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(55) The preparation and structural characterization of another Pt complex containing both bridging and terminal hydrido ligands, $[Pt_2H_2Ph(PEt_3)_4][BPh_4]$ (Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778), has recently appeared. No indication of bridge–terminal hydrido ligand exchange is observed at room temperature. This lack of fluxionality is presumably also a result of steric constraint. The PEt_3 ligands of each Pt center are mutually trans and would not be readily accommodated in the tbp geometry outlined above. The complex is best described as two distorted square-planar d^8 moieties sharing the bridging hydrido ligand and involving a minimal Pt–Pt interaction. Thus the complex lacks the angular strain present in complexes **1**–**5** which facilitates bridge bond cleavage.

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Preparation and Characterization of Tetraphenylarsonium *trans*-Bis(μ-acetato)-tetrachlorodimolybdate(II) Disolvates, $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2L$ (L = H_2O or CH_3OH)

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The preparation and isolation of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2L$ (L = H_2O or CH_3OH) are reported. The methanolate crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.571$ (2) Å, $b = 11.330$ (2), Å, $c = 13.397$ (2) Å, $\alpha = 75.16$ (1)°, $\beta = 67.19$ (1)°, and $\gamma = 64.24$ (1)°. The structure has been determined from 2165 X-ray counter intensities by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 0.058$ (0.073 weighted). The unit cell contains one centrosymmetric $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$, two $[(C_6H_5)_4As]^+$ ions, and two CH_3OH moieties. The anion has the trans configuration and closely approximates to D_{2h} point symmetry with dimensions Mo–Mo = 2.086 (2), $\overline{\text{Mo–O}}$ = 2.120 (13), and $\overline{\text{Mo–Cl}}$ = 2.434 (4) Å; the methanol molecules are not coordinated to the molybdenum atoms. Vibrational and electronic spectral data are reported for this material. The ν(Mo–Mo) stretching frequency of 380 cm^{-1} and the position of the first absorption maximum at 20 200 cm^{-1} are midway between the corresponding values of $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$, even though the Mo–Mo bond length for $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ is the shortest of these three complexes.

Introduction

A large number of compounds containing metal–metal quadruple bonds have now been characterized,[2,3] including a considerable range of compounds containing the Mo_2^{4+} center. Two parent complexes, from which a large number of these derivatives have been prepared, are $Mo_2(O_2CCH_3)_4$[4] and $[Mo_2Cl_8]^{4-}$.[5] Herein[6] we report the isolation, X-ray crystallographic characterization, and certain spectroscopic properties of the bis(μ-acetato)-tetrachlorodimolybdenum(II) complex, *trans*-$[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$. Spectral properties of this anion are discussed with reference to the corresponding properties of $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$.

Experimental Section

Preparation of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2L$ (L = H_2O or CH_3OH). $Mo_2(O_2CCH_3)_4$[4] (1.0 g, 2.34 mmol) was added to a solution of Ph_4AsCl (Aldrich, 1.92 g, 4.68 mmol) in deionized, degassed water (65 cm^3) under an atmosphere of purified nitrogen. Concentrated hydrochloric acid (20 cm^3), previously purged with nitrogen, was added dropwise with stirring to this solution. After ca. 8 h the orange precipitate which had formed was removed by filtration, washed twice with degassed, deionized water (10 cm^3) and methanol (2 × 5 cm^3), and dried in vacuo. Yield of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2H_2O$ was typically ca. 2 g (ca. 75%). Anal. Calcd for $C_{52}H_{50}O_6As_2Cl_4Mo_2$: C, 49.8; H, 4.0; As, 11.9; Cl, 11.3; Mo, 15.3. Found: C, 49.7; H, 3.9; As, 11.2; Cl, 11.7; Mo, 15.4. Crystals of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2CH_3OH$ suitable for X-ray crystallographic studies were obtained by recrystallization from degassed AnalaR methanol.

Data Collection and Reduction. The dark red crystals were irregular in shape. Initial values of the triclinic cell parameters were obtained from precession photographs (Mo Kα radiation, 0.710 69 Å) by a least-squares refinement based on the observed and calculated positions of spots on ($0kl$), ($h0l$), and ($hk0$) photographs. There were no systematic absences.

The crystal chosen for refinement of cell parameters and collection of intensities had a maximum dimension of ca. 0.35 mm. It was mounted on a Hilger and Watts Y290 four-circle diffractometer, with c^* a few degrees misaligned from the instrument Φ axis. Unit cell parameters and the orientation matrix were refined by a least-squares technique[7] based on the automatically determined setting angles at room temperature of 12 reflections with $34° < 2\theta < 41°$ (Mo Kα radiation; Zr filter). Values obtained were $a = 10.571$ (2) Å, $b = 11.330$ (2) Å, $c = 13.469$ (2) Å, $\alpha = 85.05$ (1)°, $\beta = 66.47$ (1)°, and $\gamma = 64.24$ (1)°. This corresponds to a type I reduced cell[8] with $a = 10.571$ (2) Å, $b = 11.330$ (2) Å, $c = 13.397$ (2) Å, $\alpha = 75.16$ (1)°, $\beta = 67.19$ (1)°, and $\gamma = 64.24$ (1)°; the matrix for transformation from initial cell to reduced cell is (–1, 0, 0; 0, –1, 0; –1, 0, 1). Data were collected, reduced, and corrected for absorption on the basis of the initial cell and then transformed to correspond to the reduced cell for all other calculations.

The unit cell volume (1324.6 $Å^3$) and formula weight (1282.6) give $Z = 1$ for a density of 1.608 g cm^{-3}. The density was measured as 1.60 ± 0.01 g cm^{-3}. For space group $P1$, no symmetry is imposed on the structure, but for $P\bar{1}$, the dimeric anion must be centrosymmetric. $P\bar{1}$ was assumed and was confirmed by successful structure solution and refinement.

Intensities were collected at room temperature for all independent reflections with $2\theta \leq 45°$. A θ–2θ scan was used, with a 1-s count at each of 80 steps of 0.01° for each reflection and a 20-s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of attenuators into the beam. The data were corrected for Lp factors, absorption, and crystal decay.[9] Absorption corrections were of the Gaussian integration type (μ 20.20 cm^{-1}, 96 grid points), with the crystal approximated by six planar

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Table I. Atomic Coordinates ($\times 10^4$)[a] and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a,b]

atom	*x*	*y*	*z*	*U*
Mo	−179 (1)	360 (1)	−752 (1)	
Cl(1)	2112 (4)	−572 (3)	−2203 (3)	
Cl(2)	−2742 (4)	1869 (3)	−448 (3)	
O(1)	419 (9)	1987 (7)	−920 (6)	
O(2)	−768 (9)	−1210 (7)	−714 (6)	
C(1)	749 (14)	2060 (12)	−139 (11)	
C(2)	1120 (19)	3235 (15)	−201 (12)	
As	−1677 (1)	4518 (1)	3749 (1)	
C(11)	−2540 (12)	6043 (11)	4494 (9)	45 (3)
C(12)	−3412 (14)	5973 (13)	5589 (10)	60 (4)
C(13)	−4145 (15)	7102 (14)	6116 (11)	69 (4)
C(14)	−4008 (15)	8292 (14)	5592 (11)	69 (4)
C(15)	−3111 (15)	8323 (14)	4533 (11)	70 (4)
C(16)	−2444 (14)	7235 (13)	3965 (11)	62 (4)
C(21)	−2792 (13)	4812 (11)	2819 (9)	46 (3)
C(22)	−4043 (14)	5939 (12)	2818 (10)	57 (3)
C(23)	−4774 (15)	6124 (13)	2106 (11)	64 (4)
C(24)	−4289 (14)	5179 (12)	1421 (10)	59 (3)
C(25)	−3109 (15)	4063 (13)	1462 (11)	65 (4)
C(26)	−2318 (15)	3822 (13)	2147 (10)	61 (4)
C(31)	340 (12)	4141 (11)	2885 (9)	42 (3)
C(32)	860 (15)	5100 (13)	2266 (11)	65 (4)
C(33)	2316 (16)	4725 (14)	1574 (11)	72 (4)
C(34)	3228 (17)	3473 (15)	1488 (12)	76 (4)
C(35)	2740 (18)	2497 (17)	2098 (13)	90 (5)
C(36)	1269 (17)	2851 (15)	2801 (12)	82 (5)
C(41)	−1737 (13)	3025 (11)	4822 (9)	47 (3)
C(42)	−2599 (15)	2358 (13)	4885 (11)	68 (4)
C(43)	−2629 (18)	1313 (16)	5736 (13)	86 (5)
C(44)	−1792 (18)	998 (17)	6370 (14)	89 (5)
C(45)	−905 (19)	1592 (17)	6308 (14)	99 (5)
C(46)	−897 (16)	2669 (15)	5480 (12)	79 (4)
O(Sol)	4381 (19)	568 (17)	−2058 (15)	179 (7)
C(Sol)	4713 (35)	503 (32)	−969 (28)	221 (14)

[a] In this and subsequent tables, estimated standard deviations in the last place of figures are given in parentheses. [b] The isotropic temperature factor takes the form $\exp[-8\pi^2(\sin^2\theta)U/\lambda^2]$.

Table II. Anisotropic Thermal Parameters ($Å^2 \times 10^3$)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	52.5 (8)	37.3 (6)	35.4 (6)	4.0 (5)	−13.1 (6)	−22.3 (6)
Cl(1)	84 (3)	65 (2)	47 (2)	−7 (2)	5 (2)	−37 (2)
Cl(2)	68 (2)	59 (2)	77 (2)	−3 (2)	−37 (2)	−19 (2)
O(1)	74 (6)	38 (5)	45 (5)	2 (4)	−20 (5)	−24 (4)
O(2)	66 (6)	45 (5)	52 (5)	−2 (4)	−16 (4)	−29 (4)
C(1)	52 (8)	43 (8)	56 (8)	−2 (6)	−3 (7)	−22 (6)
C(2)	131 (15)	73 (10)	85 (11)	−6 (9)	−12 (10)	−70 (11)
As	50.6 (9)	46.2 (8)	38.8 (7)	3.5 (6)	−12.3 (6)	−24.6 (7)

[a] The anisotropic temperature factor takes the form $\exp[-2\pi^2\cdot(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

Table III. Calculated H Atom Coordinates ($\times 10^4$)[a]

atom	*x*	*y*	*z*
H(1)	1356	3178	430
H(2)	290	4024	−243
H(3)	1944	3240	−831
H(12)	−3494	5162	5963
H(13)	−4756	7063	6854
H(14)	−4530	9065	5958
H(15)	−2940	9107	4182
H(16)	−1919	7304	3208
H(22)	−4392	6576	3303
H(23)	−5621	6904	2084
H(24)	−4789	5322	920
H(25)	−2808	3418	996
H(26)	−1495	3021	2172
H(32)	236	6004	2309
H(33)	2672	5393	1144
H(34)	4214	3257	1005
H(35)	3382	1597	2051
H(36)	916	2178	3222
H(42)	−3134	2585	4391
H(43)	−3238	841	5851
H(44)	−1836	285	6923
H(45)	−330	1315	6782
H(46)	−286	3132	5380

[a] Group isotropic thermal parameters are $U = 0.119\ (34)\ Å^2$ for methyl and $U = 0.144\ (15)\ Å^2$ for phenyl H atoms.

faces (010, $0\bar{1}0$, 210, $\bar{2}10$, 001, and $00\bar{1}$ at distances 0.222, 0.022, 0.022, 0.158, 0.135, and 0.135 mm, respectively, from a common point inside the crystal, measured with a high-power microscope and calibrated graticule). Transmission factors range from 0.526 to 0.664. Decay corrections were based on the periodic measurement of three standard reflections, the intensities of which fell by a total of 15.4, 14.7, and 11.1% during the data collection. Intensities and their estimated standard deviations were calculated as reported previously,[10] with $p = 0.05$. Of the 3785 measured independent reflections, 431 had $I < 0$, and 2165 with $I > 3\sigma(I)$ were used for structure solution and refinement.

Structure Solution and Refinement. All nonhydrogen atoms, other than those of methanol, were determined from Patterson and subsequent Fourier syntheses. Refinement was by full-matrix least-squares methods; the quantity minimized was $\sum w\Delta^2$ with $w = \{\sigma^2(F_o) + 0.002F_o^2\}^{-1}$ and $\Delta = |F_o| - |F_c|$. Refinement began with isotropic thermal parameters and rigid idealized phenyl rings; constraints were gradually removed as refinement continued. Whenever the model was altered and more parameters were introduced, the decrease in R $(=\sum|\Delta|/\sum|F_o|)$ and R_w $(=\{\sum w\Delta^2/\sum wF_o^2\}^{1/2})$ was tested[11] and found to be highly significant (significant at the 0.5% level in all cases). Atomic scattering factors for uncharged atoms, including corrections for anomalous scattering, were taken from ref 12.

With Mo, Cl, As, and acetate atoms anisotropic and phenyl carbon atoms isotropic, R was 0.080 and R_w 0.119. A difference map revealed two peaks assigned to methanol, not coordinated to the Mo atoms. The larger of these was refined as oxygen, the smaller as carbon, with isotropic thermal parameters. With R at 0.059 and R_w 0.075, another difference map contained peaks at most of the positions expected for hydrogen atoms. H atoms were included in the refinement, but their positions were calculated for idealized geometry (external bisectors of C–C–C angles for phenyl H, tetrahedral angles for CH_3, and C–H = 0.95 Å [13]) and constrained to these geometries during refinement. No hydrogen atoms were included for the methanol. Two isotropic thermal parameters were refined: one for the phenyl and one for the methyl hydrogen atoms. The final values of R and R_w were 0.058 and 0.073. The largest shift/esd ratio for the atomic coordinates in the last cycle was 0.020, and for the thermal parameters it was 0.007. The value of S $(=\{\sum w\Delta^2/[N - P]\}^{1/2})$ for N reflections and P (=180) refined parameters was 1.10; the root-mean-square deviation of a reflection of unit weight on an absolute scale of F_c $(=\{\sum w\Delta^2/\sum w\}^{1/2})$ was 2.52 electrons and showed no systematic trends with indices, $\sin\theta$, or F_o. The weighting scheme was thus shown to be consistent.[14] No extinction correction was indicated as necessary by a comparison of F_o and F_c for strong, low-angle reflections. A difference synthesis after the final cycle showed no peaks higher than 1.07 e $Å^{-3}$, the largest being close to the heaviest atoms, and no depressions lower than −0.88 e $Å^{-3}$. The two methanol atoms had high thermal parameters and a separation of 1.605 (33) Å, indicating a degree of disorder in the solvent of crystallization. There were no significant differences between $|F_c|$ and $|F_o|$ for the reflections with $0 < I < 3\sigma(I)$ omitted from the refinement. Inclusion of them gave $R = 0.096$ and $R_w = 0.086$; one refinement cycle produced no shift/esd ratio greater than 0.8 and no significant change in R and R_w.

Observed and calculated structure factors on an absolute scale (electrons) are tabulated as supplementary material. Positional and thermal parameters are given in Tables I–III, interatomic distances and bond angles in Table IV, and selected least-squares planes fitted to atomic positions in Table V.

The atomic arrangements within the cations and anions are presented in Figures 1 and 2, respectively, and the crystal packing is shown in Figure 3. There are no unusually short interatomic contacts.

Spectroscopic Measurements. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer and Raman spectra on a Cary 82 instrument by using 6328-Å excitation. Room-temperature electronic absorption spectra (8500–2000 Å) for these compounds dissolved in H_2O and CH_3OH were recorded with a Perkin-Elmer

Table IV

Cation Bond Lengths (Å)

As–C(11)	1.903 (11)	As–C(31)	1.902 (11)
As–C(21)	1.906 (12)	As–C(41)	1.926 (11)
C(11)–C(12)	1.401 (16)	C(21)–C(22)	1.383 (16)
C(12)–C(13)	1.383 (17)	C(22)–C(23)	1.371 (17)
C(13)–C(14)	1.392 (18)	C(23)–C(24)	1.382 (17)
C(14)–C(15)	1.369 (17)	C(24)–C(25)	1.343 (17)
C(15)–C(16)	1.381 (18)	C(25)–C(26)	1.373 (18)
C(16)–C(11)	1.382 (16)	C(26)–C(21)	1.415 (16)
C(31)–C(32)	1.369 (16)	C(41)–C(42)	1.383 (17)
C(32)–C(33)	1.391 (17)	C(42)–C(43)	1.420 (19)
C(33)–C(34)	1.329 (18)	C(43)–C(44)	1.336 (20)
C(34)–C(35)	1.365 (19)	C(44)–C(45)	1.342 (21)
C(35)–C(36)	1.407 (20)	C(45)–C(46)	1.424 (20)
C(36)–C(31)	1.366 (17)	C(46)–C(41)	1.357 (17)

Anion Bond Lengths (Å)

Mo–Mo′	2.086 (2)	Mo–O(2)	2.108 (8)
Mo–Cl(1)	2.437 (3)	C(1)–O(1)	1.255 (15)
Mo–Cl(2)	2.430 (4)	C(1)–O(2)′	1.293 (15)
Mo–O(1)	2.131 (8)	C(1)–C(2)	1.518 (17)

Solvent Bond Length (Å)

C(sol)–O(sol)	1.605 (33)

Cation Bond Angles (deg)

C(11)–As–C(21)	107.5 (5)	C(21)–As–C(31)	108.5 (5)
C(11)–As–C(31)	113.7 (5)	C(21)–As–C(41)	112.2 (5)
C(11)–As–C(41)	108.1 (5)	C(31)–As–C(41)	107.0 (5)
As–C(11)–C(12)	118.2 (9)	As–C(21)–C(22)	121.4 (9)
As–C(11)–C(16)	122.0 (9)	As–C(21)–C(26)	117.8 (9)
C(16)–C(11)–C(12)	119.5 (11)	C(26)–C(21)–C(22)	120.8 (11)
C(11)–C(12)–C(13)	118.9 (12)	C(21)–C(22)–C(23)	119.0 (12)
C(12)–C(13)–C(14)	121.6 (13)	C(22)–C(23)–C(24)	120.4 (13)
C(13)–C(14)–C(15)	118.4 (13)	C(23)–C(24)–C(25)	120.1 (13)
C(14)–C(15)–C(16)	121.3 (14)	C(24)–C(25)–C(26)	122.5 (13)
C(15)–C(16)–C(11)	120.1 (13)	C(25)–C(26)–C(21)	117.1 (12)
As–C(31)–C(32)	122.8 (9)	As–C(41)–C(42)	119.8 (10)
As–C(31)–C(36)	118.1 (10)	As–C(41)–C(46)	117.2 (10)
C(36)–C(31)–C(32)	118.8 (12)	C(46)–C(41)–C(42)	123.0 (13)
C(31)–C(32)–C(33)	118.9 (13)	C(41)–C(42)–C(43)	115.7 (14)
C(32)–C(33)–C(34)	122.7 (15)	C(42)–C(43)–C(44)	119.4 (16)
C(33)–C(34)–C(35)	119.6 (15)	C(43)–C(44)–C(45)	126.5 (18)
C(34)–C(35)–C(36)	118.7 (15)	C(44)–C(45)–C(46)	114.8 (17)
C(35)–C(36)–C(31)	121.3 (14)	C(45)–C(46)–C(41)	120.6 (15)

Anion Bond Angles (deg)

Mo′–Mo–Cl(1)	109.6 (1)	O(1)–Mo–O(2)	175.5 (3)
Mo′–Mo–Cl(2)	108.6 (1)	Cl(1)–Mo–O(1)	88.6 (2)
Mo′–Mo–O(1)	92.3 (1)	Cl(1)–Mo–O(2)	89.2 (2)
Mo′–Mo–O(2)	92.1 (1)	Cl(2)–Mo–O(1)	89.1 (2)
Cl(1)–Mo–Cl(2)	141.8 (1)	Cl(2)–Mo–O(2)	90.2 (2)
Mo–O(1)–C(1)	115.6 (7)	O(1)–C(1)–O(2)′	124.0 (12)
Mo–O(2)–C(1)′	116.0 (7)	O(1)–C(1)–C(2)	117.4 (12)
		O(2)′–C(1)–C(2)	118.6 (12)

[a] A prime indicates an atom related by the center of symmetry.

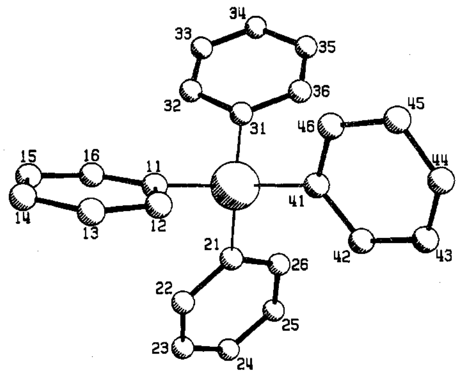

Figure 1. Arrangement of atoms within the cations of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2CH_3OH$.

Table V. Least-Squares Planes in Terms of Orthogonal Ångstrom Axes along a^*, $c \times a^*$, and c

Cation

A. Equations of Planes for the Four Phenyl Rings

(1) $0.7964X + 0.0633Y + 0.6015Z = 2.5745$

(2) $0.5873X + 0.7174Y - 0.3746Z = 0.0358$

(3) $0.3005X + 0.1434Y + 0.9429Z = 5.6695$

(4) $-0.7641X + 0.3681Y + 0.5298Z = 5.6787$

B. Deviations (Å × 10^3) of Atoms from the Planes

atom	Δ_1	Δ_2	Δ_3	Δ_4
C(*1)[a]	9	21	1	15
C(*2)	13	−16	1	−21
C(*3)	−13	−1	0	12
C(*4)	−9	14	−2	3
C(*5)	32	−9	3	−10
C(*6)	−31	−9	−2	0
As[b]	−110	68	−178	65
rms Δ	20	13	2	12

C. Dihedral Angles (deg) between Planes

(1)–(2)	73.3	(2)–(3)	94.2
(1)–(3)	35.4	(2)–(4)	112.5
(1)–(4)	105.5	(3)–(4)	71.2

Anion

A. Equations of Planes

(5) $0.2564X + 0.9260Y + 0.2772Z = 0$

(6) $0.9583X - 0.1905Y - 0.2131Z = 0$

B. Deviations (Å × 10^3) of Atoms from the Planes

atom[c]	Δ_5	Δ_6
Mo	−8	−10
Cl(1)	2	
Cl(2)	2	
O(1)		22
O(2)		−12
C(1)		13
C(2)		−25
rms Δ	5	17

C. Dihedral Angle (5)–(6) = 89.4°

[a] C(*1) means C(11), C(21), C(31), or C(41) as appropriate.

[b] As not included in the mean-plane calculation.

[c] For each atom, the centrosymmetrically related atom was also included in the calculation. Thus, the two planes intersect at the unit cell origin, and the deviations for related atoms are equal and opposite in sign.

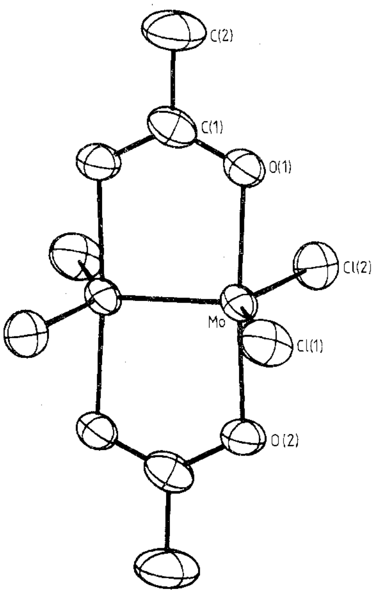

Figure 2. ORTEP representation of the thermal motions of the atoms of the anions of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2CH_3OH$.

402 spectrophotometer. Electronic absorption spectra (20 000–3000 Å) were also recorded on a Cary 14 instrument, for the powdered solids mulled in Nujol, supported on filter paper, and mounted on a glass slide attached to the copper block of an Oxford Instruments continuous-flow Cryotip which was maintained at 5 K. The fine structure observed between 5300 and 4300 Å for $[(C_6H_5)_4$-

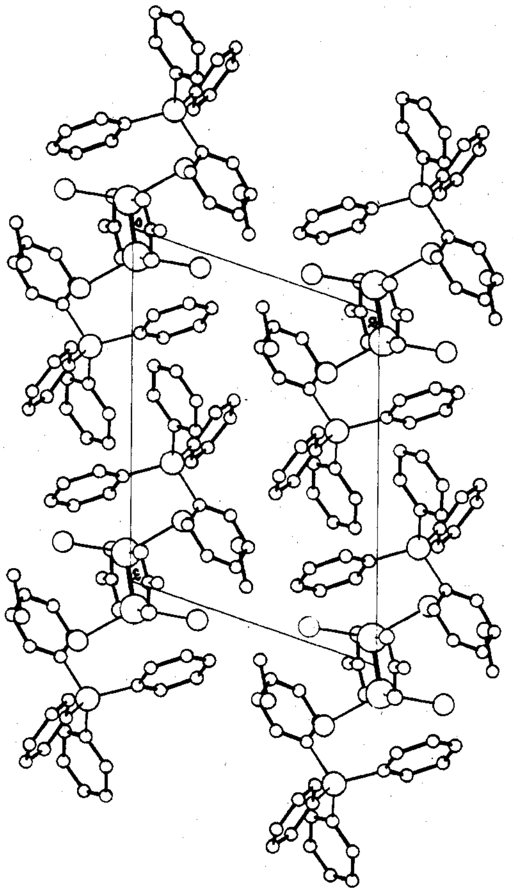

Figure 3. Projection of the crystal structure of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2CH_3OH$ down the *b* axis.

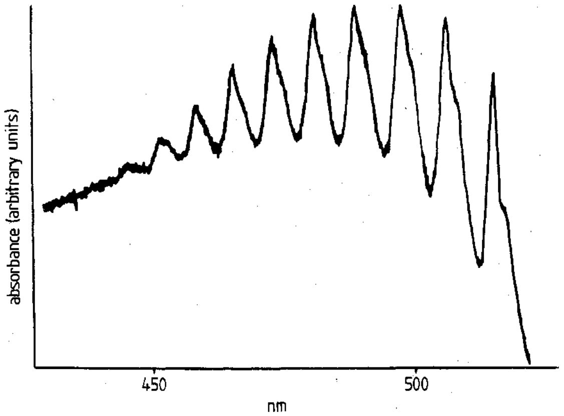

Figure 4. Lowest energy absorption of $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2H_2O$, recorded at low temperature for a Nujol mull of the sample.

$As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2H_2O$ at low temperatures is illustrated in Figure 4.

Results and Discussion

The cation structure (Figure 1) is unexceptional, and the interatomic dimensions obtained here do not differ significantly from the corresponding details reported for this ion in other crystallographic studies of similar precision.[15] The apparent shortening of the C–C bonds furthest from the arsenic is probably a libration effect,[16] and, apart from this, the deviations of the phenyl rings from a planar hexagonal structure are insignificant. The departures from a regular tetrahedral geometry about the arsenic are small, the C–As–C bond angles ranging from 107.5 (5) to 113.7 (5)°. The arsenic atom is displaced ($0.065 \leq \Delta \leq 0.178$ Å) out of the planes of the phenyl rings. The overall structure of the cation does not correspond to any of the regular arrangements possible[17] for $(C_6H_5)_4E$ species.

The anion (Figures 2 and 3) is dimeric, the two μ-acetato ligands being mutually trans, as required by the crystallographic center of symmetry. The $\{MoCl_2\}_2$ and $\{Mo_2(O_2C_2)_2\}$ units are planar, within experimental error, and the $Mo_2(O_2C_2)_2Cl_4$ moiety corresponds closely to D_{2h} (*mmm*) point symmetry. The interatomic dimensions within the anion are, as expected, comparable with the corresponding values obtained for $Mo_2(O_2CCH_3)_4$[18] and the anion of $K_4[Mo_2Cl_8]\cdot 2H_2O$.[5] The length of the Mo–Mo bond (2.086 (2) Å) is slightly shorter than that in $Mo_2(O_2CCH_3)_4$ (2.0934 (8) Å) and $[Mo_2Cl_8]^{4-}$ (2.139 (4) Å); all these bond lengths are in the range (2.064–2.183 Å)[2,3] usually taken as typical for molybdenum–molybdenum quadruple bonds. The average lengths of the other bonds within the anion (Mo–O = 2.120 (14), C–O = 1.274 (22), C–C = 1.518 (17), and Mo–Cl = 2.434 (3) Å) are not significantly different for the corresponding dimensions of the $Mo_2(O_2CCH_3)_4$ or $[Mo_2Cl_8]^{4-}$ complexes. This also applies to the bond angles involving the μ-acetato groups which in the present structure are Mo–Mo–O = 92.2 (1), O–Mo–O = 175.5 (3), Mo–O–C = 115.8 (7), and O–C–O = 124.0 (12)°. However, the Cl–Mo–Cl angle of 141.8 (1)° is significantly less than the 150° found for the corresponding angles in $[Mo_2Cl_8]^{4-}$.

Several other complexes containing two bridging and four monodentate ligands bound to a dimetal center have been structurally characterized. These include $Re_2(O_2CC_6H_5)_2I_4$,[19] $Mo_2[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Br_2$,[20] $Re_2[N_2C(C_6H_5)_3]_2Cl_4\cdot x$THF ($x$ = 0 or 1),[21] and $Mo_2(C_7H_5N_2)_2[P(C_2H_5)_3]_2Cl_2$[22] which have a trans arrangement of the bridging ligands, whereas $(NH_4)_2[Re_2(O_2CH)_2Cl_6]$[23] and $Re_2(O_2CCH_3)_2Cl_4\cdot 2H_2O$[24] have a cis arrangement of the bridging ligands. The structure favored by this last compound contrasts sharply with the trans arrangement identified in the $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ anion. We thus conclude that there are no obvious factors which lead to $M_2(LL)_2L'_4$ complexes generally adopting a cis or a trans arrangement of the bridging ligands (LL).

The IR and Raman spectra of solid $(Ph_4As)_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2L$ (L = H_2O or CH_3OH) exhibit features typical of the constituent fragments (i.e., $[(C_6H_5)_4As]^+$, coordinated CH_3CO_2, CH_3OH, or H_2O). The strong Raman effect which occurs at 380 cm^{-1} and which has no counterpart in the IR spectrum is attributed to the a_g vibration involving the stretching of the Mo–Mo bond. The following bands are attributed to the ν(Mo–O) and ν(Mo–Cl) stretching vibrations, respectively, by analogy with earlier interpretations of the vibrational spectra of $Mo_2(O_2CCH_3)_4$[25,26] and $[Mo_2Cl_8]^{4-}$:[27] 360 (w), 338 (w) cm^{-1} (Raman); 360 (m), 346 (s) cm^{-1} (IR) and 310 (w, br) cm^{-1} (Raman); 310 (s) cm^{-1} (IR). The frequency of the ν(Mo–Mo) stretching vibration is the same for both the water and the methanol solvate, and this value is intermediate between the values observed for $Mo_2(O_2CCH_3)_4$[25] and $K_4[Mo_2Cl_8]$[27] of 406 and 346 cm^{-1}, respectively. The reasons for the differences between the metal–metal stretching frequencies in $Mo_2(O_2CR)_4$ (R = CH_3, CF_3, C_2H_5, $n\text{-}C_3H_7$, C_6H_5, or C_6H_{11}), which occur in the range 400 ± 6 cm^{-1}, and $[Mo_2X_8]^{4-}$ (X = Cl or Br), which occur at 340 ± 4 cm^{-1}, have been discussed. Ketteringham and Oldham[28] concluded that these differences are, at least in part, due to different metal–metal interactions. Loewenshuss et al.,[29] however, observed that the increase in the ν(Mo–Mo) stretching frequency from $[Mo_2Cl_8]^{4-}$ to $[Mo_2(SO_4)_4]^{4-}$ (371 cm^{-1}) and $Mo_2(O_2CR)_4$ complexes could be a reflection of the stresses induced into the structure by the closed rings which the bridging ligands form with the two molybdenum atoms.

Table VI. Vibronic Structure of the Lowest Energy Visible Absorption of $(Ph_4As)_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2L$ at Low Temperature

L = H_2O				L = CH_3OH
nm	cm^{-1}			nm
516.3	19 367			513
514.4	19 435	345		
507.3	19 712		363	506
505.1	19 798	366		
498.0	20 078		352	497
496.3	20 150	359		
489.2	20 437		372	488
487.3	20 522	362		
480.8	20 799		356	479
479.0	20 878	350		
472.7	21 149		355	471
470.8	21 233	366		
464.8	21 515		357	463
463.2	21 590	350		
457.2	21 865		345	454
455.9	21 935	327		
450.6	22 192		338	447
449.0	22 273			
(442)	(22 625)			440

Table VII. Characteristics of the Lowest Electronic Absorptions for $Mo_2(O_2CCH_3)_4$ (A), $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ (B), and $[Mo_2Cl_8]^{4-}$ (C)

	A[a]	B[b]	C
$\bar{\nu}_1$ (max), cm^{-1}	22 800	20 200	19 128[c]
ϵ, M^{-1} cm^{-1}	105	490	1 050[d]
f	0.0012	0.0064	0.015[e]
$\bar{\nu}$(Mo-Mo) A_{1g}, cm^{-1}	406	380	346[f]
ν(Mo-Mo)-(excited), cm^{-1}	370	354	336[c]
ν_2(max), cm^{-1}	31 000	29 500	28 800[c]

[a] This work; THF solution. [b] This work; methanol solution. [c] Reference 30. [d] W. C. Trogler, D. K. Erwin, G. L. Geoffrey, and H. B. Gray, *J. Am. Chem. Soc.*, 100, 1160 (1978). [e] Reference 26. [f] Reference 27.

We note that the frequency of the metal–metal stretching vibration in $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ is *intermediate* between those of $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$, yet the Mo–Mo bond of this mixed ligand complex is the *shortest* of these complexes. Therefore, we favor the view that, for these complexes, the frequency of the vibration involving Mo–Mo stretching reflects the force constant typical of Mo–Mo quadruple bonds, augmented by the number and type of the bridging ligand. Consistent with this view, we note that $Mo_2(O_2CCH_3)_2(pd)_2$, which involves a Mo–Mo separation of 2.129 (1) Å and two bridging acetate and two bidentate pentane-2,4-dionate ligands,[6] has its ν(Mo–Mo) vibration at 373 cm^{-1}.

The absorption spectrum of $(Ph_4As)_2[Mo_2(O_2CCH_3)_2Cl_4]$ has been recorded from 5000 to 50 000 cm^{-1}. In methanol the lowest energy electronic absorption occurs at 20 200 cm^{-1} (ϵ 490 M^{-1} cm^{-1}, f = 0.0064); a shoulder of a slightly greater intensity is apparent at ca. 29 500 cm^{-1} on the leading edge of an intense absorption centered at ca. 35 000 cm^{-1}, which overlaps the UV absorptions characteristic of the cation. In solution the complex is extremely sensitive to oxygen which leads to a marked increase in the intensity and a slight blue shift of the lowest energy band. The lowest energy band of $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ shows well-defined vibronic fine structure at low temperatures which is better resolved for the dihydrate (Figure 4). This fine structure consists of two progressions (Table VI), 79 ± 9 cm^{-1} apart, with an average spacing of 354 ± 9 cm^{-1}. The corresponding spectrum of the methanolate is very similar, but broader features were observed (average spacing 361 cm^{-1}), one for each asymmetric doublet of the aquated species.

Polarized single-crystal electronic spectra have been recorded for $K_4[Mo_2Cl_8]\cdot 2H_2O$[30] and $Mo_2(O_2CCH_3)_4$.[26] The lowest energy transition of the former chromophore occurs at 19 128 cm^{-1} (ϵ 1050 M^{-1} cm^{-1}; f = 0.015) and is polarized primarily parallel to the metal–metal axis. At low temperatures, an irregular vibronic progression is evident on the band envelope with separations which range from 381 to 320 cm^{-1}. The spectral data, in particular the sense of the polarization, are consistent with the electronic origin of the band being due to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition, the vibronic coupling being assigned to ν(Mo–Mo) in the ${}^1A_{2u}$ state. The next highest energy spectral feature is a low-intensity, dipole-allowed transition at 28 800 cm^{-1} which has been assigned as the A_1' component of a ${}^1A_{1g} \rightarrow {}^3E_u$ transition; the corresponding ${}^1A_{1g} \rightarrow {}^1E_u$ transition was suggested to be the origin of the absorption at 31 400 cm^{-1}. $Mo_2(O_2CR)_4$ (R ≠ aromatic) compounds exhibit a weak low-energy band at ca. 23 000 cm^{-1} (ϵ ~100 M^{-1} cm^{-1}; f = 0.0012 (R = CH_3)). The polarization of this absorption band has been shown[31,32] to be inconsistent with a ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition. Gray et al.[26] accomplished a detailed spectroscopic study of $Mo_2(O_2CR)_4$ (R = H, CH_3, CD_3, or CF_3) compounds and concluded that the lowest energy band originates from the orbitally forbidden ${}^1A_{1g} \rightarrow {}^1E_g$ ($\delta \rightarrow \pi^*$) transition, with the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) suggested[33] to be associated with an intense shoulder at 30 600 cm^{-1} (in $Mo_2(O_2CH)_4$). Rich vibronic structure becomes evident at low temperature for the lowest energy band of $Mo_2(O_2CR)_4$ complexes, for $Mo_2(O_2CCH_3)_4$ this is dominated by progressions with a spacing of 374 ± 5 cm^{-1} attributed to ν(Mo–Mo) in the ${}^1E_g$ state.

Given the different assignments of the electronic absorption spectra of $[Mo_2Cl_8]^{4-}$ and $Mo_2(O_2CCH_3)_4$, it is clearly of interest to enquire into the assignment of the $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ spectrum. The situation is puzzling because the spectral characteristics, thus far determined for $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ (Table VII), are neatly intermediate between those of the other two systems and suggest a continuity of assignment for the three chromophores rather than the discontinuity thus far characterized. The lowest energy absorption can, by comparison with either $[Mo_2Cl_8]^{4-}$ or $Mo_2(O_2CCH_3)_4$, be argued to be due either to the transition (i) ($\delta \rightarrow \delta^*$) or to (ii) ($\delta \rightarrow \pi^*$). In support of (i), (a) the oscillator strength is significantly greater than the electronically forbidden ${}^1A_{1g} \rightarrow {}^1E_g$ band of $Mo_2(O_2CCH_3)_4$, and (b) there is no evidence for a splitting of this band into the two components expected for the "${}^1A_{1g} \rightarrow {}^1Eg$" transition in the D_{2h} symmetry of $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$—the absorption at ca. 29 500 cm^{-1} is clearly apparent at low temperature and shows no evidence of vibronic coupling, and a feature ca. 9000 cm^{-1} above the lowest energy band is evident for $[Mo_2Cl_8]^{4-}$ (and $Mo_2(O_2CCH_3)_4$. In favor of (ii), (a) the oscillator strength is significantly less than the electronically allowed ${}^1A_{1g} \rightarrow {}^1A_{2u}$ band of $[Mo_2Cl_8]^{4-}$, (b) the superfical appearance of the vibrational fine structure thus far determined for $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$ resembles that for $Mo_2(O_2CCH_3)_4$,[26] at a poorer resolution and minus the progression from E (Figures 1 and 2, ref 26), and (c) the absorption band deriving from the other electronic origin may be the feature of ca. 29 500 cm^{-1} or may be obscured by the intense bands above 30 000 cm^{-1}. The reduction of the ν(Mo–Mo) stretching frequency in the excited state is consistent with either of the assignments.

Clearly, further electronic spectral data, particularly polarized information, must be obtained to ascertain the assignment of the bands in the UV/vis spectrum of $[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$. An improved understanding of the order of the excited states of this complex should be valuable to the general understanding of the electronic spectra of Mo_2^{4+} complexes.

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Registry No. $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2H_2O$, 70004-02-3; $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4]\cdot 2CH_3OH$, 69109-39-3; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Triosmium Cluster Compounds Containing Isocyanide and Hydride Ligands. Crystal and Molecular Structure of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)}(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$

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The crystal and molecular structure of the compound $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)}(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$ has been determined by X-ray crystallographic methods. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ $[C_{2h}^5]$: $a = 13.651$ (4) Å, $b = 9.156$ (4) Å, $c = 18.275$ (5) Å, $\beta = 111.42$ (2)°, $V = 2126.3$ (25) Å^3, $Z = 4$, $\rho_{\text{calcd}} = 2.92$ g cm^{-3}. A uniform triangular cluster of three osmium atoms contains ten linear carbonyl groups and a $\mu\text{-}\eta^1\text{-C=N(H)}(t\text{-C}_4\text{H}_9)$ iminyl ligand. The carbon atom of the iminyl ligand symmetrically bridges one osmium–osmium bond, as is shown by the internuclear separations Os(2)–C(11) = 2.066 (8) Å and Os(3)–C(11) = 2.043 (8) Å. The iminyl bond, C(11)–N, is double with the C–N distance being 1.298 (10) Å.

Introduction

We have recently presented a detailed report of the way in which the cluster hydride complex $H_2Os_3(CO)_{10}$ reacts with isocyanide molecules and subsequently transfers hydrogen atoms to the isocyanide ligand.[1] One process involving a proton dissociation and readdition formally moves a hydrogen atom from the cluster to the nitrogen atom of the isocyanide ligand. This has been confirmed by an X-ray crystallographic analysis of the compound $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)}(\text{C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$ which is reported here.

Experimental Section

The compound $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)}(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$ was prepared from $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ by treatment with triethylamine in chloroform solution as previously reported.[1] Crystals were grown from concentrated hexanes solutions cooled to −20 °C.

All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer by using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined by using 25 randomly selected reflections obtained with the CAD-4 automatic search center, index, and least-squares routines. The space group $P2_1/n$ was determined from the systematic absences observed during data collection.

All calculations were performed on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library. Anomalous dispersion corrections[2a] were made for scattering[2b] by all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$.

Crystal data and data collection parameters are listed in Table I. A cuboidal crystal with dimensions 0.114 mm × 0.174 mm × 0.138 mm was mounted in a thin-walled glass capillary. The crystal faces

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