hydroxy-2-ethylbutyrate; the Ru=O stretch at 900 cm^{-1} present in I is absent.

Although some of the oxochromium(V) complexes give well-defined oxidation and reduction waves,[15f,18] we were unable to obtain good, reproducible CV results for our oxoruthenium(V) complexes (using CH_2Cl_2, DMSO, and CH_3CN as solvents, with (^{n}Bu$_4$N)PF$_6$ as supporting electrolyte). The reason for this is not clear, especially as oxoruthenium(V) complexes with a *trans*-dioxo unit exhibit good results.[4c,11]

Conclusions

These d^3 oxoruthenium(V) complexes show considerable similarities to the d^1 oxochromium(V) species. Both have a single unpaired electron, and they are similar structurally. The relative lack of reactivity of the oxoruthenium(V) species, especially toward organic substrates, is puzzling, though it is interesting to note that oxochromium(V) species are also quite unreactive. The ligands used in both systems, α-hydroxy carboxylic acids, lack an α-hydrogen atom, and it may be that, as proposed by Lay[15f] for oxochromium(V) hydroxy carboxylato complexes, steric protection by alkyl substituents in the α-positions is responsible for the stability of the species.

Experimental Section

Materials. Hydrated ruthenium trichloride, $RuCl_3 \cdot nH_2O$, and OsO_4 were supplied by Johnson Matthey Ltd. $RuCl_3 \cdot nH_2O$ was converted to $RuO_2 \cdot nH_2O$ as reported previously.[3c]

Improved Preparation of (^{n}Pr$_4$N)[RuO$_4$] ("TPAP") and [(Ph$_3$P)$_2$N][RuO$_4$]. Ruthenium tetraoxide vapor was generated by stirring $RuO_2 \cdot nH_2O$ (0.75 g) with sodium periodate (2.75 g) in water (15 cm^3) and swept into a second flask containing 1.0 M K_2CO_3 (20 cm^3) and 1.0 M (^{n}Pr$_4$N)OH (5 cm^3) at 0 °C. The olive green TPAP precipitated was collected after 3 h, washed with ice-cold water, and dried in vacuo. The orange mother liquor was returned to the reaction flask and passage of RuO_4 continued, with further precipitation of TPAP, until the ruthenium was consumed. Yield: 96% with respect to (^{n}Pr$_4$N)OH (ruthenium in excess). Anal. Found: C, 40.8; H, 7.9; N, 4.0. Calcd for $C_{12}H_{28}NO_4Ru$: C, 41.0; H, 8.0; N, 4.0. [(Ph$_3$P)$_2$N][RuO$_4$] was similarly prepared by using (Ph$_3$P)$_2$NCl in 1.0 M K_2CO_3. Anal. Found: C, 61.4; H, 4.2; N, 1.9. Calcd for $C_{36}H_{30}NO_4P_2Ru$: C, 61.4; H, 4.3; N, 2.0. IR: 828 cm^{-1} (strong) [ν^{as}(RuO$_2$)]. Raman (KBr disk): 843 cm^{-1} (strong) [ν^{s}(RuO$_2$)].

Preparation of (^{n}Pr$_4$N)[RuO(O$_2$COCR^{1}R^2)$_2$] [R^{1}R^2 = Et$_2$ (I), Me$_2$ (II), EtMe (III), PhMe (IV)]. The preparation of (^{n}Pr$_4$N)[RuO(O$_2$COCEt$_2$)$_2$] was typical. To a stirred solution of TPAP (0.50 g; 1.42 mmol) in acetone (25 cm^3) was added 2-hydroxy-2-ethylbutyric acid (0.375 g; 2.84 mmol). After the mixture was stirred for 24 h, a red-brown solid was isolated by addition of *n*-hexane and cooling to 5 °C for 24 h; it was washed with diethyl ether and dried in vacuo. The analogues were prepared from 2-methyl-2-hydroxypropionic, 2-methyl-2-hydroxybutyric, and 2-hydroxy-2-phenylpropionic acids, respectively. Mass spectra (negative FAB): (I) $m/z = 378$; (II) $m/z = 322$; (III) $m/z = 350$; (IV) $m/z = 446$ (due to [RuO(O$_2$COCR^{1}R^2)$_2$]$^-$ anions). Electronic spectra [nm (ϵ, dm^3 mol^{-1} cm^{-1})]: (I) 331 (3046), 365 (3261), 472 (5784); (II) 364 (3710), 460 (6771); (III) 324 (2968), 369 (3133), 466 (5928); (IV) 320 (4397), 357 (4763), 461 (6124).

Preparation of (^{n}Pr$_4$N)[RuO(O$_2$C(NH)CHEt)$_2$]. A solution of TPAP (0.40 g; 1.14 mmol) and DL-2-aminobutyric acid (0.23 g; 2.28 mmol) in acetone (25 cm^3) was stirred for 24 h. The solution was reduced to ca. 5 cm^3 in volume, and the resulting red-brown oil was triturated with diethyl ether to give a hygroscopic microcrystalline solid. This was filtered, washed with diethyl ether, and dried in vacuo.

Preparation of (Ph$_4$P)[OsO(O$_2$COCEt$_2$)$_2$]. 2-Hydroxy-2-ethylbutyric acid (0.09 g; 0.67 mmol) and (Ph$_4$P)[OsO$_4$] (0.20 g; 0.34 mmol; made by the literature method[3c]) were stirred in acetone (15 cm^3) for 48 h. Reduction in volume to ca. 5 cm^3 gave a red-purple oil, which was triturated with diethyl ether to give a hygroscopic microcrystalline solid. Electronic spectrum [nm (ϵ, dm^3 mol^{-1} cm^{-1})]: 318 (3852), 361 (4279), 460 (2941).

Instrumentation and General Experimental Details. Infrared spectra were run on a Perkin-Elmer 1720 (FTIR) instrument and Raman spectra on a Spex Ramalog 5 instrument with argon ion (5145 Å) laser excitation. ^{1}H NMR spectra were recorded on a Jeol 270 (FT) spectrometer and ^{13}C NMR spectra on a Bruker WM 250 (FT) spectrometer. ESR spectra were recorded on a Varian E12 X-band spectrometer (9.5 GHz), at low temperature with flowing liquid-nitrogen-cooled N_2 gas. Magnetic moments were determined by the Gouy method with a Johnson Matthey magnetic susceptibility balance. Mass spectra were recorded on a VG-Micromass 7070E-HS spectrometer.

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Synthesis and Characterization of Octakis(acetonitrile)dimolybdenum(II) Tetrafluoroborate

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Introduction

The preparation and properties of [M$_2$]$^{n+}$ cores surrounded only by weakly coordinated, often neutral, ligands has been of continuing interest for some years[1] although the whole body of results is not large. Reasons for this interest are first that loosely coordinated [M$_2$]$^{n+}$ species may serve as versatile starting materials in the synthesis of other complexes of the M$_2$ unit and second that they have potential catalytic activity for carbonylation and hydrogenation reactions.[1] Some examples of the previously reported compounds containing the [Mo$_2$]$^{4+}$ core surrounded partially or completely by weakly bound ligands are [Mo$_2$(H$_2$O)$_4$(CF$_3$SO$_3$)$_2$](CF$_3$SO$_3$)$_2$,[2] [Mo$_2$(NCCH$_3$)$_8$](CF$_3$SO$_3$)$_4$,[2] *cis*-[Mo$_2$(O$_2$CCH$_3$)$_2$(NCCH$_3$)$_6$](X)$_2$ (X = BF$_4^-$, CF$_3$SO$_3^-$),[3,4] [Mo$_2$(EtO$_2$CCH$_3$)$_4$](CF$_3$SO$_3$)$_4$,[5] Mo$_2$(CF$_3$SO$_3$)$_4$,[5] [Mo$_2$(en)$_4$](Cl)$_4$,[6,7] Mo$_2^{4+}$(aq),[7] *trans*-[Mo$_2$(O$_2$CCH$_3$)$_2$(dmpe)$_2$](BF$_4$)$_2$,[8] and [Mo$_2$(O$_2$CCH$_3$)$_2$(NCCH$_3$)$_5$](BF$_3$OH)$_2$.[9] Unfortunately, many of these reported procedures lead to impure products or uncertain formulations, and only in the cases of [Mo$_2$(O$_2$CCH$_3$)$_2$(NCCH$_3$)$_6$](X)$_2$ (X = BF$_4^-$, CF$_3$SO$_3^-$)[3,4] were the actual structures determined crystallographically. For [Rh$_2$]$^{4+}$, the recently reported compounds [Rh$_2$(NCCH$_3$)$_{10}$](BF$_4$)$_4$[9] and [Rh$_2$(H$_2$O)$_2$(NCCH$_3$)$_8$](PF$_6$)$_4 \cdot$2H$_2$O[10] are also of the type we are interested in here.

In this paper we report the synthesis and detailed characterization of the [Mo$_2$]$^{4+}$ compound [Mo$_2$(NCCH$_3$)$_8$(*ax*-NCCH$_3$)$_2$](BF$_4$)$_4 \cdot$2CH$_3$CN (**1**). We believe that this highly reactive compound will be of synthetic utility and perhaps also of value as a catalyst.

Experimental Section

Materials. Dimolybdenum(II) tetraacetate was prepared as reported.[11] Acetonitrile (2 L) was passed through a column (3 × 40 cm) of alumina gel (dried at 120 °C for 2 days) and then distilled from calcium hydride under an atmosphere of dry dinitrogen. Methylene chloride was distilled from phosphorus pentoxide under dinitrogen. Triethyloxonium tetrafluoroborate was used as purchased from Aldrich as a methylene chloride solution. All manipulations were performed by using standard vacuum-line and Schlenk techniques under a dry and oxygen-free atmosphere of argon.

Synthesis. Dimolybdenum(II) tetraacetate (1.00 g, 2.34 mmol) was partially dissolved in acetonitrile (30 mL) in a 100-mL three-neck flask that was equipped with a condenser and a glass rod to initiate crystallization of the product. The solution was not stirred. To this yellow solution was added triethyloxonium tetrafluoroborate (30.0 mL, 30.0 mmol, 1.0 M in CH_2Cl_2), which produced a red solution. This red color is due to the previously reported[3,4] *cis*-[Mo$_2$(O$_2$CCH$_3$)$_2$(NCCH$_3$)$_6$](BF$_4$)$_2$ species. The dimolybdenum(II) tetraacetate was dissolved completely upon warming the solution to reflux. The solution became brown after being refluxed for 1 day. It was then vigorously refluxed for 10 days. During this period, a large crop of bright blue microcrystals formed. The reaction mixture was cooled to room temperature and the supernatant liquid decanted.

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Table I. Crystal Data for $Mo_2(NCCH_3)_{10}](BF_4)_4{\cdot}2CH_3CN$ (**1**)

formula	$Mo_2F_{16}N_{12}C_{24}B_4H_{36}$
fw	1031.73
space group	$P2_1/n$
a, Å	9.586 (3)
b, Å	22.013 (7)
c, Å	10.975 (5)
β, deg	108.26 (4)
V, Å^3	2199 (3)
Z	2
d_{calcd}, g/cm^3	1.558
cryst size, mm	0.60 × 0.41 × 0.36
μ(Mo Kα), cm^{-1}	6.545
data colln instrument	Enraf-Nonius CAD-4
radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
orientation reflns: no.; range (2θ), deg	5; $19 < 2\theta \leq 32$
temp, °C	−80
scan method	ω–2θ
data colln range (2θ), deg	$4 \leq 2\theta \leq 50$
no. of unique data, tot. with $F_o^2 > 3\sigma(F_o^2)$	3616, 2502
no. of params refined	262
transm factors: max, min	1.00, 0.64
R^a	0.0864
$R_w{}^b$	0.1066
quality-of-fit indicator^c	2.108
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	3.13, 2.68, 1.74

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

The solid was rinsed with methylene chloride (4 × 10 mL) until the wash solution was clear. The solid was further rinsed with diethyl ether (3 × 10 mL). When the product was dried under vacuum for 8 h at 35 °C, 1.32 g (59% yield) of a bright blue solid, $[Mo_2(NCCH_3)_8(\mathit{ax}\text{-}NCCH_3)_{0.5}](BF_4)_4$, was isolated. Prolonged drying at elevated temperatures caused decomposition to a black intractable material.

The yield has been found to depend on the scale of the reaction. A 1.00-g scale and a 2.00-g scale of $Mo_2(O_2CCH_3)_4$ yielded 60% and 40%, respectively. The purest form of the material can be obtained by dissolving 200 mg of the product in acetonitrile (15 mL), filtering, and precipitating large dark blue crystals by slow diffusion of methylene chloride (20 mL) into the acetonitrile layer. These crystals have been shown to be $[Mo_2(NCCH_3)_8(\mathit{ax}\text{-}NCCH_3)_2](BF_4)_4{\cdot}2CH_3CN$ by X-ray crystallography, as described herein. We believe that the species in solution is $[Mo_2(NCCH_3)_8(\mathit{ax}\text{-}NCCH_3)_2](BF_4)_4$.

Physical Properties. $[Mo_2(NCCH_3)_8(\mathit{ax}\text{-}NCCH_3)_2](BF_4)_4$ is not stable in acetonitrile in air, as the solution turns purple and then decomposes to a brown color. Furthermore, the solid is hygroscopic. The solid dissolves in acetonitrile and ethanol/acetonitrile solutions. It is virtually insoluble in other common solvents and slowly decomposes in acetone. The complex reacts easily with other ligands, such as phosphines, to give other complexes of $[Mo_2]^{4+}$.

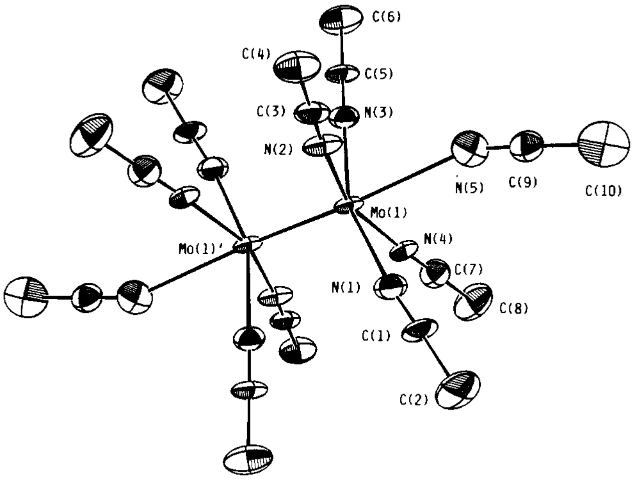

Figure 1. ORTEP drawing of the $[Mo_2(NCCH_3)_{10}]^{4+}$ core in $[Mo_2(NCCH_3)_{10}](BF_4)_4{\cdot}2CH_3CN$ (**1**). The atoms are represented by ellipsoids at the 50% probability level.

Table II. Selected Bond Distances (Å) and Angles (deg) for $[Mo_2(NCCH_3)_{10}](BF_4)_4{\cdot}2CH_3CN$ (**1**)^a

Distances			
Mo(1)–Mo(1)′	2.187 (1)	N(5)–C(9)	1.13 (2)
Mo(1)–N(1)	2.141 (9)	N(6)–C(11)	1.10 (3)
Mo(1)–N(2)	2.138 (10)	C(1)–C(2)	1.47 (2)
Mo(1)–N(3)	2.123 (9)	C(3)–C(4)	1.47 (2)
Mo(1)–N(4)	2.113 (10)	C(5)–C(6)	1.48 (2)
N(1)–C(1)	1.130 (13)	C(7)–C(8)	1.48 (2)
N(2)–C(3)	1.12 (2)	C(9)–C(10)	1.49 (2)
N(3)–C(5)	1.145 (14)	C(11)–C(12)	1.46 (3)
N(4)–C(7)	1.14 (2)	Mo(1)–N(5)	2.600 (13)
Angles			
Mo(1)′–Mo(1)–N(1)	101.8 (3)	N(1)–C(1)–C(2)	178 (2)
Mo(1)′–Mo(1)–N(2)	98.1 (3)	N(2)–C(3)–C(4)	179 (1)
Mo(1)′–Mo(1)–N(3)	97.6 (3)	N(3)–C(5)–C(6)	178 (2)
Mo(1)′–Mo(1)–N(4)	100.2 (3)	N(4)–C(7)–C(8)	180 (1)
N(1)–Mo(1)–N(2)	87.4 (4)	N(5)–C(9)–C(10)	178 (2)
N(1)–Mo(1)–N(3)	160.4 (4)	N(6)–C(11)–C(12)	177 (3)
N(1)–Mo(1)–N(4)	86.1 (4)	N(1)–Mo(1)–N(5)	80.5 (4)
N(2)–Mo(1)–N(3)	92.2 (4)	N(2)–Mo(1)–N(5)	79.2 (4)
N(2)–Mo(1)–N(4)	161.5 (4)	N(3)–Mo(1)–N(5)	80.2 (4)
N(3)–Mo(1)–N(4)	88.3 (3)	N(4)–Mo(1)–N(5)	82.7 (4)
Mo(1)–N(1)–C(1)	174 (1)	Mo(1)–N(5)–C(9)	155.3 (9)
Mo(1)–N(2)–C(3)	175.0 (9)	N(5)–C(9)–C(10)	178 (2)
Mo(1)–N(3)–C(5)	177 (1)	Mo(1)′–Mo(1)–N(5)	176 (1)
Mo(1)–N(4)–C(7)	175 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Spectral Measurements. ^1H NMR, UV–vis, and IR spectra were recorded on a Varian XL-200E, a Cary 17-D, and an IBM FTIR-IR44 instrument, respectively. Data for **1**: ^1H NMR (CD_3CN, 22 °C) 1.95 ppm (s); UV–vis (CH_3CN solution) 597 nm (ϵ = 1127 M^{-1} cm^{-1}, reflects some decomposition); IR (CH_3CN solution) 2360 (s), 2338 (m), 2306 (w), 1071 cm^{-1} (s). Similar bands are seen at 2325 (m), 2293 (s), 2247 (w), and 1059 cm^{-1} (vs) for the Nujol mull. Elemental analysis was performed on solids from two different batches by Galbraith Laboratories, Inc. The analysis is consistent with the product formulation $[Mo_2(NCCH_3)_8(\mathit{ax}\text{-}NCCH_3)_{0.5}](BF_4)_4$. Anal. Calcd: C, 22.99; H, 2.89; N, 13.41; F, 34.23. Found (sample 1, sample 2): C, 22.96, 23.46; H, 3.14, 2.96; N, 13.12, 13.48; F, 32.91, 33.11.

X-ray Crystallography. Crystals were grown as described. The crystals are extremely sensitive to air and moisture, and form an oil immediately when placed in mineral oil saturated with acetonitrile. The crystals decompose slowly (5–10 min) upon being coated with epoxy. In light of the sensitive nature of this material, a crystal was chosen directly from the Schlenk tube and mounted on a quartz fiber with Apiezon-T grease. This was then quickly transferred to the goniometer head and put in a stream of dinitrogen gas at −80 °C. The total time of this transfer was less than 1 min. Even with this method, some minor initial decay or solvent loss was evidenced by some irregular-shaped spots on the rotation and subsequent axial photographs. Once in the cold stream, the crystal was stable and thus no decay correction was applied to the data. An empirical absorption correction was applied to the data by using six azimuthal ψ scans with a χ value near 90°. The entire contents of the unit cell, except the solvent molecule, were found from the Patterson synthesis and the first Fourier map. Subsequent refinement via alternating full-matrix least-squares calculations and Fourier maps revealed

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Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for $[Mo_2(NCCH_3)_{10}](BF_4)_4 \cdot 2CH_3CN$ (**1**)[a]

atom	x	y	z	B
Mo(1)	0.0517 (1)	0.96295 (4)	0.96348 (8)	1.83 (2)
F(1)	−0.030 (1)	0.1895 (5)	0.747 (1)	7.7 (4)
F(2)	−0.022 (1)	0.1056 (5)	0.632 (1)	8.3 (4)
F(3)	0.027 (2)	0.1983 (7)	0.568 (1)	10.4 (5)
F(4)	0.181 (1)	0.1551 (6)	0.731 (1)	10.1 (4)
F(5)	0.039 (1)	0.5785 (6)	0.3372 (8)	7.3 (3)
F(6)	−0.145 (1)	0.5689 (5)	0.157 (1)	7.1 (3)
F(7)	0.053 (2)	0.6227 (5)	0.160 (1)	9.7 (5)
F(8)	0.061 (1)	0.5226 (5)	0.169 (1)	8.4 (4)
N(1)	−0.060 (1)	0.9679 (5)	0.7615 (9)	2.6 (2)
N(2)	0.226 (1)	1.0140 (5)	0.9292 (8)	2.4 (2)
N(3)	0.191 (1)	0.9311 (5)	1.1429 (9)	2.5 (2)
N(4)	−0.094 (1)	0.8912 (4)	0.9655 (8)	2.3 (2)
N(5)	0.309 (1)	0.3777 (5)	0.615 (1)	3.6 (3)
N(6)	0.086 (2)	0.263 (1)	0.274 (2)	13.2 (9)
C(1)	−0.115 (1)	0.9650 (6)	0.654 (1)	2.8 (3)
C(2)	−0.188 (2)	0.9629 (8)	0.515 (1)	5.1 (4)
C(3)	0.315 (1)	1.0382 (6)	0.904 (1)	2.4 (3)
C(4)	0.434 (1)	1.0704 (6)	0.873 (1)	3.4 (3)
C(5)	0.262 (1)	0.9124 (6)	1.240 (1)	2.5 (3)
C(6)	0.355 (2)	0.8877 (7)	1.364 (1)	4.3 (4)
C(7)	−0.169 (1)	0.8505 (6)	0.960 (1)	2.7 (3)
C(8)	−0.266 (2)	0.7975 (7)	0.953 (2)	4.7 (4)
C(9)	0.288 (1)	0.3457 (6)	0.688 (1)	3.0 (3)
C(10)	0.261 (2)	0.3024 (7)	0.783 (2)	5.0 (5)
C(11)	0.183 (3)	0.250 (1)	0.354 (2)	7.7 (7)
C(12)	0.317 (2)	0.2332 (9)	0.457 (2)	6.4 (6)
B(1)	0.038 (2)	0.1603 (9)	0.668 (2)	3.9 (4)
B(2)	0.008 (2)	0.5736 (8)	0.205 (1)	3.6 (4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

the solvent molecule and resulted in the final residuals as listed in Table I.

Results and Discussion

Crystal Structure. The structure of $[Mo_2(NCCH_3)_{10}](BF_4)_4 \cdot 2CH_3CN$ (**1**) consists of a discrete, centrosymmetric $[Mo_2(NCCH_3)_{10}]^{4+}$ core as shown in Figure 1. The dimolybdenum core resides on an inversion center. Each molybdenum atom is bonded to the other molybdenum atom [Mo(1)–Mo(1)′ = 2.187 (1) Å], four nitrogen atoms of the equatorial acetonitriles [$Mo(1)-N_{eq,av}$ = 2.129 (6) Å], and one nitrogen atom in the axial position [$Mo(1)-N_{ax}$ = 2.600 (13) Å]. The BF_4^- counterions refined nicely with no apparent disorder. All Mo–N–C angles are close to 180° as expected, except Mo(1)–N(5)–C(9), which is 155.3 (9)°. A crystal packing diagram reveals that the interstitial acetonitrile molecule [N(6)–C(11)–C(12)] "pushes" on the weakly bonded axial acetonitrile to cause this deviation from the norm. Relevant crystallographic information is presented in Tables I–III.

Attempts have been made to determine crystallographically the structure of $[Mo_2(NCCH_3)_{10}](O_3SCF_3)_4$, but all crystals to date have been badly twinned.

Synthesis and Spectroscopic Characterization. It is of extreme importance that the acetonitrile be freshly and rigorously purified. Pure solid that is dissolved in impure acetonitrile gives either green or purple solutions that decompose to a brown solution in less than 1 day. The nature of these color changes has not been established.

The presence of only one peak in the ^1H NMR spectrum indicates that the CH_3CN ligands are labile and undergo rapid exchange with the CD_3CN solvent. This behavior has been seen in the $Mo_2(O_2CCH_3)_2(NCCH_3)_6^{2+}$ complex before.[3] We attempted to record the ^1H NMR spectrum in acetone-d_6, but complex **1** decomposed. The ^1H NMR spectrum for $Mo_2(NCCH_3)_{10}(O_3CCF_3)_4$ in acetone-d_6 was reported[2] to have a peak at 1.55 ppm (s). Complex **1** is again very sensitive to impurities, and on several occasions our sample dissolved in CD_3CN to give a green solution that exhibited many broad peaks in the region of 1.4–2.2 ppm and slowly decomposed to a brown solution.

Complex **1** dissolves in pure acetonitrile to give an intensely colored blue solution. This solution has an electronic absorption peak at 597 nm, which may be assigned to the δ–δ^* transition in this unusually long Mo–Mo quadruple bond. Comparison of the values here, 597 nm and 2.187 (9) Å, with those in the typical species[12] $Mo_2Cl_8^{4-}$, namely, 530 nm and 2.138 (4) Å, is instructive. The IR spectrum of this solution has bands at 2360 (s), 2338 (m), 2306 (w), and 1071 cm^{-1} (s). When solutions of crude material (not recrystallized) are investigated by IR spectroscopy, peaks consistent with the presence of a bridging acetate (i.e. 1575 and 668 cm^{-1}) are evident. These acetate peaks disappear on recrystallization.

Conclusion. We have presented in this paper the first structurally characterized example of a complex containing a $[Mo_2]^{4+}$ core surrounded completely by neutral ligands. Although exhibiting an extreme sensitivity to various conditions, complex **1** has been fully characterized not only by X-ray crystallography but also by ^1H NMR, IR, and UV–vis spectroscopy. The compound's sensitivity to its environment foreshadows an exciting and varied chemistry, which is currently under investigation.

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Supplementary Material Available: Full tables of bond distances and angles and a table of the general displacement parameter expressions (5 pages); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

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Identification and Characterization of Trinuclear Molybdenum–Sulfur Clusters by Fast Atom Bombardment (FAB) Mass Spectrometry

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In the past few years, a variety of new complexes containing the cluster cores $[Mo_3S_4]^{4+}$, $[Mo_3S(S_2)_3]^{4+}$, and $[Mo_4S_4]^{n+}$ (n = 4–6) has been investigated.[2-9] The elucidation of composition and structure is sometimes tedious, since conventional spectroscopic methods (UV–vis, NMR, IR) and elemental analysis provide only limited information. Fast atom bombardment (FAB) mass spectrometry[10] has been widely used as a soft ionization technique for the identification and analysis of nonvolatile and thermally labile compounds.[11] For the characterization of molybdenum–sulfur clusters, mass spectrometry has occasionally been employed by Kuchen and co-workers;[2,12] however, the authors reported that they could not obtain useful spectra by using the FAB method.[13] In our laboratory, a variety of novel $Mo_3S(S_2)_3$ complexes has been prepared and characterized. With a 3-nitrobenzyl alcohol (3-NBA) matrix, FAB mass spectrometry has been found to be a powerful tool for the identification of the new molybdenum–sulfur clusters. In this contribution, positive (FAB$^+$) and negative (FAB$^-$) ion mass spectrometry of a representative series of $Mo_3S(S_2)_3$ complexes with Br$^-$, 8-hydroxyquinoline (Hoxq), *N*,*N*-diethyldithiocarbamate (dtc), 2-mercaptobenzoic acid (H_2mba), and catechol (H_2cat) are discussed.

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