Table II. Bond Distances (Å) and Bond Angles (Deg) for $V_{10}O_{26}^{4-}$

V(1)-O(1)	1.91 (2)	V(6)-O(3)	1.95 (2)
V(1)-O(11)	1.58 (1)	V(6)-O(7)	1.94 (1)
V(1)-O(14)	1.95 (2)	V(6)-O(23)	1.59 (1)
V(1)-O(15)	1.95 (1)	V(6)-O(25)	1.92 (1)
V(1)-O(21)	1.96 (2)	V(6)-O(26)	1.91 (1)
V(2)-O(19)	1.80 (1)	V(7)-O(3)	1.65 (2)
V(2)-O(21)	1.66 (2)	V(7)-O(4)	1.77 (2)
V(2)-O(22)	1.77 (1)	V(7)-O(17)	1.61 (2)
V(2)-O(24)	1.59 (2)	V(7)-O(19)	1.78 (2)
V(3)-O(1)	1.71 (2)	V(8)-O(2)	1.78 (1)
V(3)-O(2)	1.82 (1)	V(8)-O(18)	1.59 (2)
V(3)-O(16)	1.78 (1)	V(8)-O(22)	1.81 (1)
V(3)-O(20)	1.58 (2)	V(8)-O(26)	1.69 (2)
V(4)-O(5)	1.58 (2)	V(9)-O(8)	1.59 (2)
V(4)-O(6)	1.79 (2)	V(9)-O(12)	1.82 (1)
V(4)-O(12)	1.79 (1)	V(9)-O(16)	1.77 (1)
V(4)-O(14)	1.66 (2)	V(9)-O(25)	1.67 (2)
V(5)-O(4)	1.82 (2)	V(10)-O(6)	1.81 (2)
V(5)-O(9)	1.63 (2)	V(10)-O(7)	1.68 (2)
V(5)-O(13)	1.80 (2)	V(10)-O(10)	1.61 (2)
V(5)-O(15)	1.67 (2)	V(10)-O(13)	1.76 (2)
O(1)-V(1)-O(11)	105.4 (8)	O(3)-V(6)-O(7)	86.2 (6)
O(1)-V(1)-O(14)	85.3 (7)	O(3)-V(6)-O(23)	107.4 (8)
O(1)-V(1)-O(15)	150.6 (8)	O(3)-V(6)-O(25)	145.3 (7)
O(1)-V(1)-O(21)	86.8 (7)	O(3)-V(6)-O(26)	84.1 (7)
O(11)-V(1)-O(14)	109.6 (8)	O(7)-V(6)-O(23)	106.1 (8)
O(11)-V(1)-O(15)	84.1 (7)	O(7)-V(6)-O(25)	86.4 (6)
O(11)-V(1)-O(21)	107.3 (7)	O(7)-V(6)-O(26)	150.6 (7)
O(14)-V(1)-O(15)	84.1 (7)	O(23)-V(6)-O(25)	107.3 (8)
O(14)-V(1)-O(21)	143.1 (7)	O(23)-V(6)-O(26)	103.3 (8)
O(15)-V(1)-O(21)	85.4 (7)	O(25)-V(6)-O(26)	85.9 (7)
O(19)-V(2)-O(21)	109.5 (7)	O(3)-V(7)-O(4)	108.9 (7)
O(19)-V(2)-O(22)	111.4 (7)	O(3)-V(7)-O(17)	108.7 (8)
O(19)-V(2)-O(24)	108.6 (7)	O(3)-V(7)-O(19)	110.8 (7)
O(21)-V(2)-O(22)	109.6 (7)	O(4)-V(7)-O(17)	109.8 (8)
O(21)-V(2)-O(24)	110.4 (8)	O(4)-V(7)-O(19)	108.6 (7)
O(22)-V(2)-O(24)	107.3 (7)	O(17)-V(7)-O(19)	110.1 (8)
O(1)-V(3)-O(2)	108.0 (7)	O(2)-V(8)-O(18)	109.2 (7)
O(1)-V(3)-O(16)	110.1 (7)	O(2)-V(8)-O(22)	112.4 (6)
O(1)-V(3)-O(20)	109.6 (8)	O(2)-V(8)-O(26)	108.4 (7)
O(2)-V(3)-O(16)	112.6 (6)	O(18)-V(8)-O(22)	108.0 (8)
O(2)-V(3)-O(20)	107.6 (7)	O(18)-V(8)-O(26)	108.4 (9)
O(16)-V(3)-O(20)	109.0 (7)	O(22)-V(8)-O(26)	110.4 (7)
O(5)-V(4)-O(6)	107.1 (8)	O(8)-V(9)-O(12)	109.9 (7)
O(5)-V(4)-O(12)	107.8 (8)	O(8)-V(9)-O(16)	109.1 (8)
O(5)-V(4)-O(14)	111.2 (9)	O(8)-V(9)-O(25)	109.0 (8)
O(6)-V(4)-O(12)	112.2 (7)	O(12)-V(9)-O(16)	110.2 (7)
O(6)-V(4)-O(14)	109.9 (8)	O(12)-V(9)-O(25)	109.0 (7)
O(12)-V(4)-O(14)	108.6 (8)	O(16)-V(9)-O(25)	109.6 (7)
O(4)-V(5)-O(9)	108.2 (7)	O(6)-V(10)-O(7)	110.0 (7)
O(4)-V(5)-O(13)	110.9 (8)	O(6)-V(10)-O(10)	107.7 (8)
O(4)-V(5)-O(15)	109.4 (8)	O(6)-V(10)-O(13)	111.3 (8)
O(9)-V(5)-O(13)	107.6 (8)	O(7)-V(10)-O(10)	108.0 (8)
O(9)-V(5)-O(15)	109.3 (8)	O(7)-V(10)-O(13)	110.7 (8)
O(13)-V(5)-O(15)	111.3 (8)	O(10)-V(10)-O(13)	109.0 (8)
V(3)-O(1)-V(1)	165 (1)	V(5)-O(15)-V(1)	167 (1)
V(8)-O(2)-V(3)	123.7 (8)	V(9)-O(16)-V(3)	138.1 (9)
V(7)-O(3)-V(6)	173 (1)	V(7)-O(19)-V(2)	133.5 (9)
V(7)-O(4)-V(5)	122.7 (8)	V(2)-O(21)-V(1)	158 (1)
V(10)-O(6)-V(4)	126.3 (8)	V(8)-O(22)-V(2)	131.9 (8)
V(10)-O(7)-V(6)	155 (1)	V(9)-O(25)-V(6)	165 (1)
V(9)-O(12)-V(4)	123.6 (8)	V(8)-O(26)-V(6)	178 (1)
V(10)-O(13)-V(5)	138 (1)		
V(4)-O(14)-V(1)	167 (1)		

structure (as in $V_{18}O_{48}^{12-}$[2]) by the addition of the two V(IV) tetragonal pyramids.

Registry No. $[(C_2H_5)_4N]_4V_{10}O_{26}\cdot H_2O$, 79482-74-9.

Supplementary Material Available: Tables of bond distances and angles in the tetraethylammonium ions (Table III), structure factors, and thermal parameters (47 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tetrakis(trifluoroacetato)bis(dimethyl-d_6 sulfoxide)dirhodium(II): A Structural Deuterium Isotope Effect in an Oxygen-Bonded Sulfoxide Adduct

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Although the preference of platinum group metal ions to bind dimethyl sulfoxide (Me_2SO) through the sulfur atom was recognized[1] over 20 years ago, more recent studies have found that this affinity may be offset by steric[2-4] or electronic[5,6] factors imparted to the metal ion through the coordinated ligand atoms. Thus, steric effects favor oxygen-bonded Me_2SO ligands in the crowded four-coordinate $[M(Ph_2PCH_2CH_2PPh_2)(Me_2SO)Cl]^+$ complexes[4] (M = Pd^{II}, Pt^{II}), electronic effects govern oxygen coordination of Me_2SO in $Rh_2(O_2CCF_3)_4(Me_2SO)_2$,[6] while both steric and electronic factors play a role in the mixed oxygen- and sulfur-bonded complexes of $Pd(Me_2SO)_4^{2+}$,[3] $Rh(Me_2SO)_3Cl_3$,[7] and $Ru(Me_2SO)_4Cl_2$.[8]

During our previous work[6] involving the correlation of S–O bond lengths with ν(S–O) frequencies in Me_2SO adducts of $Rh_2(O_2CR)_4$ compounds, the perdeuterated compound $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ was prepared in order to aid in the assignment of the infrared spectrum of the Me_2SO adduct. Earlier studies[9,10] have noted that the advantage derived from recording the infrared spectra of both Me_2SO and $Me_2SO\text{-}d_6$ compounds stems from the near degeneracy of the S–O stretching and methyl rocking vibrations in the normal Me_2SO complex while in the $Me_2SO\text{-}d_6$ analogue these vibrations are well separated. Since the preparation of $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ afforded a crystalline product, several of the crystals were examined on an X-ray diffractometer. Unexpectedly, all of the crystals examined possessed a triclinic cell which was not the same as that for the corresponding $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ complex.[6]

In this paper we describe the structure of the $Me_2SO\text{-}d_6$ adduct of $Rh_2(O_2CCF_3)_4$, which has been refined with the inclusion of all deuterium atoms. This structure is compared to that of the undeuterated adduct[6] which has been further refined with the inclusion of all hydrogen atoms. The two structures represent, to our knowledge, the first example of a crystal packing modification in a transition-metal complex effected solely by the substitution of deuterium for hydrogen.

Experimental Section

Rhodium(II) trifluoroacetate was prepared by the procedure given by Kitchens and Bear[11] and converted to the anhydrous form by heating at 150 °C for 30 min. Glistening dark blue irregularly shaped crystals of $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ were obtained directly upon evaporation of a 1:1 mixture of benzene–chloroform containing $Rh_2(O_2CCF_3)_4$ and excess practical grade Bio-Rad $Me_2SO\text{-}d_6$.

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X-ray Crystallography. Collection of Data. A crystal of $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ having the dimensions 0.10 × 0.15 × 0.35 mm was mounted on a glass fiber with epoxy cement and examined on an Enraf-Nonius CAD-4 diffractometer using a random search procedure. A total of 25 reflections were located, centered, and indexed producing a triclinic cell which did not transform to a cell of higher symmetry upon application of a Delaunay reduction. Several other crystals were examined and none produced a cell identical with the one for $Rh_2(O_2CCF_3)_4(Me_2SO)_2$.[6] The final cell constants were obtained from 25 reflections with $17° < 2\theta < 33°$. Crystal data for $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, $Rh_2S_2F_{12}O_{10}C_{12}D_{12}$, are as follows: triclinic, $a = 9.699$ (1) Å, $b = 14.664$ (2) Å, $c = 8.614$ (2) Å, $\alpha = 91.42$ (1)°, $\beta = 91.24$ (1)°, $\gamma = 83.32$ (1)°, $V = 1216.2$ (5) Å^3; $Z = 2$; mol wt 826.21; $d_c = 2.26$ g cm^{-3}; $F(000)$ μ(Mo K$\bar{\alpha}$) 788; μ(MoK$\bar{\alpha}$) = 16.388 cm^{-1}; space group $P\bar{1}$.

Intensity data were collected for 4281 unique reflections having indices $+h,\pm k,\pm l$ out to $2\theta = 50°$. A scan width of $\Delta\omega = (0.65 + 0.35 \tan\theta)°$ was used and other data collection parameters were identical with those cited previously.[12] No crystal decomposition was noted during the 34 h of X-ray exposure time. The formulas used to derive the intensity and its standard deviation have been given before.[13]

Corrections for Lorentz and polarization effects were applied to the data as well as a correction for absorption. The absorption correction was based on an empirical method using Ψ scans (Ψ = 0–360° every 10°) for χ values near 90°. Nine sets of Ψ scans were collected for 420, 42$\bar{1}$, 410, 411, 31$\bar{1}$, 311, 22$\bar{1}$, 43$\bar{1}$, and 75$\bar{1}$ and averaged to yield maximum, minimum, and average transmission values of 1.00, 0.93, and 0.97, respectively.

Structure Solution and Refinement.[14] **$Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$.** The positions of the two independent Rh atoms were derived from a three-dimensional Patterson function. Four cycles of least-squares refinement of these positions with isotropic temperature factors and a scale factor produced residuals of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.36$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.46$$

A combination of difference Fourier syntheses followed by least-squares refinement located all 38 nondeuterium atoms in the asymmetric unit. Anisotropic temperature factors were assigned to Rh, S, F, O, and C atoms, and the structure was further refined. A difference Fourier synthesis now revealed the positions of 10 of the 12 deuterium atoms, and these were refined with fixed isotropic thermal parameters of 7.0 Å^2. The positions of D(202) and D(203) were calculated by assuming an idealized tetrahedral geometry about C(20) with C–D distances of 0.95 Å. The entire structure was then refined to convergence with 50 atoms, 373 variable parameters, and 3371 data with $I > 3\sigma(I)$. Final agreement factors were $R_1 = 0.025$ and $R_2 = 0.035$ with the esd of an observation of unit weight having a value of 1.058. In the final least-squares cycle, the largest shift/error ratio for a variable parameter was 0.42. A final difference Fourier map showed the largest peak equal to 0.32 e Å^{-3}. A table of observed and calculated structure factor amplitudes with $I > 3\sigma(I)$ is available.[15]

$Rh_2(O_2CCF_3)_4(Me_2SO)_2$. This structure has been reported before[6] with all 19 nonhydrogen atoms included in the refinement producing final residuals of $R_1 = 0.042$ and $R_2 = 0.070$ for 172 variable parameters with 1984 data having $I > 3\sigma(I)$. From the final difference Fourier map, the positions of the six methyl hydrogen atoms were located and the entire structure was refined with isotropic thermal parameters for all hydrogen atoms. Final residuals of $R_1 = 0.038$ and $R_2 = 0.060$ were obtained with 25 atoms included in the refinement, 196 variable parameters, and 1984 data. The final esd of an observation of unit weight was 1.651. The largest peak in the final difference Fourier map was 0.52 e Å^{-3}, and the seven highest peaks were all associated with the fluorine atoms indicative of a very small amount of disorder about the threefold axes of the CF_3 groups. A listing of observed and calculated structure factor amplitudes for this refinement is available.[15]

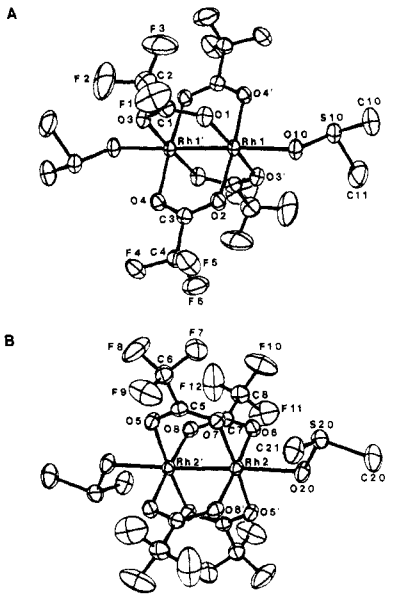

Figure 1. View of the two independent molecules (A and B) in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ with thermal ellipsoids scaled so as to enclose 40% of their electron density. Each molecule resides on a crystallographic center of inversion located at the midpoint of the Rh–Rh bond.

Results and Discussion

Table I records the final positional and thermal parameters for the two independent dinuclear molecules of $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, and Table II presents the nondeuterium bond distances and angles. Bond distances and angles involving the deuterium atoms appear in Table IIA.[15] The final positional and anisotropic thermal parameters for $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ are given in Table III,[15] and Table IV[15] includes the bond distances and angles for this compound. Least-squares planes for the two structures are compiled in Table V.[15]

Description of the Structures. Two crystallographically unique dinuclear molecules are contained in the unit cell of $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, and these are shown in Figure 1. Each molecule resides on a crystallographic center of inversion with Rh–Rh distances of 2.409 (1) and 2.407 (1) Å for molecules A and B, respectively. The Rh–Rh bond lengths are within the range found for $Rh_2(O_2CCF_3)_4L_2$ complexes, which extends from 2.399 (1) Å (L = Me_2SO_2[12]) to 2.486 (1) Å (L = PPh_3[16]). The rhodium atoms exhibit distorted octahedral geometries typical of $M_2(O_2CR)_4L_2$ complexes[17] with axial Rh and O($Me_2SO\text{-}d_6$) atoms and equatorial trifluoroacetate oxygen atoms. The Rh atoms in A and B are displaced 0.076 and 0.075 Å, respectively, out of the equatorial oxygen atom plane (Table V[15]) toward the axial ligands. The $Me_2SO\text{-}d_6$ molecules coordinate through their oxygen atoms at slightly (0.029 Å) different distances in molecules A and B, but this difference has essentially no effect on the Rh–Rh distances due to the weakly bonding character of axial oxygen donor ligands.[18] As seen in Figure 2, the two dinuclear molecules pack in a zigzag fashion in the unit cell forming a 55° dihedral angle between the equatorial carboxylate oxygen atom planes.

The structure of $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ has been described before,[6] and inclusion of the methyl hydrogen atoms into the refinement leads to significant changes (i.e., $>3\sigma$) only in the S–C(6) bond length and the O(5)–S–C(5) and F(4)–

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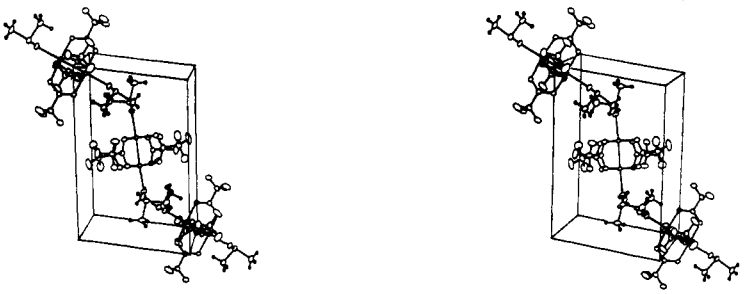

Figure 2. Stereoview of the unit cell contents in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ as seen down the *c* axis with the *a* axis horizontal and the *b* axis vertical. The origin is located in the upper front left corner. Vibrational ellipsoids are drawn at the 20% probability level except the deuterium atoms which were made arbitrarily small for clarity. Molecule A is shown in the center of the cell with two dinuclear units of molecule B residing about (0, 0, 0) and (1, 1, 1).

C(4)–F(6) bond angles. Apart from the different number of independent dinuclear molecules per unit cell, the Me_2SO (Z = 1) and $Me_2SO\text{-}d_6$ (Z = 2) adducts of $Rh_2(O_2CCF_3)_4$ have Rh–Rh distances which differ by more than 0.01 Å, a change that must be attributed solely to differences in packing forces in the two structures. The molecular packing is influenced by the orientation of the sulfoxide ligands with respect to the RhO_4 "face" of the $Rh_2(O_2CCF_3)_4$ molecules. Figure 3 displays the orientations adopted by the Me_2SO ligands in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ (A and B) and $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ (C). Particularly noteworthy in these two structures is the Rh–O–S angle. In the $Me_2SO\text{-}d_6$ adduct it has values of 120.1 (2) and 120.0 (2)° for molecules A and B, while in the Me_2SO adduct it increases to 132.3 (2)°. In contrast to the zigzag pattern of molecular packing in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, the Me_2SO analogue packs with all Rh–Rh vectors and carboxylate oxygen equatorial planes parallel, and this arrangement of dinuclear molecules is shown in Figure 4.

The geometries of the Me_2SO and $Me_2SO\text{-}d_6$ ligands are closely similar with minor differences that cannot be attributed solely to the effects of deuteration since the packing arrangements differ. The S–O and mean S–C bond lengths in the Me_2SO ligand are 1.517 (3) and 1.778 (7) Å, respectively, while the corresponding bond lengths in the $Me_2SO\text{-}d_6$ molecules average 1.516 (3) and 1.769 (7) Å. These S–O bond lengths are practically identical with the S–O distance of 1.513 (5) Å found in Me_2SO itself.[19] However, these distances contrast sharply with the S–O bond length found in S-bonded complexes such as $Rh_2(O_2CCH_3)_4(Me_2SO)_2$,[5] which decreases by about 0.40 Å to 1.477 (5) Å. This is consistent with an *increase* in the S–O bond order. Angular variations between the normal and deuterated Me_2SO adducts of $Rh_2(O_2CCF_3)_4$ are somewhat more pronounced with average O–S–C and C–S–C angles in Me_2SO having values of 107.0 (3) and 97.7 (3)° while the corresponding mean angles in the deuterated molecule are 104.9 (3) and 99.4 (4)°.

Structural Isotope Effects. The two structures described here represent an unusual example of a packing modification in a transition-metal complex which is associated with the substitution of CD_3 for CH_3 groups in the axial sulfoxide ligands. The scope of the present work, however, does not rule out the possibility that both crystal forms exist for the normal and deuterated Me_2SO adducts of $Rh_2(O_2CCF_3)_4$.

A survey of the literature[20] on the structures of normal and deuterated forms of the same compound reveals relatively few examples of space group changes induced by isotopic substitution. Structural differences between compounds that differ only in whether they contain protium or deuterium may be attributed to variations in the zero-point vibrational amplitudes

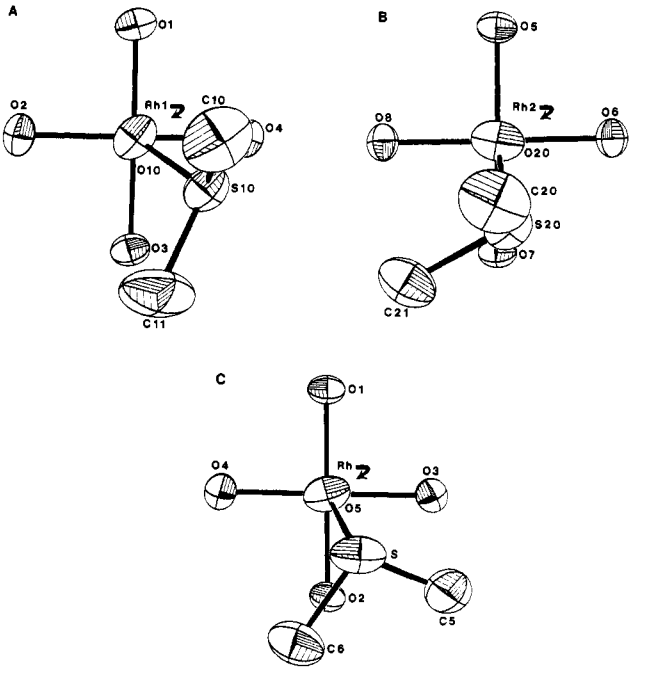

Figure 3. Orientations of the Me_2SO molecules relative to the RhO_4 moieties in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$ (molecules A and B) and $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ (C). Thermal ellipsoids are drawn at the 50% probability level. Primed atoms are not specifically labeled but are readily derived by comparison with the atom labeling scheme in Figure 1.

of protium and deuterium.[21] In an ionic crystal such as hydrazinium hydrogen oxalate,[22] the effect of isotopic substitution is to switch from the centrosymmeric space group $P2_1/m$ containing a symmetrical hydrogen bond to the acentric space group $P2_1$ containing a disordered arrangement of deuterium atoms.

More pertinent to our results is the work of McBride et al.,[23] who studied the effect on the crystal structure of azobis(isobutyronitrile), $NCC(CH_3)_2NNC(CH_3)_2CN$, of changing from CH_3 to CD_3. The deuterio and protio compounds each form both monoclinic and triclinic crystals, and in each case the unit cell for the deuterated compound had a cell volume 0.2–0.3% smaller than that of the protio compound. This suggests that a CD_3 group has a smaller van der Waals radius than a CH_3 group, but only to a very slight extent. In this case the methyl groups make up a rather substantial part (ca. 30%) of the volume of the molecule, and still, the effect is almost negligible. There are also some other types of evidence[24] that the effective

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.48289 (3)	0.42146 (2)	0.52304 (3)	2.82 (1)	1.91 (1)	2.24 (1)	−0.705 (9)	0.43 (1)	−0.028 (9)
Rh(2)	0.10688 (3)	0.03253 (2)	0.02474 (3)	1.95 (1)	2.31 (1)	2.28 (1)	−0.679 (9)	0.078 (9)	−0.094 (9)
S(10)	0.4082 (1)	0.23932 (7)	0.7062 (1)	4.31 (5)	3.09 (4)	3.22 (4)	−1.12 (4)	0.68 (4)	0.25 (3)
S(20)	0.3462 (1)	0.13405 (8)	0.2100 (1)	3.41 (4)	4.17 (5)	3.64 (4)	−1.35 (4)	−0.54 (4)	0.18 (4)
F(1)	0.8868 (4)	0.3468 (3)	0.2350 (4)	5.9 (2)	10.3 (2)	8.5 (2)	1.0 (2)	2.3 (1)	−4.3 (2)
F(2)	0.9452 (3)	0.4770 (3)	0.2724 (5)	6.3 (1)	8.5 (2)	14.9 (2)	−0.3 (1)	6.5 (1)	2.3 (2)
F(3)	0.9669 (3)	0.3809 (3)	0.4498 (4)	4.4 (1)	15.5 (3)	7.3 (2)	2.5 (2)	−0.6 (1)	1.3 (2)
F(4)	0.3496 (3)	0.5401 (2)	−0.0297 (3)	5.9 (1)	4.3 (1)	3.04 (9)	−0.5 (1)	−0.4 (1)	0.72 (9)
F(5)	0.3552 (4)	0.3970 (2)	0.0021 (3)	10.2 (2)	3.5 (1)	3.7 (1)	−1.2 (1)	−0.9 (1)	−0.9 (1)
F(6)	0.1835 (3)	0.4888 (3)	0.0846 (3)	3.6 (1)	12.2 (2)	5.2 (1)	−1.9 (1)	−0.4 (1)	0.4 (2)
F(7)	−0.0443 (3)	0.1059 (2)	0.5279 (3)	4.9 (1)	8.6 (2)	3.1 (1)	−0.6 (1)	−0.1 (1)	−1.7 (1)
F(8)	−0.2244 (3)	0.0423 (3)	0.4888 (3)	8.5 (2)	10.8 (2)	4.7 (1)	−4.7 (1)	3.5 (1)	−1.9 (1)
F(9)	−0.2132 (4)	0.1749 (2)	0.4015 (4)	9.6 (2)	6.7 (2)	5.2 (1)	4.3 (1)	−0.7 (1)	−1.6 (1)
F(10)	0.2535 (4)	−0.2405 (2)	0.2830 (4)	12.3 (2)	5.7 (2)	6.1 (2)	2.4 (2)	−3.0 (2)	0.7 (1)
F(11)	0.2770 (4)	−0.2779 (2)	0.0528 (4)	9.9 (2)	5.3 (2)	8.1 (2)	2.8 (2)	2.4 (2)	0.2 (1)
F(12)	0.1011 (4)	−0.3069 (2)	0.1682 (6)	5.8 (2)	5.4 (1)	24.5 (4)	−1.1 (1)	−1.5 (2)	7.3 (2)
O(1)	0.6743 (3)	0.3835 (2)	0.4352 (3)	3.5 (1)	2.8 (1)	3.8 (1)	−0.3 (1)	1.0 (1)	−0.1 (1)
O(2)	0.3987 (3)	0.4162 (2)	0.3061 (3)	4.5 (1)	2.7 (1)	2.7 (1)	−1.39 (9)	−0.3 (1)	0.16 (9)
O(3)	0.7080 (3)	0.5309 (2)	0.3930 (3)	3.1 (1)	3.0 (1)	3.6 (1)	−0.78 (9)	0.8 (1)	0.1 (1)
O(4)	0.4285 (3)	0.5634 (2)	0.2623 (3)	4.0 (1)	2.4 (1)	2.5 (1)	−0.75 (9)	0.01 (9)	0.02 (9)
O(5)	−0.1683 (3)	0.0112 (2)	0.1921 (3)	2.6 (1)	3.6 (1)	2.9 (1)	−0.90 (9)	0.59 (9)	−0.43 (9)
O(6)	0.1889 (3)	−0.0912 (2)	0.1073 (3)	2.6 (1)	2.8 (1)	3.8 (1)	−0.32 (9)	−0.4 (1)	0.4 (1)
O(7)	0.0318 (3)	0.0725 (2)	0.2383 (3)	2.9 (1)	3.3 (1)	2.6 (1)	−1.06 (9)	0.27 (9)	−0.44 (9)
O(8)	−0.0118 (3)	−0.1519 (2)	0.0610 (3)	3.0 (1)	2.4 (1)	3.6 (1)	−0.79 (9)	0.11 (9)	0.47 (9)
O(10)	0.4470 (3)	0.2730 (2)	0.5498 (3)	4.7 (1)	2.5 (1)	3.0 (1)	−1.4 (1)	0.7 (1)	0.09 (9)
O(20)	0.3069 (3)	0.0933 (2)	0.0542 (3)	2.9 (1)	4.4 (1)	4.0 (1)	−1.6 (1)	0.4 (1)	−1.0 (1)
C(1)	0.7416 (4)	0.4465 (3)	0.3943 (4)	2.9 (2)	3.8 (2)	2.6 (1)	−0.4 (1)	0.5 (1)	−0.4 (1)
C(2)	0.8883 (5)	0.4128 (4)	0.3389 (6)	3.6 (2)	5.4 (2)	4.9 (2)	0.3 (2)	1.1 (2)	0.2 (2)
C(3)	0.3898 (4)	0.4870 (3)	0.2277 (4)	2.9 (2)	2.8 (2)	2.6 (1)	−0.4 (1)	0.2 (1)	−0.1 (1)
C(4)	0.3189 (4)	0.4783 (3)	0.0686 (4)	4.0 (2)	3.6 (2)	2.6 (2)	−0.9 (2)	0.0 (1)	−0.1 (1)
C(5)	−0.0865 (4)	0.0546 (2)	0.2708 (4)	3.0 (2)	2.5 (1)	2.4 (1)	−0.2 (1)	0.2 (1)	0.0 (1)
C(6)	−0.1429 (4)	0.0951 (3)	0.4241 (5)	3.1 (2)	4.9 (2)	3.0 (2)	−0.3 (2)	0.4 (1)	−0.8 (2)
C(7)	0.1128 (4)	−0.1543 (3)	0.1043 (4)	2.8 (2)	2.9 (2)	2.7 (1)	0.0 (1)	0.2 (1)	0.0 (1)
C(8)	0.1828 (5)	−0.2468 (3)	0.1541 (5)	4.2 (2)	3.0 (2)	4.1 (2)	0.2 (2)	0.1 (2)	0.3 (2)
C(10)	0.4544 (6)	0.1182 (3)	0.6945 (6)	7.6 (3)	3.4 (2)	6.3 (3)	−1.2 (2)	1.4 (2)	1.3 (2)
C(11)	0.2272 (6)	0.2426 (5)	0.7011 (8)	4.6 (2)	8.1 (3)	9.6 (4)	−1.6 (2)	2.2 (2)	2.6 (3)
C(20)	0.5020 (5)	0.1811 (4)	0.1729 (7)	3.7 (2)	6.3 (3)	6.7 (3)	−2.1 (2)	−0.4 (2)	−1.2 (2)
C(21)	0.2326 (5)	0.2373 (3)	0.2344 (6)	4.5 (2)	4.2 (2)	6.2 (2)	−1.6 (2)	0.6 (2)	−1.6 (2)

atom	x	y	z	atom	x	y	z
D(101)	0.417 (5)	0.100 (3)	0.597 (6)	D(201)	0.559 (5)	0.132 (3)	0.148 (6)
D(102)	0.415 (5)	0.096 (4)	0.764 (6)	D(202)[c]	0.535	0.211	0.263
D(103)	0.563 (5)	0.108 (3)	0.702 (6)	D(203)[c]	0.490	0.223	0.090
D(111)	0.185 (5)	0.301 (4)	0.716 (6)	D(211)	0.265 (6)	0.278 (4)	0.301 (6)
D(112)	0.195 (5)	0.205 (4)	0.622 (6)	D(212)	0.133 (6)	0.216 (3)	0.268 (6)
D(113)	0.202 (5)	0.217 (4)	0.790 (6)	D(213)	0.245 (5)	0.272 (3)	0.153 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Deuterium atoms were assigned $B_{iso} = 7.0$ Å^2. [c] Calculated deuterium atom position.

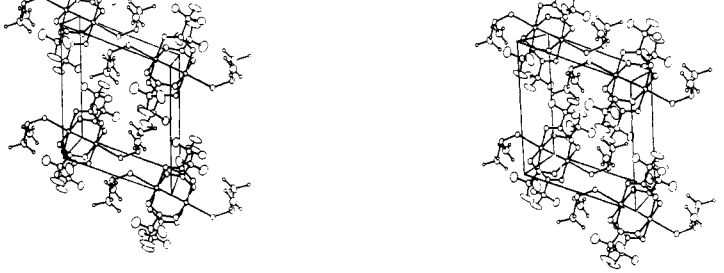

Figure 4. Stereoview of the packing in $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ showing the alignment of the dirhodium units. The thermal elllipsoids are drawn at the 20% probability level except the hydrogen atoms have been made arbitrarily small for clarity. The view is looking down the *a* axis with the *b* axis vertical and the *c* axis horizontal. The origin is in the upper front right corner.

size of CD_3 is slightly less than that of CH_3.

It may well be that this "size" effect, essentially localized in the methyl groups themselves, is responsible for the different crystal structures of the protio and deuterio dirhodium compounds we have studied. However, since the effect is so small on a "per methyl group" basis, and since the methyl groups constitute such a small fraction of the volume of $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, many aspects of what we have observed remain uncertain or obscure.

Doubtless, the two crystal structures must be of comparable though not exactly equal stability for both the protio and

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Table II. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$

Distances

Rh(1)-Rh(1′)	2.409 (1)	F(4)-C(4)	1.319 (5)
O(1)	2.032 (3)	F(5)-C(4)	1.324 (5)
O(2)	2.026 (3)	F(6)-C(4)	1.314 (5)
O(3′)	2.042 (3)	F(7)-C(6)	1.315 (5)
O(4′)	2.040 (3)	F(8)-C(6)	1.311 (5)
O(10)	2.263 (3)	F(9)-C(6)	1.302 (5)
Rh(2)-Rh(2′)	2.407 (1)	F(10)-C(8)	1.300 (6)
O(5′)	2.039 (3)	F(11)-C(8)	1.312 (5)
O(6)	2.033 (3)	F(12)-C(8)	1.261 (6)
O(7)	2.040 (2)	O(1)-C(1)	1.253 (5)
O(8′)	2.029 (3)	O(2)-C(3)	1.245 (4)
O(20)	2.234 (3)	O(3)-C(1)	1.243 (5)
S(10)-O(10)	1.515 (3)	O(4)-C(3)	1.250 (4)
C(10)	1.781 (6)	O(5)-C(5)	1.252 (5)
S(10)-C(11)	1.749 (7)	O(6)-C(7)	1.249 (5)
S(20)-O(20)	1.516 (3)	O(7)-C(5)	1.245 (5)
C(20)	1.771 (6)	O(8)-C(7)	1.254 (5)
C(21)	1.776 (6)	C(1)-C(2)	1.533 (6)
F(1)-C(2)	1.303 (6)	C(3)-C(4)	1.530 (5)
F(2)-C(2)	1.296 (6)	C(5)-C(6)	1.520 (5)
F(3)-C(2)	1.273 (6)	C(7)-C(8)	1.513 (6)

Angles

Rh(1′)-Rh(1)-O(1)	88.00 (8)	Rh(2)-O(6)-C(7)	117.4 (2)
O(2)	87.83 (7)	Rh(2)-O(7)-C(5)	118.2 (2)
O(3′)	87.88 (8)	Rh(2)-O(8′)-C(7′)	117.9 (2)
O(4′)	87.76 (7)	Rh(1)-O(10)-S(10)	120.1 (2)
O(10)	176.29 (7)	Rh(2)-O(20)-S(20)	120.0 (2)
O(1)-Rh(1)-O(2)	89.8 (1)	O(1)-C(1)-O(3)	130.1 (4)
O(3′)	175.9 (1)	C(2)	113.9 (4)
O(4′)	89.5 (1)	O(3)-C(1)-C(2)	116.0 (4)
O(1)-Rh(1)-O(10)	91.4 (1)	F(1)-C(2)-F(2)	105.5 (5)
O(2)-Rh(1)-O(3′)	89.6 (1)	F(1)-C(2)-F(3)	106.5 (5)
O(2)-Rh(1)-O(4′)	175.6 (1)	F(1)-C(2)-C(1)	111.5 (4)
O(10)	88.5 (1)	F(2)-C(2)-F(3)	109.2 (5)
O(3′)-Rh(1)-O(4′)	90.7 (1)	C(1)	112.0 (4)
O(10)	92.7 (1)	F(3)-C(2)-C(1)	111.8 (4)
O(4′)-Rh(1)-O(10)	95.9 (1)	O(2)-C(3)-O(4)	129.1 (4)
Rh(2′)-Rh(2)-O(5′)	88.45 (8)	O(2)-C(3)-C(4)	114.6 (3)
O(6)	88.08 (8)	O(4)-C(3)-C(4)	116.3 (3)
O(7)	87.30 (7)	F(4)-C(4)-F(5)	106.6 (3)
O(8′)	87.70 (8)	F(6)	107.7 (4)
O(20)	176.31 (8)	C(3)	113.0 (3)
O(5′)-Rh(2)-O(6)	88.9 (1)	F(5)-C(4)-F(6)	108.3 (4)
O(7)	175.7 (1)	C(3)	111.6 (4)
O(8′)	90.8 (1)	F(6)-C(4)-C(3)	109.5 (3)
O(20)	88.1 (1)	O(5)-C(5)-O(7)	129.2 (3)
O(6)-Rh(2)-O(7)	91.0 (1)	C(6)	115.1 (3)
O(8′)	175.8 (1)	O(7)-C(5)-C(6)	115.7 (3)
O(20)	93.2 (1)	F(7)-C(6)-F(8)	105.6 (4)
O(7)-Rh(2)-O(8′)	88.8 (1)	F(9)	108.0 (4)
O(20)	96.1 (1)	C(5)	112.7 (4)
O(8′)-Rh(2)-O(20)	91.0 (1)	F(8)-C(6)-F(9)	108.3 (4)
O(10)-S(10)-C(10)	104.3 (2)	C(5)	112.1 (4)
C(11)	105.9 (3)	F(9)-C(6)-C(5)	109.8 (3)
C(10)-S(10)-C(11)	99.4 (4)	O(6)-C(7)-O(8)	128.8 (4)
O(20)-S(20)-C(20)	103.7 (2)	C(8)	115.1 (4)
C(21)	105.8 (2)	O(8)-C(7)-C(8)	116.0 (4)
C(20)-S(20)-C(21)	99.4 (3)	F(10)-C(8)-F(11)	103.8 (4)
Rh(1)-O(1)-C(1)	117.1 (3)	F(12)	108.7 (5)
Rh(1)-O(2)-C(3)	118.0 (2)	C(7)	111.8 (4)
Rh(1)-O(3′)-C(1′)	116.9 (2)	F(11)-C(8)-F(12)	108.1 (5)
Rh(1)-O(4′)-C(3′)	117.3 (2)	C(7)	109.6 (4)
Rh(2)-O(5′)-C(5′)	116.8 (2)	F(12)-C(8)-C(7)	114.2 (4)

deuterio compounds. It might well be asked if the isolation of a different structure for each compound has not arisen merely from the fact that slightly different conditions prevailed during crystallization in each case. We believe the conditions of temperature, concentration, etc., were the same, but of course there may have been slight differences of which we were unaware. A related question in whether both types of crystals may have been present in each case. While we did not check exhaustively, each batch appeared to be homogeneous in this respect. We cannot, however, rule this out altogether.

There are several small but real differences in the intramolecular dimensions from one structure to the other. These are presumably the result of the different intermolecular contacts and not direct consequences of the isotopic substitution. It may also be noted that a comparison of the cell volumes for the Me_2SO and $Me_2SO\text{-}d_6$ adducts of $Rh_2(O_2CCF_3)_4$ shows that the protio compound occupies 614.2 Å^3 per dinuclear molecule while the deuterio compound has an effective volume of 608.2 Å^3. This change of ca. 1% in volume is far too large to be a direct consequence of the smaller effective volume of CD_3; it is simply a consequence of the overall change in packing. It is interesting, however, that the deuterio compound has the structure with the tighter packing.

Acknowledgment. We thank the Robert A. Welch Foundation for financial support, Engelhard Industries for a loan of rhodium trichloride, and Dr. S. Bellard, University Chemical Laboratory, Cambridge, for a literature survey of crystal structures determined in both deuterated and undeuterated forms.

Registry No. $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, 79769-93-0; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0.

Supplementary Material Available: Tables IIA (bond distances and angles involving deuterium atoms in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$), III (final positional and thermal parameters), IV (bond distances and angles for $Rh_2(O_2CCF_3)_4(Me_2SO)_2$), V (least-squares planes for both compounds), and listings of observed and calculated structure factors for the two compounds (29 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and The University of Texas at Austin, Austin, Texas 78712

Crystal and Molecular Structure of the Sulfamide $(t\text{-BuNH})_2SO_2$

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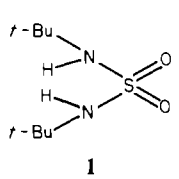
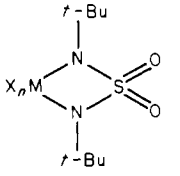
Received April 13, 1981

It has been demonstrated recently[3] that the sulfamide (t-BuNH)$_2SO_2$ (**1**) is a very useful precursor for the synthesis



1



2

e.g., M = P, X = Cl, n = 1
M = P, X = F, n = 1
M = P, X = NMe_2, n = 1

of novel heterocycles such as **2**. Interestingly, if the steric bulk of the N-alkyl group is reduced, it is not possible to isolate heterocycles like **2** and only polymeric materials or ring-opened products can be isolated.[4]

We are aware of only two previous X-ray crystal structures on sulfamides. The structure of the parent compounds $(H_2N)_2SO_2$ has been determined by Trueblood and Mayer,[5] and

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(2) The University of Texas at Austin.
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