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Trimolybdenum Cluster Compounds with Two Capping Ethynylidyne Groups

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Three compounds containing equilateral-triangular trimolybdenum clusters capped on both sides by ethynylidyne (CCH₃) groups are described: [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]SbF₆·3H₂O (1), [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](CF₃SO₃)₂ (2), and [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](p-CH₃C₆H₄SO₃)₂·10H₂O (3). All three are obtained by suitable workup of the reaction mixture after refluxing Mo(CO)₆ with a 10:1 v/v mixture of acetic acid and acetic anhydride. For the last two permanganate oxidation is used. The crystal structures of the three compounds have been solved and refined. In 1, where there are five electrons for the Mo₃ cluster, the Mo-Mo bond orders are ⁵/₆ and the mean Mo-Mo distance is 2.814 (5) Å; this is about 0.06 Å longer than that in a closely related cluster with Mo-Mo bond orders of 1.0. In 2 and 3, which each contain a bicapped Mo₃ cluster with only four electrons, and hence a bond order of ²/₃, the mean Mo-Mo distances are 2.883 (1) Å and 2.892 (1) Å, i.e., about 0.13 Å longer than for the Mo-Mo bonds of order 1.0. The cation in 1 has one unpaired electron showing an essentially constant *g* factor slightly above 2.0 in the range 4–300 K according to bulk susceptibility measurements. It shows no EPR spectrum but has a sharp 360-MHz ¹H NMR spectrum in which the resonance of the O₂CCH₃ protons is shifted to 14 ppm downfield while that of the CCH₃ protons is broadened and shifted 85 ppm downfield. The cations in 2 and 3 appear to be paramagnetic, but the temperature dependence is unusual and still under study. The cation gives an ¹H NMR spectrum with lines at 15.6 and 27.1 ppm with relative intensities of 3.3 to 1.0.

Introduction

From reactions of Mo(CO)₆ with acetic acid one may obtain, in addition to Mo₂(O₂CCH₃)₄, trinuclear metal-atom-cluster compounds of three types. We have already presented a brief overview of this chemistry,² describing the isolation and characterization of compounds with cations of general form [Mo₃(μ₃-X)(μ₃-Y)(O₂CCH₃)₆(H₂O)₃]ⁿ⁺ in which X = Y = O, X = Y = CCH₃, or X = O, Y = CCH₃. We have also presented a detailed report³ on the third type of cation in which *n* = 1 and there is a set of Mo-Mo single bonds linking the metal atoms in the Mo₃ equilateral triangle. In this paper we present a detailed report on compounds containing two μ₃-CCH₃ groups, where the positive charge, *n*, may be 1 or 2. We shall describe fully the following three compounds: [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]SbF₆·3H₂O (1), [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](CF₃SO₃)₂ (2), and [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](p-CH₃C₆H₄SO₃)₂·10H₂O (3).

Experimental Section

Preparations. The first stage in the preparation of all compounds was the reaction of 1.0 g of Mo(CO)₆ with a mixture of 100 mL of acetic acid and 10 mL of acetic anhydride. This reaction was carried out in a single-neck, round-bottom flask equipped with a reflux condenser. The mixture was refluxed for about 12 h (i.e., overnight) under an atmosphere of nitrogen. After it had cooled to room temperature, still under nitrogen, the dark brown reaction mixture was filtered (in air) to separate the yellow crystalline Mo₂(O₂CCH₃)₄ and the filtrate was then diluted with 100 mL of water and the entire volume poured on a Dowex 50W-X2 cation-exchange column. From this point on, procedures differ for the different products.

[Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]SbF₆·3H₂O (1). The column may be eluted with either 0.1 M HCl or 0.1 M CF₃CO₂H, and the resulting green-brown eluate solution is stripped to dryness on a rotary evaporator. The dark solid is then dissolved in methanol and passed through a Dowex 50W-X2 column that has been prepared in methanol. Upon elution of this column with a 0.1 M NaSbF₆ solution in methanol, a green-brown fraction is obtained, and on slow evaporation in air this affords beautifully crystalline material. The formula, [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]SbF₆·3H₂O, was established by X-ray crystallography. The yields are typically about 0.20 g. The water is evidently carried through from the original aqueous solution and/or

Table I. Crystallographic Data

compd no.	1	2	3
space group	<i>P</i> 2 ₁ / <i>a</i>	<i>R</i> 3̄ <i>c</i>	<i>C</i> m <i>c</i> m
unit cell parameters			
<i>a</i> , Å	18.316 (5)	11.697 (2)	13.141 (3)
<i>b</i> , Å	14.630 (5)		26.464 (4)
<i>c</i> , Å	11.970 (5)	40.842 (2)	13.939 (3)
α, deg			
β, deg	92.56 (5)		
γ, deg			
<i>V</i> , Å ³	3204 (1)	4839 (1)	4847 (2)
<i>Z</i>	4	6	4
ρ, g cm ⁻³ , calcd	2.16	2.158	1.736
measd	2.16 ^a	2.16	
cryst size, mm	0.13 × 0.17 × 0.43	0.15 × 0.20 × 0.20	0.80 × 0.30 × 0.10
μ(Mo Kα), cm ⁻¹	20.86	13.8	9.32
radiation used	Mo Kα	Mo Kα	Mo Kα
scan range, deg of 2θ	5–46	3–60	3–52
scan mode	ω/2θ	ω/2θ	ω/2θ
no. of unique data	4363	1340	1781
<i>R</i> ^b	0.049	0.026	0.069
<i>R</i> ₁ ^c	0.056	0.038	0.087
goodness of fit	<i>d</i>	1.24	2.20

^a Measured by flotation in toluene/1,1,2,2-tetrabromoethane. ^b *R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^c *R*₂ = Σ*w*^{1/2}||*F*_o| - |*F*_c||/Σ*w*^{1/2}|*F*_o|.
^d Not calculated.

carried in the methanol, which was not specially dried.

[Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](CF₃SO₃)₂ (2) and [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃](p-CH₃C₆H₄SO₃)₂·10H₂O (3). The green-brown aqueous solution obtained by eluting the column with 0.1 M HCl is oxidized by addition of 0.1 M KMnO₄ solution, which is added slowly, dropwise toward the end, to avoid having any appreciable excess. This red solution is then poured on a Dowex 50W-X2 column and the column washed with 0.1 M HCl, which does not remove the red band. The red band is then eluted with either a 1 M solution of CF₃SO₃H or a 0.5 M solution of p-CH₃C₆H₄SO₃H, and the eluates are allowed to evaporate slowly in air to yield well-crystallized specimens of 2 or 3, respectively. The yields are essentially quantitative. Anal. Calcd for 2: C, 20.62; H, 2.88; S, 6.12; Mo, 27.45. Found: C, 20.6, 20.6, 21.1, 20.5; H, 2.83, 2.90, 2.85, 2.94; S, 5.87, 5.90, 6.10; Mo, 27.1. Calcd for 3: C, 28.64; H, 5.03; S, 5.03; Mo, 22.64. Found: C, 28.66; H, 4.80; S, 5.19; Mo, 22.2.

X-ray Crystallography. Compound 1. Data for this compound were collected on a Philips 1100/20 four-circle diffractometer. Accurate cell parameters were obtained from 25 centered reflections and are listed, along with other crystallographic data, in Table I. Intensities were corrected for background, polarization, and Lorentz factors, but no absorption corrections were deemed necessary.

- (1) (a) The Hebrew University. (b) Texas A&M University. (c) The Technion.
(2) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243.
(3) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779.

Table II. Positional and Thermal Parameters for $[\text{Mo}_3(\text{CCH}_3)_2(\text{OAc})_6(\text{H}_2\text{O})_3]\text{SbF}_6 \cdot 3\text{H}_2\text{O}^a$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	62044 (2)	17669 (3)	82242 (5)	170 (3)	196 (3)	228 (3)	-6 (2)	10 (2)	34 (2)
Mo(2)	67413 (2)	11735 (3)	61794 (5)	155 (3)	193 (3)	214 (3)	-1 (2)	6 (2)	-2 (2)
Mo(3)	74287 (2)	6126 (3)	82204 (5)	150 (3)	181 (3)	225 (3)	1 (2)	6 (2)	9 (2)
O(11)	5185 (2)	1545 (3)	7343 (4)	21 (2)	29 (2)	42 (3)	3 (2)	0 (2)	7 (2)
O(12)	5623 (2)	1035 (3)	5732 (4)	22 (2)	36 (3)	28 (2)	-6 (2)	-2 (2)	2 (2)
C(11)	5097 (4)	1226 (4)	6353 (7)	28 (4)	17 (3)	46 (5)	0 (3)	0 (3)	6 (3)
C(12)	4323 (4)	1076 (7)	5864 (8)	8 (3)	73 (6)	61 (5)	-10 (5)	-12 (3)	-2 (3)
O(21)	6087 (2)	3060 (3)	7370 (4)	31 (2)	25 (2)	26 (3)	1 (2)	1 (2)	3 (2)
O(22)	6467 (2)	2547 (3)	5738 (4)	31 (2)	30 (2)	24 (2)	5 (2)	0 (2)	0 (2)
C(21)	6235 (3)	3179 (4)	6354 (6)	16 (3)	27 (4)	31 (4)	-3 (3)	-8 (3)	1 (2)
C(22)	6145 (5)	4121 (5)	5835 (6)	52 (5)	25 (4)	37 (4)	11 (3)	-9 (4)	3 (3)
O(31)	7824 (2)	1485 (3)	9526 (4)	29 (2)	22 (2)	29 (2)	-2 (2)	-4 (2)	0 (2)
O(32)	6844 (2)	2387 (3)	9563 (4)	32 (3)	26 (2)	33 (2)	-5 (2)	-4 (2)	2 (2)
C(31)	7472 (4)	2154 (5)	9921 (6)	23 (4)	22 (3)	30 (4)	-2 (3)	-7 (3)	-3 (3)
C(32)	7843 (5)	2706 (6)	10848 (7)	60 (6)	51 (5)	36 (4)	-30 (4)	-16 (4)	0 (4)
O(41)	6901 (2)	21 (3)	9605 (4)	23 (2)	28 (2)	36 (3)	7 (2)	4 (2)	10 (2)
O(42)	5916 (2)	922 (3)	9587 (4)	30 (2)	34 (3)	29 (2)	7 (2)	9 (2)	3 (2)
C(41)	6318 (4)	272 (5)	9977 (6)	44 (5)	34 (4)	31 (4)	11 (3)	3 (3)	4 (4)
C(42)	6024 (5)	-239 (7)	10976 (9)	54 (6)	69 (7)	71 (7)	42 (6)	32 (5)	23 (5)
O(51)	6967 (2)	-201 (3)	5738 (4)	24 (2)	22 (2)	28 (2)	-5 (2)	2 (2)	4 (2)
O(52)	7487 (2)	-648 (3)	7370 (4)	28 (2)	21 (2)	27 (2)	-3 (2)	0 (2)	4 (2)
C(51)	7243 (3)	-806 (5)	6375 (6)	23 (3)	23 (4)	27 (4)	-2 (3)	9 (3)	0 (3)
C(52)	7314 (5)	-1781 (5)	5960 (7)	53 (5)	21 (4)	44 (4)	-11 (3)	-3 (4)	6 (3)
O(61)	8378 (2)	849 (3)	7319 (4)	23 (2)	26 (2)	29 (3)	5 (2)	7 (2)	0 (2)
O(62)	7847 (2)	1297 (3)	5701 (4)	29 (3)	31 (2)	28 (2)	5 (2)	5 (2)	-3 (2)
C(61)	8403 (3)	1138 (4)	6314 (6)	12 (3)	25 (4)	38 (4)	-5 (3)	0 (3)	-4 (2)
C(62)	9156 (4)	1260 (7)	5824 (7)	20 (4)	72 (6)	54 (5)	17 (4)	19 (4)	-10 (4)
C(1)	7194 (3)	1871 (4)	7529 (5)	20 (3)	19 (3)	24 (3)	-2 (2)	0 (2)	1 (2)
CMe(1)	7707 (4)	2702 (6)	7524 (7)	40 (5)	39 (5)	49 (5)	-3 (4)	2 (4)	-7 (4)
C(2)	6377 (3)	499 (3)	7574 (5)	19 (3)	16 (3)	19 (3)	1 (2)	4 (2)	-5 (2)
CMe(2)	5885 (4)	-344 (5)	7597 (7)	20 (4)	31 (4)	55 (5)	-1 (3)	5 (3)	-8 (3)
OW(1)	5407 (2)	2531 (3)	9157 (4)	36 (3)	38 (3)	33 (2)	0 (2)	8 (2)	16 (2)
OW(2)	6645 (2)	1169 (3)	4331 (4)	38 (3)	31 (3)	28 (2)	1 (2)	0 (2)	4 (2)
OW(3)	8294 (2)	-167 (3)	9116 (4)	24 (2)	27 (2)	35 (2)	1 (2)	0 (2)	6 (2)
Sb	48840 (2)	68344 (3)	77271 (5)	346 (3)	519 (3)	395 (3)	41 (2)	-43 (2)	-80 (2)
F(1)	4506 (3)	7723 (5)	6727 (5)	89 (4)	102 (5)	82 (4)	45 (4)	-11 (3)	14 (4)
F(2)	5152 (2)	7763 (4)	8746 (4)	63 (3)	68 (3)	60 (3)	-4 (2)	17 (2)	-18 (2)
F(3)	5792 (3)	6972 (4)	7062 (5)	61 (3)	112 (5)	68 (3)	-3 (3)	19 (2)	-8 (3)
F(4)	4636 (4)	5903 (4)	6708 (5)	148 (6)	81 (4)	77 (4)	-17 (3)	-35 (4)	-31 (4)
F(5)	5316 (3)	5924 (5)	8714 (5)	79 (4)	106 (5)	74 (4)	13 (3)	-2 (3)	28 (3)
F(6)	3968 (3)	6692 (4)	8399 (6)	54 (3)	69 (3)	139 (6)	10 (3)	18 (3)	-16 (2)
OW(4)	6513 (3)	4730 (4)	8626 (4)	60 (3)	55 (3)	41 (3)	-2 (2)	0 (2)	3 (3)
OW(5)	4653 (3)	4070 (4)	8850 (5)	46 (3)	56 (3)	77 (4)	0 (3)	-4 (3)	16 (3)
OW(6)	7261 (4)	5941 (5)	7110 (6)	83 (5)	93 (5)	79 (5)	-4 (4)	32 (4)	-16 (4)

^a Positional parameters are $\times 10^5$ for Mo and Sb and $\times 10^4$ for the light atoms. Thermal parameters are $\times 10^4$ for Mo and Sb and $\times 10^3$ for the light atoms.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 2^{a,b}

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.14229 (2)	0.0000 (0)	0.2500 (0)	1.104 (6)	1.153 (7)	1.535 (9)	0	-0	-0
S	0.0000 (0)	0.0000 (0)	0.09452 (3)	2.07 (3)	2	3.12 (4)	1	0	0
F	-0.0227 (3)	-0.1150 (2)	0.03780 (6)	9.3 (1)	4.68 (7)	4.7 (1)	3.50 (7)	-0.6 (1)	-1.62 (8)
O(S)	0.0895 (2)	0.1348 (2)	0.10291 (6)	3.79 (9)	2.47 (7)	5.1 (1)	0.50 (6)	0.68 (9)	-1.20 (7)
O(W)	0.3270 (2)	0.0000 (0)	0.25000 (0)	1.34 (5)	1.59 (6)	4.0 (1)	0	0	0
O(1)	0.1119 (1)	-0.1489 (1)	0.28306 (4)	1.67 (4)	1.84 (4)	2.31 (6)	0.94 (3)	-0.04 (4)	0.47 (4)
O(2)	0.2594 (1)	0.1507 (1)	0.28327 (4)	1.69 (4)	1.80 (4)	2.42 (6)	0.90 (3)	-0.47 (4)	-0.59 (4)
C	0.0000 (0)	0.0000 (0)	0.05019 (13)	2.9 (2)	2	3.6 (2)	1	0	0
C(1)	0.0000 (0)	0.0000 (0)	0.28035 (9)	2.0 (1)	1	1.6 (1)	0	0	0
C(2)	0.0000 (0)	0.0000 (0)	0.31686 (9)	2.3 (1)	2	1.6 (1)	1	0	0
C(3)	0.0014 (2)	-0.2428 (2)	0.29293 (6)	2.00 (6)	1.71 (5)	1.98 (8)	0.98 (4)	-0.15 (6)	0.19 (5)
C(4)	0.0034 (3)	-0.3373 (3)	0.31705 (7)	2.65 (7)	3.15 (7)	3.9 (1)	1.35 (5)	0.20 (8)	1.99 (8)
atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
H(1)	0.334 (3)	0.408 (3)	0.6570 (8)	4.0 (8)	H(4)	0.059 (3)	0.401 (3)	0.2558 (8)	3.6 (8)
H(2)	0.333 (4)	0.294 (3)	0.6679 (17)	7.1 (11)	H(5)	0.062 (3)	0.067 (3)	0.6763 (8)	4.8 (10)
H(3)	0.297 (4)	0.044 (4)	0.3574 (11)	6.7 (12)					

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

^b Estimated standard deviations in the least significant digits are shown in parentheses.

The structure was solved and refined with use of procedures in routine use at the Technion. The positions of the four heaviest atoms (3 Mo, Sb) were found by using the MULTAN direct-methods program. The remaining atoms were then located in successive Fourier maps,

and the structure was refined with use of the SHELX-77 program package. All 44 (nonhydrogen) atoms were refined anisotropically in two blocks, the first of which included the trimolybdenum cation and the second the SbF_6^- ion and the three water molecules of

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 3^a

atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Mo(1)	0.0000 (0)	0.18208 (5)	0.25000 (0)	2.24 (6)	1.32 (5)	0.97 (5)	0	0	0
Mo(2)	0.0000 (0)	0.27668 (4)	0.35375 (7)	2.53 (4)	1.48 (3)	1.17 (3)	0	0	-0.09 (4)
S(1)	0.0000 (0)	0.2863 (2)	0.7500 (0)	6.4 (3)	3.1 (2)	3.2 (2)	0	0	0
O(1)	0.1053 (5)	0.1634 (2)	0.3586 (4)	3.3 (3)	2.1 (2)	1.8 (2)	0.2 (2)	-0.8 (2)	-0.2 (2)
O(2)	0.1040 (5)	0.2360 (2)	0.4386 (4)	3.6 (3)	2.2 (2)	1.9 (2)	0.3 (2)	-0.5 (2)	-0.3 (2)
O(3)	0.1029 (5)	0.3358 (2)	0.3305 (4)	4.2 (3)	2.1 (2)	1.9 (2)	-0.7 (2)	-0.4 (3)	0.2 (2)
OW(1)	0.0000 (0)	0.1009 (4)	0.2500 (0)	2.7 (6)	1.5 (4)	2.3 (5)	0.7 (4)	0	0
OW(2)	0.0000 (0)	0.3175 (3)	0.4866 (7)	5.1 (7)	0.9 (4)	1.8 (5)	0	0	0
C(A)	0.0949 (10)	0.2447 (4)	0.2500 (0)	5.6 (5)	1.9 (3)	1.9 (4)	0	0	-0.3 (3)
C(1)	0.1358 (7)	0.1919 (3)	0.4265 (7)	2.7 (4)	2.4 (4)	2.3 (4)	-0.2 (3)	-0.2 (4)	0.3 (3)
C(2)	0.2171 (9)	0.1720 (4)	0.4923 (8)	5.0 (5)	3.2 (4)	3.6 (4)	0.3 (4)	-2.5 (4)	0.3 (4)
C(3)	0.1344 (11)	0.3534 (5)	0.2500 (0)	2.7 (6)	2.8 (5)	2.7 (5)	-0.3 (5)	0	0
C(4)	0.2110 (16)	0.3944 (7)	0.2500 (0)	9 (1)	5.6 (8)	3.6 (7)	-4.9 (7)	0	0
C(A1)	0.2080 (11)	0.2455 (5)	0.2500 (0)	2.3 (6)	3.5 (6)	3.4 (6)	-0.0 (5)	0	0

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
S(2)	0.2275 (5)	0.0000 (0)	0.5000 (0)	4.4 (1)	OW(6)	0.0427 (16)	0.4706 (8)	0.350 (2)	9.5 (7)
O(S1)	0.0706 (11)	0.2991 (5)	0.664 (1)	3.7 (3)	OW(7)	0.0693 (25)	0.4439 (12)	0.650 (3)	17.0 (14)
O(S2)	0.0834 (22)	0.3057 (11)	0.750 (0)	6.9 (7)	C(10)	0.0000 (0)	0.2198 (8)	0.7500 (0)	3.0 (4)
O(S3)	0.2626 (24)	0.0480 (11)	0.530 (2)	4.6 (7)	C(11)	0.0000 (0)	0.1935 (7)	0.6658 (14)	5.0 (4)
O(S4)	0.2573 (22)	0.0080 (11)	0.602 (2)	4.3 (6)	C(12)	0.0000 (0)	0.1411 (7)	0.6670 (15)	5.3 (4)
O(S5)	0.2609 (22)	0.0403 (10)	0.443 (2)	4.0 (6)	C(13)	0.0000 (0)	0.1137 (9)	0.7500 (0)	4.4 (5)
OW(3)	0.1750 (9)	0.0536 (4)	0.250 (0)	4.2 (2)	C(14)	0.0000 (0)	0.0571 (12)	0.7500 (0)	6.6 (7)
OW(4)	0.0000 (0)	0.4149 (7)	0.510 (2)	10.2 (5)	C(15)	0.1049 (12)	0.0000 (0)	0.5000 (0)	3.8 (3)
OW(5)	0.1431 (15)	0.4001 (7)	0.686 (1)	6.5 (4)	C(16)	0.0508 (8)	0.0417 (4)	0.4639 (8)	3.6 (2)

^a The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkabB_{12} + 2hlacB_{13} + 2klbcB_{23})]$ where a , b , and c are reciprocal lattice constants.

crystallization. With the initial assumption that the capping units were OCH₃ groups, the refinement converged at $R_1 = 0.063$. When these were changed to CCH₃ groups, the value of R_1 dropped to 0.049. The final positional and thermal parameters for this structure are listed in Table II. With $Z = 4$ for this compound the formula unit is the asymmetric unit, and no crystallographic symmetry is imposed on any component.

Compounds 2 and 3. Data for both of these compounds were collected on an Enraf-Nonius CAD-4F automated diffractometer. Least-squares analysis of the setting angles of 25 reflections in the range $25^\circ \leq 2\theta \leq 32^\circ$, obtained with use of the automatic search routine, provided the cell parameters listed in Table I. Data collection was conducted according to standard procedures that have been described many times previously,⁴ and the solution and refinement of these two structures were carried out by standard procedures.⁵ A number of data relevant to these phases of the work are presented in Table I.

Compound 2 gave no special difficulty and refined smoothly to very good figures of merit. The entire Mo₃ cation resides on a site of 32 (D_3) symmetry, and the CF₃SO₃ anions are on positions of 3 (C_3) symmetry.

Compound 3, however, had a proclivity to form very thin platelike crystals. However, with persistence it was possible to obtain a few crystals with acceptable, if not desirable, shape. The systematic absences allowed three space groups, $Cmcm$, $Cmc2_1$, and $Ama2$. Because of the unfavorable shape of the crystal the special CAD-4 data collection routine for flat crystals was employed. The diffraction vector $[1,0,0]$ was chosen as x , parallel to the incident beam and perpendicular to the face of the crystal, and all data were collected at the smallest angles with respect to this direction so as to minimize the effects of nonuniform dimensions. Of the 2573 observations made, 1781 had $I > 3\sigma(I)$ and were considered observed.

The structure of 3 was solved by using a Patterson map in the centric space group $Cmcm$ to find the positions of the molybdenum atoms, which were seen to form a trinuclear cluster having mm crystallographic symmetry. A series of alternating electron density maps and least-squares refinements allowed the location of all atoms in the cation. However, the p -CH₃C₆H₄SO₃ anions were found to be highly disordered, and this led to an attempt to refine the structure in the acentric

space group $Ama2$, but this resulted in distances and angles within the anions that were not chemically satisfactory. Ultimately, the structure was converged in $Cmcm$ with use of anisotropic thermal parameters for the cationic species. At this point, the two p -toluenesulfonate groups were refined at two different sites in the unit cell. The first anion sits on a crystallographic mirror plane and is bisected longitudinally by a second mirror plane. This results in only a simple twofold disorder of the SO₃ group. The sulfur atom was refined anisotropically, and the carbon and oxygen atoms were refined isotropically. The second p -toluenesulfonate ion is found at a site of $2/m$ crystallographic symmetry with the twofold rotation axis passing through the CH₃ and SO₃ groups. This again results in disorder of the SO₃ group. Furthermore, the mirror plane produces a positional disorder between the SO₃ and CH₃ groups of this anion. The most suitable model for refinement at the isotropic level involved refining the CH₃ and S positions as fractionally occupied by a S atom alone. Therefore a multiplicity for the S atom of 0.38 was chosen to represent the S atom and CH₃ group along the twofold axis. Inclusion of the two anionic groups in the model as well as a total of 10 lattice water molecules produced the final refinement parameters presented in Table I.

Magnetic Measurements. These were made on an automated, temperature-programmed Faraday Balance at the H. C. Ørsted Institute, University of Copenhagen, by Dr. Eric Pedersen and co-workers. Details may be secured from Dr. Pedersen.

Nuclear Magnetic Resonance Measurements. These were kindly provided by R. E. Willson, Shell Development Company. ¹H spectra were recorded at 360 MHz, and chemical shifts are in ppm downfield from Me₄Si. For the [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]⁺ ion the spectrum, Figure 1, consists of two peaks at 14.6 and 85.2 ppm with measured relative intensities of 3.5 to 1.0. For the [Mo₃(CCH₃)₂(O₂CCH₃)₆(H₂O)₃]²⁺ ion the spectrum, Figure 2, has two peaks at 15.6 ppm and 27.1 ppm with measured relative intensities of 3.3 to 1.0.

Visible Spectra. These were measured on a Cary 14 spectrophotometer in aqueous solution. For compounds 1 and 2 the spectra are shown in Figure 3. The peak positions and intensities in nm and 10⁻³ cm⁻¹ (ϵ , L mol⁻¹ cm⁻¹) are as follows: 1, 590, 16.9 (340), ~420, ~23.8 (sh); 2, 549, 18.2 (850), 456, 21.9 (850), 382, 26.2 (1060).

Results

Structures. Compound 1. The structure of the trinuclear cation and the atomic numbering scheme are shown in Figure 4, and a packing diagram is presented as a stereopair in Figure 5. The bond lengths and angles are listed in Tables V and

(4) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* 1979, 18, 3558.

(5) Crystallographic computing on these two structures was done on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX using the Enraf-Nonius Structure Determination Package with some local modifications.

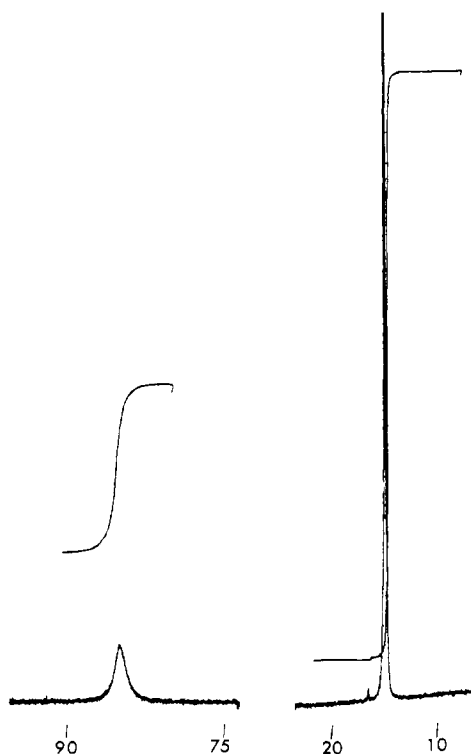


Figure 1. 360-MHz ^1H NMR spectrum of the $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ ion in aqueous solution. Chemical shifts are in ppm downfield from Me_4Si . Exact peak positions and relative intensities are listed in the Experimental Section.

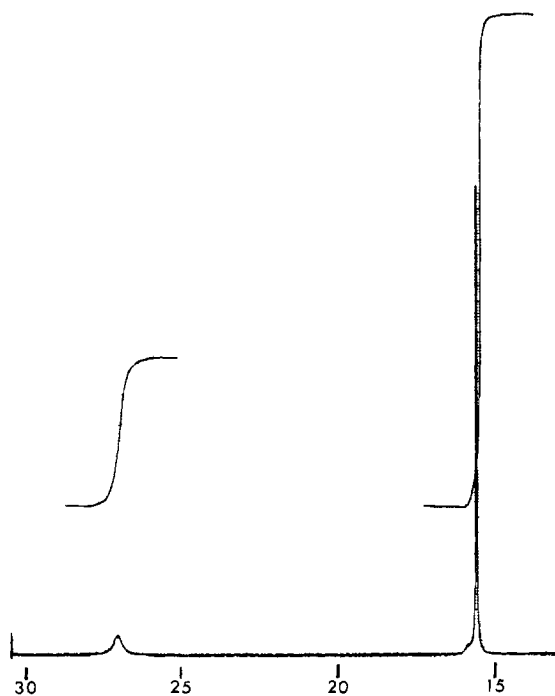


Figure 2. 360-MHz ^1H NMR spectrum of the $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$ ion in aqueous solution. Chemical shifts are in ppm downfield from Me_4Si . Exact peak positions and relative intensities are listed in the Experimental Section.

VI, respectively. In Table VII are the hydrogen bond distances based on $\text{O}\cdots\text{O}$ or $\text{O}\cdots\text{F}$ contacts less than 3.0 Å. It may be noted that the SbF_6^- octahedron is slightly irregular, with cis $\text{F}-\text{Sb}-\text{F}$ angles ranging from 87.9 to 92.2° and $\text{Sb}-\text{F}$ distances ranging from 1.871 (7) to 1.926 (7) Å. However, most of this irregularity seems to be due to hydrogen bonding since the $\text{Sb}-\text{F}$ distances to fluorine atoms not involved in hydrogen

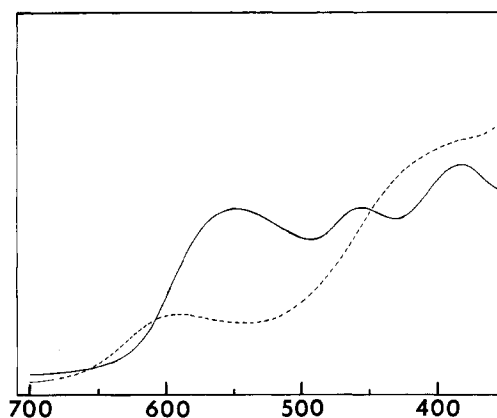


Figure 3. Visible spectra of compound 1 (---) and compound 2 (—). The horizontal scale is in nm. For exact peak positions and molar absorbances see the Experimental Section.

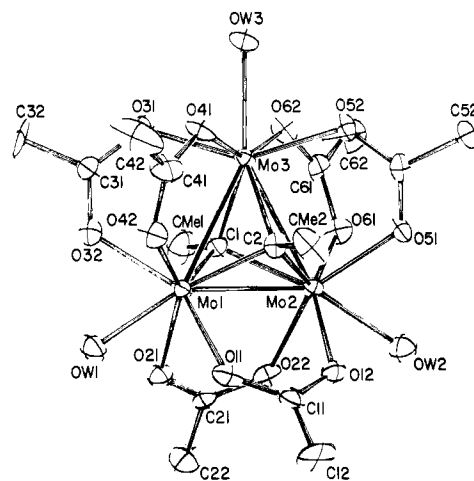


Figure 4. The $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ cation in compound 1. Atoms are represented by thermal vibration ellipsoids at the 40% level, and the labeling scheme is shown.

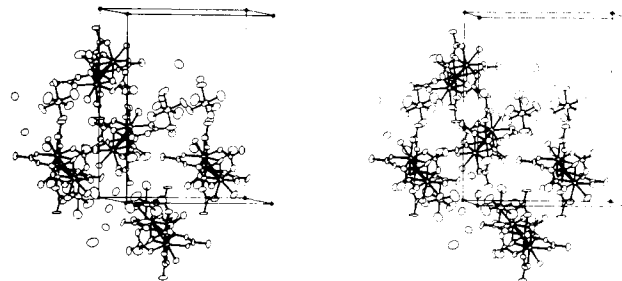


Figure 5. A stereoview of the packing in crystals of compound 1.

bonding are all in the narrow range 1.871–1.887 Å while the other two, where the fluorine atoms are hydrogen bonded, have values of 1.904 (6) and 1.926 (7) Å.

Compound 2. The structure of the $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$ ion as it occurs in this compound is shown in Figure 6. The cation has D_3 symmetry. The packing of cations and anions in the unit cell is shown in stereo in Figure 7. The bond lengths and angles in this compound are listed in Table VIII.

Compound 3. The trinuclear cation in this compound is depicted in Figure 8 where the atom labeling scheme is defined. Unlabeled atoms are related to those that are by one of the two crystallographic mirror planes. One of these contains the Mo_3 cluster while the other passes through Mo(1), C(A), C(A1), C(3), and C(4). The bond lengths and bond angles are listed in Table IX.

Table V. Bond Distances (Å) for
 $[\text{Mo}_3(\text{CCH}_3)_2(\text{OAc})_6(\text{H}_2\text{O})_3]\text{SbF}_6 \cdot 3\text{H}_2\text{O}$

Mo(1)–Mo(2)	2.8155 (8)	O(12)–C(11)	1.275 (9)
Mo(1)–Mo(3)	2.8075 (7)	O(11)–C(12)	1.52 (1)
Mo(1)–O(11)	2.127 (5)	O(21)–C(21)	1.269 (9)
Mo(1)–O(21)	2.157 (4)	O(22)–C(21)	1.267 (8)
Mo(1)–O(32)	2.146 (5)	C(21)–C(22)	1.52 (1)
Mo(1)–O(42)	2.132 (5)	O(31)–C(31)	1.274 (8)
Mo(1)–C(1)	2.035 (6)	O(32)–C(31)	1.257 (8)
Mo(1)–C(2)	2.042 (5)	C(31)–C(32)	1.51 (1)
Mo(1)–OW(1)	2.185 (5)	O(41)–C(41)	1.23 (1)
Mo(2)–Mo(3)	2.8200 (8)	O(42)–C(41)	1.277 (9)
Mo(2)–O(12)	2.103 (4)	C(41)–C(42)	1.53 (1)
Mo(2)–O(22)	2.132 (5)	O(51)–C(51)	1.259 (8)
Mo(2)–O(51)	2.125 (4)	O(52)–C(51)	1.275 (8)
Mo(2)–O(62)	2.138 (5)	C(51)–C(52)	1.52 (1)
Mo(2)–C(1)	2.054 (6)	O(61)–C(61)	1.278 (9)
Mo(2)–C(2)	2.075 (6)	O(62)–C(61)	1.249 (8)
Mo(2)–OW(2)	2.211 (5)	C(61)–C(62)	1.53 (1)
Mo(3)–O(31)	2.122 (4)	C(1)–CMe(1)	1.54 (1)
Mo(3)–O(41)	2.139 (5)	C(2)–CMe(2)	1.530 (9)
Mo(3)–O(52)	2.112 (4)	Sb–F(1)	1.878 (7)
Mo(3)–O(61)	2.116 (5)	Sb–F(2)	1.877 (5)
Mo(3)–O(1)	2.056 (5)	Sb–F(3)	1.887 (6)
Mo(3)–O(2)	2.050 (5)	Sb–F(4)	1.871 (7)
Mo(3)–OW(3)	2.194 (4)	Sb–F(5)	1.926 (7)
O(11)–O(11)	1.28 (1)	Sb–F(6)	1.904 (6)

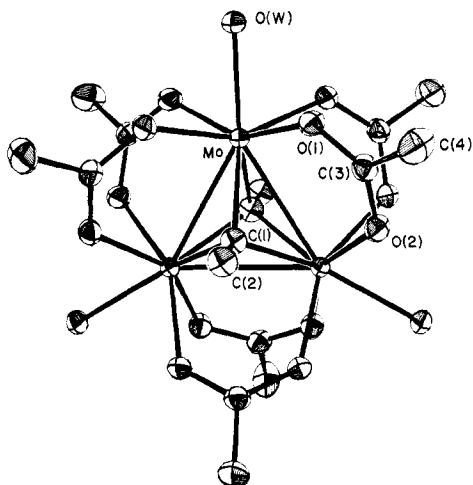


Figure 6. The $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$ cation in compound 2. Atoms are represented by thermal vibration ellipsoids at the 40% level, and the labeling scheme is defined.

Spectroscopic and Magnetic Properties. The characteristic visible spectra for the two trinuclear cations are shown in Figure 3. We shall not at present discuss assignments for these spectra, but MO calculations⁶ suggest some possibilities, and this matter will be discussed in a future paper.

The magnetic results are of mixed character. For the +1 cation in 1, the bulk susceptibility supports straightforwardly the presence of one unpaired electron. For the +2 cation, where the calculations⁶ suggest that both singlet or triplet states are possible, the magnetic susceptibility is indicative of paramagnetism but does not conform simply to a triplet state. The fact that the ^1H NMR spectra are observed in both cases with appreciable shifts but only moderate line broadening suggests that both the +1 and +2 ions are paramagnetic in solution and that the electron spin relaxation processes are quite fast.

Discussion

Authentication of the Ethylidyne Groups. It is pertinent here, as in the case of the $[\text{Mo}_3(\text{O})(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$

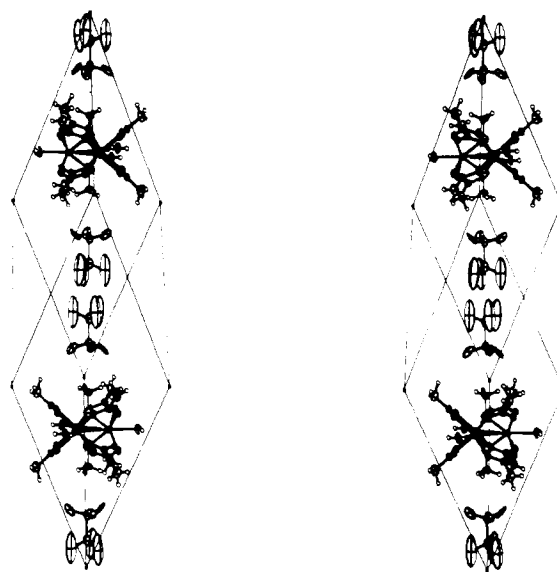


Figure 7. A stereoview of the packing in crystals of compound 2. A rhombohedral cell is shown although the structure was refined with use of the equivalent hexagonal setting.

ion,³ and even more necessary, to present very carefully the evidence in support of the CCH_3 capping groups. Compound 2, described in this paper, was previously discussed⁷ but with the formulation $[\text{Mo}_3(\text{OC}_2\text{H}_5)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_2$. The basis for this formulation was threefold. (1) The formation reaction, from $\text{CH}_3\text{CO}_2\text{H}$ and $\text{Mo}(\text{CO})_6$, seemed likely to generate $\text{CH}_3\text{CH}_2\text{O}$ groups. (2) The chemical analysis agreed well with this formulation but not with one having OCH_3 groups, so that this possibility was rejected even though the β -carbon atoms of the putative OCH_2CH_3 groups could not be found in the crystal structure. (3) Considering that the compound was stable against aqueous acid and permanganate, the idea that it might be an organometallic compound did not occur to anyone at that time.

The evidence that has now accumulated to show that the capping groups are CCH_3 and not either OCH_3 or OCH_2CH_3 is of many kinds and, taken in toto, is definitive.

(1) Crystallographic Evidence. We have already described the refinement of each of the three structures. In each instance, refinement has been carried to convergence with both O and C at the capping positions, and in each case the change from O to C was strongly supported in two ways. First, in each case the residuals, R_1 and R_2 , became lower, and the goodness of fit parameter improved. Second, when the capping atom was refined as oxygen, the thermal ellipsoid was unrealistically large, whereas when the identity was changed to carbon it became small and reasonable. The behavior in each of these compounds was essentially the same as in the case of $[\text{Mo}_3(\text{O})(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\text{BF}_4 \cdot 9\text{H}_2\text{O}$, which we have already described and depicted in detail.³ Finally, it must be mentioned that there has not been any indication of the presence of a third atom in any of the four crystallographically independent capping groups in the three structures reported here.

(2) Analytical and Density Evidence. In the comparison of the measured density and carbon analysis with values calculated for the three possible assignments of capping groups, i.e., $\text{C}_2\text{H}_5\text{O}$, CH_3O , and CH_3C , it is clear that only the latter can be simultaneously consistent with both kinds of data. The force of the argument for compound 2 is clear from Table X. The analytical figures for elements other than carbon are nearly

(6) Unpublished work by B. E. Bursten, A. Fang, and M. B. Hall.

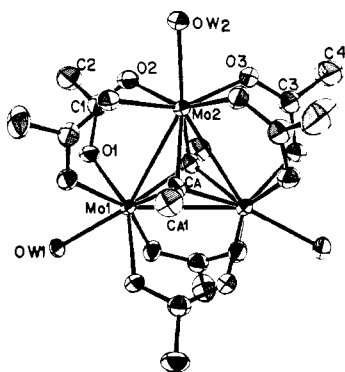
(7) Bino, A.; Ardon, M.; Maor, I.; Kaftory, M.; Dori, Z. *J. Am. Chem. Soc.* 1976, 98, 7093.

Table VI. Important Bond Angles (Deg) for $[\text{Mo}_3(\text{CCH}_3)_2(\text{OAc})_6(\text{H}_2\text{O})_3]\text{SbF}_6 \cdot 3\text{H}_2\text{O}$

Mo(2)-Mo(1)-Mo(3)	60.20 (2)	Mo(2)-Mo(3)-O(61)	81.7 (1)	Mo(1)-Mo(2)-C(2)	46.4 (1)	O(41)-C(41)-O(42)	125.7 (7)
Mo(2)-Mo(1)-O(11)	81.7 (1)	Mo(2)-Mo(3)-C(1)	46.7 (1)	Mo(1)-Mo(2)-OW(2)	148.8 (1)	O(41)-C(41)-C(42)	118.6 (7)
Mo(2)-Mo(1)-O(21)	83.7 (1)	Mo(2)-Mo(3)-C(2)	47.2 (1)	Mo(3)-Mo(2)-O(12)	125.8 (1)	O(42)-C(41)-C(42)	115.7 (7)
Mo(2)-Mo(1)-O(32)	125.4 (1)	Mo(2)-Mo(3)-OW(3)	149.3 (1)	Mo(3)-Mo(2)-O(22)	125.4 (1)	Mo(2)-O(51)-C(51)	126.4 (4)
Mo(3)-Mo(1)-O(42)	126.5 (1)	O(31)-Mo(3)-O(41)	79.8 (1)	Mo(3)-Mo(2)-O(51)	81.7 (1)	Mo(3)-O(52)-C(51)	125.8 (4)
Mo(2)-Mo(1)-C(1)	46.8 (1)	O(31)-Mo(3)-O(52)	149.1 (1)	Mo(3)-Mo(2)-O(62)	82.2 (1)	O(51)-C(51)-O(52)	123.5 (6)
Mo(2)-Mo(1)-C(2)	47.3 (1)	O(31)-Mo(3)-O(61)	90.9 (1)	Mo(3)-Mo(2)-C(1)	46.7 (1)	O(51)-C(51)-C(52)	120.1 (6)
Mo(2)-Mo(1)-OW(1)	150.4 (1)	O(31)-Mo(3)-C(1)	79.4 (2)	Mo(3)-Mo(2)-C(2)	46.5 (1)	O(52)-C(51)-C(52)	116.4 (6)
Mo(3)-Mo(1)-O(11)	126.2 (1)	O(31)-Mo(3)-C(2)	127.7 (2)	Mo(3)-Mo(2)-OW(2)	151.4 (1)	Mo(3)-O(61)-C(61)	126.8 (4)
Mo(3)-Mo(1)-O(21)	126.1 (1)	O(31)-Mo(3)-OW(3)	74.8 (1)	O(12)-Mo(2)-O(22)	79.1 (1)	Mo(2)-O(62)-C(61)	125.7 (4)
Mo(3)-Mo(1)-O(32)	81.1 (1)	O(41)-Mo(3)-O(52)	93.1 (1)	O(12)-Mo(2)-O(51)	92.5 (1)	O(61)-C(61)-O(62)	123.5 (6)
Mo(3)-Mo(1)-O(42)	83.0 (1)	O(41)-Mo(3)-O(61)	150.6 (1)	O(12)-Mo(2)-O(62)	149.8 (1)	O(61)-C(61)-C(62)	117.9 (6)
Mo(3)-Mo(1)-C(1)	47.0 (1)	O(41)-Mo(3)-C(1)	125.5 (2)	O(12)-Mo(2)-C(1)	127.1 (2)	O(62)-C(61)-C(62)	118.5 (6)
Mo(3)-Mo(1)-C(2)	46.8 (1)	O(41)-Mo(3)-C(2)	79.1 (2)	O(12)-Mo(2)-C(2)	79.3 (2)	Mo(1)-C(1)-Mo(2)	87.0 (2)
Mo(3)-Mo(1)-OW(1)	149.4 (1)	O(41)-Mo(3)-OW(3)	75.7 (1)	O(12)-Mo(2)-OW(2)	73.3 (1)	Mo(1)-C(1)-Mo(3)	86.7 (2)
O(11)-Mo(1)-O(21)	80.4 (2)	O(52)-Mo(3)-O(61)	80.6 (1)	O(22)-Mo(2)-O(51)	151.3 (1)	Mo(1)-C(1)-CMe(1)	128.1 (4)
O(11)-Mo(1)-O(32)	150.8 (1)	O(52)-Mo(3)-C(1)	127.1 (2)	O(22)-Mo(2)-O(62)	94.0 (1)	Mo(3)-C(1)-Mo(3)	86.6 (2)
O(11)-Mo(1)-O(42)	92.9 (2)	O(52)-Mo(3)-C(2)	79.3 (2)	O(22)-Mo(2)-C(1)	79.0 (2)	Mo(2)-C(1)-CMe(1)	128.0 (4)
O(11)-Mo(1)-C(1)	126.0 (2)	O(52)-Mo(3)-OW(3)	74.3 (1)	O(22)-Mo(2)-C(2)	124.5 (2)	Mo(3)-C(1)-CMe(1)	126.4 (5)
O(11)-Mo(1)-C(2)	79.7 (2)	O(61)-Mo(3)-C(1)	79.0 (2)	O(22)-Mo(2)-OW(2)	75.4 (1)	Mo(1)-C(2)-Mo(2)	86.3 (2)
O(11)-Mo(1)-OW(1)	74.9 (2)	O(61)-Mo(3)-C(2)	126.9 (2)	O(51)-Mo(2)-O(62)	79.4 (1)	Mo(1)-C(2)-Mo(3)	86.7 (2)
O(21)-Mo(1)-O(32)	91.3 (1)	O(61)-Mo(3)-OW(3)	75.0 (1)	O(51)-Mo(2)-C(1)	126.1 (2)	Mo(1)-C(2)-CMe(2)	128.7 (4)
O(21)-Mo(1)-O(42)	148.1 (1)	C(1)-Mo(3)-C(2)	75.2 (2)	O(51)-Mo(2)-C(2)	79.8 (2)	Mo(2)-C(2)-Mo(3)	86.3 (2)
O(21)-Mo(1)-C(1)	79.2 (2)	C(1)-Mo(3)-OW(3)	142.7 (2)	O(51)-Mo(2)-OW(2)	75.9 (1)	Mo(2)-C(2)-CMe(2)	127.6 (4)
O(21)-Mo(1)-C(2)	129.1 (2)	C(2)-Mo(3)-OW(3)	142.0 (2)	O(62)-Mo(2)-C(1)	79.2 (2)	Mo(3)-C(2)-CMe(2)	127.1 (4)
O(21)-Mo(1)-OW(1)	74.9 (1)	Mo(1)-O(11)-C(11)	126.0 (4)	O(62)-Mo(2)-C(2)	126.7 (2)	F(1)-Sb-F(2)	89.5 (2)
O(32)-Mo(1)-O(42)	79.6 (1)	Mo(2)-O(12)-C(11)	125.7 (4)	O(62)-Mo(2)-OW(2)	76.5 (1)	F(1)-Sb-F(3)	87.9 (2)
O(32)-Mo(1)-C(1)	78.8 (2)	O(11)-C(11)-O(12)	123.6 (7)	C(1)-Mo(2)-C(2)	74.7 (2)	F(1)-Sb-F(4)	91.0 (3)
O(32)-Mo(1)-C(2)	125.5 (2)	O(11)-C(11)-C(12)	119.1 (6)	C(1)-Mo(2)-OW(2)	143.0 (2)	F(1)-Sb-F(5)	177.2 (2)
O(32)-Mo(1)-OW(1)	75.9 (1)	O(12)-C(11)-C(12)	117.3 (7)	C(2)-Mo(2)-OW(2)	142.2 (2)	F(1)-Sb-F(6)	92.2 (2)
O(42)-Mo(1)-C(1)	127.7 (2)	Mo(1)-O(21)-C(21)	123.6 (4)	Mo(1)-Mo(3)-Mo(2)	60.04 (2)	F(2)-Sb-F(3)	89.2 (2)
O(42)-Mo(1)-C(2)	79.2 (2)	Mo(2)-O(22)-C(21)	128.7 (4)	Mo(1)-Mo(3)-O(31)	83.3 (1)	F(2)-Sb-F(4)	178.8 (3)
O(42)-Mo(1)-OW(1)	73.2 (2)	O(21)-C(21)-O(22)	123.3 (6)	Mo(1)-Mo(3)-O(41)	81.6 (1)	F(2)-Sb-F(5)	90.8 (2)
C(1)-Mo(1)-C(2)	75.9 (2)	O(21)-C(21)-C(22)	119.5 (6)	Mo(1)-Mo(3)-O(52)	125.8 (1)	F(2)-Sb-F(6)	90.8 (2)
C(1)-Mo(1)-OW(1)	143.0 (2)	O(22)-C(21)-C(22)	117.2 (6)	Mo(1)-Mo(3)-O(61)	125.3 (1)	F(3)-Sb-F(4)	89.8 (3)
C(2)-Mo(1)-OW(1)	141.1 (2)	Mo(3)-O(31)-C(31)	125.0 (4)	Mo(1)-Mo(3)-C(1)	46.4 (1)	F(3)-Sb-F(5)	89.3 (2)
Mo(1)-Mo(2)-Mo(3)	59.76 (2)	Mo(1)-O(32)-C(31)	126.9 (4)	Mo(1)-Mo(3)-C(2)	46.5 (1)	F(3)-Sb-F(6)	179.9 (3)
Mo(1)-Mo(2)-O(12)	82.9 (1)	O(31)-C(31)-O(32)	123.6 (6)	Mo(1)-Mo(3)-OW(3)	150.7 (1)	F(4)-Sb-F(5)	88.7 (3)
Mo(1)-Mo(2)-O(22)	80.6 (1)	O(31)-C(31)-C(32)	117.7 (6)	Mo(2)-Mo(3)-O(31)	126.0 (1)	F(4)-Sb-F(6)	90.2 (3)
Mo(1)-Mo(2)-O(51)	126.0 (1)	O(32)-C(31)-C(32)	118.7 (6)	Mo(2)-Mo(3)-O(41)	126.1 (1)	F(5)-Sb-F(6)	90.6 (2)
Mo(1)-Mo(2)-O(62)	125.3 (1)	Mo(3)-O(41)-C(41)	126.1 (5)	Mo(2)-Mo(3)-O(52)	82.4 (1)		
Mo(1)-Mo(2)-C(1)	46.2 (1)	Mo(1)-O(42)-C(41)	123.6 (4)				

Table VII. Hydrogen Bond Distances (Å) in Compound 1

OW(3)-F(6)	2.707 (8)	OW(5)-OW(1)	2.658 (8)
OW(4)-F(5)	2.809 (9)	OW(6)-OW(2)	2.722 (8)
OW(4)-OW(3)	2.713 (8)		

Figure 8. The $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$ cation in compound 3. Atoms are represented by thermal vibration ellipsoids at the 40% level, and the labeling scheme is defined.

insensitive to the identity of the capping groups, but the calculated values for carbon vary markedly. The value calculated for CH_3O caps is much too low, while that for $\text{C}_2\text{H}_5\text{O}$ caps could be considered acceptable. On the other hand, the density calculated for $\text{C}_2\text{H}_5\text{O}$ caps is much too high while that calculated for CH_3O caps might be considered acceptable. Clearly, neither of these alkoxide-type capping groups is ac-

Table VIII. Bond Distances and Bond Angles for $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_2$ (2)

Bond Distances, Å			
Mo-Mo'	2.883 (1)	O(1)-C(3)	1.273 (2)
O(1)	2.089 (2)	O(2)-C(3)	1.266 (3)
O(2)	2.101 (1)	C(3)-C(4)	1.490 (3)
O(W)	2.161 (2)	C(1)-C(2)	1.491 (4)
C(1)	2.075 (2)	O(2)-H(4)	0.83 (3)
S-O(S)	1.431 (2)	C(2)-H(5)	0.81 (3)
S-C	1.811 (1)	C(4)-H(1)	0.91 (4)
C-F	1.334 (2)	H(2)	0.85 (6)
		H(3)	0.80 (5)
Bond Angles Deg			
Mo'-Mo-O(1)	125.08 (4)	Mo-O(1)-C(3)	126.9 (1)
Mo'-Mo-O(1)'	81.53 (1)	O(2)-C(3)	127.5 (1)
O(2)	124.38 (4)	O(1)-C(3)-O(2)	123.4 (2)
O(2)'	80.69 (4)	C(4)	117.6 (2)
C(1)	46.01 (4)	O(2)-C(3)-C(4)	119.0 (2)
O(1)-Mo-O(1)'	151.42 (3)	Mo-C(1)-Mo'	87.98 (8)
O(2)'	92.81 (8)	C(2)	126.68 (6)
O(2)''	80.57 (9)	C(1)-C(2)-H(5)	110 (2)
C(1)	79.15 (6)	H(5)-C(2)-H(5)	108 (2)
C(1)'	125.74 (4)	O(S)-S-O(S)'	114.46 (8)
O(W)	75.71 (2)	C	103.8 (1)
O(2)-Mo-O(2)'	153.09 (8)	S-C-F	112.3 (2)
C(1)	78.48 (6)	F-C-F'	106.5 (2)
C(1)'	124.95 (5)	H(4)-O(W)-H(4)'	102 (4)
O(W)	76.55 (4)	C(3)-C(4)-H(1)	119 (2)
C(1)-Mo-C(1)'	73.4 (1)	H(2)	108 (4)
O(W)	143.32 (6)	H(3)	111 (3)
		H(1)-C(4)-H(2)	105 (4)
		-H(3)	99 (4)
		H(2)-C(4)-H(3)	116 (5)

Table IX. Bond Distances and Bond Angles for $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot 10\text{H}_2\text{O}$ (3)

Bond Distances, Å							
Mo(1)–Mo(2)	2.891 (1)	Mo(2)–Mo(2)'	2.892 (1)	C(1)–O(1)	1.274 (7)	C(3)–O(3)	1.282 (6)
O(1)	2.110 (4)	O(2)	2.105 (4)	O(2)	1.250 (7)	C(4)	1.48 (1)
C(A)	2.074 (9)	O(3)	2.094 (4)	C(2)	1.504 (9)	C(A)–C(A1)	1.49 (1)
O(W1)	2.147 (8)	C(A)	2.088 (6)				
		O(W2)	2.144 (6)				
S(1)–O(S1)	1.55 (1)	C(10)–C(11)	1.36 (1)	S(2)–O(S3)	1.41 (2)	C(15)–C(16)	1.41 (9)
O(S2)	1.21 (2)	C(11)–C(12)	1.39 (2)	O(S4)	1.49 (2)	C(16)–C(16)'	1.33 (1)
C(10)	1.76 (1)	C(12)–C(13)	1.37 (2)	O(S5)	1.40 (2)		
		C(13)–C(14)	1.50 (3)	C(15)	1.61 (1)		
Bond Angles, Deg							
Mo(2)–Mo(1)–Mo(2)'	60.03 (3)	Mo(1)–Mo(2)–Mo(2)'	59.99 (2)				
O(1)	81.0 (1)	O(2)	80.7 (1)				
O(1)'	124.1 (1)	O(3)	124.7 (1)				
C(A)	46.2 (2)	C(A)	45.8 (2)				
O(W1)	149.99 (2)	O(W2)	150.3 (2)				
O(1)–Mo(1)–O(1)'	82.0 (2)	Mo(2)–Mo(2)–O(2)	124.2 (1)				
O(1)''	91.7 (2)	O(3)	81.1 (1)				
O(1)'''	152.9 (2)	C(A)	46.2 (2)				
C(A)	78.0 (2)	O(W2)	149.8 (2)				
O(W1)	76.5 (1)	O(2)–Mo(2)–O(2)'	81.0 (2)				
C(A)'	125.5 (2)	O(3)	92.9 (2)				
C(A)–Mo(1)–C(A)'	73.9 (5)	O(3)'	152.8 (2)				
O(W1)	143.1 (2)	C(A)	78.1 (2)				
Mo(1)–O(1)–C(1)	126.9 (4)	C(A)'	124.7 (2)				
Mo(2)–O(2)–C(1)	128.2 (4)	O(W2)	76.8 (2)				
O(1)–C(1)–O(2)	123.2 (6)	O(3)–Mo(2)–O(3)'	80.5 (2)				
C(2)	118.0 (6)	C(A)	79.0 (3)				
O(2)–C(1)–C(2)	118.8 (6)	C(A)'	125.5 (2)				
Mo(2)–O(3)–C(3)	127.9 (5)	O(W2)	75.9 (2)				
O(3)–C(3)–O(3)'	122.0 (8)	C(A)–Mo(2)–C(A)'	73.3 (4)				
C(4)	119.0 (4)	O(W2)	143.3 (2)				
Mo(1)–C(A)–C(A1)	127.8 (7)	O(S3)–S(2)–O(S4)	109 (1)				
Mo(2)–C(A)–C(A1)	126.2 (4)	O(S5)	114 (1)				
O(S1)–S(1)–O(S1)'	101.1 (7)	C(15)	109 (1)				
O(S2)	116.6 (6)	O(S4)–S(2)–O(S5)	111 (1)				
C(10)	102.6 (4)	C(15)	105.2 (8)				
S(1)–C(10)–C(11)	120.7 (7)	O(S5)–S(2)–C(15)	108.2 (9)				
C(11)–C(10)–C(11)'	119 (1)	S(2)–C(15)–C(16)	120.4 (5)				
C(10)–C(11)–C(12)	120 (1)	C(16)–C(15)–C(16)'	119 (1)				
C(11)–C(12)–C(13)	123 (1)	C(15)–C(16)–C(16)'	120.4 (5)				
C(12)–C(13)–C(12)'	116 (2)						
C(14)	122.1 (9)						

Table X. Analytical and Density Figures for Possible Formulations of Compound 2, $[\text{Mo}_3\text{X}_2(\text{OAc})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_2$

X	% C	density
	20.62 ± 0.06 (found)	2.16 ± 0.01 (found)
C ₇ H ₅ O	19.94	2.234
CH ₃ O	18.19	2.179
CH ₃ C	20.62	2.158

ceptable on both counts. The combined effect of the analytical and density data is to demand that the capping groups simultaneously satisfy two requirements: They must contain two carbon atoms, and they must contain a *total* of two atoms. Ergo, they must be C₂H_n. From the fact that the C–C bonds are perpendicular to the Mo₃ plane we must identify them as C–CH₃ groups. For compound 1 the density supports the CCH₃ assignment, and for compound 3 the carbon analysis does so. In view of the preparative chemistry it is also reasonable to believe that whatever is the case for one of these compounds must be so for the others as well.

One other structural point to be mentioned is that in these three structures the C–CH₃ distances, average values of which are listed in Table XI, are comparable to that in the previously discussed O₂CCH₃ compound. All of them are acceptable as C–C distances, but they would be anomalously long as O–C distances.

Comparison and Correlation of Structures. We now have a total of four accurately measured structures, one for the

Table XI. Bond Distances in CCH₃-Capped Trimolybdenum Cluster Cations, $[\text{Mo}_3(\mu_3\text{-X})(\mu_3\text{-Y})(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{n+}$

X	Y	n	no. Mo–Mo electrons	Mo–Mo, Å	Mo–(μ ₃ -C), Å	C–CH ₃ , Å
O	CCH ₃	1	6	2.753 (1)	2.054 (16)	1.514 (12)
CCH ₃	CCH ₃	1	5	2.815 (7)	2.052 (10)	1.535 (10)
CCH ₃	CCH ₃	2	4	2.883 (1)	2.075 (2)	1.491 (4)
CCH ₃	CCH ₃	2	4	2.892 (1)	2.083 (6)	1.49 (1)

$[\text{Mo}_3(\text{O})(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ ion, one for the $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ ion and two for the $[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$ ion. Table XI lists the four compounds and several of the important bond lengths therein. We have already commented on the C–C distances in the CCH₃ capping groups. The Mo–(μ₃-C) distances are also constant within the uncertainties. However, there are large and highly significant differences among the Mo–Mo bond lengths from one type of cation to another.

The variation in Mo–Mo distances fits very well the pattern expected from the changes in bond orders. As noted in Table XI, the number of electrons present in molecular orbitals that provide the Mo–Mo bonding changes from six to four. When there are six such electrons we have a mean Mo–Mo bond order of 1.0, which is equivalent to a set of three Mo–Mo electron-pair bonds. When the total number of electrons in these orbitals drops first to 5 and then to 4, the bond orders drop to ⁵/₆ and ²/₃, respectively. The Mo–Mo distances,

accordingly, increase from 2.753 (1) to 2.815 (7) Å in the first step and then to 2.883 (1)–2.892 (1) Å in the second. The magnitude of the increase per $1/6$ unit of bond order, ca. 0.065 Å, is consistent with the general pattern presented by other tri- and hexanuclear cluster structures.

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Supplementary Material Available: Tables of calculated and observed structure factors (39 pages). Ordering information is given on any current masthead page.

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Molecular and Electronic Structures of Three Pyridine- and Piperidine-Substituted Chromium Carbonyl Compounds: $\text{Cr}(\text{CO})_5(\text{C}_5\text{H}_5\text{N})$, $\text{Cr}(\text{CO})_5(\text{C}_5\text{H}_{10}\text{NH})$, and $\text{cis-Cr}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})[\text{P}(\text{OMe})_3]$

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The problem of metal-ligand bonding in $\text{Cr}(\text{CO})_5\text{L}$ compounds, and related ones, where L is an aliphatic amine or an aromatic amine, has been addressed by X-ray work on a novel crystalline solid containing equimolar amounts of $\text{Cr}(\text{CO})_5\text{NHC}_5\text{H}_{10}$ and $\text{Cr}(\text{CO})_5\text{NC}_5\text{H}_5$ and on $\text{cis-Cr}(\text{CO})_4(\text{HNC}_5\text{H}_{10})[\text{P}(\text{OMe})_3]$ as well as by Fenske-Hall calculations on $\text{Cr}(\text{CO})_5\text{NH}_3$ and other data collected from the literature. The theoretical results show that in the $\text{Cr}(\text{CO})_5\text{L}$ compounds the $b_1(d_{z^2})$ orbital lies above the $a_1(d_{z^2})$ orbital in agreement with some but contrary to other previous proposals. The structures show that the replacement of an aliphatic by an aromatic amine has no significant effect on the structure of the $\text{Cr}(\text{CO})_5$ group and that the two substituents $\text{C}_5\text{H}_{10}\text{NH}$ and $\text{P}(\text{OMe})_3$ exert their structural effects on the $\text{Cr}(\text{CO})_4$ residue essentially independently. The crystals containing the $\text{Cr}(\text{CO})_5(\text{C}_5\text{H}_{10}\text{NH})$ and $\text{Cr}(\text{CO})_5(\text{C}_5\text{H}_5\text{N})$ molecules belong to space group $P2_1/n$ and have the following unit cell parameters: $a = 13.851$ (2) Å, $b = 11.026$ (1) Å, $c = 17.693$ (2) Å, $\beta = 109.93$ (2)°, $V = 2540$ (1) Å³, and $Z = 4$. The structure was refined with use of 2209 data to $R_1 = 0.041$ and $R_2 = 0.049$. The compound $\text{cis-Cr}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})[\text{P}(\text{OMe})_3]$ crystallized in space group $P2_12_12_1$ with $a = 8.088$ (1) Å, $b = 11.587$ (2) Å, $c = 18.431$ (2) Å, $V = 1727.4$ (5) Å³, and $Z = 4$. Refinement using 1326 data converged with $R_1 = 0.043$ and $R_2 = 0.054$ for the preferred enantiomorph.

Introduction

There is a mountainous volume of literature on the subject of metal-ligand π bonding in metal carbonyls and substituted metal carbonyls. After so many attempts by so many authors, employing such a variety of physical, chemical, and theoretical methods, it may seem presumptuous to suppose that one more contribution can significantly affect our general understanding of the problem. In some respects, the situation is already well understood while in others the attainment of an unambiguous consensus seems as elusive a goal as ever. Nevertheless, we have the temerity to offer a few additional experimental results (which mostly have the virtue of being unambiguous facts) and observations (which are heuristic rather than dogmatic) to this important but tortuous problem.

With respect to molecules of the type $\text{Cr}(\text{CO})_5\text{L}$, there are two questions we shall deal with: (1) How does the replacement of one CO ligand in $\text{Cr}(\text{CO})_6$ affect the bonding and the pattern of molecular orbitals when the ligand L is one with little or no π -acceptor capacity? (2) Does the ligand pyridine show any significant ability to act as a π acceptor, especially when compared as directly as possible with an aliphatic amine, which is assumed to have none, or with a phosphite, which is assumed to be a fairly effective π acceptor?

To deal with the first question, we have employed both Fenske-Hall nonempirical molecular orbital calculations and the results of infrared and X-ray crystallographic studies of $\text{Cr}(\text{CO})_5(\text{HNC}_5\text{H}_{10})$, where $\text{C}_5\text{H}_{10}\text{NH}$ is piperidine. To deal with the second question, we have made accurate structure

Table I. Infrared Spectral Data for the Amine Derivatives^a

compd	ν_{CO} , cm ⁻¹
$\text{Cr}(\text{CO})_5(\text{NHC}_5\text{H}_{10})$	2069 (A_1 '), 1933 (E), 1917 (A_1 ')
$\text{Cr}(\text{CO})_5(\text{NC}_5\text{H}_5)$	2071 (A_1 '), 1939 (E), 1920 (A_1 ')
$\text{cis-Cr}(\text{CO})_4(\text{NHC}_5\text{H}_{10})[\text{P}(\text{OCH}_3)_3]$	2020 (A'), 1921 (A'), 1897 (A''), 1870 (A')

^a Spectra were recorded in hexane solution and are accurate to ± 1 cm⁻¹.

determinations of three molecules, $\text{Cr}(\text{CO})_5(\text{HNC}_5\text{H}_{10})$ (1), $\text{Cr}(\text{CO})_5\text{NC}_5\text{H}_5$ (2), and $\text{Cr}(\text{CO})_4(\text{HNC}_5\text{H}_{10})[\text{P}(\text{OMe})_3]$ (3). As a matter of pure, and entirely unanticipated, good luck we obtained a crystalline substance containing 1 and 2 in a 1:1 ratio and thus obtained the structures of both molecules in one neat package. The structure of 3 gives us the desired structural comparison of the effects of a non- π -accepting ligand, $\text{C}_5\text{H}_{10}\text{NH}$, and a fairly good π -accepting ligand in the same molecule where each has its own trans-CO group along with two CO groups that are simultaneously cis to both substituents.

Experimental Section

Preparation of Metal Carbonyl Amine Compounds. $\text{Cr}(\text{CO})_5\text{NH-C}_5\text{H}_{10}$ was prepared from $\text{Cr}(\text{CO})_6$ (Strem Chemical Co.) and piperidine (Aldrich Chemical Co., 98%) by the previously published photochemical technique in the THF solvent.² Both reagents were used as received. Yellow crystals suitable for X-ray analysis were obtained from hexane solution at 0 °C. The IR spectrum in the $\nu(\text{CO})$ region displayed the expected three bands (Table I).

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