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Synthesis, Structure, and Properties of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$

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$Mo_2(O_2CCF_3)_4$ reacts with (unsymmetrical) *N,N*-dimethylethylenediamine (udmed) in ethanol or acetonitrile to form a crystalline product. Solid-state IR studies both bridging bidentate and ionic trifluoroacetates. A single-crystal X-ray study of the orange blades indicates that the complex exists as $[Mo_2(O_2CCF_3)_3(Me_2NCH_2CH_2NH_2)_2](O_2CCF_3)$, in which the two udmed ligands bind as axial–equatorial chelates to each of the metals. There is hydrogen bonding between $Mo_2(O_2CCF_3)_3(udmed)_2^+$ cations and free $CF_3CO_2^-$ anions to form one-dimensional chains. The cation has idealized C_{2v} symmetry; bond distances include Mo–Mo = 2.132(2) Å, Mo–O(av) = 2.11(1) Å, Mo–N(eq, av) = 2.21(1) Å, and Mo–N(ax, av) = 2.58(2) Å. The compound crystallizes in the monoclinic space group $I2/a$ at 294 K, with $a = 20.319(10)$ Å, $b = 9.903(5)$ Å, $c = 30.260(16)$ Å, $\beta = 94.65(4)°$, $Z = 8$, $V = 6069(5)$ Å^3, $R = 0.0743$, and $R_w = 0.0807$. The ^{19}F NMR spectrum (CD_3CN solution at −20 °C) indicates a bridging: nonbridging trifluoroacetate ratio of 1.2:1, unlike the 3:1 ratio found in the solid state.

Introduction

Ethylenediamine has been a favorite ligand of coordination chemists since Werner established the concepts of coordination chemistry.[1] Bowen and Taube first used it in dimolybdenum(II) chemistry when they reported the preparation of $[Mo_2(en)_4]Cl_4$.[2] Efforts to obtain this material in a form suitable for diffraction studies have failed to date. Peacock and Fraser[3] later inferred a possible structure on the basis of ORD measurements of dimolybdenum complexes of chiral 1,2-diamines.

Practical interest in the chemistry of dimolybdenum complexes stems from studies by Wilkinson[4] of the use of $Mo_2(O_2CCH_3)_4$ as a hydrogenation catalyst. Eichhorn *et al.*[5–7] have reported the reactions of $Mo_2(O_2CCH_3)_4$ with ethylenediamine and several N-methylated derivatives and have characterized a number of solid complexes. Recently, Kerby *et al.*[8] reported the production of alkyne derivatives from a quadruply-bonded dimolybdenum complex.

The coordination chemistry of $Mo_2(O_2CCF_3)_4$ with Lewis bases has been well characterized.[9–18] Reaction with pyridine leads to a solid product in which the pyridine ligands occupy axial positions,[10] and similar structure are suggested for adducts with weaker bases. Infrared studies of reactions with bipyridine suggested that bipyridine coordinates as a chelating but not as a bridging ligand; the specific product obtained depends on the reaction solvent.[11,12] Two such products were recently characterized crystallographically.[13] Andersen[14] suggested that coordination complexes of $Mo_2(O_2CCF_3)_4$ with monodentate Lewis bases can be divided into two distinct groups. One group, with strong Lewis bases that are sterically small, forms equatorial adducts, whereas weaker or larger bases occupy axial sites.

During an ^{19}F NMR study of the solution reactions between $Mo_2(O_2CCF_3)_4$ and *N,N*-dimethylethylenediamine (udmed), we observed the formation of a crystalline solid in the NMR tube. Since trifluoroacetate is much less basic than acetate,[19] we anticipated that the trifluoroacetate ligand would be more susceptible to displacement by another ligand. We report here the synthesis and characterization of the solid-state $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$, analogous to the acetate complex.[6,7]

Experimental Section

All reactions and sample manipulations were performed under argon or nitrogen or *in vacuo*. *N,N*-Dimethylethylenediamine (udmed), obtained from Aldrich, was distilled twice and stored under argon. Acetonitrile (Fisher), redistilled, and ethanol (Florida Distillers) were stored over molecular sieves. Dimolybdenum trifluoroacetate, $Mo_2(O_2CCF_3)_4$, was synthesized via a modification of the procedure reported by Cotton and Norman.[9] In our synthesis, the mixture of dimolybdenum acetate (2.0 g), trifluoroacetic acid (30 mL), and trifluoroacetic anhydride (3 mL) was refluxed for approximately $^1/_2$ h after all the solid had dissolved. The mixture was then cooled to −20 °C. The solid was recovered by filtration, washed with hexane, and dried *in vacuo*. This method seems to eliminate most (if not all) of the contamination described by Santure and Sattelberger[18] as resulting from the original procedure. The preparation was never adjusted to a larger scale.

Synthesis of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$. In a typical experiment, udmed (30 μL, 0.273 mmol) was combined with dried ethanol or acetonitrile (1.2 mL) and the mixture was degassed. The degassed mixture was transferred on a vacuum line into a flask containing $Mo_2(O_2CCF_3)_4$ (72.2 mg, 0.112 mmol) cooled to −196 °C. As the ligand deposited on the solid, an immediate color change from yellow to orange occurred. The mixture was allowed to warm to room temperature over 12 h; the solid dissolved and reacted to produce an orange solid. This product was filtered out, washed with a 2-mL portion of pentane under argon, and dried *in vacuo* (total yield 59.3 mg, 0.723 mmol, 64.6%). IR (cm^{-1}): 3207 w, 3120 w, 2888 vw, 2844 vw, 1702 m, 1669 m, 1630 w, 1608 m, 1470 vw, 1459 vw, 1397 vw, 1365 vw, 1201 s, 1065 w, 856 m, 826 m, 790 m, 773 m, 732 s, 723 w.

Spectroscopic Studies. IR spectra (4000–400 cm^{-1}) were recorded on a Perkin-Elmer 983 grating spectrophotometer for Fluorolube and Nujol mulls on KBr plates and solid KBr pellets. To ensure that decomposition of the solid did not occur, samples were prepared and spectra recorded

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Table I. Summary of Crystallographic Data for $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$

empirical formula	$C_{16}H_{24}F_{12}Mo_2N_4O_8$
space group	$I2/a$
fw	820.3
cell dimens	
a, Å	20.319(10)
b, Å	9.903(5)
c, Å	30.260(16)
β, deg	94.65(4)
Z	8
V, Å^3	6069(5)
T, K	294
wavelength, Å	0.710 73
calcd density, g/cm^3	1.796
abs coeff, cm^{-1}	9.20
data collcn range	$3.0° \leq 2\theta \leq 45.0°$
no. of reflns collected	4391
unique (merging R)	3980 (7.81%)
obsd ($F_o > 4\sigma(F_o)$)	2018
R^a	0.0743
$R_w{}^a$	0.0807
goodness-of-fit	1.62

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

under an inert atmosphere. ^{19}F NMR spectra were obtained on Varian EM-390 and Bruker AM 400 spectrometers at 84.67 and 376.5 MHz, respectively, in 5 mm diameter tubes; samples were prepared and capped under argon. Acetonitrile-d_3 (Aldrich) was used as an internal lock solvent on the AM 400; internal α,α,α-trifluorotoluene (Aldrich) was used as lock on the EM-390 (10% in acetonitrile). Chemical shifts (δ) are reported relative to external α,α,α-trifluorotoluene, which was assigned $\delta = -63.6$ ppm relative to CCl_3F.

X-ray Structure Determination of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$. A small blade was mounted on the end of a glass fiber. Initial study indicated a C-centered monoclinic unit cell with $a = 35.062(11)$ Å, $b = 9.904(3)$ Å, $c = 20.309(7)$ Å, and $\beta = 120.65(2)°$; this transforms to a more nearly orthogonal I-centered cell with $a = 20.309(7)$ Å, $b = 9.904(3)$ Å, $c = 30.262(9)$ Å, and $\beta = 94.61(3)°$. However this crystal did not scatter well and significantly decomposed over the 3 days of data collection. Another blade was obtained from an identically produced batch of product; it was mounted and coated with epoxy to protect it from the atmosphere. Crystallographic data for the latter crystal are summarized in Table I. ω scans from the second crystal were broader than those of the first, and one such scan was not entirely Gaussian in shape. Axial photographs confirmed the axis lengths and the crystal class. The unit cell, was determined by centering 25 reflections in the 2θ range 17–28°.

Data were collected using the 2θ–θ scan technique and processed on a computer-controlled four-circle Nicolet R3m/V crystal diffractometer with Mo Kα radiation. Two reflections established as standards were checked routinely for deviations of positions and intensities after every 100 reflections. The data were corrected for an approximate 10% intensity decay over the data collection. Lorentz and polarization corrections and empirical absorption corrections based on ψ scans were performed. Systematic absences were consistent with space groups $I2/a$ and Ia (nonstandard settings of $C2/c$ (No. 15) and Cc (No. 9), respectively). Intensity statistics favored the centrosymmetric $I2/a$. Positions of the molybdenum atoms were located by direct methods.[20] Other atoms were recovered from difference maps calculated after least-squares refinement of the Mo atoms.

All of the CF_3 groups were seriously disordered; these groups were refined as rigid fragments with a single (refined) C–F distance and tetrahedral angles. The C–C distances in the carboxylates were fixed ($d_{C-C} = 1.50$ Å),[9] and a common isotropic temperature factor was assigned for all F atoms bonded to a given C atom. In the last cycles of refinement, these restrictions were relaxed; this resulted in some changes in site occupancies of the disordered F's and a small drop in R and R_w from 0.0749 and 0.0824 to the final values reported here.

Results and Discussion

Synthesis. Yellow $Mo_2(O_2CCF_3)_4$ rapidly changes color to orange as the udmed/solvent mixture condenses on the solid. As the mixture warms to room temperature over 12 h, the solid dissolves and reacts with udmed to form a crystalline product, as shown in eq 1. Infrared spectra indicate that the 1:2 adduct is the only product obtained, even when a large excess (1:10) of udmed is used.

$$Mo_2(O_2CCF_3)_4 + 2udmed \xrightarrow{EtOH} [Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3) \quad (1)$$

The product, a mass of small orange bladelike crystals, was isolated by filtration and stored *in vacuo*. The solid turns black in laboratory air after a few hours; however, solutions decompose immediately upon exposure to air, turning from dark orange to dark muddy brown.

We have obtained single crystals only by direct synthesis. Several attempts at recrystallization were unsuccessful; the solutions decomposed after several days even though they remained under vacuum in an argon-filled outer container. From solubility and decomposition studies, both ethanol and acetonitrile were appropriate solvents for this reaction. However, only ethanol produced sufficiently large single crystals for X-ray diffraction studies.

Infrared Spectrum. IR spectra recorded on each batch of material were identical, regardless of the $Mo_2(O_2CCF_3)_4$ to udmed ratio over the range 1:2 to 1:10. Besides indicating that the same product was formed in each reaction, the spectra also provided much structural information prior to the X-ray structure determination. Garner[11,12] and Andersen[14] have demonstrated the utility of infrared spectroscopy for distinguishing the several possible coordination modes of trifluoroacetate.

The infrared spectrum of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$ clearly indicates that both bridging and ionic trifluoroacetate groups are present. On the basis of Garner's work,[11,12] we assign bands at 1702, 826, 798, and 723 cm^{-1} to the OCO asymmetric stretching mode, the C–C stretching mode, and the OCO and CF_3 deformation modes, respectively, for ionic CF_3CO_2. Bands at 1608, 856, 773, and 732 cm^{-1} represent the corresponding modes for bridging CF_3CO_2 groups; the band at 1630 cm^{-1} may also represent an OCO asymmetric stretch. Absorptions at 1201 and 1065 cm^{-1} are C–F stretching bands.[9,11,12,21] Weak absorptions at 3207 and 3120 cm^{-1} are typical of N–H stretches in solid complexes.[22] C–H stretching and bending modes for udmed occur at 2888, 2844, 1470, 1459, 1397, and 1365 cm^{-1}.[22,23] The IR spectra of $[Mo_2(O_2CCF_3)_4(udmed)_2]$ do not define the coordination mode of udmed.

Solid-State Structure. An ORTEP diagram of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$ is shown in Figure 1. Fractional coordinates, bond distances, and bond angles are listed in Tables II–IV, respectively.

The combination of a small, rather low-quality crystal and the extensive disorder (all of the CF_3 groups are disordered) led to a data set with a relatively low proportion of observed reflections at high 2θ angles and to relatively large uncertainties in cell constants, atomic positions, and the derived bond distances and angles. The structure determination allows us to identify the solid and to make useful comparisons with other structures.

The structure consists of the $Mo_2(O_2CCF_3)_3(udmed)_2{}^+$ cation and the $CF_3CO_2{}^-$ anion, joined by hydrogen bonding. There is no crystallographic symmetry imposed on the structure; however

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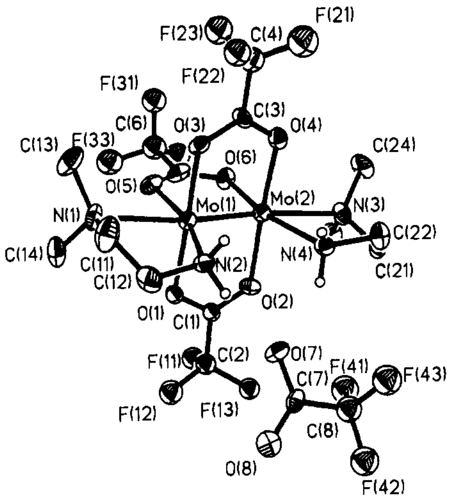

Figure 1. Molecular structure of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$. The thermal ellipsoids are scaled to 20% probability.

the cation has idealized C_{2v} symmetry. The packing diagram of this structure, shown in Figure 2, displays the cation–anion hydrogen bonding. This arrangement leads to a one-dimensional zigzag cation–anion chain through the crystal.

Some of the first one-dimensional chains comprising $Mo_2(O_2CCH_3)_4$ units came from compounds with the general formula $Mo_2(O_2CCH_3)_4[Me_2ECH_2CH_2EMe_2]$ (E = P, N).[6] In these structures, the bidentate ligand links $Mo_2(O_2CCH_3)_4$ units by coordinating to an axial site on each dimer. The acetate forms similar chains with *N,N'*-dmed (sdmed).[6,7] This linkage is different from that of the structure reported here for $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$, in which the cation and anion are held together by hydrogen bonds. Eichhorn, Kerby, *et al.*[6,7] have reported solid complexes of $Mo_2(O_2CCH_3)_4$ with udmed and *N*-methylethylenediamine (nmed) which have the same composition and coordination sphere as the trifluoroacetate analogue but are "tetramers", with the formula $\{[Mo_2(O_2CCH_3)_3(amine)_2](O_2CCH_3)\}_2$. This unit consists of two cations and two anions, held together in hydrogen-bonded rings instead of the chains formed by the trifluoroacetate. It is clear that the coordination mode of udmed is not influenced by carboxylate basicity, at least in the solid state.

The general composition of the udmed product $[Mo_2(O_2CCF_3)_4(diamine)_2]$ is identical to those of two $Mo_2(O_2CCF_3)_4(bipyridine)_2$ adducts recently characterized by Dunbar and Christou.[13] However, the structure described here differs from those of the bipyridine adducts. In both bipyridine complexes, the amines act as diequatorial chelates. In one, there are two bridging and two anionic trifluoroacetates; in the other, all four trifluoroacetates are monodentate. In the udmed complex, there are three bridging trifluoroacetates, and the diamines act as axial–equatorial chelates.

The conformation about the metal core of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$ is virtually eclipsed; the average dihedral angle is 1.2(8)°. The Mo–Mo bond distance, 2.132(2) Å, is 0.042 Å longer than the Mo–Mo bond in $Mo_2(O_2CCF_3)_4$, 2.090(4) Å.[9] It is similar to the Mo–Mo bond distances in the diaxial adducts $[Mo_2(O_2CCF_3)_4(py)_2]$, 2.129(2) Å,[10] and $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, 2.128(1) Å.[17] It is slightly longer than the distances reported for the diequatorial adducts $[Mo_2(O_2CCF_3)_4(PBu_3)_2]$, 2.105(1) Å,[18] $[Mo_2(O_2CCF_3)_4(PPhEt_2)_2]$, 2.100(1) Å,[15] and $[Mo_2(O_2CCF_3)_4(PMePh_2)_2]$, 2.107(2) Å.[15] It lies between those reported for the $Mo_2(O_2CCF_3)_4(bipyridine)_2$ complexes (2.181(2) and 2.077(1) Å for the bridged and unbridged isomers, respectively).[13] It is also slightly longer than the 2.100–2.105-Å Mo–Mo bonds found in the polymeric axial adducts $Mo_2(O_2CCH_3)_4$ (LL) (LL = tmed, dmpe, $H_2N(CH_2)_3NH_2$, (pda), sdmed;[6,7] it compares more closely with the bonds in structurally similar acetate complexes with udmed and nmed (2.124(2) and 2.130(2) Å, respectively).[7]

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	5848(1)	2095(2)	3717(1)	50(1)
Mo(2)	4925(1)	2899(2)	3878(1)	48(1)
O(1)	5435(6)	201(12)	3533(4)	53(5)
O(2)	4470(6)	1019(13)	3679(4)	59(5)
C(1)	4807(10)	101(14)	3537(6)	56(8)
C(2)	4473(5)	−1176(10)	3370(4)	66(6)
F(11)	4347(9)	−1925(17)	3709(4)	83(7)
F(12)	4857(6)	−1845(18)	3123(6)	89(7)
F(13)	3918(6)	−899(14)	3139(5)	69(6)
F(14)	4756(17)	−2161(24)	3601(10)	98(15)
F(15)	3842(7)	−1175(38)	3421(12)	131(19)
F(16)	4563(16)	−1352(31)	2952(5)	74(13)
O(3)	6301(5)	3986(13)	3873(4)	56(5)
O(4)	5342(7)	4819(13)	4047(4)	62(6)
C(3)	5958(10)	4947(14)	4019(6)	58(8)
C(4)	6273(6)	6281(11)	4148(4)	83(7)
F(21)	5854(8)	7262(20)	4184(8)	131(11)
F(22)	6701(9)	6633(19)	3868(6)	89(9)
F(23)	6594(11)	6064(21)	4535(5)	106(9)
F(24)	6021(12)	7132(23)	3850(7)	94(11)
F(25)	6097(12)	6640(23)	4536(5)	74(10)
F(26)	6913(7)	6293(29)	4151(9)	128(14)
O(5)	6064(7)	1467(14)	4379(4)	72(6)
O(6)	5105(7)	2283(14)	4543(4)	66(5)
C(5)	5643(12)	1672(22)	4651(4)	65(9)
C(6)	5827(7)	1313(14)	5129(3)	102(8)
F(31)	6141(10)	2318(15)	5332(6)	101(8)
F(32)	5298(7)	1041(22)	5332(6)	115(9)
F(33)	6212(10)	252(18)	5150(6)	122(9)
F(34)	5501(16)	2102(30)	5380(10)	132(18)
F(35)	6459(8)	1515(35)	5216(10)	96(14)
F(36)	5689(16)	57(17)	5210(10)	87(14)
N(1)	7045(8)	1460(21)	3548(7)	78(8)
C(13)	7537(9)	2085(28)	3879(8)	119(12)
C(14)	7117(11)	11(24)	3584(7)	97(12)
C(11)	7087(11)	2004(29)	3115(8)	109(12)
C(12)	6482(11)	1812(23)	2842(7)	86(10)
N(2)	5900(6)	2483(14)	3007(4)	54(6)
N(3)	3762(8)	3540(18)	4067(6)	70(7)
C(23)	3415(10)	2450(20)	4287(7)	77(10)
C(24)	3766(10)	4710(22)	4337(7)	94(11)
C(21)	3440(10)	3822(23)	3609(7)	79(10)
C(22)	3861(10)	4602(21)	3334(6)	72(9)
N(4)	4479(7)	3812(15)	3255(4)	58(6)
O(7)	419(6)	3377(14)	2361(4)	74(6)
O(8)	608(6)	4680(13)	2946(5)	72(6)
C(7)	799(5)	3875(20)	2663(7)	56(8)
C(8)	1523(5)	3548(16)	2661(5)	92(8)
F(41)	1747(11)	3884(28)	2282(6)	112(12)
F(42)	1886(11)	4125(26)	2983(7)	116(12)
F(43)	1570(11)	2235(17)	2707(9)	118(12)
F(44)	1688(12)	2887(27)	2313(6)	123(12)
F(45)	1695(12)	2847(28)	3017(7)	120(12)
F(46)	1839(11)	4702(17)	2684(9)	101(11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The Mo–O bond distances, 2.11(1) Å, are typical for those found in dimolybdenum carboxylate structures.[5–7,9,10,13,15,17,18] The Mo–N bonds show a notable difference between the longer axial bonds (2.602(17) and 2.555(16) Å) and the shorter equatorial bonds (2.194(13) and 2.218(13) Å). The longer axial distances, associated with the methylated nitrogens, indicate weak bonding interactions. There are comparable to those found for the pyridine adduct (2.548(8) Å)[10] but are generally shorter than those noted for the acetate complexes with en,[5] tmed,[6] sdmed,[7] pda,[7] udmed,[7] or nmed.[7] The equatorial Mo–N distances found here compare closely to those in $[Mo_2(O_2CCH_3)_2(en)_4](O_2CCH_3)_2 \cdot en$[5] and $[Mo_2(O_2CCH_3)_3(amine)_2](O_2CCH_3)$[7] (amine = udmed, nmed) and are slightly longer than those found in the bipyridine complexes.[13] The difference in axial and equatorial bond distances

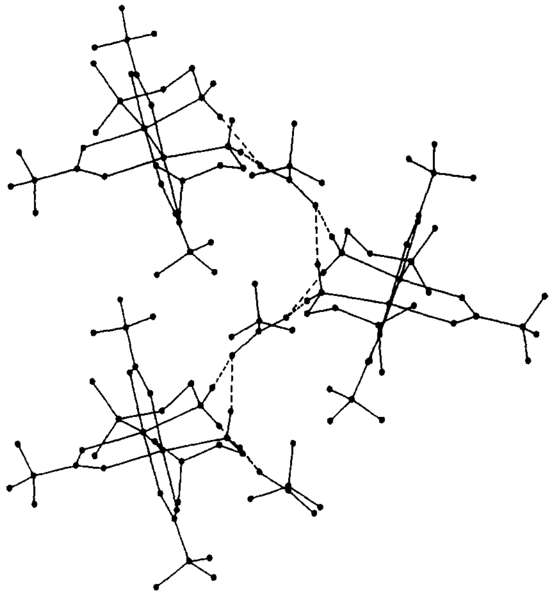

Figure 2. Molecular packing of $[Mo_2(O_2CCF_3)_3(udmed)_2](O_2CCF_3)$. N–H- -O hydrogen-bonding interactions are indicated by dashed lines.

Table III. Bond Lengths (Å)

Mo(1)–Mo(2)	2.132(2)	Mo(1)–O(1)	2.110(12)
Mo(1)–O(3)	2.124(13)	Mo(1)–O(5)	2.111(13)
Mo(1)–N(1)	2.602(17)	Mo(1)–N(2)	2.194(13)
Mo(2)–O(2)	2.143(13)	Mo(2)–O(4)	2.127(13)
Mo(2)–O(6)	2.105(11)	Mo(2)–N(3)	2.555(16)
Mo(2)–N(4)	2.218(13)	O(1)–C(1)	1.281(24)
O(2)–C(1)	1.235(22)	C(1)–C(2)	1.502(18)
C(2)–F(11)	1.308(18)	C(2)–F(12)	1.306(20)
C(2)–F(13)	1.307(17)	C(2)–F(14)	1.306(28)
C(2)–F(15)	1.305(19)	C(2)–F(16)	1.306(20)
O(3)–C(3)	1.279(21)	O(4)–C(3)	1.268(24)
C(3)–C(4)	1.504(19)	C(4)–F(21)	1.303(22)
C(4)–F(22)	1.310(23)	C(4)–F(23)	1.311(21)
C(4)–F(24)	1.307(24)	C(4)–F(25)	1.305(22)
C(4)–F(26)	1.301(19)	O(5)–C(5)	1.251(24)
O(6)–C(5)	1.269(26)	C(5)–C(6)	1.507(16)
C(6)–F(31)	1.307(21)	C(6)–F(32)	1.309(20)
C(6)–F(33)	1.308(23)	C(6)–F(34)	1.305(33)
C(6)–F(35)	1.306(21)	C(6)–F(36)	1.303(23)
N(1)–C(13)	1.493(28)	N(1)–C(14)	1.446(31)
N(1)–C(11)	1.426(33)	C(11)–C(12)	1.436(30)
C(12)–N(2)	1.477(26)	N(3)–C(23)	1.477(27)
N(3)–C(24)	1.416(28)	N(3)–C(21)	1.510(27)
C(21)–C(22)	1.462(30)	C(22)–N(4)	1.514(25)
O(7)–C(7)	1.251(21)	O(8)–C(7)	1.254(24)
C(7)–C(8)	1.507(15)	C(8)–F(41)	1.309(23)
C(8)–F(42)	1.305(25)	C(8)–F(43)	1.310(23)
C(8)–F(44)	1.305(26)	C(8)–F(45)	1.307(26)
C(8)–F(46)	1.310(23)		

is quite typical; the axial[17] and equatorial[15] isomers of $[Mo_2(O_2CCF_3)_4(PMePh_2)_2]$ have Mo–P distance of 2.99 and 2.51 Å, respectively. In the equatorial isomer, two trifluoroacetates act as chelates, coordinating both axial and equatorial sites. These Mo–O distances are near 2.80 and 2.14 Å.

The Mo–Mo–O angles are typically near 91.5°, similar to those reported for bridging carboxylates in dimolybdenum carboxylate structures.[5–7,9,10,13,15,17,18] The Mo–Mo–N (equatorial) bond angles, near 105.6°, are comparable to those in the acetate complexes $[Mo_2(O_2CCH_3)_2(en)_4](O_2CCH_3)\cdot en$[5] and $[Mo_2(O_2CCH_3)_3(amine)_2](O_2CCH_3)$[7] (amine = udmed, nmed). They also resemble the Mo–Mo–Cl bond angles in salts of $Mo_2Cl_8^{4-}$,[24–26] along with the Mo–Mo–C bond angles in $Li(THF)_4Mo_2Me_8$.[27] The (equatorial) Mo–Mo–N bond angles are larger than the

Table IV. Bond Angles (deg)

Mo(2)–Mo(1)–O(1)	93.1(3)	Mo(2)–Mo(1)–O(3)	89.6(3)
O(1)–Mo(1)–O(3)	176.8(5)	Mo(2)–Mo(1)–O(5)	90.6(4)
O(1)–Mo(1)–O(5)	92.1(5)	O(3)–Mo(1)–O(5)	89.7(5)
Mo(2)–Mo(1)–N(1)	171.6(4)	O(1)–Mo(1)–N(1)	95.3(6)
O(3)–Mo(1)–N(1)	82.1(5)	O(5)–Mo(1)–N(1)	89.4(6)
Mo(2)–Mo(1)–N(2)	105.8(4)	O(1)–Mo(1)–N(2)	87.0(5)
O(3)–Mo(1)–N(2)	90.6(5)	O(5)–Mo(1)–N(2)	163.6(5)
N(1)–Mo(1)–N(2)	74.4(6)	Mo(1)–Mo(2)–O(2)	88.7(4)
Mo(1)–Mo(2)–O(4)	92.8(4)	O(2)–Mo(2)–O(4)	176.8(5)
Mo(1)–Mo(2)–O(6)	91.3(4)	O(2)–Mo(2)–O(6)	93.1(5)
O(4)–Mo(2)–O(6)	89.7(5)	Mo(1)–Mo(2)–N(3)	172.4(4)
O(2)–Mo(2)–N(3)	83.9(5)	O(4)–Mo(2)–N(3)	94.7(5)
O(6)–Mo(2)–N(3)	87.2(6)	Mo(1)–Mo(2)–N(4)	105.3(4)
O(2)–Mo(2)–N(4)	88.7(5)	O(4)–Mo(2)–N(4)	88.1(5)
O(6)–Mo(2)–N(4)	163.3(5)	N(3)–Mo(2)–N(4)	76.5(5)
Mo(1)–O(1)–C(1)	116.2(10)	Mo(2)–O(2)–C(1)	120.0(12)
O(1)–C(1)–O(2)	121.7(15)	O(1)–C(1)–C(2)	119.0(14)
O(2)–C(1)–C(2)	119.3(17)	C(1)–C(2)–F(11)	109.0(12)
C(1)–C(2)–F(12)	110.2(13)	C(1)–C(2)–F(13)	110.5(11)
C(1)–C(2)–F(14)	106.5(15)	C(1)–C(2)–F(15)	112.4(19)
C(1)–C(2)–F(16)	110.1(17)	F(11)–C(2)–F(12)	109.0(13)
F(11)–C(2)–F(13)	108.8(13)	F(12)–C(2)–F(13)	109.2(12)
F(14)–C(2)–F(15)	109.4(23)	F(14)–C(2)–F(16)	109.2(20)
F(15)–C(2)–F(16)	109.3(22)	Mo(1)–O(3)–C(3)	119.7(11)
Mo(2)–O(4)–C(3)	116.7(10)	O(3)–C(3)–O(4)	121.1(14)
O(3)–C(3)–C(4)	120.7(16)	O(4)–C(3)–C(4)	118.1(14)
C(3)–C(4)–F(21)	114.2(14)	C(3)–C(4)–F(22)	110.9(14)
C(3)–C(4)–F(23)	104.9(13)	C(3)–C(4)–F(24)	104.7(14)
C(3)–C(4)–F(25)	109.3(15)	C(3)–C(4)–F(26)	114.4(17)
F(21)–C(4)–F(22)	109.2(15)	F(21)–C(4)–F(23)	109.2(16)
F(22)–C(4)–F(23)	108.2(15)	F(24)–C(4)–F(25)	108.9(16)
F(24)–C(4)–F(26)	109.5(18)	F(25)–C(4)–F(26)	109.7(18)
Mo(1)–O(5)–C(5)	118.5(12)	Mo(2)–O(6)–C(5)	117.6(10)
O(5)–C(5)–O(6)	121.9(13)	O(5)–C(5)–C(6)	117.6(18)
O(6)–C(5)–C(6)	120.1(15)	C(5)–C(6)–F(31)	110.1(14)
C(5)–C(6)–F(32)	110.5(14)	C(5)–C(6)–F(33)	109.7(14)
C(5)–C(6)–F(34)	108.5(17)	C(5)–C(6)–F(35)	108.7(18)
C(5)–C(6)–F(36)	111.4(17)	F(31)–C(6)–F(32)	109.0(15)
F(31)–C(6)–F(33)	108.8(15)	F(32)–C(6)–F(33)	108.8(16)
F(34)–C(6)–F(35)	109.2(21)	F(34)–C(6)–F(36)	109.6(21)
F(35)–C(6)–F(36)	109.4(22)	Mo(1)–N(1)–C(13)	110.8(13)
Mo(1)–N(1)–C(14)	108.4(13)	C(13)–N(1)–C(14)	107.6(17)
Mo(1)–N(1)–C(11)	102.4(13)	C(13)–N(1)–C(11)	112.0(19)
C(14)–N(1)–C(11)	115.6(20)	N(1)–C(11)–C(12)	111.5(20)
C(11)–C(12)–N(2)	114.7(18)	Mo(1)–N(2)–C(12)	110.7(10)
Mo(2)–N(3)–C(23)	113.8(12)	Mo(2)–N(3)–C(24)	111.7(12)
C(23)–N(3)–C(24)	108.6(17)	Mo(2)–N(3)–C(21)	100.4(12)
C(23)–N(3)–C(21)	111.1(15)	C(24)–N(3)–C(21)	111.1(16)
N(3)–C(21)–C(22)	113.0(16)	C(21)–C(22)–N(4)	110.3(16)
Mo(2)–N(4)–C(22)	111.3(10)	O(7)–C(7)–O(8)	122.9(13)
O(7)–C(7)–C(8)	117.2(16)	O(8)–C(7)–C(8)	119.8(14)
C(7)–C(8)–F(41)	111.0(15)	C(7)–C(8)–F(42)	113.2(16)
C(7)–C(8)–F(43)	106.0(15)	C(7)–C(8)–F(44)	115.3(15)
C(7)–C(8)–F(45)	107.8(16)	C(7)–C(8)–F(46)	106.6(15)
F(41)–C(8)–F(42)	109.1(17)	F(41)–C(8)–F(43)	108.6(20)
F(42)–C(8)–F(43)	108.9(18)	F(44)–C(8)–F(45)	109.2(18)
F(44)–C(8)–F(46)	108.9(19)	F(45)–C(8)–F(46)	108.8(18)

Mo–Mo–P angles for the substituted phosphine adducts $Mo_2(O_2CCF_3)_4(PBu_3)_2$,[18] $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$, and $Mo_2[O_2CCF_3)_4(PPh_2CH_3)_2$.[15] The axial Mo–Mo–N angles are nearly linear at 172.4(4) and 171.6(4)°. They are typical of those found in other axial amine–dimolybdenum complexes.[5–7,10]

NMR Spectrum. The ^{19}F NMR spectrum (376.5 MHz) of this compound in acetonitrile-d_3 at −20 °C consists of two major peaks of approximately equal area at −73.6 and −76.6 ppm plus several other small peaks around −73 ppm and a small peak at −76.0 ppm. We attribute the −73 ppm peaks to bridging bidentate trifluoroacetates[14,16,18] and the −75 and −76 ppm peaks to nonbridging (monodentate and/or anionic) trifluoroacetates. The ratio of bridging to nonbridging trifluoroacetates is 1.2:1, on the basis of integration of the spectrum. At low field or higher temperature, the spectrum shows line broadening; a study at low

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field (84.67 MHz) shows that this line broadening is reversible with temperature change. These results suggest that the solid-state species is not a major species in solution. The solution contains a number of species; the temperature-dependent line widths indicate that these species undergo exchange. The major species contains two bridging and two nonbridging trifluoroacetates; diamines and solvent presumably occupy other coordination sites on the dimolybdenum core. Its structure could be related to those of the equatorial phosphine adducts[14,15,18] or the $Mo_2(O_2CCH_3)_4$·en adduct.[5] This difference between solution and solid-state structures is not unknown for dimolybdenum chemistry; the trifluoroacetate–pyridine system also features different solution and solid-state species.[16] The lability of these complexes is also well established.[13,16,18] We are currently investigating the solution reactions of $Mo_2(O_2CCF_3)_4$ with several diamines; these results will be reported later.[28]

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Supplementary Material Available: Complete listings of data collection and solution refinement parameters, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients and a stereoview of the unit cell (6 pages). Ordering information is given on any current masthead page.

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