-O, have been detected. These types of binding were realized in two series of sulfone and selenone metal complexes, polymeric mono-adducts $\{Rh_2(O_2CCF_3)_4 \cdot (R_2XO_2)\}_\infty$ (X = S, R = Me (**1a**); R = Ph (**2a**); X = Se, R = Ph (**4a**)) and discrete bis-adducts $[Rh_2(O_2CCF_3)_4 \cdot (R_2XO_2)_2]$ (X = S, R = Ph (**2b**); X = Se, R = Me (**3b**)). The compositions and structures of new compounds have been confirmed by NMR and IR spectroscopy, chemical analyses, and X-ray diffraction studies. Compounds **3b** and **4a** are the first crystallographically characterized metal complexes having selenone ligands coordinated to the metal centers. Preparation and X-ray study of analogous metal complexes of sulfone and selenone ligands allow, for the first time, tracking the structural changes induced by metal coordination. In addition, the X-ray structure of dimethyl selenone, Me_2SeO_2 (**3**), an analogue of Me_2SO_2, has been determined. Geometries of coordinated sulfone and selenones ligands have been compared with those of the corresponding "free" molecules.

Introduction

As part of a broad study of the comparative ligating properties of small organosulfur and organoselenium molecules, we recently reported that dimethyl sulfoxide (Me_2SO) and dimethyl selenoxide (Me_2SeO) display different thermal stability and reactivity under similar experimental conditions.[1] In the present work we extend this research to classes of molecules containing two terminal oxo functions, namely, sulfones and selenones, R_2SO_2 and R_2SeO_2 (R = Me and Ph).

In contrast to well-demonstrated donor properties of sulfoxides R_2SO,[2] sulfones are very weak donors and show very limited coordination chemistry. Sulfones are widely used in organic synthesis.[3] They are effective enhancers of polymerase chain reaction DNA amplification.[4a] Dimethyl sulfone (methylsulfonylmethane; MSM) is a popular dietary supplement of low toxicity, used in a variety of conditions including pain, inflammation, allergies, arthritis, parasitic infections, and the maintenance of normal keratin levels in hair, skin, and nails.[4b−c] It has been investigated for treatment of interstitial cystitis[4d] and murine autoimmune lymphoproliferative disease,[4e] and has been found to readily cross the blood−brain barrier.[4f] Sulfone reactivity and chemical bonding,[5] as well as mechanisms of rearrangements and decomposition[6] are of current interest. Structural data on a variety

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of sulfones are available,[7] but information on their complexation has thus far been limited to lithium,[8] with only one work aimed at studying the sulfone coordination by transition metal centers.[9] Two more examples have been mentioned for the whole transition metal series, namely, diethyl sulfone cobalt[10] and tetramethylene sulfone copper complexes.[11] Coordination complexes of sulfones with mercury(II) will soon be reported.[12]

Selenones have been much less studied than their sulfur analogues and are only infrequently used in organic synthesis.[13] Several selenones, including diphenyl selenone,[14] have been crystallographically characterized.[15] Selenones have been studied as potential antitumor agents,[16] and the biological reduction of dimethyl selenone has been reported.[17a−c] Preliminary results indicate that dimethyl (**3**) and diphenyl (**4**) selenones are more effective than the corresponding dimethyl (**1**) and diphenyl (**2**) sulfones, respectively, in inhibiting endothelial cell chemotaxis toward extracellular matrix proteins.[17d] Early reports of the biological formation of dimethyl selenone were shown to be incorrect; dimethyl selenenyl sulfide, MeSeSMe, with the same nominal mass was shown to be the actual product.[17c] Near K-edge X-ray absorption spectroscopy of dimethyl selenone is useful for distinguishing this compound in admixture with other selenium species in complex matrices.[17e,f]

Table 1. Numbering of Sulfones, Selenones, and Their Metal Complexes

L	Me_2SO_2 **1**	Ph_2SO_2 **2**	Me_2SeO_2 **3**	Ph_2SeO_2 **4**
$[Rh_2]$:L = 1:1	**1a**	**2a**		**4a**
$[Rh_2]$:L = 1:2	**1b**	**2b**	**3b**	

Ligating properties of selenones toward metal centers, to our knowledge, have not been previously reported. Therefore we attempted to compare the reactivity of sulfone R_2SO_2 ligands with that of the corresponding selenones R_2SeO_2 (in both cases R = Me and Ph) toward a model coordinatively unsaturated metal complex having two centers of Lewis acidity, $[Rh_2(O_2CCF_3)_4]$. We have extensively used dirhodium(II) tetrakis(trifluoroacetate) for testing reactivity of various donor molecules. The electron-withdrawing effect of four trifluoroacetate groups significantly enhances the Lewis acid properties of the rhodium centers so as to allow coordination of extremely weak donors, the latest examples being 1,4-diiodo-1,3-butadiyne[18] and corannulene.[19] Good volatility and good solubility of this model complex allow us to use both solution and gas-phase coordination reactions for preparation of adducts with controlled stoichiometries in crystalline form. The presence of two acidic metal centers in selected metal complex accounts for structural flexibility and structural diversity of the donor−acceptor products formed. In this work we present our findings on the reactivity of weak donor molecules having two terminal oxo functions as potential coordination sites, R_2XO_2 (R = Me, Ph; X = S, Se).

Results and Discussion

To test the donor properties of terminal oxo functions of sulfones, Me_2SO_2 (**1**) and Ph_2SO_2 (**2**), their coordination reactions with the bidentate electrophilic complex $[Rh_2(O_2CCF_3)_4]$ have been studied under controlled reaction conditions in the gas phase and solution. First, sublimation of the dirhodium complex in the presence of the corresponding volatile sulfone molecules was performed followed by deposition of donor−acceptor products in crystalline form. The ratio of components in the solid state was controlled to afford two products of the composition $[Rh_2]:R_2SO_2 = 1:1$ (Table 1), namely, $[Rh_2(O_2CCF_3)_4\cdot(O_2SR_2)]$, where R = Me (**1a**) and Ph (**2a**).

The compositions and structures of both products were revealed by elemental analysis and by single-crystal X-ray studies. Both complexes are built on the bridging μ_2-O,O′ coordination mode of sulfone ligands that link two rhodium centers of the two neighboring dimetal complexes through both oxygen atoms. This results in the formation of infinite 1D polymeric chains in **1a** and **2a** (Figures 1 and 2). There are two independent dirhodium molecules in complexes **1a** and **2a** with their geometrical characteristics being very

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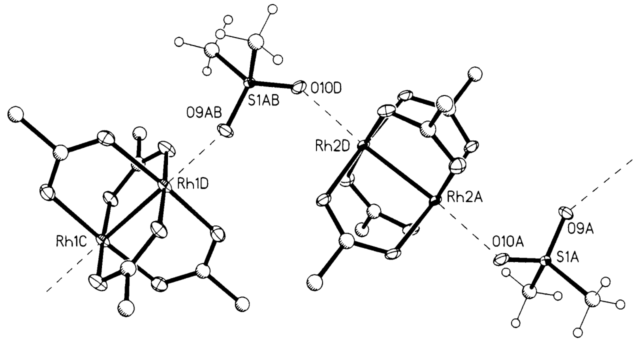

Figure 1. A fragment of a 1D polymer $\{Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}O_2SMe_2)\}^1_\infty$ (**1a**) showing the alternating arrangement of $[Rh_2(O_2CCF_3)_4]$ and dimethyl sulfone molecules. Rhodium, sulfur, and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii. Fluorine atoms are omitted for clarity. Dashed lines indicate axial coordination to rhodium atoms (this has been used for Figures 2 and 6).

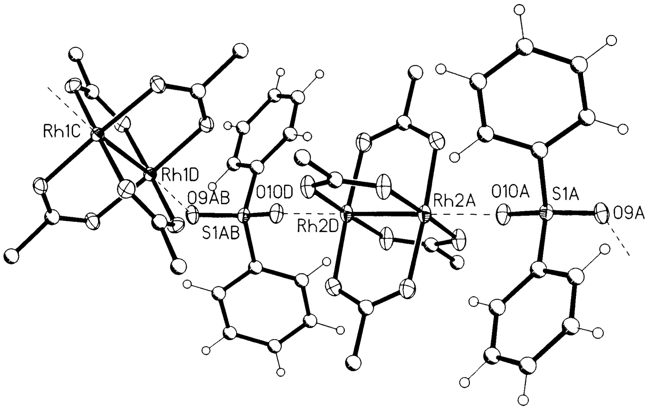

Figure 2. A fragment of a 1D polymer $\{Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}O_2SPh_2)\}^1_\infty$ (**2a**).

similar and typical for adducts with weakly bound σ-donor ligands (Table 2).

The two Rh−O axial distances in complex **1a** are slightly different, 2.287(4) and 2.307(4) Å, while the S−O bond distances of the ligand in **1a** differ insignificantly, 1.438(5) and 1.449(5) Å. For comparison, the S−O bond distance in the uncomplexed dimethyl sulfone molecule is 1.45 Å.[20] The angles around the S atoms for complexed and uncomplexed sulfones are also similar. It is interesting to compare the geometrical parameters of the mono-adduct **1a** with those of the bis-adduct, $[Rh_2(O_2CCF_3)_4\cdot(Me_2SO_2)_2]$ (**1b**), prepared earlier[9] from solutions containing $[Rh_2(O_2CCF_3)_4]$ and an excess of dimethyl sulfone. For **1b** an average Rh−O axial distance of 2.287(3) Å is very similar to that in **1a**. It should also be noted that, in $[Rh_2(O_2CCF_3)_4\cdot(Me_2SO_2)_2]$, virtually no difference was detected between the S−O bond lengths for coordinated and uncoordinated oxygen atoms (1.455(3) vs 1.450(4) Å).

The two Rh−O axial contacts in the mono-adduct **2a** are 2.290(4) and 2.301(4) Å, and the two S−O distances of diphenyl sulfone are the same, 1.443(4) Å. A direct comparison of the coordinated sulfone in **2a** with the structure of diphenyl sulfone (the S−O distance is 1.44 Å[21]) is not informative since the SO_2 groups in pure diphenyl sulfone are involved in formation of hydrogen bonds responsible for solid state supramolecular aggregation.[7c]

In the present work the electronic effect of two different substituents R on the sulfur atoms of disubstituted sulfones **1** and **2** is not seen, since average axial Rh−O distances are almost identical for dimethyl and diphenyl sulfone complexes **1a** and **2a**, 2.297 vs 2.296 Å, respectively. At the same time there is a noticeable difference in the two S−O−Rh angles in polymer **2a**, 127.2(2) vs 163.9(3)°, but not in **1a**, in which the corresponding angles are more similar, 130.3(3)° and 139.9(3)°. This difference can be explained by steric or packing effects caused by the phenyl substituents in **2a**.

By analogy with the earlier work,[9] solution coordination of the dirhodium complex in the presence of an excess of diphenyl sulfone affords a bis-adduct complex, $[Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)_2]$ (**2b**), which has been isolated as a dichloromethane solvate. The structure of **2b** consists of centrosymmetric discrete molecules $[Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)_2]$ (Figure 3) having sulfone ligands coordinated to the dirhodium core at both axial sites through only one oxygen atom. The Rh−O axial distance is 2.306(2) Å, and the S−O−Rh angle is 132.1(1)°. In contrast to the dimethyl sulfone bis-adduct **1b**, in complex **2b** there is a noticeable difference in the S−O distances to the coordinated compared to the uncoordinated oxygen atom, e.g., 1.456(2) vs 1.428(2) Å.

When studying reactivity of dimethyl and diphenyl selenone ligands toward the dirhodium complex in the gas phase at 110−140 °C, decomposition of both Se-containing ligands has been observed yielding only oily, unidentifiable products. Therefore, in the case of more thermally sensitive selenones, Me_2SeO_2 and Ph_2SeO_2, we have been limited to solution coordination reactions and to the use of standard solvent diffusion methods for crystal growth.

For the ligands **1**, **2**, and **4** the crystal structures have been reported, while that of dimethyl selenone (**3**) has not. To compare the geometry of the coordinated molecule with its "free" form, an X-ray structural characterization of **3** has been accomplished in this work. Molecules of Me_2SeO_2 are distorted tetrahedrons with C_{2v} symmetry (Figure 4).

The Se−O and Se−C bond lengths of 1.626(1) and 1.905(2) Å are longer than those in the corresponding sulfone **1**. The O−Se−O angle of 114.75(10)° is greater than the ideal tetrahedral value, while the C−Se−C angle of 107.6(1)° is slightly less than tetrahedral (Table 2). In the solid state structure of **3** hydrogen bonds C−H···O are responsible for supramolecular aggregation of Me_2SeO_2 molecules. Hydrogen atoms are located along the directions of electron lone pairs of oxygen atoms with O···H contacts and angles C−H···O being in the ranges 2.44−2.56 Å and 145−157°, respectively.

From the system containing dirhodium complex and dimethyl selenone (**3**), the product **3b** has been crystallized from solutions in low yield. This product was shown by X-ray diffraction study to have a discrete bis-adduct structure

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Table 2. Selected Distances (Å) and Angles (deg) in Complexes $\{Rh_2(O_2CCF_3)_4\cdot(Me_2SO_2)\}^1_\infty$ (**1a**), $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)\}^1_\infty$ (**2a**), $[Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)_2]\cdot 2CH_2Cl_2$ (**2b**$\cdot 2CH_2Cl_2$), $[Rh_2(O_2CCF_3)_4\cdot(Me_2SeO_2)_2]$ (**3b**), $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SeO_2)\}^1_\infty$ (**4a**), and $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SeO_2)\}^1_\infty\cdot 1,2\text{-}C_2H_4Cl_2$ (**4a′**$\cdot 1,2\text{-}C_2H_4Cl_2$)

	1a	**2a**	**2b**	**3b**	**4a**	**4a′**
Rh−Rh[a]	2.3951(9)	2.3947(9)	2.3973(4)	2.4104(7)	2.4045(4)	2.3988(6)
Rh−O_{TFA}[a]	2.032(5)	2.035(5)	2.030(2)	2.037(3)	2.037(2)	2.035(3)
Rh−$O_{S(Se)}$	2.287(4) 2.307(4)	2.301(4) 2.290(4)	2.306(2)	2.272(3)	2.265(2)	2.243(3) 2.266(2)
Rh−Rh−O[a]	177.47(11)	177.54(11)	177.26(5)	178.67(8)	179.10(5)	175.72(7)
Rh−O−S(Se)	130.3(3) 139.9(3)	127.2(2) 163.9(3)	132.07(13)	127.2(2)	125.05(11)	120.36(12) 142.30(15)
S(Se)−O_{coord}[a]	1.444(5)	1.443(4)	1.456(2)	1.640(3)	1.635(2)	1.628(3)
S(Se)−$O_{uncoord}$			1.428(2)	1.624(3)		
S(Se)−C	1.744(7)	1.757(6)	1.759(3)	1.901(5)	1.908(3)	1.911(3)
O−S(Se)−C	108.3(3)	108.0(3)	107.84(14)	110.2(2)	107.10(12)	109.00(17)
C−S(Se)−C	106.7(3)	107.7(3)	106.33(13)	104.1(2)	109.98(17)	107.13(16)
O−S(Se)-O	116.6(3)	116.9(2)	118.53(13)	112.1(2)	118.38(14)	113.46(13)

[a] Data are averaged for two independent dirhodium units (**1a**, **2a**, **3b**, and **4a′**).

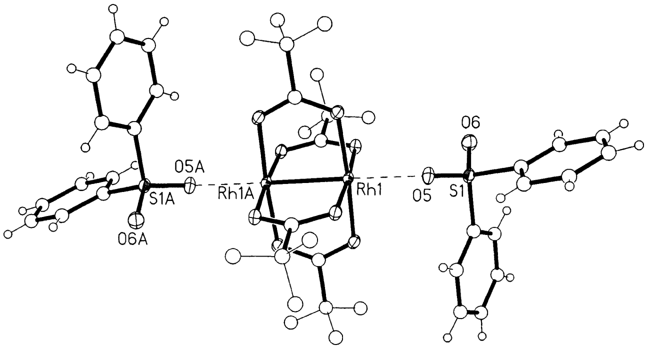

Figure 3. A perspective drawing of the $[Rh_2(O_2CCF_3)_4\cdot(O_2SPh_2)_2]$ (**2b**) molecule. Rhodium, sulfur, and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. Carbon, fluorine, and hydrogen atoms are shown as spheres of arbitrary radii (this has also been used for Figure 5).

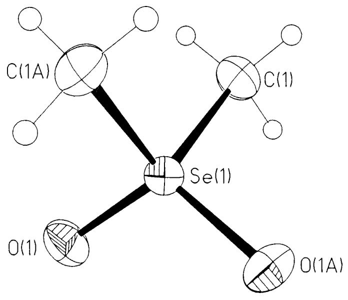

Figure 4. A perspective drawing of the Me_2SeO_2 (**3**) molecule. Selenium, oxygen, and carbon atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

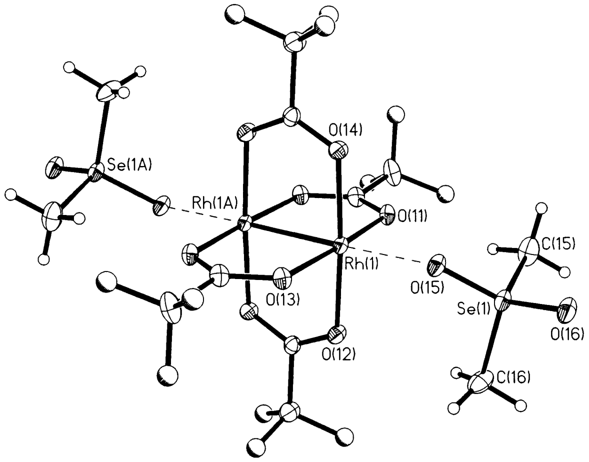

Figure 5. A perspective drawing of the $[Rh_2(O_2CCF_3)_4\cdot(O_2SeMe_2)_2]$ (**3b**) molecule.

$[Rh_2(O_2CCF_3)_4\cdot(\eta^1\text{-}O_2SeMe_2)_2]$ (Figure 5) in which dirhodium molecules have two terminally coordinated dimethyl selenones. There are two crystallographically independent centrosymmetric molecules in **3b**, but their geometrical characteristics are very close. The average Rh−O distance for these two molecules of 2.272(3) Å is slightly shorter than that in analogous sulfur complex **1b** (2.287(3) Å[9]). In contrast to **1b**, there is a noticeable elongation of the Se−O bond involved in coordination (average 1.640(3) Å) versus the uncoordinated Se−O bond (1.624(3) Å). The latter value is virtually the same as in the structure of free ligand **3** mentioned above. The observed structural changes upon coordination confirm stronger metal−ligand interactions in **3b** than in analogous complex **1b**, a fact which stems from higher polarization of the Se−O bond compared to the S−O bond.

From the system containing dirhodium complex and diphenyl selenone **4** only one product was isolated in the form of single crystals of sufficient quality for an X-ray study. This product was confirmed to be a 1D polymer (Figure 6) built on the bridging coordination of selenone, $\{Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}O_2SePh_2)\}^1_\infty$ (**4a**). This complex was also crystallized as a dichloroethane solvate (**4a′**). Complexes **4a** and **4a′** exhibit different symmetry but show a similar general structural motif as found in **2a**, and that allows us to make a direct structural comparison of the sulfur and selenium analogues.

In contrast to **2a**, the dirhodium molecule in **4a** is centrosymmetric; therefore the Se−O−Rh angles in **4a** are both 125.05(11)°. The axial Rh−O interaction in **4a**, 2.265(2) Å, is slightly shorter than that in the analogous sulfur adduct **2a**. The corresponding Se−O bond distance is 1.635(2) Å.

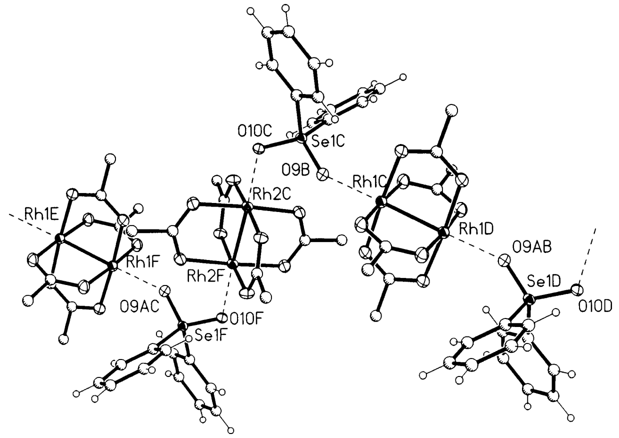

Figure 6. A fragment of a 1D structure of **4a**, $\{Rh_2(O_2CCF_3)_4\cdot(\mu_2\text{-}O_2\text{-}SePh_2)\}^1_\infty$.

Similarly to **1a** and **2a**, there are two crystallographically independent dirhodium units in complex **4a′**. One Rh−O axial distance is slightly longer than the other (2.243(3) vs 2.266(2) Å), and the corresponding Se−O distances are also different, 1.621(3) and 1.634(3) Å. This can be compared with the Se−O distance of 1.620 Å in uncomplexed diphenyl selenone. The latter was calculated using atom coordinates of Ph_2SeO_2 reported in a very short communication.[15c] In contrast to **4a**, the Se−O−Rh angles are different in **4a′**, e.g., 142.30(15)° and 120.36(12)°. The observed differences in some geometrical parameters of **4a** and **4a′** are probably crystallographically imposed.

For the purpose of comparison, the main structural parameters of analogous 1D chain complexes **1a**, **2a**, and **4a** are listed in Table 2. The geometrical characteristics of the rigid dirhodium units in all complexes are nearly constant, regardless of the nature of the coordinated R_2XO_2 molecules and their coordination mode. The only noticeable difference is that the Se−O bond of diphenyl selenone is distinctly longer than the S−O bond in diphenyl sulfone, and that results in slightly shorter Rh−O axial contacts in **4a** compared to analogous complex **2a**. The same trend is observed in isostructural bis-adduct complexes **1b** and **3b**.

A direct comparison of the geometric characteristics of free and coordinated R_2XO_2 (X = S and Se) ligands studied here shows that their complexation by the dirhodium complex is weak (Table 3). The S(Se) atoms of coordinated sulfone/selenone molecules display a distorted tetrahedral coordination with average angles around the central atoms being very similar to those in their "free" forms. Coordination of R_2XO_2 to the rhodium centers of $[Rh_2(O_2CCF_3)_4]$ does not perturb the structures of ligands as there is no significant elongation of the S−O or Se−O bonds nor noticeable alternation of angles around the S(Se) atoms. This is confirmed by IR spectroscopy for the products. The only previously characterized example, containing μ_2-O,O′-diethyl sulfone, was indirectly produced by the cleavage of the dithiolate C−S bond.[10] The infrared spectrum of that product exhibited strong characteristic bands for bridging diethyl sulfone. Compared to the S−O absorption for a free ligand, the bands were red shifted by about 100 cm^{-1} as a result of weakening of the S−O bond upon coordination. Our IR data for the complexed dimethyl sulfone in **1a** does not reveal such drastic changes. In agreement with the earlier work,[9] the ligand ν_{sym} (1143 cm^{-1}) has shifted only to 1120 cm^{-1}, while ν_{asym} at 1307 has moved to 1270 cm^{-1} in complex **1a**.

Conclusions

This work is the first comparative study of coordination properties of analogous sulfone and selenone molecules. The reactivity of these weak donors was enhanced by using dirhodium(II,II) tetrakis(trifluoroacetate) complex that has prominent electrophilic properties. Preparation and X-ray study of metal complexes, and direct comparison of selenium and sulfur analogues under similar experimental conditions has revealed similarities in their coordination modes but different thermal stability and reactivity. The stronger bonding of the dirhodium complex with selenone compared to sulfone oxygen is indicated by the shorter Rh−O(Se) bonds compared to Rh−O(S) bonds and by the relative lengthening of complexed vs uncomplexed Se−O bonds in selenones compared to complexed vs uncomplexed S−O bonds in sulfones. This difference in bonding in sulfones and selenones has potentially significant implications for studies comparing their biological activity, as will be discussed in more detail elsewhere.[17d]

Coordination of R_2XO_2 was found to be very weak as manifested by X-ray crystallography and IR spectroscopy. Two different coordination modes of sulfones and selenones have been revealed upon coordination by $[Rh_2(O_2CCF_3)_4]$, namely, η^1-O and μ_2-O,O′. The former is observed in discrete bis-adduct types of complexes, while the latter is found in products of 1:1 composition that have extended chain structures. We note that this is the first structural characterization of coordinated selenones.

One of the major observations made in this work is the fact that the geometry (distances and angles) of complexed alkyl sulfones and selenones is not different from that of the uncomplexed ligands. In other words, coordination by the dirhodium complex does not perturb ligand structures. This finding is important for our ongoing work with low molecular weight organosulfur and selenium molecules that are liquids or low-melting solids for which direct structural characterization cannot be accomplished.

The structure of dimethyl selenone is also reported here for the first time. The solid state packing in the structure of **3** is characterized by multiple hydrogen bonding to the oxo atoms of selenone. That may affect the distances and angles in the molecule compared to the true "free" ligand structure in the gas phase. Interestingly, all efforts to volatilize **3** have thus far led only to decomposition[22] as was also found in the case of dimethyl selenoxide.[1] That is the reason that gas phase structural data for **3** are unavailable.

Experimental Section

General Data. All manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk techniques. The $[Rh_2(O_2CCF_3)_4]$ without any exogenous ligands

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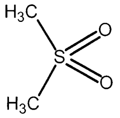
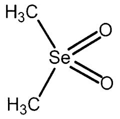
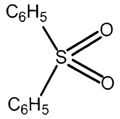
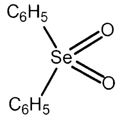
[22] Block, E.; Gillies, W. Unpublished results.

Table 3. Geometric Characteristics of "Free" and Coordinated R_2XO_2 Molecules (X = S, Se; R = Me, Ph)

Molecule	Bond (Å), Angle (deg)	"Free" Ligand	Coord. Ligand μ_2-O,O'	Coord. Ligand η^1-O
Dimethyl Sulfone 	S=O S-C O-S-O C-S-O C-S-C	1.446(3) 1.765(5) 117.3(2) 108.5(1) 104.8(2) (**1**) [20b]	1.444(5) 1.744(7) 116.6(3) 108.3(3) 106.7(3) (**1a**) [this work]	1.453(4) 1.764(4) 115.5(2) 109.3(3) 103.5(4) (**1b**) [9]
Dimethyl Selenone 	Se=O Se-C O-Se-O C-Se-O C-Se-C	1.626(1) 1.905(2) 114.75(10) 108.56(8) 107.6(1) (**3**) [this work]		1.640(3) 1.901(5) 112.1(2) 110.2(2) 104.1(2) (**3b**) [this work]
Diphenyl Sulfone 	S=O S-C O-S-O C-S-O C-S-C	1.437(2) 1.768(2) 119.2(1) 108.1(1) 104.1(1) (**2**) [21]	1.442(4) 1.758(5) 116.9(2) 108.0(2) 107.6(2) (**2a**) [this work]	1.442(2) 1.759(3) 118.53(13) 107.84(14) 106.33(13) (**2b**) [this work]
Diphenyl Selenone 	Se=O Se-C O-Se-O C-Se-O C-Se-C	1.620 1.908 117.9 108.1 105.7 (**4**) [15c][a]	1.635(2) 1.908(3) 118.4(1) 107.1(1) 110.0(2) (**4a**) [this work]	

[a] Distances and angles are calculated using atomic coordinates in ref 15c.

was prepared according to the literature procedures.[23] Dimethyl and diphenyl sulfones were purchased from Aldrich and dried in a vacuum for 24 h prior to use. Dimethyl[17a] and diphenyl selenones[14] were prepared according to modified literature procedures. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. NMR spectra were obtained using Varian Gemini or XL-300 spectrometers at 300 MHz for ^1H and 75.1 MHz for ^{13}C. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Syntheses. $[Rh_2(O_2CCF_3)_4\cdot(O_2SMe_2)]$ (1a). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.066 g, 0.10 mmol) and Me_2SO_2 (0.005 g, 0.005 mmol) was sealed in an evacuated (10^{-2} atm) 10 × 70 mm glass ampule. The ampule was then placed in an electric furnace having a temperature gradient along the length of the tube. The ampule was kept at 165 °C for a week to afford green crystals of **1a** deposited in the coldest end of the tube where the temperature was set ca. 160 °C. Yield: 0.049 g, 65%. Anal. Calcd: C, 15.97; H, 0.80. Found: C, 16.10; H, 0.89. IR (KBr, cm^{-1}): 2940w, 1667s, 1662s, 1231s, 1190s, 1166s, 1194w, 1002w, 948w, 860m, 804w, 786m, 739w, 694w, 542w, 528w, 464w.

$[Rh_2(O_2CCF_3)_4\cdot(O_2SPh_2)]$ (2a). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.045 g, 0.07 mmol) and Ph_2SO_2 (0.015 g, 0.07 mmol) was sealed in an evacuated glass ampule. The ampule was then placed in the electric furnace and kept at 130 °C for 2 days. This resulted in green crystals of **2a** deposited in the coldest end of the tube where the temperature was set ca. 120 °C. Yield: 0.034 g, 55%. Anal. Calcd: C, 27.42; H, 1.15. Found: C, 27.55; H, 1.23. IR (KBr, cm^{-1}): 2968m, 2906w, 1675s, 1657s, 1455m, 1416w, 1268s, 1224w, 1193m, 1163m, 1101s, 1017s, 879m, 861s, 802s, 740m, 702m, 684m.

Table 4. Crystallographic Data for Sulfone Complexes: $\{Rh_2(O_2CCF_3)_4\cdot(Me_2SO_2)\}^1_\infty$ (**1a**), $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)\}^1_\infty$ (**2a**), and $[Rh_2(O_2CCF_3)_4\cdot(Ph_2SO_2)_2]\cdot 2CH_2Cl_2$ (**2b**·$2CH_2Cl_2$)

	1a	**2a**	**2b**
formula	$Rh_2SO_{10}F_{12}C_{10}H_6$	$Rh_2SO_{10}F_{12}C_{20}H_{10}$	$Rh_2S_2O_{12}F_{12}Cl_4C_{34}H_{24}$
fw	752.03	876.16	1264.27
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.062(2)	11.1098(9)	8.3668(7)
b (Å)	9.681(1)	11.9417(9)	9.4711(8)
c (Å)	13.244(2)	12.9680(9)	14.2118(12)
α (deg)	103.70(2)	96.876(7)	86.2260(10)
β (deg)	102.63(2)	112.277(8)	73.8870(10)
γ (deg)	106.55(1)	110.450(4)	88.1540(10)
V (Å^3)	1029.7(3)	1427.2(2)	1079.5(2)
Z	2	2	1
ρ_{calcd} ($g\cdot cm^{-3}$)	2.425	2.039	1.945
μ (mm^{-1})	1.859	1.358	1.220
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
transm factors		0.7277−0.8762	0.7263−0.9415
temp (K)	213(2)	213(2)	173(2)
data/restr/params	2603/36/316	4663/48/418	4809/0/338
*R*1,[a] *wR*2[b]			
$I > 2\sigma(I)$	0.0413, 0.1036	0.0508, 0.1326	0.0344, 0.0826
all data	0.0428, 0.1060	0.0564, 0.1391	0.0400, 0.0854
quality-of-fit[c]	1.048	1.043	1.048

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

$[Rh_2(O_2CCF_3)_4\cdot(O_2SPh_2)_2]$ (2b). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.030 g, 0.05 mmol) and Ph_2SeO_2 (0.035 g, 0.16 mmol) was dissolved in CH_2Cl_2 (10 mL). The mixture was stirred overnight

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(23) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19.

Table 5. Crystallographic Data for Dimethyl Selenone (**3**) and Selenone Complexes: $[Rh_2(O_2CCF_3)_4\cdot(Me_2SO_2)_2]$ (**3b**), $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SeO_2)\}^1_\infty$ (**4a**), and $\{Rh_2(O_2CCF_3)_4\cdot(Ph_2SeO_2)\}^1_\infty\cdot C_2H_4Cl_2$ (**4a′**·$C_2H_4Cl_2$)

	3	3b	4a	4a′
formula	$SeO_2C_2H_6$	$Rh_2Se_2O_{12}F_{12}C_{12}H_{12}$	$Rh_2SeO_{10}F_{12}C_{20}H_{10}$	$Rh_2SeO_{10}F_{12}Cl_2C_{22}H_{14}$
fw	141.03	939.96	923.06	1022.01
crystal system	monoclinic	triclinic	orthorhombic	triclinic
space group	$C2/c$	$P\bar{1}$	$Pbcn$	$P\bar{1}$
a (Å)	8.8118(9)	9.3124(9)	10.1378(6)	11.8427(7)
b (Å)	8.4480(9)	10.337(2)	20.4656(12)	12.9521(8)
c (Å)	6.9904(7)	13.974(2)	13.1423(8)	13.2926(8)
α (deg)		83.767(3)		108.9900(10)
β (deg)	120.184(2)	72.945(3)		97.7230(10)
γ (deg)		80.511(3)		117.0250(10)
V (Å^3)	449.82(8)	1265.8(3)	2726.7(3)	1618.2(2)
Z	4	2	4	2
ρ_{calcd} (g·cm^{-3})	2.082	2.466	2.249	2.098
μ (mm^{-1})	8.183	4.322	2.680	2.429
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
transm factors	0.2914−0.6851	0.3212−0.8813	0.4627−0.8557	0.6973−0.7760
temp (K)	243(2)	173(2)	173(2)	173(2)
data/restr/params	528/0/37	24369/0/368	3295/6/221	7268/53/450
$R1$,[a] $wR2$[b]				
$I > 2\sigma(I)$	0.0154, 0.0420	0.0545, 0.1374	0.0300, 0.0780	0.0363, 0.0970
all data	0.0158, 0.0422	0.0784, 0.1451	0.0340, 0.0806	0.0390, 0.0970
quality-of-fit[c]	1.162	0.944	1.031	1.050

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

and then filtered to give a green solution. Hexanes (10 mL) were carefully layered on the top of the CH_2Cl_2 solution. After 2−3 days when the layers had mixed, the volume of the mixture was reduced by $^1/_2$. The concentrated solution was refrigerated to afford green crystals of **2b** as a CH_2Cl_2 solvate in 12 h. Yield: 0.029 g, 50%. IR (KBr, cm^{-1}): 3065w, 1661s, 1449s, 1319m, 1310s, 1298m, 1232s, 1199s, 1154s, 1132w, 1107m, 1069w, 1024w, 862m, 786m, 780m, 761m, 740s, 731s, 700m, 691s, 682m. ^1H NMR (acetone-d_6, 22 °C) δ 7.65 (m), 8.01 (m).

Dimethyl Selenone, Me_2SeO_2 (3). 3-Chloroperoxybenzoic acid (10.35 g, 65%, 39.0 mmol) in CH_2Cl_2 (25 mL) was added dropwise to dimethyl selenide (1.41 g, 13.0 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 2 h at 20 °C, and the white cloudy solution was concentrated in vacuo and extracted with ethyl ether (3 × 20 mL). The ether-soluble byproduct 3-chlorobenzoic acid was separated from the crude solid dimethyl selenone by vacuum filtration. The crude selenone was recrystallized from MeOH to give the title compound as colorless, odorless crystals. Yield: 0.78 g, 43%; mp 147−148 °C (lit. 148 °C[16a]). ^1H NMR (DMSO-d_6, 22 °C): δ 3.27 (s). ^{13}C NMR (DMSO): δ 42.97. By comparison, dimethyl selenoxide, a low-melting colorless solid, shows ^1H NMR ($CDCl_3$) δ 2.60 (s) and ^{13}C NMR ($CDCl_3$) δ 33.46.

Diphenyl Selenone, Ph_2SeO_2 (4). Diphenyl selenide (5.33 g, 22.9 mmol) was added dropwise to peracetic acid (13.9 g, 183.0 mmol) at 0 °C. The reaction mixture was stirred for 4 days at room temperature and brought to pH 7 with Na_2CO_3. The salt was filtered off, and the filtrate was concentrated to give a solid residue. The residue was extracted with CH_2Cl_2 (3 × 100 mL), concentrated in vacuo, and chromatographed (1:15 MeOH:CH_2Cl_2) to afford the title compound as a white solid. Yield: 3.71 g, 61%; mp 142−143 °C. ^1H NMR (CD_3OD): δ 7.73 (m, 3H), 8.02 (m, 2H). ^{13}C NMR (CD_3OD): δ 127.96, 131.88, 135.89, 143.37. IR (neat, cm^{-1}): ν 1063, 1444.

$[Rh_2(O_2CCF_3)_4\cdot(O_2SeMe_2)_2]$ (3b). A solution containing $[Rh_2(O_2CCF_3)_4]$ (0.039 g, 0.06 mmol) in 10 mL of benzene was carefully layered on top of a solution of Me_2SeO_2 (0.012 g, 0.08 mmol) in $CHCl_3$ (10 mL). After several days when the layers had mixed, green crystals of product **3b** had precipitated out. Yield: 0.020 g, 43%. IR (KBr, cm^{-1}): 2990w, 2930w, 1666s, 1462w, 1409w, 1234m, 1196s, 1166s, 1038w, 886s, 862s, 789m, 745s. ^1H NMR (acetone-d_6, 22 °C): δ 3.30 (broad).

$[Rh_2(O_2CCF_3)_4\cdot(O_2SePh_2)]$ (4a). A mixture of $[Rh_2(O_2CCF_3)_4]$ (0.030 g, 0.05 mmol) and Ph_2SeO_2 (0.012 g, 0.05 mmol) was dissolved in CH_2Cl_2 (10 mL). The mixture was stirred overnight and then filtered to give a green solution. Hexanes (10 mL) were carefully layered on top of the CH_2Cl_2 solution to afford green crystals of **4a** in a week. Yield: 0.025 g, 59%. Anal. Calcd: C, 26.02; H, 1.09. Found: C, 26.15; H, 1.11. This compound was also crystallized as a dichloroethane solvate (**4a′**). IR (KBr, cm^{-1}): 2965w, 2906w, 1676s, 1658s, 1613w, 1451w, 1263s, 1230m, 1210w, 1197s, 1190s, 1175w, 1150w, 1160m, 1100s, 1062w, 1022w, 889m, 858w, 843w, 802s, 748w, 744m, 737m, 708w, 680m, 670w.

X-ray Crystallographic Procedures. Single crystals of all compounds were obtained as described above. X-ray diffraction experiments for **1a** and **2a** were carried out on a Nonius FAST diffractometer with an area detector at −60 °C using Mo Kα radiation. Fifty reflections were used in cell indexing, and about 250 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[24] The intensities for **2a** were also corrected for anisotropy effects using a local adaptation of the program SORTAV.[25] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[26]

The X-ray intensity data for **2b**, **3**, **3b**, **4a**, and **4a′** were measured at −100 °C (−30 °C for **3**; Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 1800 W power. The crystals were mounted on a goniometer head with

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(24) Pflugrath, J.; Messerschmitt, A. MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

(25) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(26) (a) Kabsch, W. J. *Appl. Crystallogr.* **1988**, *21*, 67. (b) Kabsch, W. J. *Appl. Crystallogr.* **1988**, *21*, 916.

silicon grease. The detector was placed at a distance of 6.14 cm from the crystal. For each experiment a total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm for a cubic unit cell to a maximum 2θ angle of 56.56° (0.75 Å resolution). The final cell constants are based upon the refinement of the XYZ-centroids of several thousands reflections above $20\sigma(I)$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical method (SADABS).

All crystals of **3b** were twins. Initial resolution of the twinning using the Gemini program (Gemini, Bruker AXS Inc., Madison, WI) suggested that there were still reflections that were not indexed by the two Gemini components found. Examination of the data set with an unpublished program by George Sheldrick for the brute force identification of multiple twin components revealed a four-component twin. The data were processed as a four-component twin using prerelease versions of SAINT and TWINABS (Bruker AXS Inc., Madison, WI, 2003).

The structures were solved and refined by full-matrix least-squares procedures on $|F^2|$ with Software Package SHELXTL-97, version 6.12.[27] The coordinates of rhodium atoms for the structures were found in direct method E maps. The remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps.[27] Hydrogen atoms of **2b**, **3**, and **4a** were located and refined independently. For all other structures, hydrogen atoms were included at idealized positions for structure factor calculations. The fluorine atoms of CF_3 groups in some experiments were disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine atoms and disordered atoms of solvent molecules. Relevant crystallographic data for all compounds are summarized in Tables 4 and 5. Selected bond lengths and angles are given in Table 2. Table 3 contains geometric parameters of “free” sulfones and selenones **1**−**4** compared with the data for coordinated ligands.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0302130

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(27) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.