support of this work. We also thank Dr. J. M. Williams and Dr. M. Beno of Argonne National Laboratory for some useful discussions and some help with graphics.

Registry No. $[Mo_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)(CF_3SO_3H)_2 \cdot 5H_2O$, 82598-68-3.

Supplementary Material Available: Tables of structure factors and thermal vibration parameters for both crystals (23 pages). Ordering information is given on any current masthead page.

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Structural and Bonding Studies of the Hexachlorobis(μ-chloro)(μ-hydrido)dimolybdenum(III) Ion, $[Mo_2Cl_8H]^{3-}$

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The preparations and structures of two compounds containing the $[Mo_2Cl_8H]^{3-}$ ion are reported. The pyridinium salt, $(C_5NH_6)_3[Mo_2Cl_8H]$ (**1**), crystallizes in space group $P\bar{1}$ with $a = 10.550$ (1) Å, $b = 15.162$ (2) Å, $c = 8.392$ (1) Å, $\alpha = 99.14$ (1)°, $\beta = 111.68$ (1)°, $\gamma = 81.22$ (1)°, $V = 1225.1$ (5) Å^3, and $Z = 2$. Using 2786 reflections and 257 variables, refinement led to $R_1 = 0.026$ and $R_2 = 0.040$. The mean values of important dimensions of the $[Mo_2Cl_8H]^{3-}$ ion are Mo–Mo = 2.371 (1) Å, Mo–Cl$_b$ = 2.492 (4) Å, Mo–Cl$_t$(trans to Cl) = 2.389 (11) Å, Mo–Cl$_t$(trans to H) = 2.489 (15) Å, Mo–H = 1.68 (6) Å, and ∠Mo–H–Mo = 89.6 (3)°. The second compound, $[N(C_2H_5)_4]_2[H_5O_2][Mo_2Cl_8H]$ (**2**), crystallizes in space group *Pnma* with $a = 15.436$ (3) Å, $b = 10.578$ (2) Å, $c = 19.233$ (2) Å, $V = 3140$ (2) Å^3, and $Z = 4$. For the $[Mo_2Cl_8H]^{3-}$ ion, the principal dimensions are Mo–Mo = 2.384 (1) Å, Mo–Cl$_b$ = 2.474 (1) Å, Mo–Cl$_t$(trans to Cl) = 2.398 (4) Å, Mo–Cl$_t$(trans to H) = 2.517 (1) Å, Mo–H = 1.793 (4) Å, and ∠Mo–H–Mo = 83.3 (2)°. Using the average dimensions of the $[Mo_2Cl_8H]^{3-}$ ion calculated from those reported here for structure **2**, an SCF–Xα–SW calculation has been carried out to learn more about the electronic structure of this ion and to make comparisons with the earlier results of Ginsberg on the $[Mo_2Cl_9]^{3-}$ ion.

Introduction

The $[Mo_2X_8H]^{3-}$ ions, X = Cl, Br, were discovered in 1969 and 1973, respectively,[2,3] but only in 1976 was their true identity as μ-H complexes established.[4] In their alkali metal salts these anions occupy sites of $\bar{6}m2$ (D_{3h}) symmetry and are disordered, thus making it impossible to establish their true structures. It was only in 1979[5] that the $[Mo_2Cl_8H]^{3-}$ ion was structurally characterized in a compound, $(C_5NH_6)_3[Mo_2Cl_8H]$, in which there was no crystallographic symmetry greater than its own inherent C_{2v} symmetry (actually, in this instance, no crystallographic symmetry whatever) imposed upon it. It was possible in this case, and also in another compound[6] where a crystallographic mirror plane passes through the midpoint of the Mo–Mo bond, to locate and refine isotropically the μ-H atom. Subsequently we have obtained another compound containing the $[Mo_2Cl_8H]^{3-}$ ion and obtained a third characterization, again including the μ-H atom. In this paper we present that structure as well as a full report on the pyridinium compound, which had been given only in preliminary form earlier, and compare the three independent structures. In addition, because of (a) the chemical importance[7] of the $[Mo_2X_8H]^{3-}$ ions and (b) the peculiar relationship that they have to the $[Mo_2X_9]^{3-}$ ions,[8,9] in which all bridging groups are halide ions (4-electron donors) instead of only two halide ions and an H^- ion (2-electron donor), we wanted to make a detailed comparison of the bonding in the two cases, $[Mo_2Cl_8H]^{3-}$ and $[Mo_2Cl_9]^{3-}$. An SCF–Xα–SW study of the latter has recently been published by Ginsberg,[10] and we have now carried out such a study on $[Mo_2Cl_8H]^{3-}$.

Table I. Crystallographic Parameters

parameter	compd 1	compd 2
space group	$P\bar{1}$	*Pnma*
a, Å	10.550 (1)	15.436 (3)
b, Å	15.162 (2)	10.578 (2)
c, Å	8.392 (1)	19.233 (2)
α, deg	99.14	90.0
β, deg	111.68	90.0
γ, deg	81.22	90.0
V, Å^3	1225.1 (5)	3140 (2)
d_{calcd}, g/cm^3	1.943	1.637
Z	2	4
fw	716.8	774.0
cryst size, mm	0.3 × 0.2 × 0.2	0.6 × 0.3 × 0.2
μ(Mo Kα), cm^{-1}	21.61	14.71
range 2θ, deg	$0 < 2\theta \leqslant 45$	$0 < 2\theta \leqslant 50$
no. of unique data	2952	3834
no. of data, $F_o^2 > 3\sigma(F_o^2)$	2786	2485
no. of variables	257	160
R_1	0.026	0.035
R_2	0.040	0.049
goodness of fit	1.008	1.222
largest shift[a]	0.04	0.01

[a] Ratio of shift to esd of a positional parameter in the last cycle of refinement.

Procedures

Preparations. The two compounds were prepared in practically the same way. $Mo_2(O_2CCH_3)_4$ (0.20 g) was dissolved in 50 mL of hot (60 °C) 12 M hydrochloric acid. To this solution was added either pyridinium hydrochloride (0.20 g) or tetraethylammonium chloride (0.20 g). The solutions were then cooled and evaporated in a stream of nitrogen, giving either dark brown crystals of **1** or yellow-brown crystals of **2**.

Crystal Structure Determinations. These were carried out routinely as described in detail many times before.[11] Data were collected on

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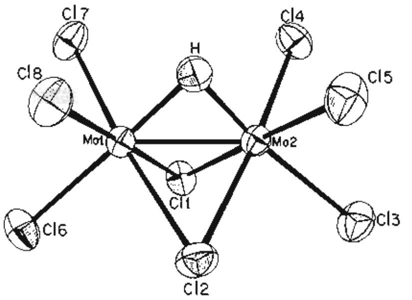

Figure 1. ORTEP drawing of the $[Mo_2Cl_8H]^{3-}$ ion as found in $(C_5NH_6)_3[Mo_2Cl_8H]$ (**1**). Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of its electron density.

an Enraf-Nonius CAD-4 diffractometer; the structures were solved easily by Patterson methods and refined smoothly with use of the standard Enraf-Nonius software. The crystallographic data for both compounds are summarized in Table I. In both cases hydrogen atoms were introduced at calculated positions in the $[C_5NH_6]^+$ and NEt_4^+ ions and assigned isotropic thermal parameters of 5.0 Å^2, but they were not refined. Their contributions to the calculated structure factors were included, and they were shifted after each cycle. Their final positional parameters are available as Tables S1 and S2 in the supplementary material. The hydrogen atoms of the $H_5O_2^+$ ion in **2** could not be located in electron density maps, and they were omitted entirely from the refinement. Anisotropic thermal parameters for all non-hydrogen atoms are listed in supplementary Tables S3 and S4, and the bond lengths and bond angles for the $C_5NH_6^+$ and $N(C_2H_5)_4^+$ ions are listed in Tables S5 and S6. Tables of observed and final calculated structure factors are also included in the supplementary material.

Computational Details. The Xα–SW calculation on $[Mo_2Cl_8H]^{3-}$ was performed analogously to our earlier calculations of Mo_2L_6 complexes.[12] Atomic coordinates were obtained from the crystal structure of **2** and were idealized to C_{2v} symmetry. Sphere radii were chosen with use of the nonempirical scheme of Norman[13] and were very similar to those of the Xα–SW calculation[10] on $[Mo_2Cl_9]^{3-}$. A Watson sphere[14] of radius equal to the outer sphere and with a charge of 3+ was used to stabilize the levels of the anion.

Spherical harmonics through $l = 2$ were used in the basis for the Mo and Cl atoms, and a single $l = 0$ spherical harmonic was the basis for the H atom. Electronic transition energies were obtained with Slater's transition-state formalism[15] in a spin-polarized fashion so as to allow the calculations of singlet rather than multiplet-averaged energies.

A table of atomic coordinates and sphere radii is available as supplementary material.

Structural Results

Compound 1. This pyridinium compound, $(C_5NH_6)_3[Mo_2Cl_8H]$, forms triclinic crystals in the space group $P\bar{1}$. The entire formula unit is the asymmetric unit, and therefore no crystallographic symmetry is imposed on either the cations or the anion. The atomic positional parameters of all non-hydrogen atoms as well as the bridging hydrogen atom in the $[Mo_2Cl_8H]^{3-}$ ion are listed in Table II. The anion is depicted in Figure 1, and the bond lengths and angles are listed in Table III. The bond lengths and angles in the pyridinium cations, which are all normal, are available as supplementary material (Table S5).

Table II. Positional Parameters for All Non-Hydrogen Atoms and the μ-H Atom in Compound 1

atom	*x*	*y*	*z*
Mo(1)	0.73217 (3)	0.83222 (2)	0.33428 (4)
Mo(2)	0.71948 (3)	0.68663 (2)	0.39333 (4)
Cl(1)	0.50345 (9)	0.77269 (7)	0.2260 (1)
Cl(2)	0.73914 (10)	0.81311 (7)	0.6273 (1)
Cl(3)	0.58836 (10)	0.60810 (7)	0.5085 (1)
Cl(4)	0.69137 (11)	0.57412 (7)	0.1492 (1)
Cl(8)	0.95120 (10)	0.88619 (7)	0.4536 (1)
Cl(6)	0.61196 (11)	0.98676 (7)	0.3578 (2)
Cl(7)	0.72199 (11)	0.83527 (7)	0.0456 (1)
Cl(5)	0.93033 (10)	0.61290 (8)	0.5675 (1)
N(1)	0.2740 (4)	0.9623 (3)	0.2089 (5)
N(2)	0.5913 (5)	0.3560 (4)	0.2032 (6)
N(3)	0.1707 (5)	0.5325 (3)	0.2583 (5)
C(1)	0.2882 (5)	0.9569 (3)	0.0591 (7)
C(2)	0.1918 (5)	0.9229 (4)	−0.0832 (6)
C(3)	0.0847 (5)	0.8914 (3)	−0.0711 (7)
C(4)	0.0715 (5)	0.8978 (3)	0.0889 (7)
C(5)	0.1690 (5)	0.9362 (3)	0.2287 (6)
C(6)	0.5215 (4)	0.2883 (3)	0.1877 (5)
C(7)	0.5681 (5)	0.2253 (3)	0.2857 (7)
C(8)	0.6998 (5)	0.2247 (3)	0.4083 (7)
C(9)	0.7756 (5)	0.2915 (3)	0.4226 (6)
C(10)	0.7208 (5)	0.3596 (3)	0.3214 (6)
C(11)	0.2647 (5)	0.5590 (4)	0.2252 (7)
C(12)	0.2327 (6)	0.6235 (4)	0.1151 (7)
C(13)	0.0925 (8)	0.6575 (3)	0.0451 (7)
C(14)	0.0013 (6)	0.6256 (4)	0.0959 (7)
C(15)	0.0440 (5)	0.5637 (4)	0.2005 (7)
H[a]	0.815 (4)	0.725 (2)	0.312 (5)

[a] An isotropic thermal parameter was refined to a value of 3.0 (9) Å^2.

Table III. Bond Distances (Å) and Angles (Deg) in the $[Mo_2Cl_8H]^{3-}$ Ion in $(C_5H_6N)_3[Mo_2Cl_8H]$ (1)

	Distances		
Mo(1)–Mo(2)	2.371 (1)		
–Cl(1)	2.499 (1)	Mo(2)–Cl(1)	2.486 (1)
–Cl(2)	2.494 (1)	–Cl(2)	2.490 (1)
–Cl(6)	2.504 (10)	–Cl(3)	2.474 (1)
–Cl(7)	2.392 (1)	–Cl(4)	2.407 (1)
–Cl(8)	2.370 (1)	–Cl(5)	2.386 (1)
–H	1.742 (4)	Mo(2)–H	1.620 (6)
	Angles		
Mo(1)–H–Mo(2)	89.6 (3)	Cl(1)–Mo(1)–Cl(8)	176.53 (4)
–Cl(1)–Mo(2)	56.81 (2)	Cl(2)–Mo(1)–Cl(7)	174.36 (4)
–Cl(2)–Mo(2)	56.82 (2)	H–Mo(1)–Cl(6)	178.5 (2)
H–Mo(1)–Cl(1)	91.7 (2)	–Cl(7)	83.7 (2)
–Cl(2)	91.8 (2)	–Cl(8)	87.8 (2)
H–Mo(2)–Cl(1)	95.2 (2)	Cl(1)–Mo(1)–Cl(6)	88.22 (4)
–Cl(2)	95.0 (2)	–Cl(7)	91.15 (4)
Cl(1)–Mo(1)–Cl(2)	85.63 (4)	Cl(2)–Mo(1)–Cl(6)	89.68 (4)
–Mo(2)–Cl(2)	86.02 (4)	–Cl(8)	90.95 (4)
Cl(6)–Mo(1)–Cl(7)	94.86 (4)	Cl(1)–Mo(2)–Cl(5)	176.12 (4)
–Cl(8)	92.37 (4)	Cl(2)–Mo(2)–Cl(4)	174.89 (4)
Cl(7)–Mo(1)–Cl(8)	92.20 (4)	H–Mo(2)–Cl(3)	172.3 (2)
Cl(3)–Mo(2)–Cl(4)	91.85 (4)	–Cl(4)	82.5 (2)
–Cl(5)	90.98 (4)	–Cl(5)	84.3 (2)
Cl(4)–Mo(2)–Cl(5)	94.00 (4)	Cl(1)–Mo(2)–Cl(3)	89.90 (4)
		–Cl(4)	89.75 (4)
		Cl(2)–Mo(2)–Cl(3)	91.02 (4)
		–Cl(5)	90.18 (4)

In this case the μ-H atom is not constrained by symmetry to be equidistant from the two Mo atoms, and the two Mo–H distances differ by 0.14 Å. Their mean value, 1.69 Å, is also less, by 0.04–0.10 Å from the Mo–H distances found in the other two compounds (vide infra). The coordinates of the μ-H atom in this structure are probably less accurate than those in the other cases. The other dimensions of the $[Mo_2Cl_8H]^{3-}$ ion are obtained with precision equal to or better than that obtained elsewhere. If C_{2v} symmetry is assumed to be intrinsic to the anion, the Mo–Cl distances within sets of what should be equivalent ones are significantly scattered in view of their individual esd's, all of which are 0.001 Å. Thus, the four bonds

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(11) See, for example, ref 6 and other papers cited therein.

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Table IV. Positional Parameters for all Non-Hydrogen Atoms and the μ-H Atom in Compound **2**

atom	x	y	z
Mo	0.311260	0.362679	0.383147
Cl(1)	0.357306	0.529249	0.297330
Cl(2)	0.179294	0.470854	0.409768
Cl(3)	0.385768	0.463562	0.477880
Cl(4)	0.240980	0.250000	0.285523
Cl(5)	0.446951	0.250000	0.354271
H[a]	0.270235	0.250000	0.444544
O(1)	0.360045	0.750000	0.397900
O(2)	0.475745	0.750000	0.482334
N(1)	0.362612	0.250000	0.703072
C(1)	0.409198	0.364137	0.674169
C(2)	0.371368	0.490532	0.695563
C(3)	0.269897	0.250000	0.679053
C(4)	0.254997	0.250000	0.602277
C(5)	0.361454	0.250000	0.781619
C(6)	0.447797	0.250000	0.816912
N(2)	0.101323	0.750000	0.599135
C(7)	0.068761	0.637348	0.560114
C(8)	0.095881	0.510843	0.591006
C(9)	0.069187	0.750000	0.672895
C(10)	−0.026823	0.750000	0.679691
C(11)	0.198613	0.750000	0.603511
C(12)	0.246559	0.750000	0.538009

[a] An isotropic thermal parameter was refined to a value of 1.63 $Å^2$.

Table V. Bond Distances (Å) and Angles (Deg) in $[N(C_2H_5)_4]_2(H_5O_2)[Mo_2Cl_8H]$ (2)

Distances

Mo–Mo′	2.384 (1)
–Cl(1)	2.517 (1)
–Cl(2)	2.392 (1)
–Cl(3)	2.404 (1)
–Cl(4)	2.474 (1)
–Cl(5)	2.473 (1)
–H	1.793 (4)
O···H···O	2.414 (15)

Angles

Mo–H–Mo′	83.3 (2)	H–Mo–Cl(1)	175.5 (1)
–Cl(4)–Mo′	57.59 (3)	–Cl(2)	82.9 (1)
–Cl(5)–Mo′	57.63 (4)	–Cl(3)	88.0 (2)
H–Mo–Cl(4)	91.4 (2)	Cl(4)–Mo–Cl(1)	87.90 (4)
–Cl(5)	97.3 (1)	–Cl(2)	91.12 (4)
Cl(4)–Mo–Cl(5)	88.21 (5)	–Cl(3)	176.85 (4)
Cl(1)–Mo–Cl(2)	92.63 (4)		
–Cl(3)	92.93 (4)	Cl(5)–Mo–Cl(1)	87.19 (4)
Cl(2)–Mo–Cl(3)	91.88 (4)	–Cl(2)	179.31 (5)
		–Cl(3)	88.79 (5)

to terminal Cl atoms that are trans to bridging Cl atoms range from 2.370 to 2.407 Å in length, and the four bonds to bridging Cl atoms range from 2.486 to 2.499 Å. It is clear, however, that the bridge bonds are significantly longer than those to the terminal Cl atoms trans to them, by about 0.10 Å. The two bonds to terminal Cl atoms that are trans to μ-H are about as long as the bonds to bridging Cl atoms. Thus, it is evident that the μ-H atom has a considerable structural trans effect, which is ca. 0.10 Å greater than that of Cl.

Compound 2. In this compound, with only four formula units in an orthorhombic unit cell belonging to the space group *Pnma*, the NEt_4^+ cations and the $[Mo_2Cl_8H]^{3-}$ anion are each bisected by the mirror planes at $b = {}^1/_4$ and ${}^3/_4$. The positional parameters for all non-hydrogen atoms as well as μ-H are listed in Table IV, and the bond lengths and angles for the anion as well as the O···O distance in the $H_5O_2^+$ ion are reported in Table V. Bond lengths and angles in the NEt_4^+ ions are available as supplementary material (Table S6).

The symmetry plane contains the μ-H and μ-Cl atoms, Cl(4) and Cl(5), of the anion. The terminal chlorine atoms are numbered Cl(1) (trans to μ-H), Cl(2) (trans to Cl(5)), and Cl(3) (trans to Cl(4)). The structure is essentially identical with that in compound **1** except for the rigorous mirror symmetry, and no drawing is given.

Table VI. Some Mean Dimensions of the $[Mo_2Cl_8H]^{3-}$ Ion in Three Compounds and Grand Average Values[a]

dimens[b]	1[c]	2[c]	3[d]	grand av
Mo–Mo, Å	2.371 (1)	2.384 (1)	2.375 (2)	2.377 [4]
Mo–H, Å	1.74	1.793 (4)	1.728 (2)	1.73 [3]
	1.62			
Mo–H–Mo, deg	89.6 (3)	83.3 (2)	86.8 (1)	86.6 [20]
Mo–Cl_b, Å	2.499 (1)	2.474 (1)	2.466 (3)	2.477 [4]
	2.494 (1)			
	2.486 (1)	2.473 (1)	2.465 (3)	
	2.490 (1)			
Mo–$Cl_{t,Cl}$, Å	2.407 (1)	2.392 (1)	2.393 (2)	2.394 [3]
	2.386 (1)			
	2.392 (1)	2.404 (1)	2.395 (3)	
	2.370 (1)			
Mo–$Cl_{t,H}$, Å	2.504 (1)	2.517 (1)	2.500 (3)	2.502 [7]
	2.474 (1)			

[a] Numbers in brackets are variances, obtained from the expression $[(\Sigma\Delta_i^2)/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value from the arithmetic mean and n is the total number of values averaged. Values duplicated by symmetry were counted twice. [b] Cl_b is a bridging chlorine atom. $Cl_{t,Cl}$ and $Cl_{t,H}$ are terminal chlorine atoms trans to Cl_b and H, respectively. [c] This work. [d] Reference 6.

Table VII. Correlation of the Orbital Energies of the Mo-Based Orbitals of $[Mo_2Cl_9]^{3-}$ and $[Mo_2Cl_8H]^{3-}$

$[Mo_2Cl_9]^{3-}$		$[Mo_2Cl_8H]^{3-}$	
orbital	energy, eV	orbital	energy, eV
23e′	−2.45	$14a_1$	−1.96
		$10b_2$	−2.83
18e″	−2.84	$11b_1$	−2.82
		$8a_2$	−2.86
$18a_2$″	−3.78	$10b_1$	−3.45
17e″	−5.22	$7a_2$	−4.43
		$9b_1$	−4.92
22e′[a]	−5.48	$13a_1$[a]	−5.41
		$9b_2$	−5.99
$21a_1$′	−6.60	$12a_1$	−6.93

[a] Highest occupied molecular orbital.

Comparison of Structures. There are now three independent structural studies providing dimensions for the $[Mo_2Cl_8H]^{3-}$ ion. In addition to compounds **1** and **2** reported here, there is the structure of the compound $[N(C_2H_5)_4]_3(H_5O_2)[Mo_2Cl_8H][MoCl_4O(H_2O)]$ (**3**) described elsewhere.[6] In Table VI some of the critical dimensions of the $[Mo_2Cl_8H]^{3-}$ ion as found in these three compounds are listed for comparison and grand average values given.

Variations in the Mo–Mo distance from one compound to another are statistically significant only in the case of compound **1** vs. **2**, but as far as chemical significance is concerned, this bond length is essentially constant at 2.377 [7] Å. This is effectively identical with that in $Rb_3[Mo_2Cl_8H]$, 2.38 (1) Å, where the anion is disordered on a site of D_{3h} symmetry.[2] It is far shorter than the Mo–Mo distances found for the $[Mo_2Cl_9]^{3-}$ ion in $Cs_3[Mo_2Cl_9]$,[10] 2.66 (1) Å, and in $K_3[Mo_2Cl_8H]$, 2.53 (1) Å. We shall discuss this point further below in connection with the electronic structure calculations.

The Mo–H distance and Mo–H–Mo angle show the widest variation and the variances, 0.06 Å for the former and 3° for the latter, probably give a reasonable approximation to the proper esd's for the mean values of 1.75 Å and 86.6°, respectively. It is still one of our objectives to obtain suitable crystals for a neutron diffraction study to establish these dimensions of the Mo–H–Mo unit with more accuracy.

Table VIII. Converged Valence Orbital Energies (eV) and Atomic Spheres Populations (percent)

orbital	*E*	Mo	H	Cl_b	$Cl_{t,H}$	$Cl_{t,Cl}$	inner sphere	outer sphere
$14a_1$	−1.958	30	4	5	4	8	29	20
$11b_1$	−2.822	68	0	5	11	7	3	4
$10b_2$	−2.829	52	0	17	0	20	5	5
$8a_2$	−2.858	63	0	7	0	22	3	4
$10b_1$	−3.450	78	0	2	4	7	8	1
$7a_2$	−4.431	78	0	5	3	6	7	1
$9b_1$	−4.918	76	0	1	4	10	7	1
$13a_1$ (HOMO)	−5.415	68	0	10	0	10	9	1
$9b_2$	−5.990	66	0	6	6	12	9	1
$12a_1$	−6.931	42	3	6	13	27	5	3
$6a_2$	−7.573	0	0	13	23	52	8	3
$8b_1$	−7.621	1	0	21	47	20	6	4
$8b_2$	−7.622	0	0	10	11	67	9	2
$11a_1$	−7.673	9	4	3	54	21	5	5
$5a_2$	−7.763	0	0	1	36	50	10	3
$10a_1$	−7.777	2	1	21	46	19	5	6
$7b_2$	−7.822	1	0	8	37	41	10	3
$7b_1$	−8.043	3	0	9	21	55	9	4
$4a_2$	−8.123	3	0	12	7	65	10	3
$6b_2$	−8.134	3	0	44	2	38	10	3
$9a_1$	−8.342	14	1	12	21	42	4	6
$5b_2$	−8.579	6	0	17	22	39	12	3
$6b_1$	−8.657	10	0	1	22	50	13	3
$5b_1$	−8.725	13	0	0	56	19	2	9
$8a_1$	−8.820	6	0	18	7	55	10	4
$3a_2$	−9.034	12	0	12	13	51	8	4
$4b_2$	−9.046	13	0	34	8	28	14	2
$4b_1$	−9.079	11	0	5	7	64	8	4
$7a_1$	−9.219	33	0	2	14	36	12	2
$6a_1$	−9.689	14	0	45	4	17	17	1
$3b_1$	−9.753	13	0	43	5	26	10	2
$2a_2$	−9.782	24	0	40	5	22	6	2
$5a_1$	−10.364	25	2	44	1	19	7	2
$3b_2$	−10.644	35	0	41	0	21	1	1
$4a_1$	−11.758	48	37	2	8	1	2	1
$2b_1$	−19.680	1	0	0	91	3	0	5
$3a_1$	−19.688	other essentially pure Cl 2s orbitals (like $2b_1$)						
$1a_2$	−19.839							
$2b_2$	−19.846							
$2a_1$	−19.927							
$1b_1$	−19.985							
$1b_2$	−20.546							
$1a_1$	−20.687							

The general pattern of variation in the Mo–Cl distances is consistent with C_{2v} symmetry, degraded by packing forces in crystal environments of lower than C_{2v} symmetry. The general relationships among Mo–Cl bond lengths, in the notation of Table VI, are as follows: Mo–$Cl_{t,Cl}$ < Mo–$Cl_{t,H}$ by about 0.11 [2] Å; Mo–$Cl_{t,Cl}$ < Mo–Cl_b by about 0.08 [2] Å; Mo–$Cl_{t,H}$ ≈ Mo–Cl_b.

Bond angles at the Mo atoms do not deviate by more than ±3° from 90° except for those involving μ-H, but the uncertainties in these are surely underestimated by the calculated esd's, and it is not profitable to discuss them further.

The $H_5O_2^+$ Ion in 2. The $H_5O_2^+$ ion has been observed many times[16] and in several cases has been definitely characterized by neutron diffraction.[17-21] In general the O···O distances fall in the range 2.40–2.45 Å, although there are two reports of shorter ones, viz., 2.370 (5)[21] and 2.336 (14) Å.[6] In compound **2** the O···O distance, 2.414 (15) Å, is in the typical range and therefore requires no special comment.

Computational Results

The replacement of a bridging Cl ligand in $[Mo_2Cl_9]^{3-}$ by an H ligand raises the following questions regarding the electronic structure of $[Mo_2Cl_8H]^{3-}$. (1) To what extent is the reduction in molecular symmetry from essentially D_{3h} to C_{2v} reflected in the symmetry of the molecular orbitals? (2) Is the interaction of the H atom with the dinuclear unit localized or are the interactions of all three bridging ligands delocalized over a number of MO's? (3) What is the effect on the electron distribution and energetics of the central $Mo_2(\mu_3\text{-}X)_3$ grouping of replacing one 4 e ligand, Cl, with a 2 e ligand, H? (4) To what extent is the shortening of the Mo–Mo bond in the $[Mo_2Cl_8H]^{3-}$ anion relative to that in $[Mo_2Cl_9]^{3-}$ due to electronic effects?

The first question may be answered by looking at the splitting of the degenerate e′ and e″ orbitals of $[Mo_2Cl_9]^{3-}$ upon symmetry reduction to C_{2v}; such an analysis is similar to that carried out for $Co(CO)_3NO$ vs. $Ni(CO)_4$ and $Mn(CO)_4NO$ vs. $Fe(CO)_5$.[22] Under the coordinate system used for the calculation on $[Mo_2Cl_8H]^{3-}$, the representations of D_{3h} symmetry correlate as

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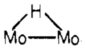
D_{3h}	C_{2v}	D_{3h}	C_{2v}
a_1'	a_1	a_1''	a_2
a_2'	b_2	a_2''	b_1
e'	$a_1 + b_2$	e''	$a_2 + b_1$

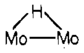
The principally metal-based MO's of the calculations on $[Mo_2Cl_9]^{3-}$ and $[Mo_2Cl_8H]^{3-}$ are compared in Table VII. It is seen that the ordering of MO energies is nearly the same, although the 22e′, 17e″, and 23e′ MO's of $[Mo_2Cl_9]^{3-}$ split by 0.5–0.8 eV upon symmetry reduction. The 18e″ orbital does not split much, consistent with its description as an antibonding orbital. It is apparent that the substitution of a bridging H ligand does perturb the electronic symmetry of the molecule but not enough to influence profoundly the ordering of the MO's.

A list of all filled MO's for $[Mo_2Cl_8H]^{3-}$ excluding the krypton cores of the molybdenum atoms and the neon cores of the chlorine atoms is presented in Table VIII, which also includes the lowest seven unoccupied MO's, all of which have major contributions from the molybdenum atoms.

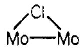
On the basis of the partitioning of each MO into the spatial regions defined by the atomic spheres, the bridging hydrido ligand contributes no more than 4% to any filled orbital except the $4a_1$ MO. This MO, which has an energy of −11.76 eV, is energetically between the Cl 3p and 3s levels and is roughly 48% Mo and 37% H in character. It represents a strong interaction between the Mo–Mo π-bonding orbital and the H 1s orbital in the Mo–H–Mo plane. Taking this together with the $13a_1$ MO, which is also Mo–Mo π bonding, we propose that the



interaction is essentially a three-center 4-electron one and essentially divorced from the Mo–Cl_b and Mo–Cl_t interactions. In fact, the strong mixing of Mo–H–Mo and Mo–Mo bonding has no parallel in the results for $[Mo_2Cl_9]^{3-}$. We believe, therefore, that the



interaction is stronger than that in



and that this additional strength is mainly responsible for the shorter Mo–Mo bond lengths in $[Mo_2Cl_8H]^{3-}$ systems.

Replacement of the bridging Cl ligand with a bridging H ligand affects the relative energetics of the bridging and terminal Cl ligands as well. In the calculation on $[Mo_2Cl_9]^{3-}$ it is noted that the nonbonding 3p and 3s orbitals on the bridging Cl ligands have a more negative effective charge. In $[Mo_2Cl_8H]^{3-}$ the opposite is the case; the nonbonding orbitals of the bridging Cl ligands are lower in energy than those of the terminal ligands. Thus, it would appear that the bridging Cl ligands in $[Mo_2Cl_8H]^{3-}$ are more effective charge donors than are the terminal ligands, probably as a result of decreased donor competition due to the bridging H ligand.

Structural comparison of $[Mo_2Cl_9]^{3-}$ and $[Mo_2Cl_8H]^{3-}$ shows two significant bond length changes: The Mo–Mo bond shortens by at least 0.20 Å while the Mo–$Cl_{t,H}$ bond lengthens. We believe that both of these changes are due in part to electronic effects in the hydrido bridging system. The strong bonding of the H ligand to the Mo atoms, in conjunction with its smaller size, should in effect "pull" the Mo atoms closer together. Additionally, the absence of p lone pairs on the H ligand does not allow it to donate charge into Mo–Mo antibonding orbitals, as a bridging Cl does. Such differences in the interactions of lone pairs with Mo–Mo antibonding orbitals has recently been shown to be an important factor in the Mo–Mo bond lengths of oxo-bridged Mo trimers.[23] The trans influence of the H ligand on the terminal Cl ligands is reminiscent of the same effect on axial ligands bound to dimetal units, particularly dirhodium tetracarboxylates.[24,25] We believe the source of the trans influence in the systems at hand is similar, namely, the stronger Mo–H bonding makes donation from a ligand trans to the H ligand both energetically and spatially less favorable.

It is apparent that the stronger Mo–Mo interaction in $[Mo_2Cl_8H]^{3-}$ than in $[Mo_3Cl_9]^{3-}$ should affect the spectroscopic and magnetic properties of it. The HOMO–LUMO separation in the hydrido species is about twice as great as that in $[Mo_2Cl_9]^{3-}$, a reflection of the greater bonding and antibonding natures of the HOMO and LUMO, respectively. A spin-polarized calculation of the lowest allowed excitation, $^1B_1 \leftarrow {}^1A_1$ ($13a_1 \rightarrow 9b_1$) yields a predicted value of 6300 cm^{-1} for this transition. Attempts to observe this low-energy band in these laboratories were made, but sample decomposition to intensely green $MoOCl_4$ did not allow definitive spectroscopic data to be obtained.

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Registry No. $(C_5NH_6)_3[Mo_2Cl_8H]$, 69706-30-5; $[N(C_2H_5)_4]_2[H_5O_2][Mo_2Cl_8H]$, 82598-71-8; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of structure factors for both structures, positional parameters of hydrogen atoms, anisotropic parameters of hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, bond lengths and angles in the $C_5NH_6^+$ and $N(C_2H_5)_4^+$ ions, and atomic coordinates and other input for the SCF–Xα–SW calculation (30 pages). Ordering information is given on any current masthead page.

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