

Figure 2. Solid-state ^{13}C NMR spectra obtained for TOT clathrates. Only the guest lines are shown, under normal (b, d, f) and dipolar dephasing (a, c, e) conditions.

dipolar dephasing technique.⁶ The ratio I_{DD}/I of ^{13}C line intensities obtained under dipolar dephasing and normal CP/MAS conditions is a semiquantitative measure of the dynamic state of the molecule or molecular group. For example, for rigidly held methylene or methine carbons $I_{\text{DD}}/I = 0$, whereas for a methyl group rotating about its threefold axis $I_{\text{DD}}/I \approx 0.6$ when a dipolar dephasing time of $40 \mu\text{s}$ is used. More extensive molecular motion further increases I_{DD}/I up to a maximum value of 1.

In Figure 2 the guest lines are shown under normal and dipolar dephasing conditions. For the chloride and bromide the C_2 methylene carbons have $I_{\text{DD}}/I \sim 0$ for the major enantiomer and a value of ~ 0.4 for the minor enantiomer. The I_{DD}/I ratios for the methyl carbons show a similar trend. The major enantiomer value is ~ 0.6 , that for the minor enantiomer ~ 0.9 . The observations suggest that the major enantiomer is held essentially rigidly in the TOT cage (except for small angle librations), whereas the minor enantiomer is more mobile, the I_{DD}/I values suggesting some sort of single-axis rotation for the encaged molecules. In case of the alcohol, the C_2 methylene carbons for the two enantiomers dephase to the same extent ($I_{\text{DD}}/I \sim 0.4$) so that both enantiomers have the same degree of rotational freedom in the cage. Chiral discrimination, therefore, is related to the tightness of fit of a guest molecule in the cage, which ultimately must relate back to nonspecific guest-host van der Waals interactions and which seems to be reflected more by the dynamic guest properties than the static equilibrium guest positions determined by diffraction techniques. Of course, although diffraction techniques can detect positional disorder as for the major 2-bromobutane enantiomer guest in the TOT cages, no information can be obtained about the motion taking place between disorder sites. The minor 2-bromobutane enantiomer could not be located at all, presumably because of excessive disorder.

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In the case of the *sec*-butyl compounds studied here, the differences in guest dynamics between major and minor enantiomers is especially pronounced, the major enantiomer being static in the cage, whereas the minor enantiomer is mobile. For many other guest-host systems the differences may be rather less pronounced, and perhaps more detailed information will be required, i.e., the degree of motional anisotropy and motional rates, in accordance with the concept of a guest-host dynamic coupling coefficient proposed by Lehn⁷ in the case of solution complexes.

Registry No. TOT, 4399-52-4; (\pm)-2-chlorobutane, 53178-20-4; (\pm)-2-bromobutane, 5787-31-5; (\pm)-2-iodobutane, 52152-71-3; (\pm)-2-butanol, 15892-23-6.

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Ruthenium(IV) and Osmium(IV) Chalcogen Complexes of Carbon Monoxide

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The ability of ruthenium and osmium complexes in the +2 and to a lesser extent in the +3 oxidation states to coordinate π -acid ligands such as carbon monoxide is well documented.²⁻⁴ We wish to report that a series of Ru(IV) and Os(IV) complexes of sterically hindered thiolate and selenolate ligands^{5,6} bind CO to provide rare examples of $\text{M}^{\text{IV}}(\text{CO})$ compounds. These compounds, $\text{M}(\text{SR})_4(\text{CO})$,^{7,8} are readily prepared at room temperature and atmospheric pressure by flushing CO over methylene chloride solutions of $\text{M}(\text{SR})_4(\text{CH}_3\text{CN})$.⁶

$\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (**1**) has been structurally characterized by X-ray diffraction.⁹ The overall structure (Figure 1) is similar to that of the parent complex,⁶ $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CH}_3\text{CN})$ (**2**), with the CO occupying the axial position of the trigonal-bipyramidal coordination sphere.¹⁰ The Ru-S

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(5) 2,3,5,6-Tetramethylbenzenethiolate = $[\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}]^-$; 2,4,6-triisopropylbenzenethiolate = $[\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2]^-$.

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(7) Typical synthesis: A methylene chloride solution of $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CH}_3\text{CN})$ (1.0 g, 0.92 mM) was stirred in an atmosphere of CO for 10 min. EtOH was then added slowly to crystallize the product which was filtered in air. Black crystals of $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CO})$ were acquired in 75% yield.

(8) $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$: IR (CHCl_3) 2040 cm^{-1} , UV/vis (CHCl_3) 408 (63700), 320 (sh) (14700), 270 nm (sh) (16700). IR $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CO})$ (CHCl_3) 2032 cm^{-1} ; Os($\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (CHCl_3) 2020 cm^{-1} .

(9) $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (CHCl_3) crystallizes from $\text{CHCl}_3/\text{EtOH}$ in the triclinic space group $P\bar{1}$ with $a = 12.507$ (1) Å, $b = 17.297$ (4) Å, $c = 11.200$ (6) Å, $\alpha = 98.01$ (4)°, $\beta = 97.76$ (4)°, $\gamma = 110.56$ (1)°, $V = 2202$ (3) Å³, $Z = 2$. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by using normal Patterson and difference Fourier methods. Final least-squares refinement gave $R = 0.064$ and $R_w = 0.082$ for 2592 reflections with $|F_o| > 3\sigma(|F_o|)$.

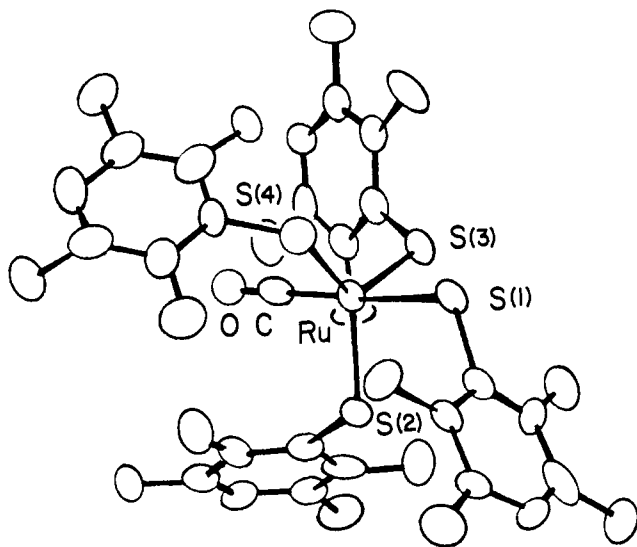


Figure 1. Structure of $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})$; selected bond lengths (\AA): Ru-S1, 2.409 (3); Ru-S2, 2.210 (3); Ru-S3, 2.223 (3); Ru-S4, 2.207 (3); Ru-C, 1.880 (12); C-O, 1.163 (11).

distances $[\text{Ru}-\text{S}_e(\text{av}) = 2.213$ (7) \AA ; $\text{Ru}-\text{S}_a = 2.409$ (3) \AA] in **1** are not significantly different from those in **2**. However, the Ru-C distance (1.880 (12) \AA) in **1** is 0.2 \AA shorter than the Ru-N distance in **2**. As in the structure of **2**, the Ru-S-C planes of the equatorial thiolate ligands are perpendicular to the $\text{Ru}(\text{S}_e)_3$ plane. In **1** the phenyl rings of all three equatorial thiolates are oriented in the direction of the CO (the 3-up isomer), whereas in **2** two of the aromatic rings are projected toward the CH_3CN and one toward the axial sulfur (the 2-up, 1-down isomer).¹¹

The binding of CO to metals in the +4 oxidation state is very unusual.¹² In this instance, the observed chemistry can be rationalized by a bonding scheme in which there is significant donation of electron density from the sulfur ligands to the metal. The d^4 electrons fill the $1e$ (d_{xz} , d_{yz}) metal orbitals which are engaged in π -back-bonding to the CO. The σ lone pair orbitals of the S_e atoms and both the σ and the $3p$ lone pair orbitals of the S_a atom can overlap with these metal orbitals and may augment the back-bonding to CO. The $3p$ lone pair electrons of the S_e atoms can donate into the empty $2e$ (d_{xy} , $d_{x^2-y^2}$) metal orbitals. This $p\pi-d\pi$ bonding accounts for the short Ru-S_e distances and the slow rotation of the ligands about the Ru-S_e bonds.¹¹

To further assess the effect of the electron-donating ability of the coordinated ligand atoms, the analogous selenium complexes were synthesized and studied.^{13,14} The structure of $\text{Ru}(\text{Se}-$

(10) The bond angles (deg) that define the geometry of the $[\text{Ru}(\text{SR})_4(\text{CO})]$ core are S1-Ru-C = 175.5 (3), S1-Ru-S2 = 89.0 (1), S1-Ru-S3 = 84.3 (1), S1-Ru-S4 = 84.5 (1), S2-Ru-S3 = 116.6 (1), S2-Ru-S4 = 121.6 (1), S2-Ru-C = 95.3 (3), S3-Ru-S4 = 120.3 (1), S3-Ru-C = 95.0 (3), S4-Ru-C = 92.1 (3), Ru-S_e-C = 113 (2), Ru-S_a-C = 113.0 (3), and Ru-C-O = 178 (1).

(11) The ^1H NMR spectra of all the $\text{M}(\text{XR})_4\text{L}$ compounds are complex. For example, **2** in DCCl_3 shows five singlets between δ 6.6 and 7.2 which are assigned to the aromatic proton of the thiolate ligands, ten singlets between δ 1.8 and 2.7 which are assigned to the methyl groups of the thiolate ligands, and two resonances at δ 1.0 and 0.89 assigned to the CH_3CN ligand. An interpretation of this spectrum indicates that both the 3-up isomer and the 2-up, 1-down isomer are present in solution and that these two isomers are not interconverting rapidly on the NMR time scale.

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(13) $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CH}_3\text{CN})$ UV/vis (CHCl_3) 390 (18 500), 282 nm (20 900); $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})$ IR (CHCl_3) 2019 cm^{-1} .

(14) $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CH}_3\text{CN})$ crystallizes from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ in the triclinic space group $P\bar{1}$ with $a = 12.251$ (2) \AA , $b = 19.351$ (3) \AA , $c = 10.714$ (2) \AA , $\alpha = 99.91$ (1) $^\circ$, $\beta = 115.09$ (1) $^\circ$, $\gamma = 74.31$ (1) $^\circ$, $V = 2210$ (1) \AA^3 , $Z = 2$. The structure was solved using the heavy atom method. Final least-squares refinement gave $R = 0.059$ and $R_w = 0.083$ using 4346 reflections with $|F_o| > 3\sigma(|F_o|)$.

$2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CH}_3\text{CN})$ (**3**), in which all three equatorial phenyl rings are directed toward the CH_3CN ligand, is similar to the structure of **1**.¹⁵ The Ru-Se distances [$\text{Ru}-\text{Se}_e(\text{av}) = 2.322$ (6) \AA ; $\text{Ru}-\text{Se}_a = 2.495$ (3) \AA] reflect the increase in radius of the Se atoms.¹⁶ The Ru-N distance (2.042 (6) \AA) in **3** is shorter than the corresponding Ru-N distance (2.096 (5) \AA) in the thiolate analogue **2**, which suggests that Se (compared to S) is more capable of increasing the π -basicity of the metal. This observation is also confirmed by the decrease in the CO stretching frequency (by 21 cm^{-1}) in $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})$ compared to **1**.

The CO stretching frequency provides a good monitor of the π -basicity of the metal center. A decrease in the ν_{CO} corresponds to an increase in the effective π -basicity of the metal; the following trends for ν_{CO} are observed:^{8,13} $\text{Ru} > \text{Os}$; $\text{M}(\text{SR})_4(\text{L}) > \text{M}(\text{SeR})_4(\text{L})$; $\text{M}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{L}) > \text{M}(\text{S}-2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_4(\text{L})$. Changes in the chalcogenide ligand or metal have only small effects on the redox potential of the metal center.¹⁷ In contrast, the nature of the axial ligand, L, has a marked effect on the reduction potential ($[\text{M}(\text{XR})_4(\text{L})] + e^- \rightleftharpoons [\text{M}(\text{XR})_4(\text{L})]^-$). A shift of the reduction potential to more positive values corresponds to an increase in the π -acceptor ability of L; the following trends for $E_{1/2}$ are observed for $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{L})$: -0.28 V (L = CO); -0.64 V (L = *tert*-butyl isocyanide); -0.85 V (L = CH_3CN).

The ability of sulfur ligands to increase the π -basicity of metal centers may be an important factor in understanding the mechanism of metal sulfide heterogeneous catalysts.^{18,19} For instance, it is interesting to note that ruthenium and osmium sulfides show the highest rate of hydrodesulfurization catalysis of any binary metal sulfide.²⁰ We are studying the chemistry of coordinatively unsaturated $\text{M}(\text{SR})_x$ complexes as simple models for the MS_x surface species which have been proposed as active sites of the heterogeneous catalysts.²¹

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Registry No. **1**, 96212-08-7; **1⁻**, 96212-16-7; **1⁺**, 96212-17-8; **2**, 96290-35-6; **2⁻**, 96212-12-3; **2⁺**, 96212-13-4; **3**, 96212-09-8; **3⁻**, 96212-14-5; **3⁺**, 96212-15-6; $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})$, 96212-10-1; $\text{Ru}(\text{S}-2,4,6\text{-}i\text{-P}_3\text{C}_6\text{H}_2)_4(\text{CO})$, 96227-26-8; $\text{Ru}(\text{S}-2,4,6\text{-}i\text{-P}_3\text{C}_6\text{H}_2)_4(\text{CH}_3\text{N})$, 96290-73-2; $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{L})$ (L = *t*-butyl isocyanide), 96212-11-2; $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})^-$, 96212-18-9; $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})^+$, 96212-19-0.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters and an ORTEP diagram of $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CH}_3\text{CN})$ (7 pages). Ordering information is given on any current masthead page.

(15) The bond angles (deg) that define the geometry of the $[\text{Ru}(\text{SeR})_4\text{N}]$ core are Se1-Ru-N = 176.6 (1), Se1-Ru-Se2 = 86.42 (3), Se1-Ru-Se3 = 90.07 (3), Se1-Ru-Se4 = 84.11 (3), Se2-Ru-Se3 = 120.82 (4), Se2-Ru-Se4 = 119.23 (4), Se2-Ru-N = 92.7 (1), Se3-Ru-Se4 = 119.06 (4), Se3-Ru-N = 93.2 (1), Se4-Ru-N = 93.5 (1); Ru-Se_e-C = 108.8 (7), and Ru-Se_a-C = 109.0 (2).

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(17) (a) Cyclic voltammetric data for the $[\text{M}(\text{XR})_4\text{L}]^2$ compounds (obtained in CH_2Cl_2 with 0.20 M (*n*-Bu₄N)BF₄ as the supporting electrolyte and the SCE as the reference electrode) show a 1e⁻ reduction and a 1e⁻ oxidation. The potentials ($E_{pc} + E_{pa})/2 = E_{1/2}$ and (ΔE_p) for the $z = 0/-1$ couple and E_{pa} for the $z = +1/0$ couple are as follows: -0.78 (90 mV) and +0.79 for **2**; -0.74 (60 mV) and +0.7 for **3**; -0.36 (80 mV) and +1.12 for **1**; -0.36 (90 mV) and +0.86 for $\text{Ru}(\text{Se}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4(\text{CO})$.

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