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A Complex Reaction Product of Dimolybdenum Tetraacetate with Aqueous Hydrochloric Acid. Structural Characterization of the Hydrido-Bridged $[Mo_2Cl_8H]^{3-}$ Ion, the $[Mo(O)Cl_4(H_2O)]^-$ Ion, and an $H_5O_2^+$ Ion with an Exceptionally Short Hydrogen Bond

Avi Bino and F. Albert Cotton*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843.

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Abstract: From a solution prepared by dissolving $Mo_2(O_2CCH_3)_4$ in 12 M HCl and heating to 70 °C in air followed by addition of tetraethylammonium chloride, deep yellow crystals of $[(C_2H_5)_4N]_3(H_5O_2)[Mo_2Cl_8H][MoCl_4O(H_2O)]$ are slowly deposited. This compound was identified and fully characterized by X-ray crystallography. It contains three entities of structural interest. First, the diaquahydrogen ion, $H_5O_2^+$, occurs here with an O···H···O distance shorter by ca. 0.07 Å than any previously reported in this ion; indeed, at 2.34 (1) Å, it is comparable to the few shortest O···H···O bonds known. Second, the $[Mo_2Cl_8H]^{3-}$ ion, with a μ-H atom, is here found in an ordered condition and the hydrogen atom has been located and refined in one of the bridging positions; the Mo-H distances are 1.73 Å. Third, a full structural description of the $[trans\text{-}MoCl_4O(H_2O)]^-$ ion is given. The Mo═O distance is 1.66 (1) Å while Mo—OH_2 is 2.33 (1) Å. This remarkable compound forms orthorhombic crystals, space group *Pnma*, with $a = 26.785$ (7) Å, $b = 10.454$ (2) Å, $c = 16.874$ (4) Å, $V = 4725$ (2) Å,^{3} and $Z = 4$. Using 1868 reflections having $I > 3\sigma(I)$ the structure was refined to discrepancy indices of $R_1 = 0.046$ and $R_2 = 0.064$ and a goodness-of-fit index of 1.35.

Introduction

In the first structural-chemical studies of reactions of the quadruply bonded dimolybdenum tetraacetate with aqueous hydrochloric acid the desired result was the preparation and characterization of the $[Mo_2Cl_8]^{4-}$ ion, and this was accomplished about 10 years ago by a suitable choice of reaction conditions.[1] It was noted at the same time that under other

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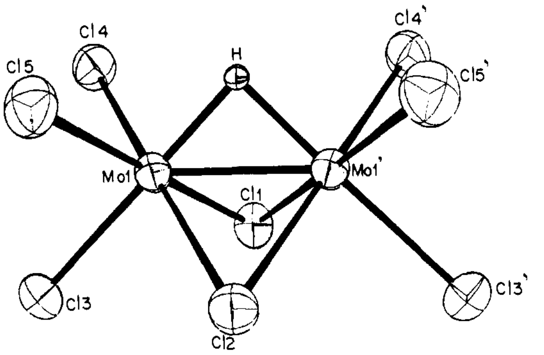


Figure 1. The $[Mo_2Cl_8H]^{3-}$ ion, showing the atom numbering scheme.

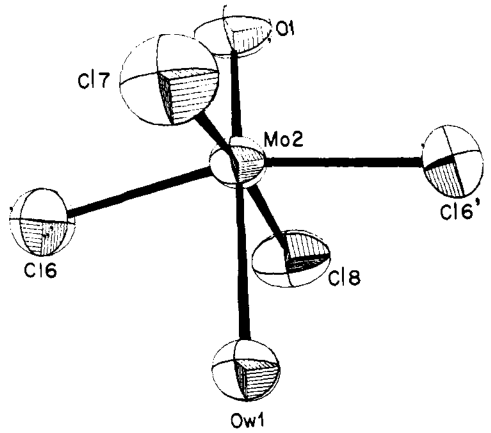


Figure 2. The $[MoCl_4O(H_2O)]^-$ ion, showing the atom numbering scheme.

conditions, particularly at higher temperature, limited oxidation of the metal occurred and other products were obtained. In fact, only a few months after the $Mo_2Cl_8^{4-}$ ion was first reported, compounds to which the formulas $M^I_3Mo_2Cl_8$ were assigned were described and the structure of "$Rb_3Mo_2Cl_8$" was presented in detail.[2] It was a distinctly curious feature of this structure that the "$Mo_2Cl_8^{3-}$ " ion was located on a site of $\overline{6}\,m2$ symmetry and two μ-Cl atoms were disordered over three positions; the structure was qualitatively identical with that of the $M^IMo_2Cl_9$ compounds except for the $\frac{2}{3}$ occupancy of the bridging positions. It was later found that "$Cs_2Mo_2Br_8$" and other "$M^I_3Mo_2Br_8$" compounds were analogous structurally.[3] There was, however, a remarkable and important quantitative difference between the $M^I_3Mo_2X_9$ compounds and these "$M^I_3Mo_2X_8$" compounds: the latter have Mo-Mo distances that are 0,3-0.4 Å shorter than those in their $M^I_3Mo_2X_9$ analogues.

This curious situation was greatly illuminated by the recent demonstration that the "$Mo_2X_8^{3-}$ " ions are actually $Mo_2X_8H^{3-}$ ions.[4,5a] The "vacant" bridging position is not in fact vacant but occupied by a bridging hydrogen—or, better, hydride ion. However, because of the disordering of the μ-H and μ-X atoms only indirect chemical and spectroscopic proofs of the reality of μ-H were possible.

Recently, in an effort to account for what appeared to be curious chemical and structural properties of a substance with the apparent composition "$W_4(OPr\text{-}i)_{14}$", it was hypothesized that this too contained bridging hydrogen atoms (being, thus, $W_4(OPr\text{-}i)_{14}H_2$) and this notion stimulated studies that have led to the direct observation of the bridging hydrogen atoms in $W_4(OPr\text{-}i)_{14}H_2$[6] as well as in the $[Mo_2X_8H]^{3-}$ ions and the approximate measurement of their positions by X-ray diffraction.

In the case of the $[Mo_2X_8H]^{3-}$ ions what was clearly needed were compounds in which this unit would be present in an ordered fashion with the μ-H in an unobscured position, accessible to direct observation. A number of such compounds have now been obtained and structurally investigated.[7] When the cation used is tetraethylammonium, complex substances are obtained. The one reported here has allowed full characterization of the $[Mo_2Cl_8H]^{3-}$ ion but, in addition, it provides two other interesting subjects for study: the $[MoCl_4O(H_2O)]^-$ ion and the diaquahydrogen ion, $H_5O_2^+$, the latter in an unprecedented form with a hydrogen-bonded O···O distance far shorter than any previously observed for this species and about as short as *any* other O···H···O type hydrogen bond ever reported.

Experimental Section

Preparation. $Mo_2(O_2CCH_3)_4$ (0.1 g), prepared by a literature method,[8] was dissolved in 25 mL of 12 M HCl. The solution was stirred and heated to ca. 70 °C. $(C_2H_5)_4NCl$ (0.2 g) was added and the solution was left to stand in an open beaker. After 7 days deep yellow crystals which had formed were collected; yield 80 mg. These crystals appear to be stable indefinitely in the normal laboratory atmosphere.

X-ray Crystallography. A crystal of dimensions 0.1 × 0.1 × 0.2 mm was attached to the end of a glass fiber and mounted on a Syntex P$\overline{1}$ four-circle diffractometer. Mo Kα (λ = 0.710 730 Å) radiation, with a graphite crystal monochromator in the incident beam, was used.

Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the orthorhombic system, space group *Pnma* or *Pna*2$_1$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range 25° $< 2\theta <$ 35° giving a = 26.785 (7) Å, b = 10.454 (2) Å, c = 16.874 (4) Å, and V = 4725 (2) Å^3. With these dimensions and Z = 4 (for the formula $Mo_3Cl_{12}O_4N_3C_{24}H_{68}$, mol wt 1176.08) the density is calculated to be 1.653 g/cm^3. The density determined by flotation in a mixture of carbon tetrachloride and acetone was 1.61 ± 0.05 g/cm^3.

Data were measured by θ-2θ scans. A total of 1973 reflections in the range 0° $< 2\theta <$ 45° were collected of which 1868 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.[9] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 14.72 cm^{-1}; no absorption correction was applied.

The heavy atoms positions were obtained from a three-dimensional Patterson function. The structure was refined[10] in space group *Pnma* to convergence using anisotropic thermal parameters for all the metal atoms, the chlorine atoms, and the oxygen atoms. The rest of the atoms were refined using isotropic temperature parameters. The centric space group *Pnma* rather than the acentric *Pna*2$_1$ was chosen (a) because the statistics indicated a centric space group and (b) on the basis of the distribution of peaks in the Patterson function. It is confirmed by the successful refinement.

The discrepancy indices, $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/\Sigma w|F_o|^2$ had final values of R_1 = 0.046 and R_2 = 0.064 with a goodness-of-fit parameter equal to 1.35. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results

The positions and thermal parameters of all atoms are listed in Table I. The structure contains two kinds of cation; (1) $N(C_2H_5)_4^+$, of which there are three crystallographically independent ones; (2) the diaquahydrogen ion, $H_5O_2^+$, which lies on a special position such that both oxygen atoms and the shared hydrogen atom must be on a mirror plane at $y = \frac{1}{4}$. It also contains two kinds of anion; (1) the $[MoCl_4O(H_2O)]^-$ ion, which has crystallographic mirror symmetry and deviates only slightly from $C_{4v}(4m)$ symmetry; (2) the $[Mo_2Cl_8H]^{3-}$ ion, which also has mirror symmetry and, within the uncertainties, $C_{2v}(mm)$ symmetry. The $N(C_2H_5)_4^+$ ions are of no particular interest and require no discussion. One $(N(C_2H_5)_4^+$ ions was

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	X	Y	Z	$B(1.1)$	atom	X	Y	Z	$B(1.1)$
Mo(1)	0.15914(3)	0.13641(9)	0.12567(5)	2.31(3)	C(14)	0.3117(10)	0.750(0)	0.1900(15)	8.4(7)
Mo(2)	0.90552(5)	0.25000(0)	0.31786(9)	2.37(6)	C(15)	0.2136(7)	0.750(0)	0.3560(10)	4.2(4)
Cl(1)	0.2006(1)	0.2500(0)	0.2355(2)	3.2(2)	C(16)	0.2107(9)	0.750(0)	0.4499(14)	7.5(6)
Cl(2)	0.0812(1)	0.2500(0)	0.1585(3)	2.6(2)	C(31)	0.1580(6)	0.424(2)	0.4812(10)	7.8(4)
Cl(3)	0.1340(1)	−0.0312(3)	0.2236(2)	3.8(1)	C(32)	0.0382(7)	0.436(2)	0.4021(11)	8.1(5)
Cl(4)	0.2362(1)	0.0299(3)	0.0976(2)	3.2(1)	C(33)	0.0515(10)	0.340(3)	0.4759(16)	5.2(6)
Cl(5)	0.1183(1)	0.0292(3)	0.0182(2)	4.4(1)	C(34)	0.1143(10)	0.325(3)	0.5085(16)	4.9(6)
Cl(6)	0.8923(1)	0.0273(3)	0.3234(2)	5.8(2)	C(35)	0.0796(10)	0.323(3)	0.3685(16)	5.4(6)
Cl(7)	0.9177(2)	0.2500(0)	0.4581(3)	4.3(2)	C(36)	0.1412(10)	0.343(3)	0.4099(16)	5.1(6)
Cl(8)	0.8757(2)	0.2500(0)	0.1857(3)	5.4(2)	H	0.677(4)	0.2500(0)	0.443(6)	1.(2)
O(1)	0.9653(4)	0.2500(0)	0.2928(7)	2.9(5)					
Ow(1)	0.8210(4)	0.2500(0)	0.3517(7)	3.3(5)	$B(2.2)$	$B(3.3)$	$B(1.2)$	$B(1.3)$	$B(2.3)$
Ow(2)	0.3232(7)	0.2500(0)	0.4869(11)	11(1)	1.93(3)	2.55(3)	−0.06(4)	0.23(3)	0.05(4)
Ow(3)	0.3336(5)	0.2500(0)	0.6243(8)	8.3(8)	3.26(6)	3.84(7)	0	0.23(6)	0
N(1)	0.4939(5)	0.7500(0)	0.3405(7)	2.7(3)	2.7(2)	3.1(2)	0	−0.7(1)	0
N(2)	0.2688(5)	0.7500(0)	0.3268(8)	4.0(3)	2.9(2)	4.4(2)	0	0.5(2)	0
N(3)	0.0960(5)	0.2500(0)	0.4423(8)	3.6(3)	3.0(1)	3.6(1)	−0.5(1)	0.4(1)	0.5(1)
C(1)	0.4599(4)	0.635(1)	0.3464(7)	3.6(2)	2.9(1)	4.9(1)	0.6(1)	0.9(1)	0.1(1)
C(2)	0.4878(5)	0.504(1)	0.3448(8)	5.0(3)	3.6(1)	3.5(1)	−0 4(1)	−0.7(1)	−0.4(1)
C(3)	0.5326(6)	0.750(0)	0.4069(10)	3.7(4)	3.3(1)	7.7(2)	0.5(1)	1.8(2)	0.3(2)
C(4)	0.5096(8)	0.750(0)	0.4923(13)	6.0(5)	8.5(3)	4.2(2)	0	0.1(2)	0
C(5)	0.5237(6)	0.750(0)	0.2636(10)	3.3(3)	7.5(3)	4.5(2)	0	−0.9(2)	0
C(6)	0.4915(7)	0.750(0)	0.1890(11)	5.0(4)	7.2(8)	4.6(6)	0	0.8(5)	0
C(11)	0.2994(5)	0.633(1)	0.3557(9)	6.1(3)	3.8(6)	6.0(6)	0	0.8(5)	0
C(12)	0.2741(6)	0.502(2)	0.3312(9)	6.8(4)	13(1)	5.1(8)	0	0.6(8)	0
C(13)	0.2617(7)	0.750(0)	0.2363(12)	4.8(4)	3.9(6)	7.0(7)	0	−1.0(7)	0

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

Table II. Bond Lengths and Bond Angles in the $[Mo_2Cl_8H]^{3-}$ Ion

bond lengths, Å		bond angles, deg	
Mo(1)-Mo(1)′	2.375(2)	Cl(1)-Mo(1)-Cl(2)	88.9(1)
Cl(1)	2.466(3)	Cl(3)	87.8(1)
Cl(2)	2.465(3)	Cl(4)	89.1(1)
Cl(3)	2.500(3)	Cl(5)	179.1(1)
Cl(4)	2.393(2)	H	92.5(1)
Cl(5)	2.395(3)	Cl(2)-Mo(1)-Cl(3)	87.8(1)
H	1.728(2)	Cl(4)	178.0(1)
		Cl(5)	90.5(1)
bond angles, deg		H	93.4(1)
Mo(1)-Cl(1)-Mo(1)′	57.58(8)	Cl(3)-Mo(1)-Cl(4)	92.1(1)
Cl(2)-Mo(1)′	57.59(8)	Cl(5)	92.8(1)
H-Mo(1)′	86.8(1)	H	178.8(1)
		Cl(4)-Mo(1)-Cl(5)	91.5(1)
		H	86.7(1)
		Cl(5)-Mo(1)-H	86.9(1)

Table III. Bond Lengths and Bond Angles in the $[MoCl_4O(H_2O)]^-$ Ion

bond lengths, Å		bond angles, deg	
Mo(2)-Cl(6)	2.357(3)	O(1)-Mo(2)-Cl(6)	98.9(1)
Cl(7)	2.389(5)	Cl(7)	96.9(4)
Cl(8)	2.368(5)	Cl(8)	94.9(4)
O(1)	1.657(9)	O(W1)	179.4(5)
O(W1)	2.333(13)	Cl(6)-Mo(2)-Cl(6)	162.1(2)
		Cl(7)	88.9(1)
		Cl(8)	89.2(1)

subjected to twofold disorder, but otherwise all atoms in these ions refined uneventfully to give unremarkable results. Their bond distances and angles are listed in a table included in the supplementary material.

The $H_5O_2^+$ ion and the anions are each of unusual interest and will be discussed in some detail. The $[Mo_2Cl_8H]^-$ and $[MoCl_4O(H_2O)]^-$ ions are depicted in Figures 1 and 2, respectively, and their internal dimensions are listed in Tables II and III, respectively.

Discussion

The $[Mo_2Cl_8H]^{3-}$ Ion. This work was begun with the objective of obtaining the best possible X-ray crystallographic characterization of this ion and the other interesting structural elements came as unexpected bonuses. It is, therefore, fitting to discuss the $[Mo_2Cl_8H]^{3-}$ ion first. As indicated in the Introduction, an ion of this composition is of unusual interest, but the previous structural work was incapable of either providing exact information on the position of the hydrogen atom or giving the intrinsic structure (whose symmetry could be no higher than *mm*) of the ion. Both of these features were obscured by the disordering of the ion on a site of high symmetry ($\bar{6}m2$). We now have direct and accurate information on both of these points.

From Figure 1 and Tables II and IV it can be seen that the ion has $C_{2v}(mm)$ symmetry to well within the experimental uncertainties. One of the two mirror planes is a rigorous, crystallographic one; it contains the three bridging atoms, H, Cl(1), and Cl(2). The other one should contain Cl(3), Mo(1), H, Mo(1)′, and Cl(3)′. The equation for the plane containing the two metal atoms, Cl(3) and Cl(3)′, which is necessarily perpendicular to the crystallographic mirror plane, was determined and the deviations of Cl(1), Cl(2), Cl(4), Cl(5), and H from it were calculated. These results are presented in Table IV. The pairs of distances from this plane to Cl(4) and Cl(5) and to Cl(1) and Cl(2) are virtually identical and the H atom lies in the plane to within the experimental uncertainties.

It is also found that pairs of Mo-Cl distances that should be equal under *mm* symmetry are identical within the errors. Thus, we have the Mo-Cl(1) and Mo-Cl(2) distances with values of 2.465 (3) and 2.466 (3) Å while the Mo-Cl(4) and Mo-Cl(5) distances are 2.393 (2) and 2.395 (3) Å.

The position of the bridging hydrogen atom is clearly defined. Its distance from each of the Mo atoms is 1.728 (2) Å

Table IV. The Virtual Symmetry Plane in $[Mo_2Cl_8H]^{3-}$ and Deviations from It

equation of plane defined by Mo(1), Mo(1)′, Cl(3):
$0.9261X + 0.3772Z + 4.7474 = 0$

atom	deviation, Å
H	−0.02(11)
Cl(1)	−1.728(4)
Cl(2)	1.725(4)
Cl(4)	−1.733(3)
Cl(5)	1.697(3)

according to the least-squares refinement in which it is assigned an isotropic thermal vibration parameter, which refined to the very reasonable value of 1 (2) Å². We doubt if this type of investigation, using X-ray data, is capable of affording a truly meaningful estimate of the uncertainty in the position of a hydrogen atom and we therefore caution that the esd for the Mo-H distance should not be accorded the same status as the esd's for other bond lengths. An esd of perhaps 0.02 Å, that is, ten times higher, might be a more realistic estimate of the reliability of the result. The angle Mo-H-Mo is found to be 86,8 (1)° but again a larger error range, perhaps ±1.0°, would be more credible.

One of the most important features of our results for the $[Mo_2Cl_8H]^{3-}$ ion, second only to the fact that they provide direct evidence for the presence of a bridging hydrogen atom (and show its position with fair accuracy), is that they show the true structure of the anion. In previous work the disordering of these ions on sites of $\bar{6}m2$ symmetry concealed completely the interesting and highly important variation among the terminal Mo-Cl distances. There is now seen to be a very strong trans effect by the μ-H atom, so that the chlorine atoms trans to μ-H have Mo-Cl bond distances ca. 0.10 Å greater than those trans to μ-Cl atoms. Indeed, the Mo-Cl(3) distances are even longer than the Mo-(μ-Cl) distances, by ca. 0.03 Å.

Our results concerning the position of the μ-H atom should be compared with the prediction made from the vibrational spectrum by Katovic and McCarley.[5] These authors, who were the first to observe both the symmetric and the antisymmetric ν(Mo-H) modes, employed a simplified vibrational analysis, in which certain elements of the kinetic energy matrix were neglected or approximated, to estimate the Mo-H-Mo angle, for which they derived a value of 77.6°. This, in conjunction with the known Mo-Mo distance, allowed them to estimate the Mo-H distance as 1.90 Å. It seems to us unlikely, but not impossible, that our results could be in error by enough to account for the difference between our results and these estimates, We are optimistic that crystals sufficiently large for neutron diffraction study can be obtained in the near future and feel it unproductive to carry the discussion further at this time except for one additional comment. In view of the large trans effect of μ-H just noted, it is clear that there *may* be a significant interaction constant between ν(Mo-H) and ν(Mo-Cl) vibrations, whereas the vibrational analysis used to make the estimates did not allow for this. In other words, the explicit approximations made may have been satisfactory but this implicit (and seemingly reasonable) one may not be.[5b]

Finally, one must again[3] comment on the fact that the replacement of *one* μ-Cl by μ-H, in going from $[Mo_2Cl_9]^{3-}$ to $[Mo_2Cl_8H]^{3-}$, causes an enormous contraction, 0.28 Å, in the Mo-Mo distance. The fact that the Mo-H-Mo system must be a three-center, two-electron bond whereas an Mo-Cl-Mo unit may contain, and probably does contain, a three-center, four-electron bond should be carefully noted in this context. We shall defer analysis of this problem until we have completed a projected study of the $[Mo_2Br_8H]^{3-}$ ion, where an even larger effect of the same kind is observed.

The $[MoOCl_4(H_2O)]^-$ Ion. This important type of complex has been structurally characterized in several other compounds, but only within the last few years. In the present case it has a crystallographic mirror plane which contains the molybdenum atom, the two oxygen atoms, and the chlorine atoms Cl(7) and Cl(8). The bond distances and angles are listed in Table III. For comparison with the other results available for this ion, as well as those for two related species, average values of Mo—Cl distances and O=Mo—Cl angles were computed using C_{4v} symmetry. The distances and angles involving Cl(6) were double weighted in these averages.

Table V gives the average dimensions for the $[MoCl_4O(H_2O)]^-$ ion as found here and in another compound (where it has fully crystallographic C_{4v} symmetry). It also gives dimensions for the related ion with a different ligand trans to the short Mo=O bond and for the five-coordinate $[MoCl_4O]^-$ ion. The two sets of results for the $[MoCl_4O(H_2O)]^-$ ion agree fully within the limits of error. For the $[MoOCl_4\{OP(OMe)_2\}]^-$ ion the Mo=O distance appears to be shorter but the esd is large and 1.60 (2) Å is not significantly different from 1.66 (1) Å. It would appear that the most reliable value for use in calculations concerning electronic or vibrational problems is 1.66 Å.

Comparison of the $[MoCl_4O(H_2O)]^-$ and $[MoCl_4O]$ structures is instructive but fully in accord with reasonable expectation. The Mo=O distance appears to decrease on removing the water molecule, from 1.66 (1) to 1.61 (1) Å, but strictly speaking this decrease is not unequivocal because of the magnitudes of the estimated standard deviations. A decrease of some 0.03 Å in the Mo-Cl distances is statistically unequivocal since it is roughly five times greater than its estimated standard deviation. The most striking and unambiguous change upon removal of the sixth, weakly held ligand is the increase, by ca. 7°, in the O=Mo—Cl angle. The loss of the sixth ligand from $[MoCl_4O(H_2O)]^-$ allows rehybridization of the metal orbitals so that increases in the Mo=O and Mo—Cl bond strengths can compensate for the breaking of the weak Mo—OH₂ bond.

Table V. Bond Lengths and Angles in $[MoOCl_4]^-$ and $[MoOCl_4L]^-$ Ions[a]

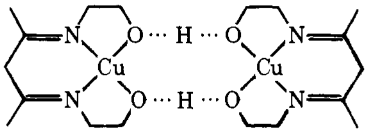
	$[MoOCl_4(H_2O)]^-$	$[MoOCl_4(H_2O)]^-$	$[MoOCl_4\{PO(OMe)_2\}]^-$	$[MoOCl_4]^-$
Mo=O, Å	1.657 (9)	1.672 (15)	1.604(23)	1.610(10)
Mo—Cl, Å	2.368 ± 0.011	2.359(3)	2.368 ± 0.008	2.333(3)
∠O=Mo—Cl(deg), mean	97.4 ± 1.5	99.0(9)	96.2 ± 1.1	105.2(1)
∠O=Mo—L, deg	179.4(5)	180.00[b]	178.7(9)	
Mo—L, Å	2.333(13)	2.393(15)	2.179(18)	
ref	this work	*c*	*d*	*e*

[a] Figures in parentheses are esd's in individual values; figures given as ± are mean deviations from the unweighted arithmetic mean of two or more values. [b] Required by symmetry. [c] C. D. Garner, L. H. Hill, F. E. Mobbs, D. L. McFadden, and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1202 (1977). [d] M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1984 (1975). [e] C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 853 (1977).

The Diaquahydrogen Ion. Though once considered a rarity, the $H_5O_2^+$ ion has now been found in over 12 compounds[11] and in a number of cases fully defined by neutron diffraction.[12-16] The O···O separation in all definitive determinations has been in the range 2,41–2.45 Å, Moreover, good quality X-ray and neutron measurements of this distance have shown good agreement, as, for example, in the cases of $[H_5O_2][C_6H_2(NO_2)_3SO_3]\cdot 2H_2O$[12] where X-ray and neutron values were 2.427 (2) and 2.436 (2) Å, and $[H_5O_2][C_6H_4(CO_2)(SO_2)_3]\cdot H_2O$ where values of 2.404 (2) and 2.414 (2) Å were obtained by X-ray[13a] and neutron[13b] work, respectively. There have also been cases where large discrepancies occurred.[14,15] In these cases it is thought that there is some inadequacy in the handling of the X-ray data or the refinement. There is no reason to believe that there is any inherent tendency of the X-ray method to give results that are inaccurate by any significant amount.

The only $H_5O_2^+$ ion with a reported O···H···O distance by neutron diffraction below 2,41 Å is in $(H_5O_2^+)_3(PW_{12}O_{40}^{3-})$,[16] where a distance of 2.370 (5) Å, rising to 2.414 Å after correction for thermal motion, was found. However, the $H_5O_2^+$ ion in this case is disordered and appears to have an essentially planar (!) arrangement of all seven atoms.

The $H_5O_2^+$ ion found in our compound has an O···O distance of 2.336 (14) Å. This is considerably, i.e,, ≥0.07 Å, below any of the previously known definitive values, It is, in fact, shorter by a very considerable amount than any previously reported O···O H-bonded distances except those reported by Bertrand et al.,[17] 2,31 (1) and 2.33 (1) Å, in the compound shown as **1**. For an O···H···O distance as short as this, it is clearly of great interest to determine the O–H distances and we are attempting to grow crystals suitable for neutron diffraction study.



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Supplementary Material Available: A table of bond distances and angles in the tetraethylammonium ions and a table of structure factors (10 pages). Ordering information is given on any current masthead page.

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