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Exchange Interactions in Tris[*cis*-di-μ-hydroxo-bis(ethylenediamine)chromium(III)]chromium(III) Tris(dithionate) Octahydrate

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The tetranuclear complex $[Cr\{(OH)_2Cr(en)_2\}_3]^{6+}$, the chromium(III) analogue of Werner's brown salt, has been prepared and magnetochemically investigated. There is a dominating antiferromagnetic exchange interaction between the central and each of the three peripheral chromium ions. Next-nearest-neighbor exchange has to be included to obtain quantitative agreement with the observed magnetic susceptibilities.

1. Introduction

The complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, often referred to as Werner's brown salt, has been known for a long time.[1] It exhibits a triangular planar array of Co^{3+} ions as schematically shown in Figure 1.[2] Because of the similarities in the chemistry of cobalt(III) and chromium(III) complexes, the chromium(III) analogue of Werner's brown salt was the subject of some speculation before it was prepared. For some time it was believed that the Pfeiffer complex, $[Cr_4(OH)_6(en)_6]^{6+}$, had the same triangular structure as Werner's brown salt.[3] X-ray work later demonstrated that the Pfeiffer complex is structurally related to the rhodoso complex $[Cr_4(OH)_6(NH_3)_{12}]^{6+}$ with a planar rhombic array of the chromium(III) centers.[4] The isolation of $[Cr\{(OH)_2Cr(en)_2\}_3](NO_3)_6{\cdot}xH_2O$, the "true" analogue of Werner's brown salt, was reported only recently by Andersen and Berg.[5] The complex was found to occur, along with a number of other mono- and polynuclear chromium(III) complexes, in aqueous acid solutions containing chromium(III) and ethylenediamine (en).[6] It was isolated by chromatographic techniques.

Because of its structure (Figure 1), the title complex is of interest from a magnetochemical point of view. As in other polynuclear chromium(III) complexes, exchange interactions between the chromium centers are expected to split the electronic ground state and thus give rise to abnormal magnetic behavior at low temperatures. The main attraction lies in the fact that to a first approximation the exchange interaction should be describable by only one empirical parameter J.

2. Experimental Section

Preparation of $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$. A procedure to prepare the iodide salt was described in detail by Andersen and Berg.[6] It was closely followed.

The iodide was recrystallized once and then dissolved in a minimum amount of water. Well-ground solid $Na_2S_2O_6$ was added, and the solution was left in a refrigerator for a few days. During that time well-developed single crystals of $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$ were growing. They were separated and could be kept at 5 °C without deterioration. Anal. Calcd for $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$: C, 11.13; H, 5.45; N, 12.98; Cr, 16.05. Found: C, 11.62; H, 5.52; N, 12.90; Cr, 15.16. The product was further characterized by powder X-ray diffraction using Cu Kα radiation. The following monoclinic unit cell parameters with those of the Co(III) analogue[2] in parentheses were determined: $a = 9.50$ (2) (9.464 (1)) Å, $b = 22.31$ (3) (22.355 (5)) Å, $c = 22.86$ (4) (22.725 (2)) Å, and $\beta = 94.3$ (3)° (94.33 (1)°). The unit cell is very close to that determined by Thewalt for the analogous cobalt(III) compound. It is safe to conclude that the two compounds are isostructural. The geometry of the tetranuclear complexes is that shown schematically in Figure 1.

Magnetic Susceptibility. Magnetization measurements were performed on freshly ground polycrystalline material. A moving-sample technique, which has been described elsewhere, was used for the measurements.[7] On the basis of magnetization curves at 1.7 and 4.2 K, two sets of susceptibility data were collected under the following conditions: $H = 0.502T$ for 4 K < T < 50 K and $H = 1.009T$ for 20 K < T < 280 K.

After application of a diamagnetic correction, the molar susceptibility χ_M' was transformed to μ_{eff}^2 ($\mu_{eff}^2 = 8\chi_M'T$). Molecular parameters were obtained by a least-squares fitting procedure[8] using the formulas in section 3.

3. Theory

3.1. Exchange Interactions. The crystal structure of the title compound has not been determined. Since it is isostructural with practically identical unit cell parameters to the corresponding cobalt(III) compound, geometry and size of the two tetranuclear complexes can be assumed to be the same. In the crystal structure of $[Co\{(OH)_2Co(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$ it was found that within experimental accuracy all four Co^{3+} ions lie in a plane and the three distances Co_1–Co_4, Co_2–Co_4, and Co_3–Co_4 (cf. Figure 1) are identical.

By neglecting next-nearest-neighbor exchange and considering only bilinear terms, we are left with one dominant exchange parameter J. The corresponding Heisenberg operator takes the simple form

$$\hat{H}_{ex} = J(\vec{S}_1{\cdot}\vec{S}_4 + \vec{S}_2{\cdot}\vec{S}_4 + \vec{S}_3{\cdot}\vec{S}_4) \tag{1}$$

Here we are assuming that all the interacting chromium centers have virtually pure spin angular momenta. This is known to be a good approximation for $(t_2)^3$ systems.

In order to evaluate the eigenvalues of (1), it is most convenient to choose the following coupling scheme:

$$\begin{aligned} \vec{S}_{12} &= \vec{S}_1 + \vec{S}_2 \\ \vec{S}_{123} &= \vec{S}_{12} + \vec{S}_3 \\ \vec{S} &= \vec{S}_{123} + \vec{S}_4 \end{aligned} \tag{2}$$

The resulting wave functions are of the form

$$|\{(S_1,S_2)S_{12},S_3\}S_{123}S_4SM\rangle \tag{I}$$

or simply, since $S_1 = S_2 = S_3 = S_4 = {}^3/_2$

$$|S_{12}S_{123}SM\rangle \tag{II}$$

The eigenvalues of the exchange operator (1) are now easily evaluated:

$$E(S_{123}S) = \frac{J}{2}\left[S(S+1) - S_{123}(S_{123}+1) - \frac{15}{4}\right] \tag{3}$$

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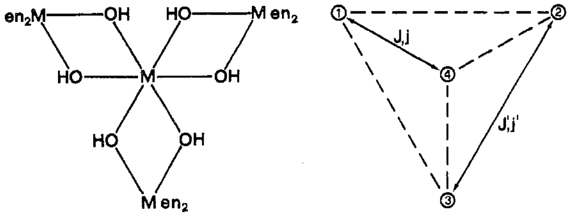

Figure 1. Schematic structure of Werner's brown salt (M = Co^{3+}), $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, and its chromium(III) analogue (M = Cr^{3+}). The exchange coupling scheme for the chromium(III) complex is shown on the right.

The energies do not depend on S_{12}, leaving part of the 44-fold degeneracy of the ground state untouched. Eighteen energy levels $E(S_{123}S)$ are obtained.

In the analysis of the magnetochemical results introduction of higher order terms in the empirical Hamiltonian proved necessary. Including the additional interactions defined in Figure 1, we obtain

$$\begin{aligned}\hat{H}_{ex} = {} & J(\vec{S}_1\cdot\vec{S}_4 + \vec{S}_2\cdot\vec{S}_4 + \vec{S}_3\cdot\vec{S}_4) + \\ & J'(\vec{S}_1\cdot\vec{S}_2 + \vec{S}_2\cdot\vec{S}_3 + \vec{S}_3\cdot\vec{S}_1) - j[(\vec{S}_1\cdot\vec{S}_4)^2 + (\vec{S}_2\cdot\vec{S}_4)^2 + \\ & (\vec{S}_3\cdot\vec{S}_4)^2] - j'[(\vec{S}_1\cdot\vec{S}_2)^2 + (\vec{S}_2\cdot\vec{S}_3)^2 + (\vec{S}_3\cdot\vec{S}_1)^2] \end{aligned} \quad (4)$$

Matrix elements of (4) in the basis of (I) are most easily obtained by using tensor operator techniques. Fano and Racah[9] have developed a formalism, which has been brought to chemists' attention by Griffith[10] and which is directly applicable to our problem.

Applying that formalism, we obtain (5) for a general matrix

$$\begin{aligned}
& \langle S_{12}S_{123}S|\hat{H}_{ex}|S'_{12}S'_{123}S\rangle = \delta(S_{12}S'_{12})[(2S_{123}+1)(2S'_{123}+1)]^{1/2} \times \\
& (-1)^{S_{123}+S'_{123}+S_{12}+S}\left[(15J + {}^{15}/_2 j)\begin{Bmatrix} S_{123} & S'_{123} & 1 \\ {}^3/_2 & {}^3/_2 & S \end{Bmatrix} \times \right. \\
& \left. \begin{Bmatrix} S_{123} & S'_{123} & 1 \\ {}^3/_2 & {}^3/_2 & S_{12} \end{Bmatrix} + 30j\begin{Bmatrix} S_{123} & S'_{123} & 2 \\ {}^3/_2 & {}^3/_2 & S \end{Bmatrix}\begin{Bmatrix} S_{123} & S'_{123} & 2 \\ {}^3/_2 & {}^3/_2 & S_{12} \end{Bmatrix}\right] + \\
& [(2S_{123}+1)(2S'_{123}+1)(2S_{12}+1)(2S'_{12}+1)]^{1/2} \times \\
& [(-1)^{2S'_{123}+S_{12}+S'_{12}+S} + (-1)^{2S'_{123}+S}] \times \\
& \left[(15J + {}^{15}/_2 j)\begin{Bmatrix} S_{123} & S'_{123} & 1 \\ {}^3/_2 & {}^3/_2 & S \end{Bmatrix}\begin{Bmatrix} S_{123} & S'_{123} & 1 \\ S'_{12} & S_{12} & {}^3/_2 \end{Bmatrix}\begin{Bmatrix} S_{12} & S'_{12} & 1 \\ {}^3/_2 & {}^3/_2 & {}^3/_2 \end{Bmatrix} - \right. \\
& \left. 30j\begin{Bmatrix} S_{123} & S'_{123} & 2 \\ {}^3/_2 & {}^3/_2 & S \end{Bmatrix}\begin{Bmatrix} S_{123} & S'_{123} & 2 \\ S'_{12} & S'_{12} & {}^3/_2 \end{Bmatrix}\begin{Bmatrix} S_{12} & S'_{12} & 2 \\ {}^3/_2 & {}^3/_2 & {}^3/_2 \end{Bmatrix}\right] + \\
& \delta(S_{12}S'_{12})\delta(S_{123}S'_{123})(-1)^{S_{12}+1}\left[(15J' + {}^{15}/_2 j')\begin{Bmatrix} {}^3/_2 & {}^3/_2 & 1 \\ {}^3/_2 & {}^3/_2 & S_{12} \end{Bmatrix} - \right. \\
& \left. 30j'\begin{Bmatrix} {}^3/_2 & {}^3/_2 & 2 \\ {}^3/_2 & {}^3/_2 & S_{12} \end{Bmatrix}\right] + \delta(S_{123}S'_{123})[(2S_{12}+1)(2S'_{12}+1)]^{1/2} \times \\
& [(-1)^{S_{123}+S_{12}+S'_{12}+3/2} + (-1)^{S_{123}+3/2}]\left[(15J' + {}^{15}/_2 j') \times \right. \\
& \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ {}^3/_2 & {}^3/_2 & S_{123} \end{Bmatrix}\begin{Bmatrix} S_{12} & S'_{12} & 1 \\ {}^3/_2 & {}^3/_2 & {}^3/_2 \end{Bmatrix} + \\
& \left. \qquad 30j'\begin{Bmatrix} S_{12} & S'_{12} & 2 \\ {}^3/_2 & {}^3/_2 & S_{123} \end{Bmatrix}\begin{Bmatrix} S_{12} & S'_{12} & 2 \\ {}^3/_2 & {}^3/_2 & {}^3/_2 \end{Bmatrix}\right] \quad (5)
\end{aligned}$$

element of (4). The matrix elements are independent of M, and they are nonzero only if $S = S'$. Off-diagonal elements contain biquadratic terms only.

3.2. Magnetic Susceptibility. In the susceptibility measurements care was taken to choose the magnetic fields as small as possible in order to ensure that $W_i^{(1)}H << kT$ and $W_i^{(2)}H^2 << kT$, where $W_i^{(1)}$ and $W_i^{(2)}$ are first- and second-order Zeeman coefficients, respectively. For the calculation of susceptibilities we can therefore safely use the approximate formula

$$\begin{aligned}\chi_M' = (N\beta^2g^2/3kT)[\sum_{S_{12}S_{123}S} S(S+1)(2S+1) \\ \exp\{-E(S_{12}S_{123}S)/kT\}/\sum_{S_{12}S_{123}S}(2S+1) \\ \exp\{-E(S_{12}S_{123}S)/kT\}]\end{aligned} \quad (6)$$

where χ_M' is the susceptibility per tetrameric unit and all the remaining symbols have their usual meaning.

For the evaluation of $E(S_{12}S_{123}S)$ a 44 × 44 energy matrix has to be computed and diagonalized (see section 3.1).

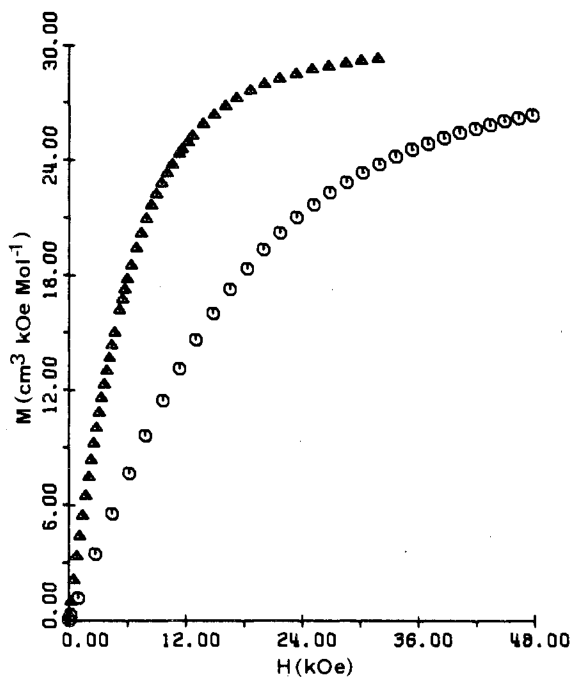

Figure 2. Magnetization measurements at 1.7 K (▲) and 4.2 K (○).

Results

Figure 2 shows the results of magnetization measurements at 1.7 and 4.2 K. The linear parts of the curves define the magnetic fields which may be used for susceptibility measurements. The temperature dependence of μ_{eff}^2 is shown in Figure 3. This representation rather than χ_M' vs. T or $\chi_M'T$ vs. T was chosen for convenience in order to be able to qualitatively compare experimental and calculated magnetic properties.

Starting at high temperatures, we see immediately that μ_{eff}^2 is markedly reduced compared to $\mu_{eff}^2 = 60$ expected for four uncoupled chromium(III) ions with $g = 2$. This is clear evidence for an overall antiferromagnetic exchange coupling in $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3\cdot 8H_2O$. The very slow increase between 100 and 280 K also shows that the exchange split levels of the ground state must be spread over at least 200 cm^{-1}. The behavior of μ_{eff}^2 at temperatures below 100 K shows that $S = 2$ and $S = 3$ levels ($\mu_{eff}^2 = 24$ and 48, respectively, for spin only) dominate the picture. A $S = 3$ level must lie lowest in energy.

This qualitative exchange splitting is in good correspondence with a theoretical prediction based on the one-parameter model (J only, eq 3). In a least-squares fit, which is also included in Figure 3, the magnitude of J was estimated to 16.2 cm^{-1}. The corresponding energy splitting pattern is shown on the left-hand side of Figure 4. As expected, the fit is not quantitative, but the agreement is remarkably good for a one-parameter model. It proves that in essence the empirical Ham-

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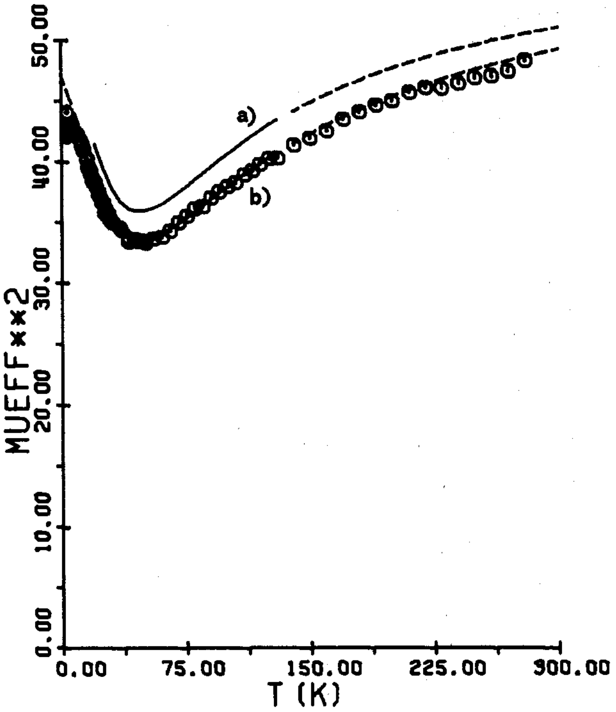


Figure 3. Temperature dependence of μ_{eff}^2. The full curves in the temperature range 20 K < T < 130 K correspond to least-squares fits using (a) one-parameter (J only) and (b) three-parameter (J, J', j) models. The broken curves are extrapolations of the susceptibility computed with the parameters obtained in the respective fits.

Table I. Final Exchange Parameters Obtained in the Least-Squares Fits[a]

adjustable parameters	J	J'	j	R
1	16.2 ± 0.9			0.074
2	17.7 ± 0.1	1.68 ± 0.03		0.0088
3	19.8 ± 0.2	1.40 ± 0.04	−1.0 ± 0.1	0.0048

[a] Only μ_{eff}^2 values for 20 K < T < 130 K were used.

iltonian (1) provides a correct picture of the exchange splitting.

Next we concentrate on the physical effects which are responsible for the differences between experimental and calculated magnetic properties. In the tetranuclear rhodoso and Pfeiffer chromium(III) complexes next-nearest-neighbor as well as biquadratic exchange terms were found to be necessary for a description of the energy splitting in the ground state. We therefore decided to include J' and j in the analysis. Table I lists the final parameter values obtained from the one (J), two (J, J') and three (J, J', and j) parameter fits. As expected the fits improve significantly on the addition of J' and j.[11] However, having neglected such effects as temperature-independent paramagnetism, intercluster interactions, and zero field splittings, we do not wish to put too much physical significance into these parameters. Next-nearest-neighbor exchange (J') of the order of 10% of nearest-neighbor exchange (J) seems a reasonable order of magnitude. The antiferromagnetic sign of J' is expected. The best fit obtained with a three-parameter model is included in Figure 3. Figure 4 shows the corresponding energy-level scheme.

The discrepancies between observed and calculated μ_{eff}^2 at the highest temperatures are an indication of slightly temperature-dependent exchange parameters. For the fits only data for 20 K < T < 130 K were used. At temperatures below 10 K the experimental values are leveling off around μ_{eff}^2 = 43 instead of converging to a value of 47, expected from theory for g = 1.98. This deviation may be the result of weak antiferromagnetic interactions between neighboring tetranuclear complexes.

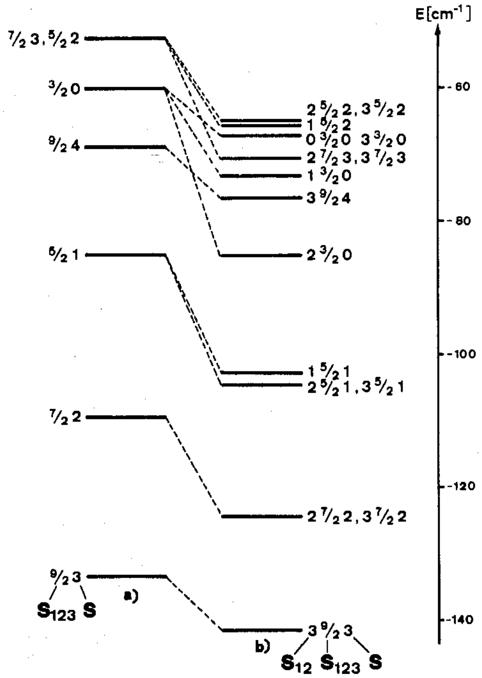
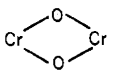


Figure 4. Energy level diagrams for the best fits in Figure 3: (a) one-parameter fit (J only); (b) three-parameter fit (J, J', j).

Discussion

The Co–Co distance found in the crystal structure of $[Co\{(OH)_2Co(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$ is 2.88 Å.[2] Co–O distances range from 1.90 to 1.92 Å and Co–O–Co angles from 96.2 to 98.0°. A large number of Co–O- - -acceptor distances suitable for hydrogen bonding were found. If we assume the corresponding chromium(III) complex in $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3{\cdot}8H_2O$ to have the same size and geometry, comparisons can be made with other dihydroxo-bridged polynuclear chromium complexes. Similar



bridging geometries[4,12,13] as well as similar values for the corresponding exchange parameter[8] were found in the tetranuclear rhodoso and Pfeiffer complexes. Both Cr–Cr and Cr–O–Cr are smaller, however, than in any dihydroxo-bridged dinuclear chromium complex.[14] In compounds containing both dinuclear and tetranuclear complexes the involvement of OH-bridging groups in hydrogen bonding was found likely to affect the exchange coupling.[8,15] This, of course, is an indication of a superexchange mechanism. On the other hand, on the basis of spectroscopic studies, direct exchange was postulated as the dominant mechanism in the coupling between chromium(III) pairs in $MgAl_2O_4$ and $ZnGa_2O_4$, where $Cr^{3+}–Cr^{3+}$ distances also lie around 2.90 Å.[16,17] We have,

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at present, no means to decide which mechanism is dominant in the tetranuclear complex under investigation.

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Registry No. $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3$, 73079-34-2; $[Cr\{(OH)_2Cr(en)_2\}_3]I_6$, 69786-52-3.

Supplementary Material Available: A listing of nonvanishing matrix elements (2 pages). Ordering information is given on any current masthead page.

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Synthesis of 1,1-Bis(fluorooxy)perhaloalkanes by Reaction of Fluorinated Carboxylic Acids with Fluorine in the Presence of Cesium Fluoride

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The reaction of CF_3CO_2H, $C_2F_5CO_2H$, n-$C_3F_7CO_2H$, and $ClCF_2CO_2H$ with F_2 in the presence of CsF at −111 °C forms the corresponding 1,1-bis(fluorooxy)perhaloalkanes in high yield. The reaction occurs in two steps in which the acidic proton is first fluorinated to form $RC(O)OF{\cdot}CsF$ or $RC(O)OF$, followed by a fast fluorination of the carbonyl oxygen forming $RCF(OF)_2$. The fluorination of $(CF_2CO_2H)_2$ forms $[CF_2CF(OF)_2]_2$, but the compound could not be characterized due to its explosiveness above −20 °C. The new compounds $RCF(OF)_2$ ($R = C_2F_5$, n-C_3F_7, $ClCF_2$) are characterized by IR, NMR, and physical properties. Additional characterization of the previously known $CF_3CF(OF)_2$ is also given.

Introduction

Compounds containing oxygen–fluorine bonds are among the most reactive compounds in chemistry.[1-3] The O–F bond is relatively weak, and this, coupled with high bond energies of oxygen and fluorine to many elements, accounts for their reactivity. During a 10-year period from 1955 to 1965, the search for high energy oxidizers for use in advanced chemical propellants spawned considerable research in this area.[4] One area of this endeavor involved the synthesis of compounds containing more than one O–F group per molecule. However, few such compounds were actually isolated and fully characterized.

In 1967, the first bis(fluorooxy) compound (other than OF_2 and O_2F_2) $CF_2(OF)_2$ was reported by several groups.[5-7] This was followed by the other new geminal compounds $CF_3CF(OF)_2$, $(CF_3)_2C(OF)_2$,[8] and $SeF_4(OF)_2$[9] and by several nongeminal compounds $FO(CF_2)_3OF$,[10] $FO(CF_2)_4OF$, $FO(CF_2)_5OF$,[11] and $FOCF_2OOCF_2OF$.[12] No other fully characterized examples have appeared in the chemical literature. Five of these examples are best prepared by the CsF-catalyzed fluorination of carbon–oxygen double bonds, but the only geminal compound that can be prepared in this way is $CF_2(OF)_2$. As such, it has been the only geminal derivative available for further chemical studies.

We were interested in carrying out some reactions of $CF_3CF(OF)_2$. The reported method of synthesis from $NaOC(CF_3)_2OH$ and fluorine was of very low yield and always gave both $CF_3CF(OF)_2$ an $(CF_3)_2C(OF)_2$. The latter is especially prone to explosive decomposition making this method undesirable from several points of view. We therefore looked for a better preparative method. The low-temperature fluorination of CF_3CO_2H in the presence of CsF proved very effective. This reaction and its extension to several other carboxylic acids are described in this paper.[13]

Table I. Reactions of RCO_2H with F_2 in the Presence of CsF

R	molar ratio of $RCO_2H:F_2$	reacn condn temp, °C	reacn condn time, h	% yield of $RCF(OF)_2$[a]
CF_3	1.0:2.2	−78	6.0	84[b]
CF_3	1.0:2.2	−111	6.0	87[b]
CF_3	1.0:5.0	−78	6.0	85[b]
CF_3	1.0:5.0	−111	6.0	100
CF_3	1.0:5.0	−111	3.0	100
CF_3CF_2	1.0:5.0	−111	3.0	96
$CF_3CF_2CF_2$	1.0:5.0	−111	3.0	92
$ClCF_2$	1.0:5.0	−111 to −20	10.0	
		−20 to −8.5	30.0	100

[a] Based on RCO_2H and determined by GLC analysis. [b] Some byproducts were found.

Experimental Section

General Data. All compounds were handled in a Pyrex or stainless-steel vacuum system equipped with glass–Teflon or stainless-steel valves. Pressures were measured with a precision Heise Bourdon tube gauge in the metal system and a Wallace and Tiernan differential pressure gauge in the glass system. Amounts of volatile compounds were determined by *PVT* measurements by assuming ideal gas behavior. Molecular weights were determined by vapor density measurements. Temperatures were measured with a digital readout copper–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer by using a 10-cm glass cell fitted with silver chloride windows. NMR spectra were taken at low temperature on a Varian

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