Table II. Geometrical Parameters for $CrCl_2$ (Estimated Total Errors in Parentheses; Footnotes As in Table I)

	model 1[b]	model 2[c]
$r_g(Cr-Cl)_{mean}$,[d] Å	2.207 (7)	2.208 (8)
	Monomer	
$r_g(Cr-Cl)$, Å	2.207 (10)	2.200 (11)
$l(Cr-Cl)$, Å	0.090 (3)	0.089 (3)
$\kappa(Cr-Cl)$, $Å^3$	4.5×10^{-5} (18)	4.3×10^{-5} (16)
$r_g(Cl\cdots Cl)$, Å	3.612 (44)	3.644 (44)
$l(Cl\cdots Cl)$, Å	0.256 (48)	0.266 (50)
∠(Cl–Cr–Cl), deg	109.8 (24)	111.8 (25)
rel monomer amt, %	72 (5)	73 (5)
	Dimer	
$r_g(Cr-Cl_t)$, Å	2.207	2.230
$l(Cr-Cl_t)$,[e] Å	0.090	0.089
$r_g(Cr-Cl_b)$, Å	2.353 (10)	2.357 (10)
$l(Cr-Cl_b)$,[f] Å	0.120	0.119
$\angle(Cl_b-Cr-Cl_b)$, deg	82.0 (7)	82.8 (8)

Calculated Mean Amplitudes of Vibration[g]

	bent model (exptl geom)	linear model
$l(Cr-Cl)$, Å	0.087	0.090
$l(Cl\cdots Cl)$, Å	0.280	0.121

calculated for the linear geometry coincides with the one determined experimentally for linear $FeCl_2$, 0.119 Å.[10]

Chromium Dichloride. The experimental radial distribution (Figure 4) as well as the mass spectra indicated a large relative abundance of the dimeric species. The refinement eventually showed a 30% presence for the dimeric species. Considering the larger relative weight of the dimer vs. the monomer as regards scattering power, this situation considerably hindered the determination of an accurate structure for $CrCl_2$. On the other hand, our early hope for a more detailed elucidation of the dimer geometry did not prove feasible because of the strong correlation among the parameters. The refinements again yielded a highly bent geometry for the monomer; the results are compiled in two parameter sets in Table II, similarly to those for vanadium dichloride.

It has been tested thoroughly whether or not the experimental data could be approximated by a model in which the monomer was linear. In fact, an earlier electron diffraction report on chromium dichloride[20] communicated 2.20 (1) and 4.34 (5) Å for the Cr–Cl bonded and Cl···Cl nonbonded distances which in turn yield a 161° bond angle. This, taking into account the probable shrinkage,[11] would correspond to a linear equilibrium geometry. There is, in fact, a peak at 4.25 Å on our radial distribution curve (Figure 4), which could correspond to the Cl···Cl interaction of a linear monomeric $CrCl_2$ molecule. Assuming the Cl···Cl distance to appear in this peak and constraining it at various values, we refined its amplitude to very large values (0.37 Å), which is unrealistic for a *linear* molecule according to our earlier experience[10] and to the calculated values given in Table II. In this model the geometry of the dimer had to be taken such that its main nonbonded contribution, the $Cl_t\cdots Cl_b$ distance, shifts from the 4.25-Å peak to the 3.4-Å one (see curve b in Figure 4, where the corresponding part of the radial distribution curve of this model, together with the experimental curve, is indicated). This could only be achieved with unrealistically tilted terminal bonds for the dimer. In this model the $Cr\cdots Cl_t$ nonbonded distance of the dimer shifts from the 5.4-Å peak to the 4.25-Å one, causing marked disagreement between the experimental and theoretical distributions. Moreover, when the Cl···Cl distance of the monomer was allowed to vary, it shifted to the maximum at 5.4 Å, rendering the model meaningless.

Discussion

Our high-temperature gas-phase electron diffraction data are consistent with highly bent shapes of the vanadium dichloride and chromium dichloride molecules. This result represents a challenge to the spectroscopist to determine the ν_1 symmetric stretching frequency in the infrared spectrum. It also represents a challenge to the theoretical chemist to account for the structural differences among the dichlorides of first-row transition metals. Quantum-chemical calculations on manganese dichloride[21] suggest that there are two orbitals with substantial d character that markedly change their energy on bending; they are the σ (d_{z^2}) and one of the π (d_{yz}) orbitals of the linear molecule. The energy of the first decreases and that of the second increases upon bending. Thus, the bent geometry of VCl_2 and $CrCl_2$ could be rationalized with an electronic configuration in which the d_{yz} orbital would be empty and the d_{z^2} orbital half-filled, and the molecules would favor a bent geometry with a lower total energy than for the linear configuration. Unfortunately, these systems are not easily amenable to sophisticated calculations, which is especially demonstrated by the uncertainties in the determination of the bond lengths.[21] Reliable information even merely on the bond length *differences* could facilitate a better utilization of the available experimental data. A more accurate determination of the bond lengths of these dihalides from the experiment is hindered by the lack of knowledge of the difference between the lengths of the monomer bond and the terminal bond of the dimer. Further vibrational spectroscopic information would also enhance the utility of our electron diffraction data.

Acknowledgment. We express our gratitude to Professor Harald Schäfer, University of Münster, for the samples of vanadium dichloride and chromium dichloride. We appreciate the advice and encouragement from Prof. L. V. Gurvich and Prof. I. Hargittai and some auxiliary computations by Dr. B. Rozsondai.

Registry No. VCl_2, 10580-52-6; $CrCl_2$, 10049-05-5.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera distances (50 and 19 cm) for both compounds (2 pages). Ordering information is given on any current masthead page.

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(20) Kupreev, A. V., unpublished results.

(21) Hargittai, M.; Rossi, A. *Inorg. Chem.*, in press.

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Replacement of Acetate Ions in Dimolybdenum Tetraacetate by Acetonitrile Molecules: Crystal Structures of Two Compounds Containing the *cis*-$[Mo_2(O_2CCH_3)_2(CH_3CN)_4]^{2+}$ Cation

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Received August 6, 1984

Over a number of years the reactions of dimolybdenum(II) carboxylates, especially the acetate, $Mo_2(O_2CCH_3)_4$, with strong acids have provided synthetic routes to many other compounds having the Mo_2^{4+} binuclear cation at the center.[1] Doubtless the most important of such reactions is the one[2] used to obtain the $[Mo_2Cl_8]^{4-}$ ion, from which scores of other Mo_2^{4+} compounds are then prepared.

There have also been several efforts, with varying degrees of success, to replace carboxylate groups with weakly coordinating anions (e.g., $CF_3SO_3^-$) or with neutral ligands so as to obtain highly reactive complexes that might be of use synthetically. Bowen and Taube[3] were able to obtain the $Mo_2^{4+}(aq)$ ion and to form the $[Mo_2(en)_4]^{4+}$ complex, but neither of these cationic species has been obtained in a crystalline compound suitable for X-ray crystallographic characterization. Abbott and co-workers have studied reactions of $Mo_2(O_2CCH_3)_4$ with CF_3SO_3H[4] and later of $Mo_2(O_2CH)_4$ with CF_3SO_3H.[5] The former yielded,

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(2) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7, 2698; **1970**, *9*, 346.

(3) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287; *Inorg. Chem.* **1974**, *13*, 2245.

(4) Abbott, E. H.; Schoenewolf, F., Jr.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255.

(5) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774.

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apparently, impure forms of $Mo_2(O_3SCF_3)_4$ while the latter led to $[Mo_2(H_2O)_4(O_3SCF_3)_2](CF_3SO_3)_2$ from which $[Mo_2(CH_3CN)_8](CF_3SO_3)_4$ ws reportedly obtained. Again, no crystallographic characterizations were accomplished. A very recent report[6] deals with some reactions of $Mo_2(O_2CCH_3)_4$ with the acids CF_3SO_3H and HBF_4 and describes products to which the following formulas were assigned: $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$ and $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)_2$. Again, no crystallographic support for these formulations was given.

We are prompted by these reports, especially the most recent one,[6] to communicate work carried out some time ago in this laboratory. We have prepared compounds containing the title cation by two routes, one of which is different from any previously reported in this field, and we have characterized two of these compounds by X-ray crystallography.

Experimental Section

All manipulations were carried out under an argon or nitrogen atmosphere with use of standard Schlenk techniques. All solvents were dried by conventional methods and were distilled under argon immediately prior to use. $Mo_2(O_2CCH_3)_4$ was prepared by the method of Cotton and Brignole.[7] Et_3OBF_4 (Aldrich) and CF_3SO_3H (3M) were used as received. Infrared spectra were obtained on an IBM IR/85 Fourier transform spectrophotometer. Electronic spectra of acetonitrile solutions of **1** and **2** were recorded on a Cary 17 spectrophotometer.

Preparation of *cis*-$[Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2](BF_4)_2$ (1). To a stirred suspension of 428 mg (1 mmol) of $Mo_2(O_2CCH_3)_4$ in 30 mL of CH_2Cl_2 and 1 mL of CH_3CN was added 5.0 mL of a 1.0 M solution of $(C_2H_5)_3OBF_4$ in CH_2Cl_2. The liquid phase of the yellowish suspension immediately developed a bright red color, and all of the suspended $Mo_2(O_2CCH_3)_4$ went into solution in less than 1 h to give a clear, bright red solution. Stirring was stopped at this point, and the solution was left undisturbed at room temperature overnight. In this way an essentially quantitative yield of bright red, highly crystalline material was obtained. Electronic spectrum (CH_3CN solution): λ_{max} at 529 and 372 nm. Infrared spectrum (CH_3CN solution): ν_{CN} 2293 (m), 2255 (vs) cm^{-1}; $\nu_{BF_4^-}$ 1063 (vs) cm^{-1}.

Preparation of *cis*-$[Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}O_3SCF_3)_2](HO_3SCF_3)_2(THF)$ (2). To a stirred suspension of 428 mg (1 mmol) of $Mo_2(O_2CCH_3)_4$ in 25 mL of CH_3CN was added 1.5 mL of CF_3SO_3H by syringe. A bright purple-red solution, which resulted almost immediately, was stirred for 3 h. The volume was then reduced by half under vacuum, and 20 mL of a 1:1 mixture of tetrahydrofuran and benzene was added. The resulting solution was allowed to stand at room temperature for 3 days when compound **2** was deposited on large, blocky red-purple crystals in greater than 90% yield. Electronic spectrum (CH_3CN solution): λ_{max} at 535 and 390 nm. Infrared spectrum (CH_3CN solution): ν_{CN} 2293 (m), 2278 (s) cm^{-1}. Infrared spectrum ($CF_3SO_3^-$ solution): $\nu_{as}(SO_3)$ 1155 cm^{-1}; $\nu_3(SO_3)$ 1040 cm^{-1}; $\delta(SO_3)$ 638 cm^{-1}.

X-ray Crystallography.[8] Details of the crystallographic procedures are given as supplementary material. Table I contains information pertinent to the data collection and structure refinements.

Results and Discussion

Preparation of Compounds. The method by which compound **1** was prepared (eq 1) is efficient and leads readily to a pure, homogeneous, and highly crystalline product. The crystallographic results, to be discussed in detail below, show that the composition is $[Mo_2(O_2CCH_3)_2(CH_3CN)_6](BF_4)_2$; there are *six* coordinated acetonitrile molecules.

$$Mo_2(O_2CCH_3)_4 + 2(C_2H_5)_3OBF_4 \xrightarrow[CH_3CN]{CH_2Cl_2} 2CH_3CO_2C_2H_5 + 2(C_2H_5)O + [Mo_2(O_2CCH_3)_2CH_3CN)_6](BF_4)_2 \quad (1)$$

$$Mo_2(O_2CCH_3)_4 + 4CF_3SO_3H \xrightarrow{CH_3CN} 2CH_3CO_2H + [Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}O_3SCF_3)_2](CF_3SO_3H)_2 \quad (2)$$

Our compound **2** was prepared according to reaction 2, whereby a cation containing four CH_3CN groups was obtained. The preparation of compound **2** is quite similar to the procedure recently reported[6] for preparing $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$.

Table I. Crystallographic Parameters

	$Mo_2O_4C_{16}H_{24}B_2F_8N_6$	$Mo_2O_{17}N_4S_4F_{12}C_{20}H_{26}$
fw	613.75	1142.56
space group	$P2_1/m$	$Pnma$
systematic absences	$0k0$, $k = 2n$	$0kl$, $k + l = 2n$; $hk0$, $h = 2n$
a, Å	7.129 (4)	25.140 (2)
b, Å	10.647 (4)	9.652 (5)
c, Å	19.364 (4)	13.686 (3)
β, deg	99.17 (4)	
V, Å^3	1451.1 (8)	3320 (3)
Z	2	4
d_{calcd}, g/cm^3	1.405	2.246
cryst size, mm	0.35 × 0.35 × 0.20	0.40 × 0.40 × 0.30
μ(Mo Kα), cm^{-1}	10.715	11.256
data collection instrument	Enraf-Nonius CAD-4F	Nicolet P3/F
radiation (monochromated in incident beam)	Mo Kα	Mo Kα
orientation reflcns no., range (2θ), deg	25, $20 < 2\theta < 30$	25, $20.0 < 2\theta < 35.0$
temp, °C	22 ± 1	22 ± 1
scan method	θ–2θ	θ–2θ
data collecn range, 2θ, deg	$5.0 < 2\theta < 45.0$	$5.0 < 2\theta < 50.0$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1404	783
no. of parameters refined	197	188
trans factors, max, min (exptl)	1.000, 0.861	1.000, 0.752
R^a	0.067	0.067
R_w^b	0.085	0.082
quality-of-fit indicator	1.581	1.569
largest shift/esd, final cycle	0.11	0.46
largest peak, e/Å^3	0.982	0.952

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)_2/\sum w|F_o|_2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|^2)/(N_{observns} - N_{param})]^{1/2}$.

What relationship, if any, there may be between our compound **1**, $[Mo_2(O_2CCH_3)_2(CH_3CN)_6](BF_4)_2$, the cation of which has been characterized unequivocally by X-ray crystallography, and the substance formulated by Telser and Drago as $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)_2$ is hard to say.

It has been our experience that elemental analyses do not afford a satisfactory basis for characterizing precisely the compounds we have dealt with. Over a dozen attempts, using three different analytical laboratories, gave unreproducible results, none of which agreed satisfactorily with the formulas established crystallographically or with any other, related formulas. The compounds are extremely sensitive to conditions of handling, tending to decompose in various ways.

The electronic spectra of both of our compounds **1** and **2** are very similar to each other and closely resemble the electronic spectra reported by Telser and Drago. For acetonitrile solutions, **1** has bands at 529 and 372 nm and **2** has bands at 535 and 390 nm. The infrared spectrum of our compound **1** gave no indication of the BF_3OH^- ion proposed for one of the Telser and Drago compounds; this is as we would expect since the use of $(C_2H_5)_3OBF_4$ in a nonaqueous medium should unambiguously give a BF_4-containing product.

The use of $(C_2H_5)_3OBF_4$ as a reagent for removal of acetate groups from $Mo_2(O_2CCH_3)_4$ has further synthetic potential, as we shall report in the future. It can be used, for example, to prepare $[Mo_2(CH_3CN)_8](BF_4)_4$ in crystalline form. It seems to afford a more convenient route to the $[Mo_2(CH_3CN)_8]^{4+}$ cation than the reported two-step route,[5] in which the formate groups of $Mo_2(O_2CH)_4$ are destroyed by heating with CF_3SO_3H.

Structural Results. The $[Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2]^{2+}$ ion in **1** resides on a crystallographic mirror plane, which contains both metal atoms and the axial acetonitrile molecules. The structure is shown in Figure 1. Positional parameters are given in Table II. The distances and angles are listed

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(6) Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 1798.
(7) Brignole, A. B.; Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 81.
(8) All computing was carried out on a PDP 11/60 computer using the Enraf-Nonius SDP Structure Determination Package.

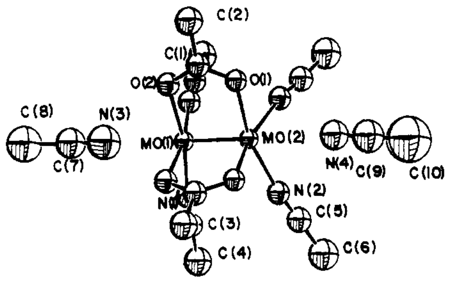

Figure 1. ORTEP diagram of the *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2}]^{2+}$ cation in **1**. Each atom is represented by its ellipsoid of thermal vibration scaled at the 50% level.

Table II. Positional Parameters and Isotropic Equivalent Thermal Parameters and Their Esd's for *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2}]^{2+}$ [a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.2390 (2)	0.250	0.65298 (8)	2.72 (3)
Mo(2)	0.0424 (2)	0.250	0.72535 (8)	2.57 (3)
O(1)	0.117 (1)	0.6103 (8)	0.3317 (4)	3.2 (2)
O(2)	0.086 (1)	0.3883 (9)	0.5938 (4)	3.8 (2)
N(1)	0.434 (1)	0.391 (1)	0.6979 (5)	3.9 (3)
N(2)	0.149 (2)	0.389 (1)	0.8009 (5)	3.8 (2)
N(3)	0.544 (3)	0.750	0.445 (1)	8.8 (6)
N(4)	0.223 (3)	0.750	0.1840 (9)	5.9 (5)
C(1)	0.932 (2)	0.430 (1)	0.6132 (6)	3.9 (3)
C(2)	0.185 (2)	0.469 (2)	0.4265 (7)	5.2 (4)
C(3)	0.529 (2)	0.468 (1)	0.7251 (7)	3.9 (3)
C(4)	0.350 (2)	0.434 (1)	0.2386 (9)	6.4 (4)
C(5)	0.189 (2)	0.459 (1)	0.8468 (7)	4.6 (3)
C(6)	0.238 (3)	0.551 (2)	0.9028 (8)	7.3 (5)
C(7)	0.452 (4)	0.750	0.487 (1)	7.1 (7)
C(8)	0.319 (5)	0.750	0.545 (2)	10 (1)
C(9)	0.272 (4)	0.750	0.136 (11)	7.4 (7)*
C(10)	0.283 (6)	0.750	0.067 (2)	15 (1)*
F(1)	0.191 (2)	0.646 (2)	0.6885 (8)	8.8 (4)*
F(2)	0.98 (1)	0.750	0.663 (5)	8 (2)*
F(3)	0.02 (1)	0.750	0.776 (4)	5 (2)*
F(4)	−0.031 (5)	0.750	0.719 (2)	15 (1)*
F(5)	0.265 (5)	0.750	0.780 (2)	13 (1)*
F(6)	0.320 (9)	0.250	0.979 (3)	14 (2)*
F(7)	0.155 (7)	0.250	0.974 (2)	15 (1)*
F(8)	0.284 (4)	0.367 (3)	1.059 (1)	19 (1)*
F(9)	0.107 (7)	0.250	1.072 (3)	9 (1)*
F(10)	0.425 (7)	0.250	1.078 (2)	14 (1)*
F(11)	0.23 (1)	0.250	0.112 (4)	7 (2)*
B(1)	0	0.750	0	7*
B(2)	0.13 (1)	0.750	0.734 (4)	7 (2)*
B(3)	0.25 (2)	0.250	0.047 (7)	8 (5)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Numbers in parentheses in this and all subsequent tables are the estimated standard deviation in the least significant digit.

Table III. Selected Bond Distances (Å) for *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2}]^{2+}$

Mo(1)–Mo(2)	2.134 (2)	N(1)–C(3)	1.136 (13)
–O(2)	2.068 (7)	N(2)–C(5)	1.159 (14)
–N(1)	2.137 (10)	N(3)–C(7)	1.11 (3)
–N(3)	2.64 (2)	N(4)–C(9)	1.04 (3)
Mo(2)–O(1)	2.079 (7)	C(3)–C(4)	1.46 (2)
–N(2)	2.132 (10)	C(5)–C(6)	1.46 (2)
–N(4)	2.77 (2)	C(7)–C(8)	1.59 (4)
O(1)–C(1)	1.251 (12)	C(9)–C(10)	1.36 (4)
O(2)–C(1)	1.291 (13)		
C(1)–C(2)	1.499 (15)		

Table IV. Selected Bond Angles (deg) for *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}CH_3CN)_2}]^{2+}$

Mo(1)–Mo(2)–O(1)	90.6 (2)	Mo(1)–N(3)–C(7)	180 (2)
–N(2)	104.6 (3)	Mo(2)–N(2)–C(5)	171.1 (9)
–N(4)	178.2 (2)	–N(4)–C(9)	157.0 (3)
Mo(2)–Mo(1)–O(2)	91.1 (2)	O(1)–C(1)–O(2)	120 (1)
–N(1)	100.8 (2)	–C(2)	118 (1)
–N(3)	175.0 (6)	O(2)–C(1)–C(2)	122 (1)
Mo(1)–O(2)–C(1)	118.8 (7)	N(1)–C(3)–C(4)	179 (1)
Mo(2)–O(1)–C(1)	119.7 (8)	N(2)–C(5)–C(6)	178 (1)
Mo(1)–N(1)–C(3)	174.7 (9)	N(3)–C(7)–C(8)	179 (3)
		N(4)–C(9)–C(10)	164 (4)

Table V. Positional Parameters and Isotropic Equivalent Thermal Parameters and Their Esd's for *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}O_3SCF_3)_2}]\mathrm{(HO_3SCF_3)_2(THF)}$ [a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.31818 (8)	0.3605 (2)	0.6829 (2)	3.05 (3)
O(3)	0.3245 (7)	0.624 (2)	0.654 (1)	6.4 (5)
N(1)	0.3728 (7)	0.407 (2)	0.793 (1)	2.5 (4)
N(2)	0.2543 (7)	0.412 (2)	0.779 (1)	4.0 (5)
O(1)	0.3796 (5)	0.357 (2)	0.579 (1)	3.5 (4)
O(2)	0.2627 (6)	0.366 (2)	0.570 (1)	4.3 (4)
C(1)	0.400 (1)	0.250	0.556 (2)	2.2 (8)
C(2)	0.250	0.250	0.544 (3)	6 (1)
C(3)	0.442 (2)	0.250	0.480 (3)	5 (1)*
C(4)	0.198 (2)	0.250	0.469 (4)	8 (2)*
C(5)	0.402 (1)	0.451 (3)	0.850 (2)	5.2 (8)
C(6)	0.441 (1)	0.501 (5)	0.927 (3)	12 (1)
C(7)	0.220 (1)	0.431 (3)	0.830 (2)	4.3 (6)
C(8)	0.171 (1)	0.483 (4)	0.887 (2)	8 (1)
C(9)	0.416 (2)	0.750	0.637 (4)	9 (2)*
C(10)	0.036 (1)	0.250	0.774 (3)	4*
S(1)	0.3495 (4)	0.750	0.677 (1)	5.4 (3)
S(2)	0.0751 (6)	0.250	0.678 (1)	12.4 (7)
F(1)	0.4421 (7)	0.637 (2)	0.650 (1)	8.7 (5)*
F(2)	0.414 (2)	0.750	0.535 (4)	18 (2)*
F(3)	−0.019 (2)	0.250	0.750	14 (1)*
F(4)	0.040 (1)	0.356 (4)	0.836 (3)	22 (1)*
O(4)	0.362 (2)	0.750	0.785 (3)	10 (1)*
O(5)	0.127 (2)	0.250	0.702 (3)	12 (1)*
O(6)	0.058 (2)	0.250	0.603 (5)	19 (2)*
O(1T)	0.192 (2)	0.750	0.511 (4)	18 (2)*
C(2B)	0.176 (2)	0.640 (8)	0.619 (5)	21 (2)*
C(4B)	0.124 (3)	0.667 (8)	0.669 (5)	28 (4)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta 2_2 + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Selected Bond Distances (Å) for *cis*-$[\mathrm{Mo_2(O_2CCH_3)_2(CH_3CN)_4(O_3SCF_3)_2}]\mathrm{(HO_3SCF_3)_2(THF)}$

Mo(1)–Mo′(1)	2.132 (4)	C(5)–C(6)	1.495 (36)
–N(1)	2.092 (18)	C(7)–C(8)	1.544 (34)
–N(2)	2.137 (19)	S(1)–C(9)	1.754 (39)
–O(1)	2.103 (13)	–O(3)	1.544 (27)
–O(2)	2.073 (16)	–O(4)	1.510 (29)
–O(3)	2.576 (15)	C(9)–F(1)	1.280 (24)
N(1)–C(5)	1.152 (26)	–F(2)	1.341 (56)
N(2)–C(7)	1.117 (27)	S(2)–C(10)	1.637 (37)
O(1)–C(1)	1.201 (19)	–O(5)	1.390 (34)
O(2)–C(2)	1.206 (21)	–O(6)	1.020 (51)
C(1)–C(3)	1.498 (43)	C(10)–F(3)	1.413 (40)
C(2)–C(4)	1.691 (44)	–F(4)	1.399 (36)

in Tables III and IV. The $Mo_2(O_2CCH_3)_2$ part of the structure has dimensions very similar to those found in other cases where there are two cis bridging acetate groups together with four other equatorial ligands.[9] Thus, the Mo–Mo distance, 2.134 (2) Å, is somewhat longer than that in the acetate,[10] where it is 2.093 (1) Å, and the bonds to the other ligands (the equatorial CH_3CN molecules) make rather large angles with the Mo–Mo axis, 100.8 (2) and 104.6 (3)°. The Mo–N distances for the equatorial

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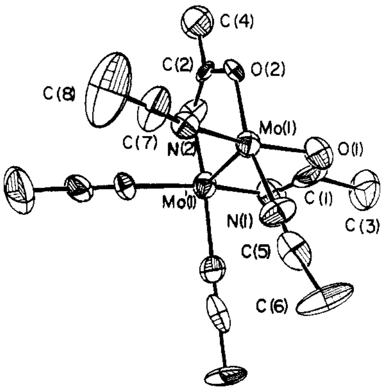

Figure 2. ORTEP diagram of the cation in **2**. Each atom is represented by its ellipsoid of thermal vibration at the 50% probability level. The axial triflate groups have been omitted for clarity.

Table VII. Selected Bond Angles (deg) for *cis*-[$Mo_2(O_2CCH_3)_2(CH_3CN)_4(O_3SCF_3)_2$]$(HO_3SCF_3)_2$(THF)

Mo(1)-Mo(1)-N(1)	103.04 (48)	Mo(1)-O(1)-C(1)	119.56 (165)
-N(2)	103.32 (56)	-O(2)-C(2)	111.88 (185)
-O(1)	89.39 (48)	-N(1)-C(5)	171.97 (208)
-O(2)	91.20 (49)	-N(2)-C(7)	176.86 (230)
-O(3)	170.51 (41)	N(1)-C(5)-C(6)	175.46 (346)
N(1)-Mo(1)-O(1)	90.75 (54)	N(2)-C(7)-C(8)	170.62 (298)

CH_3CN ligands, 2.132 (10) and 2.137 (10) Å, are similar to the Mo–O distances, 2.068 (7) and 2.079 (7) Å, whereas the axial Mo–N distances are very long, 2.64 (2) and 2.77 (2) Å. These latter long distances are in accord with the possibility of easy dissociation of the axial ligands.

The $[Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}O_3SCF_3)_2]^{2+}$ cation of **2** possesses a crystallographic mirror plane that bisects the metal–metal bond. The structure is depicted via the ORTEP diagram given in Figure 2. Positional parameters are given in Table V. Distances and angles are listed in Tables VI and VII. The distances and angles within the cation of **2** are identical with those within **1** within experimental error. The axial CF_3SO_3 anions represent the first reported example of axially coordinated triflate groups attached to a quadruple bond. The Mo–O(ax) distance is 2.576 (15) Å, with the Mo–Mo–O(ax) angle being 170.51 (41)°. There is an infinite chain of O–S–O–Mo–Mo–O–S–O linkages throughout the crystal.

Acknowledgment. We thank the National Science Foundation for support. The assistance of C. Ovalles and Professor D. J. Darensbourg in the recording of the Fourier transform infrared spectra is gratefully acknowledged.

Registry No. **1**, 98542-25-7; **2**, 98542-27-9; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Mo, 7439-98-7; $(C_2H_5)_3OBF_4$, 368-39-8.

Supplementary Material Available: Details of the crystallographic procedures and tables of observed and calculated structure factors and anisotropic thermal parameters for **1** and **2** and a listing of complete bond lengths and angles for **1** (19 pages). Ordering information is given on any current masthead page.

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Calorimetric Studies of Curium Complexation

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Received January 16, 1985

The high specific radioactivity of the common isotopes of the transplutonium elements has been a major deterrent to study of their complexation reactions by methods that require macroconcentrations of the metal ions. Radiotracer distribution techniques are satisfactory for measurement of stability constants although, in general, values of the enthalpies of complexation and, consequently, of the entropies of complexation obtained from such distribution measurements at different temperatures are less reliable.

Curium samples have become available with a relatively low specific activity (ca. 3 × 10^7 α decays/(m·mg)) due to a high isotopic content, 96.9%, of ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y). With use of milligram quantities of this material, direct calorimetric measurements could be made in the minicalorimeter[2] of the Florida State University Laboratory. The systems Cm + OAc (acetate) and Cm + EDTA (ethylenediaminetetraacetate) were chosen for study as these ligands form relatively weak (OAc) and very strong (EDTA) complexes.

Formation of transplutonium cation complexes with acetate has been investigated by a solvent extraction method over a temperature range of 0 to 55 °C.[3] The stability constants at 24 °C agreed well with the lanthanides of similar ionic radii, but the enthalpy and entropy values of the actinides were significantly more positive than those of the lanthanides. It was suggested that this might reflect more dehydration of the trivalent actinides upon complexation; however, the authors noted that the results were questionable as they were obtained by temperature variation.

The thermodynamics of complexation of Pu(III) and Am(III) by EDTA was studied by calorimetry[4] with samples of crystalline $PuCl_3$ and $AmCl_3$ dissolved in EDTA solutions. Suitable corrections for enthalpies of solution and of deprotonation were required. A measurement of $LaCl_3$ by the same technique gave a value of ΔH of complexation that did not agree well with direct solution calorimetric measurements,[5] casting doubt on the actinide values. A more recent study used solvent extraction at different temperatures and reported rather different values of ΔH and ΔS.[6]

Experimental Section

Chemicals. Solutions of $Eu(ClO_4)_3$, HCl, NaOH, $NaClO_4$, Na_2H_2EDTA, and HOAc were prepared from reagent or analytical grade chemicals in distilled, deionized water. The NaOAc buffer solution was prepared from HOAc by adjustment of the pH with NaOH solution. The ionic strength of the solution was adjusted with $NaClO_4$ to 2.0 M for the Cm + OAc titration and to 0.5 M for the Cm + EDTA runs. These values were chosen to allow comparison with literature data.

The 6.05 mg of curium was received as dry $CmCl_3$ from Oak Ridge National Laboratory. The sample was dissolved by gentle warming in 0.5 mL of 0.0409 M NH_4Cl, pH 5.83. Assay of the α decay by liquid scintillation counting confirmed that 6.0 ± 0.1 mg of Cm had been dissolved.

Procedure. The curium solution was transferred to the calorimeter cup and 4.00 mL of 2.186 M $NaClO_4$ solution added to produce a 2.00 M ($NaClO_4$) ionic strength solution of pH ca. 5.8. This solution was titrated automatically by incremental additions of a solution of acetate that was 0.02 M in HOAc, 0.08 M in NaOAc, and 2.0 M in $NaClO_4$. The procedures for operation of the computer-operated calorimetric titration have been described earlier.[7]

After the acetate experiment, the solution in the calorimeter cup was removed and made basic with NaOH to precipitate $Cm(OH)_3$; analysis of the supernatant after warming and centrifugation indicated that 2–5% of the Cm had not precipitated. The precipitate was washed and, then, dissolved in 0.5 mL of 0.552 M NH_4Cl solution to give a pH of 5.34. This solution was added to the calorimeter cup with 0.002 mL of 4 M

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