M–M σ bonds, and the bridging atoms are first-row atoms. However, the W–W and Mo–Mo bond lengths are in the range 2.69–2.73 Å, which are much longer than that found here. We believe that this difference can be attributed to one or, most likely, two factors, both of which have been discussed in connection with other M–M-bonded systems. One of these factors is the presence of two three-atom bridging groups.

Second, in the present ruthenium compound the formal oxidation number of the metal atoms is only +3 as compared to +5 in the tungsten and molybdenum compounds. As noted, and documented several times previously, in a variety of structural contexts,[18,19] an increase in the extent of ionization of the metal atoms causes a contraction of their d orbitals and this in turn causes poorer d–d overlap. Thus, we would argue that the d–d σ bond-forming potential of the Ru^{III}-Ru^{III} pair of atoms is appreciably greater than that of the W^V–W^V and Mo^V–Mo^V pairs and that this will also favor a shortening from ca. 2.70 to 2.57 Å on going from the M^V–M^V to the M^{III}–M^{III} case.

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Registry No. 1, 92669-47-1; $Ru_2(O_2CCH_3)_4Cl$, 38833-34-0; Ru, 7440-18-8.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters, complete lists of bond distances and bond angles, and details of the crystal structure determination (16 pages). Ordering information is given on any current masthead page.

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New Preparative Methods, Structure, and Nitration of Bi-oxo-capped Trimolybdenum(IV) and Tritungsten(IV) Cluster Cations

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The reaction of $Mo_2(O_2CC_6H_5)_4$ with dibenzoyl peroxide (1:2 mole ratio) in methylene chloride, followed by ethanolic workup, leads to the $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ cation. The product has been isolated as the ClO_4^- salt, which has been characterized crystallographically. The compound forms triclinic crystals in the space group $P\bar{1}$ with a = 13.837 (3) Å, b = 22.189 (5) Å, c = 11.394 (3) Å, α = 92.39 (1)°, β = 114.35 (1)°, γ = 89.02 (1)°, V = 3185 (3) Å^3, and Z = 2. Important dimensions are $Mo\text{–}Mo_{av}$ = 2.761 [1] Å, $Mo\text{–}(\mu_3\text{-}O)_{av}$ = 1.983 [6] Å, Mo–O(benzoate)$_{av}$ = 2.081 [6] Å, and $Mo\text{–}O(H_2O)_{av}$ = 2.123 [6] Å. Cross experiments utilizing $Mo_2(OAc)_4$ and dibenzoyl peroxide suggest that the reaction mechanism may involve an initial oxidative addition to the metal–metal bond. The reaction between $W(CO)_6$ and benzoic acid at 160 °C followed by ethanolic workup yields the homologous $[W_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ cation. This product has been spectroscopically characterized. The remarkable chemical stability of each trinuclear unit is demonstrated by the nitration of each of the six benzoate rings in the meta position to give a virtually quantitative yield of the analogous hexanitro compounds, which have been characterized by NMR spectroscopy.

Introduction

A variety of synthetic routes for trinuclear bicapped clusters of the general formula $[M_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{n+}$ (M = Mo, W),[2-10] has been developed over recent years. However, R has been restricted to a rather limited number of aliphatic hydrocarbons. The only bridging carboxylates recorded in the literature are the acetato,[2-8] propionato,[9,10] and pivalato[9] ligands. We have now found that the bi-oxo-capped trinuclear clusters with bridging benzoates can be prepared in excellent yields. For molybdenum this complex can be formed by the reaction of dimolybdenum tetrabenzoate ($M\overset{4}{-}M$) with 2 equiv of dibenzoyl peroxide. For the tungsten analogue a more conventional approach has been used. When a large excess of benzoic acid is reacted with $W(CO)_6$ in a melt reaction, the tungsten benzoate trimer is obtained. New evidence for the great stability of these $[M_3O_2(O_2CR)_6L_3]^{2+}$ units is afforded by the observation that under the strongly acidic conditions required for nitration of the aromatic rings, the trinuclear units remain intact and are converted to the hexa-*m*-nitro derivatives in greater than 90% isolated yield.

Experimental Section

Preparation of $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$. A weighed amount of dibenzoyl peroxide (533 mg, 2.2 mmol) was added to a suspension of $Mo_2(O_2CC_6H_5)_4$ (676 mg, 1 mmol) in 30 mL of CH_2Cl_2. This mixture was then refluxed for 10 h under argon, during which time the color of the solution changed from yellow to green, temporarily to black, and finally to a deep burgundy. At this point several workup procedures were followed.

(A) The red material **1** can be precipitated by adding hexane to a filtered solution, followed by cooling it overnight. The compound thus obtained is soluble in most nonprotic organic solvents. All attempts to grow crystals led only to microcrystalline or amorphous material.

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(B) Alternatively, **1** dissolved readily in ethanol or methanol, after the addition of a trace amount of an acid such as CF_3SO_3H, to produce a burgundy-colored solution. This solution was then diluted with 95% ethanol and chromatographed on a Dowex 50W-X2 cation-exchange column. The adsorbed burgundy material was then eluted with a 3 M ethanolic solution of perchloric acid. Crystalline material was obtained in yields >80% (based on $Mo_2(O_2CC_6H_5)_4$) by cooling the ethanolic eluate overnight. Numerous attempts to grow single crystals were made, utilizing the usual techniques such as slow diffusion, cooling, and evaporation. Typically we obtained crystals of reasonable size and shape which turned out to be extremely poor scatterers of X-rays. Finally, crystals suitable for X-ray diffraction studies were formed by very slow evaporation of the eluate.

Mixed-Ligand Reactions. Several other reactions were carried out in an effort to establish the reaction pathway. No efforts were made to crystallize any of the final products. All reaction conditions were essentially the same as previously described unless stated otherwise.

Case 1. To a suspension of $Mo_2(O_2CC_6H_5)_4$ in CH_2Cl_2 was added 1 equiv of dibenzoyl peroxide. The final trinuclear product was obtained along with a quantity of $Mo_2(O_2CC_6H_5)_4$, which was found to be approximately half of the starting amount.

Case 2. To a suspension of $Mo_2(O_2CC_6H_5)_4$ in CH_2Cl_2 was added 2 mmol of H_2O_2 (30% aqueous solution). No spectral features of a bi-oxo-capped trinuclear carboxylate were detected in the visible spectrum.

Case 3. To a suspension of $Mo_2(OAc)_4$ in CH_2Cl_2 was added 2 equiv of dibenzoyl peroxide. A deep red compound, **2**, was formed (vide infra).

Preparation of the $[W_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ Ion. A large excess of benzoic acid (20 g) was placed in a Parr Model 4751 general-purpose bomb along with 1 g of $W(CO)_6$. The mixture was then heated at 160 °C for 36 h. The brown product was purified by extracting the excess benzoic acid with hexane, leaving a dark brown compound, **3**. As with the molybdenum trimer, **3** can be dissolved in alcohols after the addition of small amounts of acid. The resulting ethanol solution was absorbed on a Dowex 50W-X2 cation-exchange column and eluted with ethanolic solutions of CF_3SO_3H, $HClO_4$, HBF_4, or HBr.

Nitration of Benzoate Rings. To 4 mL of concentrated sulfuric acid was added 1 g of either **1** or **3**. The mixture was shaken, and 4 mL of concentrated nitric acid was added dropwise. The resulting solution was then heated in a water bath at 45 °C for 10 min. Afterwards the mixture was poured on 15 g of ice and the solid products were collected on a glass frit; yields ≥90% (based on **1** or **3**).

Structural Characterization. A burgundy crystal of the molybdenum compound crystallized from an $EtOH/HClO_4$ elution was placed into a thin-walled glass capillary. The structure determination later showed this crystal to have the composition $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3C_2H_5OH$. Determination of the unit cell dimensions, recording of rotation and axial photographs, and data collection were all performed on a Syntex $P\bar{1}$ diffractometer located in a cold room at 5 °C using graphite-monochromatized Cu Kα radiation. The unit cell dimensions were determined by a least-squares fit of 15 reflections in the range of $25° \le 2\theta \le 60°$. Lorentz and polarization corrections in addition to absorption corrections were applied. Numerical parameters pertinent to data collection and refinement are listed in Table I.

The positions of the molybdenum atoms were derived from the three-dimensional Patterson function. The other non-hydrogen atoms were found in a series of alternating refinements and difference Fourier maps.[11] In these difference maps there were three locations with peak distributions suggestive for perchlorate groups. One of them refined smoothly in full occupancy while disorder became apparent at each of the remaining locations. Their multiplicities were therefore deliberately lowered to $^1/_2$. There remained several difference peaks close to the main positions which were left unaccounted for by lack of a structurally feasible model. Ethanol molecules, hydrogen bonded to the terminal water molecules, appeared likewise disordered, but here two reasonable orientations could be refined with half occupancy each. The last cycle of refinement gave residuals of $R = 0.0659$ and $R_w = 0.0879$ for the fit of 675 parameters to 5416 data. All the shift/esd parameters in the last cycle were smaller than unity, except for C(81A), where a value of 1.7 was encountered. In view of the large amount of computer time involved in the refinement and of the fact that C(81A) belongs to a disordered solvent molecule, the refinement was terminated at this point. An attempt to determine the true stoichiometry by chemical analysis was performed on two crystalline samples. Unfortunately the values were erratic. We therefore carefully determined the density by the flotation method. The calculated density fits the experimental value best if the three perchlorates are included at full multiplicity (1.60 and 1.63 [1]). Since the final difference Fourier map was featureless except around the disordered perchlorates, we conclude that the correct chemical formula is $[Mo_3O_2(O_2CPh)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$. Structure factors and thermal parameters are available as supplementary material. The atomic positional parameters are listed in Table II. The structure is illustrated in Figure 1. Principal bond lengths and angles are given in Table III.

Table I. Crystallographic Parameters

formula	$[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$
fw	1535.11 g/mol
space group	$P\bar{1}$
a, Å	13.837 (3)
b, Å	22.189 (5)
c, Å	11.394 (3)
α, deg	92.39 (1)
β, deg	114.35 (1)
γ, deg	89.02 (1)
V, Å^3	3185 (3)
Z	2
d_{exptl}, g/cm^3	1.63 [1]
d_{calcd}, g/cm^3	1.601
cryst size, mm	0.5 × 0.5 × 0.4
μ(Cu Kα), cm^{-1}	68.06
data collection instrument	Syntex $P\bar{1}$
radiation	Cu Kα
scan method	$2\theta/\theta$
data collection range, deg	$4 < 2\theta < 115$
no. of unique data	6957
no. of reflcns for which $F_o^2 \geq 3\sigma(F_o^2)$	5416
no. of parameters refined	675
R^a	0.0659
$R_w{}^b$	0.0879
quality-of-fit indicator^c	1.75
largest shift/esd, final cycle	1.77

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

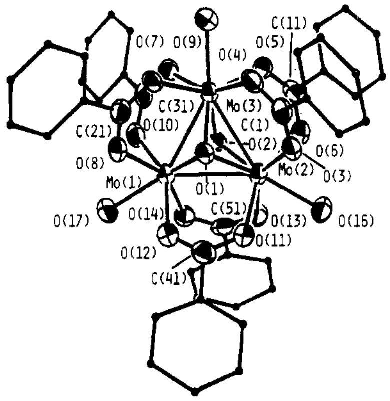

Figure 1. ORTEP drawing of the $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ion. The carbon atoms of the phenyl rings are represented as arbitrarily small circles to avoid obscuring other features. The other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

NMR Spectroscopy. ^1H NMR spectra were measured on a Varian XL-200 PFT spectrometer at 200 MHz. The results are summarized in Table IV and shown in Figure 2.

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[11] The crystallographic programs for the structural solution and refinement from the VAX-SDP software package were used on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University.

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.66076 (7)	0.27589 (4)	0.47220 (8)	3.74 (2)	C(6)	0.486 (1)	0.3533 (7)	0.058 (1)	6.5 (4)
Mo(2)	0.66076 (7)	0.22406 (4)	0.68853 (8)	3.72 (2)	C(7)	0.477 (1)	0.6771 (6)	0.028 (1)	5.7 (4)
Mo(3)	0.47116 (7)	0.25000 (5)	0.48560 (8)	3.74 (2)	C(11)	0.5054 (9)	0.8718 (6)	0.3944 (9)	4.4 (3)
Cl(1)	0.9067 (4)	0.2500 (2)	0.2032 (5)	10.0 (1)*	C(12)	0.5447 (9)	0.9333 (6)	0.396 (1)	4.7 (3)
Cl(2)	0.8741 (7)	0.5544 (4)	0.5090 (9)	8.9 (2)*	C(13)	0.475 (1)	0.9747 (7)	0.311 (1)	6.9 (4)
Cl(3)	0.1234 (8)	0.0543 (5)	0.1338 (9)	9.5 (2)*	C(14)	0.514 (1)	−0.9662 (7)	0.311 (2)	8.3 (5)
O(1)	0.4039 (5)	0.7982 (3)	0.4989 (6)	3.8 (2)	C(15)	0.617 (1)	0.0477 (7)	0.398 (1)	8.5 (4)
O(2)	0.4023 (5)	0.7016 (3)	0.4037 (6)	3.8 (2)	C(16)	0.313 (1)	−0.0072 (7)	0.516 (2)	8.2 (5)
O(3)	0.4169 (6)	0.7385 (4)	0.2037 (6)	4.6 (2)	C(17)	0.351 (1)	0.0501 (7)	0.521 (1)	6.5 (4)
O(4)	0.5696 (6)	0.7176 (4)	0.3663 (6)	4.4 (2)	C(21)	0.4902 (9)	0.2150 (5)	0.239 (1)	4.2 (3)
O(5)	0.4320 (5)	0.1646 (4)	0.5245 (6)	4.5 (2)	C(22)	0.4532 (9)	0.1839 (6)	0.112 (1)	4.5 (3)
O(6)	0.4158 (5)	0.8562 (4)	0.3152 (6)	4.3 (2)	C(23)	0.523 (1)	0.1765 (6)	0.048 (1)	5.4 (3)
O(7)	0.4294 (5)	0.2186 (4)	0.2965 (6)	4.2 (2)	C(24)	0.515 (1)	0.8521 (7)	0.072 (1)	6.0 (4)
O(8)	0.5821 (6)	0.2388 (4)	0.2855 (6)	4.4 (2)	C(25)	0.615 (1)	0.8764 (9)	0.127 (1)	8.6 (5)
O(9)	0.4331 (6)	0.3350 (3)	0.4092 (6)	4.5 (2)	C(26)	0.684 (1)	0.8690 (8)	0.064 (1)	8.0 (4)
O(10)	0.5850 (6)	0.3560 (4)	0.4009 (6)	4.4 (2)	C(27)	0.352 (1)	0.1609 (7)	0.057 (1)	6.3 (4)
O(11)	0.2192 (6)	0.8283 (4)	0.3297 (6)	4.5 (2)	C(31)	0.4945 (9)	0.3704 (6)	0.3897 (9)	4.4 (3)
O(12)	0.7794 (6)	0.2130 (3)	0.4948 (6)	4.4 (2)	C(32)	0.455 (1)	0.4335 (5)	0.351 (1)	4.8 (3)
O(13)	0.2207 (6)	0.7130 (3)	0.2146 (7)	4.4 (2)	C(33)	0.352 (1)	0.4497 (6)	0.331 (1)	6.5 (4)
O(14)	0.2189 (5)	0.6719 (4)	0.3895 (7)	4.4 (2)	C(34)	0.318 (1)	0.5070 (8)	0.292 (1)	8.0 (5)
O(15)	0.3029 (6)	0.2494 (4)	0.4008 (7)	5.3 (2)	C(35)	0.386 (1)	0.5513 (7)	0.279 (2)	8.3 (5)
O(16)	0.2554 (6)	0.8104 (4)	0.1242 (7)	4.8 (2)	C(36)	0.487 (1)	0.5353 (7)	0.297 (1)	7.8 (5)
O(17)	0.7447 (6)	0.3103 (4)	0.3700 (7)	4.8 (2)	C(37)	0.524 (1)	0.4740 (6)	0.334 (1)	6.5 (4)
O(20)	0.808 (2)	0.230 (1)	0.218 (2)	10.6 (7)*	C(41)	0.1867 (9)	0.8245 (6)	0.418 (1)	4.8 (3)
O(20A)	0.918 (3)	0.272 (2)	0.338 (3)	15 (1)*	C(42)	0.0988 (9)	0.8681 (5)	0.413 (1)	4.9 (3)
O(21)	0.809 (2)	0.266 (1)	0.087 (2)	10.5 (7)*	C(43)	0.929 (1)	0.1308 (7)	0.482 (1)	6.7 (4)
O(21A)	0.918 (3)	0.229 (2)	0.083 (3)	14 (1)*	C(44)	0.015 (1)	0.0941 (7)	0.487 (1)	7.8 (4)
O(22)	0.966 (2)	0.303 (1)	0.236 (2)	8.5 (6)*	C(45)	1.069 (1)	0.0574 (7)	0.601 (2)	7.9 (5)
O(23)	0.968 (2)	0.196 (1)	0.229 (2)	8.9 (6)*	C(46)	1.035 (1)	0.0606 (7)	0.700 (1)	6.7 (4)
O(24)	0.106 (3)	0.423 (2)	0.391 (3)	15 (1)*	C(47)	0.050 (1)	0.9029 (6)	0.305 (1)	5.9 (4)
O(25)	0.117 (2)	0.502 (1)	0.516 (3)	12.9 (9)*	C(51)	0.1851 (8)	0.6751 (5)	0.267 (1)	4.4 (3)
O(26)	0.776 (3)	0.550 (2)	0.445 (4)	18 (1)*	C(52)	0.098 (1)	0.6320 (5)	0.185 (1)	5.0 (3)
O(27)	0.895 (4)	0.577 (2)	0.435 (4)	20 (2)*	C(53)	0.072 (1)	0.6301 (6)	0.055 (1)	6.4 (4)
O(28)	0.110 (3)	0.079 (2)	0.216 (3)	14 (1)*	C(54)	0.015 (1)	0.4064 (7)	0.025 (2)	8.1 (5)
O(29)	0.113 (2)	−0.004 (1)	0.095 (3)	12.9 (9)*	C(55)	0.931 (1)	0.5573 (8)	0.033 (2)	8.1 (5)
O(30)	0.216 (3)	0.042 (2)	0.167 (4)	19 (1)*	C(56)	−1.034 (1)	0.5596 (7)	0.167 (1)	6.8 (4)
O(31)	0.100 (4)	0.078 (2)	0.037 (5)	23 (2)*	C(57)	0.050 (1)	0.5966 (6)	0.247 (1)	5.4 (3)
O(60)	0.245 (1)	0.9170 (6)	0.046 (1)	10.7 (4)*	C(60)	0.773 (2)	0.082 (1)	0.102 (2)	13.4 (8)*
O(70)	0.755 (1)	0.4165 (6)	0.302 (1)	11.1 (4)*	C(61)	0.708 (2)	0.034 (1)	0.108 (3)	16 (1)*
O(80)	0.174 (2)	0.276 (1)	0.506 (2)	8.3 (6)*	C(70)	0.773 (2)	0.418 (1)	0.169 (2)	12.9 (7)*
O(80A)	0.175 (2)	0.228 (1)	0.168 (2)	8.0 (5)*	C(71)	0.707 (2)	0.470 (1)	0.105 (3)	17 (1)*
C(1)	0.5089 (8)	0.7146 (5)	0.250 (1)	4.1 (3)	C(80A)	0.174 (3)	0.280 (2)	0.114 (4)	12 (1)*
C(2)	0.5461 (9)	0.6835 (5)	0.157 (1)	4.6 (3)	C(80)	0.823 (3)	0.781 (2)	0.477 (4)	11 (1)*
C(3)	0.650 (1)	0.6616 (8)	0.209 (1)	7.0 (4)	C(81A)	0.903 (4)	0.754 (2)	0.039 (5)	14 (2)*
C(4)	0.683 (1)	0.6287 (8)	0.117 (1)	8.0 (5)	C(81)	0.859 (4)	0.769 (2)	0.383 (4)	13 (1)*
C(5)	0.385 (1)	0.3771 (8)	0.012 (1)	8.1 (5)					

[a] Atoms marked with asterisks were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Distances and Angles[a] for $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$

	A. Bond Distances (Å)		
Mo(1)–Mo(2)	2.763 (1)	Mo(2)–O(3)	2.080 (6)
–Mo(3)	2.761 (1)	–O(6)	2.077 (6)
–O(1)	1.988 (6)	–O(11)	2.086 (6)
–O(2)	1.989 (5)	–O(13)	2.078 (6)
–O(8)	2.089 (6)	–O(16)	2.132 (6)
–O(10)	2.067 (6)	Mo(3)–O(1)	1.967 (6)
–O(12)	2.077 (6)	–O(2)	1.985 (6)
–O(14)	2.086 (6)	–O(4)	2.086 (6)
–O(17)	2.123 (6)	–O(5)	2.093 (6)
Mo(2)–Mo(3)	2.760 (1)	–O(7)	2.080 (5)
–O(1)	1.989 (5)	–O(9)	2.077 (6)
–O(2)	1.982 (6)	–O(15)	2.121 (6)
	B. Bond Angles (deg)		
Mo(2)–Mo(1)–Mo(3)	59.95 (3)	Mo(2)–O(1)–Mo(3)	88.5 (2)
Mo(1)–Mo(2)–Mo(3)	59.99 (3)	Mo(1)–O(2)–Mo(2)	88.2 (2)
Mo(1)–Mo(3)–Mo(2)	60.05 (3)	–Mo(3)	88.0 (2)
Mo(1)–O(1)–Mo(2)	88.0 (2)	Mo(2)–O(2)–Mo(3)	88.2 (2)
–Mo(3)	88.6 (2)		

[a] A complete list of bond distances and angles is available as supplementary material.

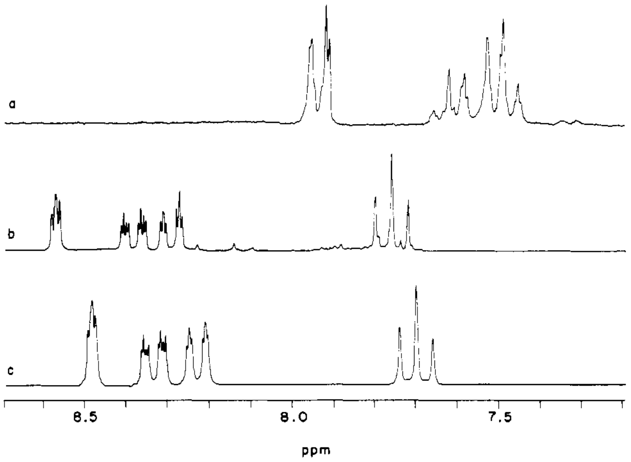


Figure 2. ^1H NMR spectra in dimethyl-d_6 sulfoxide solvent at 25 °C: (a) the $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ion; (b) the $[Mo_3O_2(O_2CC_6H_4NO_2)_6(H_2O)_3]^{2+}$ ion; (c) *m*-nitrobenzoic acid (for comparison).

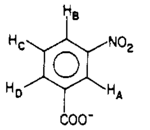
Electronic Absorption Spectra. The UV–visible spectra were measured on a Cary 17D spectrometer at 23 °C in ethanolic solution. The spectra of four trimolybdenum species are shown in Figure 3, and the spectrum of the $[W_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ion is shown

Table IV. ^{1}H NMR Spectra

A. Chemical Shifts and Coupling Constants for $[M_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$

metal	nucleus	δ	splitting, Hz
Mo	H ortho	7.940	doublet ($J_o \approx 6.9$) × quartet ($J_m, J_p \approx 1.4$)
	H meta	7.624	triplet ($J_o \approx 6.1$) × triplet ($J_m \approx 1.1$)
	H para	7.531	triplet ($J_o \approx 6.0$) × triplet ($J_m \approx 1.3$)
W	H ortho	7.934	doublet ($J_o \approx 7.2$) × quartet ($J_m, J_p \approx 1.2$)
	H meta	7.635	triplet ($J_o \approx 7.2$) × triplet ($J_m \approx 1.5$)
	H para	7.522	triplet ($J_o \approx 6.8$) × triplet ($J_m \approx 1.3$)

B. ^{1}H Chemical Shifts and Coupling Constants for $[M_3(\mu_3\text{-}O)_2(m\text{-}NO_2C_6H_4CO_2)_6(H_2O)_3]^{2+}$



metal	nucleus	δ	splitting, Hz
Mo	H_A	8.573	quartet ($J_o, J_p > 2$)
	H_B	8.296	doublet ($J_o \approx 8.3$) × triplet ($J_m, J_p \approx 1.4$)
	H_C	7.764	triplet ($J_o \approx 7.9$) × doublet ($J_p \approx 1.2$)
	H_D	8.339	doublet ($J_o \approx 6.3$) × quartet ($J_m, J_p \approx 1.3$)
W	H_A	8.607	quartet ($J_m, J_p > 2$)
	H_B	8.343	doublet ($J_o \approx 7.9$) × triplet ($J_m, J_p \approx 1.3$)
	H_C	7.817	triplet ($J_o \approx 8.0$) × doublet ($J_p \approx 1.3$)
	H_D	8.464	doublet ($J_o \approx 8.4$) × quartet ($J_m, J_p \approx 1.6$)

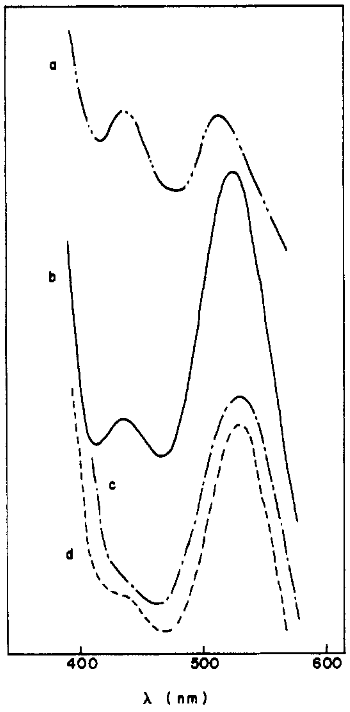


Figure 3. Visible absorption spectra of several trinuclear cations, with λ (ε) values, in nm and M^{-1} cm^{-1}, respectively, except for (b): (a) $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ 428 (460), 509 (450); (b) product obtained from the reaction of $Mo_2(O_2CCH_3)_4$ with dibenzoyl peroxide; (c) $[Mo_3O_2(O_2C\text{-}m\text{-}NO_2C_6H_4)_6(H_2O)_3]^{2+}$ 430 (517), 528 (792); (d) $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ 430 (308), 528 (666).

in Figure 4. The figure captions give wavelengths and molar extinction coefficients.

Infrared Spectroscopy. The infrared spectra of the nitrated species were measured on a Perkin-Elmer 783 spectrometer as Nujol mulls.

Results and Discussion

Synthesis. The discovery that $Mo_2(O_2CR)_4$ compounds can be obtained by reactions of $Mo(CO)_6$ with carboxylic acids led to many attempts to carry out an analogous reaction using $W(CO)_6$, but for reasons that are now well understood these were all unsuccessful,[12] and nonacidic routes to $W_2(O_2CR)_4$ compounds have now been devised.[13,14] There were early suggestions that the reactions of $W(CO)_6$ with carboxylic acids afforded trinuclear products with tungsten in an oxidation state greater than II,[15,16] but it was only in 1978 that some of these products were unequivocally characterized and shown to contain the $[W_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{n\pm}$ type clusters. All previous investigations in which the trinuclear cluster ions were properly identified have employed aliphatic carboxylic acids, although reactions leading to incompletely (and incorrectly) characterized products have been reported for benzoic, *p*-toluic, and perfluorobenzoic acids.[15] The successful preparations of compounds containing aliphatic carboxylic acids generally employed those with boiling points in the range of 100–150 °C, which allows experimentally convenient reactions that give reasonable conversions within acceptable reaction times.

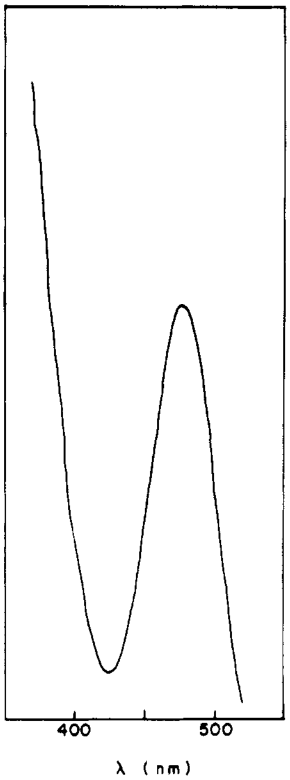


Figure 4. Visible spectrum of the $[W_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ion. The band maximum is at 475 nm with ϵ = 1080 M^{-1} cm^{-1}.

The work reported here was undertaken to find ways to obtain the crystalline tungsten and molybdenum benzoato compounds, to characterize them unambiguously, and to study their reactivities. For the tungsten compound all attempts to run the reaction in aqueous or alcoholic solution were unsuccessful. Therefore we again used the molten benzoic acid reaction. By using a cation-exchange technique, we were now able to obtain a purified compound, in contrast to the uncertain nature of the product previously obtained.[15] We also found it safer and more convenient to use a pressure bomb rather than a sealed heavy-walled glass tube, although this is not strictly necessary.

For the molybdenum compound we were unable to obtain any of the trinuclear product by reactions of $Mo(CO)_6$ with

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Table V. Comparison of Distances (Å) in Four $[Mo_3(\mu_3\text{-}O)(O_2CR)_6(H_2O)_3]Z$ Compounds[a,b]

R	Z	M-M	M-(μ_3-O)	M-O_2CR	M-OH_2	ref
C_2H_5	$(CF_3SO_3)_2\cdot CF_3SO_3H_3\cdot 4H_2O$	2.752 [2]	1.984 [4]	2.090 [4]	2.144 [4]	10
CH_3	$Br_2\cdot H_2O$	2.766 (2)	2.004 [6]	2.093 [3]	2.083 [10]	10
CH_3	$(CF_3SO_3)_2$	2.759 (1)	1.994 (5)	2.082 [7]	2.129 (6)	7
C_6H_5	$(ClO_4)_2\cdot HClO_4\cdot 3CH_3CH_2OH$	2.761 [1]	1.983 [6]	2.081 [6]	2.123 [6]	*c*

[a] Parentheses indicate esd of one value. [b] The estimated deviation in brackets is calculated as being equal to $[\Sigma_n \Delta_i / n(n-1)]^{1/2}$, in which Δ_i is the deviation of the *i*th (of *n*) value from the arithmetic mean of the *n* values. [c] This work.

benzoic acid, either in the molten state or in solvents, or from reaction of $Mo_2(O_2CCH_3)_4$ with benzoic acid. Therefore we were forced to seek some other, less obvious, route. Previously we have shown that a comproportionation reaction of $Mo_2(O_2CCH_3)_4$ and $Na_2MoO_4\cdot 2H_2O$ yields the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion[8] and also that the MoO_4^{2-} ion can be reduced with zinc or $W(CO)_6$ to yield the same ion,[6,7] but in both cases the reaction medium was a liquid consisting of pure acetic acid or a mixture of acetic acid and acetic anhydride. Neither of these approaches was thus adaptable to the preparation of the benzoate. We therefore devised the entirely new method reported here in which $Mo_2(O_2CC_6H_5)_4$ is oxidized by $[C_6H_5C(O)O]_2$, dibenzoyl peroxide. This reaction, followed by an appropriate workup procedure, affords compounds containing the $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ion in yields of 80% or better.

The mechanistic course of this new synthetic reaction is obscure. A plausible speculation, based on chemistry of M≡M bonds previously established by Chisholm and co-workers,[17] is that the first step involves an oxidative addition of the peroxide to the dimolybdenum benzoate. However, in an attempt to garner some direct evidence for this by using only 1 mol of the peroxide/mol of dimolybdenum tetraacetate, we simply obtained about half the optimum yield and recovered about half the dimolybdenum tetrabenzoate. Evidently, if the oxidative addition does occur first, subsequent participation by the peroxide occurs even more rapidly and intermediates cannot, therefore, be isolated.

The failure of a reaction using hydrogen peroxide to yield any trinuclear product tends to disfavor a simple electron-transfer mechanism and suggests instead that dibenzoyl peroxide participates in the reaction as more than just an oxidizing agent. In an experiment designed to bear on on this point, $Mo_2(O_2CCH_3)_4$ was used in place of $Mo_2(O_2CC_6H_5)_4$. The product **2** obtained appeared from its behavior on the cation-exchange column to be homogeneous, and it was shown by ^{1}H NMR spectroscopy to contain benzoate and acetate groups in a ratio of approximately 2:1. This, again, is consistent with the idea that the benzoyl peroxide is not merely an oxidizing agent but also a source of some of the carbonyl groups in the product. The apparent chromatographic homogeneity of the product suggests that it is not simply a mixture of the hexakis(acetato) and hexakis(benzoato) compounds, nor even a mixture of mixed species or isomers of one or more mixed species. We sought further evidence on this point in the visible spectrum, but without conclusive results. Figure 3 shows spectra of the pure acetate trimer, the pure benzoate trimer, and the mixed product. It is a moot point whether the spectrum of the last compound could be reproduced by a suitable combination of the pure acetate and pure benzoate spectra.

As a comparison of Figure 3 and 4 shows, the molybdenum and tungsten benzoate compounds have spectra that differ considerably in detail, although both have a band near 500 nm and steeply rising absorption at wavelengths below 400 nm.

Structure of the Trimolybdenum Cation. The $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ cation was eluted from the ion-exchange column with a 3 M ethanolic solution of perchloric acid, and the crystal used for the X-ray structure determination was selected from among those that formed upon slow evaporation of this ethanolic eluate. The complete formula for this substance appears to be $[Mo_3O_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2\cdot HClO_4\cdot 3C_2H_5OH$. However, as noted in the Experimental Section, there is considerable disordering of two of the perchlorate groups and to a lesser extent of the ethanol molecules. The trinuclear cation, on the other hand, was very well behaved, and there can be no doubt of its composition and structure, as shown in Figure 1. Because of the difficulties in refining the anionic and solvation parts of the structure, we wish to point out that the assignment of a charge of 2+ to the trinuclear cation is strongly supported by its close dimensional similarity to previously characterized $[Mo_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ cations. Some pertinent data are summarized in Table V. With the assigned charge of 2+, there are six electrons available for the formation of Mo–Mo bonds. It has been shown earlier that removal of electrons from the six-electron trinuclear bicapped structure leads to an increase in the Mo–Mo bond lengths of ca. 0.06 Å/electron.[18] On the other hand, with the charge of 2+ all bonding molecular orbitals are believed to be occupied[19] and the presence of an additional electron (so that a charge of 1+ rather than 2+ would be appropriate) is not to be expected.

The ^{1}H NMR spectrum of the trimolybdenum benzoato cation is shown in Figure 2 and tabulated in Table IV. It is clearly consistent with the presence of six equivalent phenyl groups as required by the crystal structure. For the corresponding tritungsten cation essentially the same spectrum (Table IV) was observed. These NMR spectra strongly indicate that the trinuclear cations are diamagnetic and thus provide further evidence that the charges are 2+ since for charges of 1+ or 3+ there should be an unpaired electron.

Nitration Reactions. The nitration of both the molybdenum and tungsten compounds by nitric acid in concentrated sulfuric acid, giving isolated yields of greater than 90%, vividly demonstrates, once again, the remarkable stability of trinuclear cluster compounds of this type. The nature of the products was ascertained by infrared and NMR spectroscopy. Two strong bands are found in the infrared spectrum at approximately 1350 and 1530 cm^{-1} in both compounds. These are in the normal ranges for aromatic nitro compounds.[20] The ^{1}H NMR data are tabulated in Table IV, and the spectrum of the molybdenum cation is shown in Figure 2, along with that of *m*-nitrobenzoic acid for comparison. The first thing that we can unambiguously conclude from these spectra is that nitration of all rings is substantially complete and that each ring is nitrated in the same position, viz., the meta position, as would have been expected from the ordinary meta-directing tendency of the carboxyl group. It will be noted from a close

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comparison of the spectra shown for *m*-nitrobenzoic acid and for the nitrated trinuclear compound that some of the signals in the latter case show slightly more complex splittings than those in the former. There are at least two possible reasons for this. It could be due to higher order splittings that are manifested more clearly because of the somewhat different chemical shifts in the cluster cation or to slightly better resolution in the spectrum of the cluster cation. It must also be noted that geometric isomers that may not interconvert rapidly on the NMR time scale may exist in the nitrated cluster. This isomerism would arise because for each $C_6H_4NO_2$ group two orientations (right or left) are possible. Most likely the only important effect (if any) of this on the NMR spectrum would arise from the influence of one $C_6H_4(NO_2)CO_2$ group on the other one spanning the same Mo–Mo bond. For such a pair the NO_2 groups could be syn or anti.

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Registry No. 1, 92575-20-7; 3, 92545-28-3; $[Mo_3O_2(O_2C\text{-}m\text{-}NO_2C_6H_4)_6(H_2O)_3]^{2+}$, 92622-28-1; $Mo_2(O_2CC_6H_5)_4$, 24378-22-1; $Mo_2(OAc)_4$, 14221-06-8; $W(CO)_6$, 14040-11-0; $[C_6H_5C(O)O]_2$, 94-36-0; benzoic acid, 65-85-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete bond distances and angles, and the observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Comparative Study of Structures, Including Jahn–Teller Effects, in the Saccharinate Complexes, $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$, of Chromium and Zinc, as well as Other Divalent Metal Ions

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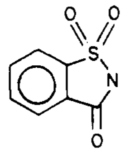
The chromium(II) and zinc(II) complexes of saccharine, $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$, have been prepared and their structures determined by X-ray crystallography. The chromium compound shows clear evidence of Jahn–Teller distortion. When the results for the two new compounds are combined with results in the literature for analogous compounds of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II}, a broad picture of structural properties vs. d-orbital population for high-spin divalent ions for the first transition series is provided. For the series Mn, Fe, Co, Ni, and Zn the expected trends are seen in the bond lengths as the high-spin configurations change, with maxima at Mn and Zn and a minimum at Ni. The bond lengths for the Cu compound deviate enormously (one Cu–O distance being greater, the other Cu–O and the Cu–N distances being less) from the values interpolated between the Ni and Zn data. For the Cr compound, the Jahn–Teller distortions take the same form as those for Cu, but they are only about half as large. The chromium and zinc compounds are isomorphous, crystallizing in space group $P2_1/c$ with $Z = 2$. The cell constants for $ZnC_{14}H_{20}O_{12}N_2S_2$ are $a = 7.934$ (1) Å, $b = 16.118$ (3) Å, $c = 7.691$ (1) Å, and $\beta = 99.90$ (1)° and for $CrC_{14}H_{20}O_{12}N_2S_2$ are $a = 8.042$ (4) Å, $b = 16.032$ (8) Å, $c = 7.804$ (4) Å, and $\beta = 100.90$ (4)°.

Introduction

Several years ago we became interested in the possibility of preparing compounds of Cr_2^{4+} and Mo_2^{4+} using the anion of saccharine (**1**) as a bridging ligand. In the course of that work, which will be reported later, we obtained a mononuclear compound, $Cr(C_7H_4NO_3S)_2(H_2O)_6$, whose structure we determined by X-ray crystallography. We then noted that a little earlier the structure of the analogous copper(II) compound had been the subject of a preliminary report.[1] Complexes of both of the high-spin ions, Cr^{2+} (d^4) and Cu^{2+} (d^9), are well-known to be subject to Jahn–Teller effects of similar character, i.e., due to an odd number of e_g electrons, which in an (idealized) octahedral environment give rise to an E ground state.[2] Both of the saccharinate structures suggested that even though the coordination sphere in these compounds, which consists of two saccharinate nitrogen atoms and four water molecules, could not provide a truly octahedral ligand field, geometric distortions of the types that are loosely, if not rigorously, called Jahn–Teller distortions were evident. However, detailed discussion of these structures was not possible since no structure of an analogous compound with a cation not subject to a Jahn–Teller effect was available for comparison.



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To supply a suitable comparison structure, we undertook the preparation and crystallographic study of the zinc saccharinate. In the meantime, however, other workers reported the structures first of the manganese[3] compound and then of the iron, cobalt, and nickel compounds[4] as well as full details of the copper structure.[4] With all of the structural data now available, it is possible to make an extensive correlation of the structural changes in a homologous series of complexes as a function of their d^n configurations. In particular, the Jahn–Teller distortions for the Cr^{II} and Cu^{II} compounds can be placed in the context of a broad range of homologous structures for ions that do not undergo Jahn–Teller distortions.

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