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A Neutron Diffraction Crystallographic Study of the Tetramethylammonium Salt of the Hexachlorobis(μ-chloro)(μ-hydrido)dimolybdenum(III) Ion, $[Mo_2Cl_8H]^{3-}$

F. Albert Cotton,*[1a] **Peter C. W. Leung,**[1b] **Wieslaw J. Roth,**[1a,c] **Arthur J. Schultz,**[1b,c] **and Jack M. Williams**[1b]

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Received April 7, 1983

Abstract: The compound $[N(CH_3)_4]_3[Mo_2Cl_8H]$ has been prepared in the form of crystals suitable for single-crystal studies of its structure by both X-ray diffraction and neutron diffraction. The results of both investigations are reported here. The principal average bond lengths (Å) in the $[Mo_2Cl_8H]^{3-}$ ion as obtained from X-ray work (22 °C), followed in each case by the result obtained in the neutron work (18 K), are as follows: Mo–Mo, 2.376 [3], 2.357 (3); Mo–H, 1.73 [1], 1.823 [7]; Mo–Cl(bridge), 2.478 [4], 2.486 [6]; Mo–Cl(terminal, trans to H), 2.498 [5], 2.490 [8]; Mo–Cl(terminal, trans to Cl), 2.394 [3], 2.401 [8]. The Mo–H–Mo angle (degrees) is 86 [1], 80.6 (2). The X-ray values are averages for all bonds in the title compound and three other compounds previously studied by X-ray diffraction. Brackets are used to indicate the esd of a mean. The title compound crystallizes in space group *Pnma* with the following unit cell edges at 22 °C (X-ray): a = 24.483 (3) Å, b = 9.655 (2) Å, c = 11.820 (2) Å. The lengths of the unit cell edges at 18 K (neutron) are as follows: a = 24.357 (4) Å, b = 9.613 (2) Å, c = 11.589 (3) Å. There are four formula units in the unit cell. Each nitrogen atom lies in a mirror plane and the $[Mo_2Cl_8H]^{3-}$ ions are bisected longitudinally by mirror planes containing Cl–Mo–(μ-H)–Mo–Cl chains of atoms. Despite the fact that the two Mo–H bonds are crystallographically independent, their lengths are not significantly different, viz., 1.816 (5) Å and 1.829 (5) Å. The neutron diffraction determined structure was refined to unit weighted and statistically weighted R values of 0.0368 and 0.0249, using data for which $F^2 > 3\sigma(F^2)$.

Several compounds containing the $[Mo_2Cl_8H]^{3-}$ ion were first reported in 1969,[2] and the bromine analogue was reported in 1973,[3] but the $[Mo_2X_8H]^{3-}$ ions were correctly formulated as H-bridged species only in 1976.[4] The first compounds prepared were alkali metal salts in which these anions, which inherently have only C_{2v} symmetry, are disordered on sites of D_{3h} symmetry. It was only in 1979, when the compound $(C_5NH_6)_3[Mo_2Cl_8H]$ was prepared and characterized by X-ray crystallography, that a detailed knowledge of the structure of the anion first became available.[5] Subsequently, the $[Mo_2Cl_8H]^{3-}$ structure was determined in two other compounds[6,7] by X-ray crystallography. The bonding has also been investigated in detail by the SCF-Xα-SW method.[7]

However, our knowledge of the molecular and electronic structure of this ion has remained imperfect because of the inability of X-ray diffraction to determine the position of the hydrogen atom nucleus with accuracy comparable to that obtained for the other atoms. For several years attempts have been made to obtain crystals of a compound containing the $[Mo_2Cl_8H]^{3-}$ ion that would be suitable for a neutron diffraction study. Two key requirements are that the crystals be sufficiently large and that there be no disorder, especially in moieties containing hydrogen atoms. We have now succeeded in obtaining suitable crystals of the tetramethylammonium compound, $[N(CH_3)_4]_3[Mo_2Cl_8H]$, obtaining a good set of neutron diffraction data and refining the structure with these data so as to obtain accurate positional parameters for the hydrogen atoms. The neutron diffraction study was preceded by an X-ray crystallographic study to be certain that the crystal was ordered and to provide starting parameters for the neutron refinement. The results of both refinements are given in this report and discussed in relation to early work.

Table I. Summary of X-ray (Room Temperature) and Neutron (18 K) Diffraction Analysis for $[N(CH_3)_4]_3Mo_2Cl_8H$

	X-ray	neutron[d]
formula	$Mo_2Cl_8N_3C_{12}H_{37}$	
formula weight	698.95	
space group	*Pnma*	
a, Å	24.483 (3)	24.357 (4)
b, Å	9.655 (2)	9.613 (2)
c, Å	11.820 (2)	11.589 (3)
α, deg	90.00	
β, deg	90.00	
γ, deg	90.00	
V, Å^3	2794 (2)	2713 (2)
Z	4	4
d_{calcd}, g/cm^3	1.661	1.711
crystal size, mm	0.5 × 0.5 × 0.5	5.2 × 0.9 × 0.8
μ, cm^{-1}	16.553	2.575
data collection instrument	Syntex P$\bar{1}$	automated four circle
radiation λ, Å	0.71073 (Mo Kα)	1.1611 (1)
scan method	ω	$\theta - 2\theta$
maximum $(\sin\theta)/\lambda$ and 2θ, Å^{-1} and deg	0.59 and 50	0.69 and 106
indices of collected reflections	$+h, +k, +l$	
no. of unique data,	2137	3571
$F_o^2 \geqslant 3\sigma(F_o^2)$	2048	2521 (2801)
no. of parameters refined	214	311
R^a	0.0321	0.0368 (0.0428)
$R_w{}^b$	0.0482	0.0249 (0.0257)
quality-of-fit indicator[c]	1.140	1.099 (1.123)
largest shift/esd, final cycle	0.27	0.10 (0.07)

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$. [d] Refinement parameters in parentheses refer to computation with a cutoff at $2\sigma(F^2)$.

Experimental Section

Preparation. The $[Mo_2Cl_8H]^{3-}$ ion was prepared by a procedure similar to the literature method.[7] Crystals of $[N(CH_3)_4]_3[Mo_2Cl_8H]$

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[1] (a) Texas A&M University. (b) Argonne National Laboratory. (c) Research collaborators, Brookhaven National Laboratory.

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Table IV. Bond Distances (Å) and Their Estimated Standard Deviations for $[N(CH_3)_4]_3Mo_2Cl_8H$: X-ray (Room Temperature) and Neutron (18 K) Diffraction Studies[a]

	X-ray	neutron
Mo(1)–Mo(2)	2.374 (1)	2.357 (3)
Cl(1)	2.473 (1)	2.480 (2)
Cl(2)	2.404 (1)	2.409 (2)
Cl(3)	2.490 (2)	2.498 (3)
H(1)	1.75 (5)	1.816 (5)
Mo(2)–Cl(1)	2.486 (1)	2.492 (2)
Cl(4)	2.383 (1)	2.393 (2)
Cl(5)	2.481 (2)	2.481 (3)
H(1)	1.73 (6)	1.829 (5)
N(1)–C(1)	1.488 (9)	1.499 (3)
C(2)	1.489 (9)	1.496 (3)
C(3)	1.492 (6)	1.497 (2)
N(2)–C(4)	1.476 (8)	1.497 (3)
C(5)	1.488 (10)	1.499 (3)
C(6)	1.487 (6)	1.495 (2)
N(3)–C(7)	1.481 (9)	1.492 (3)
C(8)	1.516 (11)	1.509 (3)
C(9)	1.457 (7)	1.493 (2)
C(1)–H(11)	0.96 (8)	1.099 (6)
H(12)	0.96 (6)	1.093 (4)
C(2)–H(21)	1.06 (8)	1.075 (6)
H(22)	0.91 (6)	1.091 (4)
C(3)–H(31)	0.86 (7)	1.091 (4)
H(32)	0.87 (7)	1.094 (4)
H(33)	1.05 (8)	1.086 (4)
C(4)–H(41)	1.13 (8)	1.081 (5)
H(42)	0.90 (6)	1.087 (4)
C(5)–H(51)	1.02 (11)	1.082 (6)
H(52)	0.99 (12)	1.084 (4)
C(6)–H(61)	0.86 (9)	1.075 (4)
H(62)	1.09 (9)	1.092 (4)
H(63)	1.03 (8)	1.097 (4)
C(7)–H(71)	0.92 (7)	1.081 (5)
H(72)	0.98 (6)	1.096 (4)
C(8)–H(81)	0.69 (11)	1.075 (6)
H(82)	1.23 (8)	1.087 (4)
C(9)–H(91)	1.07 (6)	1.085 (4)
H(92)	1.11 (14)	1.092 (4)
H(93)	0.93 (7)	1.094 (4)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

suitable for X-ray and neutron diffraction analysis were prepared by dissolving $Mo_2(O_2CCH_3)_4$ (1.0 g, 2.3 mmol) in 25 mL of hot concentrated HCl, adding excess tetramethylammonium chloride, and evaporating the solvent under the stream of nitrogen over several days.

X-ray Diffraction Analysis. A cube-shaped crystal with an approximate edge length of 0.5 mm was mounted in a glass capillary. Unit cell parameters and intensity data were obtained by using a Syntex P$\bar{1}$ diffractometer. Standard procedures, which have been described elsewhere,[6] were employed. Data were collected by using the ω scan technique. Parameters pertaining to the structure determination are compiled in Table I. Polarizaton and Lorentz corrections were applied to the intensity data.

The positions of two crystallographically independent Mo atoms were obtained by direct methods. Subsequent series of isotropic least-squares refinements and different Fourier analyses revealed the position of the remaining atoms (except methyl hydrogen atoms but including the bridging hydrogen atom). The structure was refined to convergence with all non-hydrogen atoms having anisotropic thermal parameters. The values of R and R_w at this point were 0.0391 and 0.0633, respectively. A difference Fourier map was obtained, and it appeared that the most intense peaks could be interpreted as methyl hydrogen atoms. They behaved reasonably well upon subsequent refinement of the whole set of 41 atoms. The final values of R and R_w were 0.0321 and 0.0482, respectively.

The Neutron Diffraction Analysis. Intensity data were measured with an automated four-circle diffractometer at the Brookhaven high-flux beam reactor. The wavelength of the neutron beam (1.1611 (1) Å) was selected by diffraction from the (220) planes of a germanium monochromator crystal and was calibrated against a KBr crystal (a_0 = 6.60000 (13) Å at 298 K). The crystal of $[N(CH_3)_4]_3[Mo_2Cl_8H]$ having approximate dimensions 5.2 × 0.9 × 0.8 mm was mounted inside a closed-cycle helium refrigerator (DISPLEX CS202, Air Products and Chemical, Inc.) and maintained at the nominal temperature of 18 K throughout data collection. The new lattice parameters were obtained by centering 16 strong reflections and their Friedel counterparts with 2θ between 40° and 60°, averaging the corresponding 2θ values, and making a least-squares fit to $\sin^2 \theta$.

The intensity data were measured with a $\theta/2\theta$ step-scan technique for reflections having $(\sin \theta)/\lambda < 0.69$ Å^{-1}. The scan range was varied according to $\Delta(2\theta) = 0.5\ (1 + 8.0 \tan \theta)$ for the high-angle data ($0.43 < (\sin \theta)/\lambda < 0.69$) and $\Delta(2\theta) = 2.8°$ for the low-angle reflections. The step size was varied to give approximately 60–70 steps for each scan. The integrated intensity of each reflection, I, and its variance, $\sigma^2(I)$, were evaluated from $I = C - B$ and $\sigma^2(I) = C + k^2B$, where C is the count taken in the central 80% of the scan and B is the background estimated from the outer 10% parts (i.e., $k = 4$). Lorentz and absorption corrections[8] were applied and several Friedel pairs, which had been collected to check quality of the data, were averaged to give 3571 unique data with intensity $I > 0$.

Atomic coordinates derived from the X-ray analysis were used to initiate the refinement by differential Fourier synthesis (DFS) using computing facilities at Brookhaven National Laboratory. Scattering lengths of atoms reported by Koester were used.[9] After isotropic DFS refinement the positions of three hydrogen atoms were found to be incorrect and new values of their fractional coordinates were determined from a subsequent difference Fourier map. The structure analysis was completed by using the SHELX 76 package. In the full-matrix least-squares refinement all 41 atoms were assigned anisotropic thermal parameters, U's, and an extinction correction was included. The refinements were carried out for two different cutoff limits for weak reflections, namely $F^2 < n \times \sigma(F^2)$, with n equal to 2 and 3. The corresponding number of data included in the computations were 2801 and 2581, respectively. While a negligible difference in the value of R_w was observed (0.0257 and 0.0249, respectively) a considerable improvement of the unweighted R factor (from 0.0428 to 0.0368) resulted upon exclusion of reflections with $F^2 < 3\sigma(F^2)$. However, no significant difference between the values of final atomic coordinates was found for these two cases.

Tables of observed and calculated structure factors, for both X-rays and neutrons, are available as supplementary material.

Results

The atomic positional parameters and isotropic thermal parameters (or isotropic equivalents to anisotropic thermal vibration tensors) are available (Tables II and III, supplementary material) for the X-ray and neutron data, respectively. The structure of the $[Mo_2Cl_8H]^{3-}$ ion as obtained from the neutron study is depicted in Figure 1. The three independent $N(CH_3)_4^+$ ions and the $[Mo_2Cl_8H]^{3-}$ ion all lie in mirror planes parallel to 010 at $y = {}^1/_4$ and ${}^3/_4$. The μ-H atom of the anion is not, therefore, required by crystal symmetry to be equidistant from the two independent molybdenum atoms. In fact it turns out to be so within experimental error. This and other important structural results are presented in the tables of bond lengths and bond angles, Tables IV and V, respectively.

The $N(CH_3)_4^+$ ions are well ordered. Each one is so oriented that the N atom and two C atoms, together with one H atom on

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(8) The recently determined value of μ/ρ for hydrogen was kindly provided to us by R. K. McMullan (μ/ρ = 26.446 cm^2/g); for other elements present the values of μ/ρ were taken from "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 3, p 197.

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Table V. Bond Angles (deg) and Their Estimated Standard Deviations for $[N(CH_3)_4]_3Mo_2Cl_8H$: X-ray (Room Temperature) and Neutron (18 K) Diffraction Studies[a]

	X-ray	neutron		X-ray	neutron
Mo(2)-Mo(1)-Cl(1)	61.68 (3)	61.95 (6)	H(11)-C(1)-H(12)	109 (4)	111.7 (3)
Cl(2)	117.60 (3)	117.57 (7)	H(12)-C(1)-H(12)'	111 (7)	109.4 (5)
Cl(3)	133.36 (4)	132.3 (1)	N(1)-C(2)-H(21)	112 (4)	108.1 (3)
H(1)	47 (2)	49.9 (2)	H(22)	106 (4)	108.7 (2)
Cl(1)-Mo(1)-Cl(1)'	90.66 (5)	92.22 (8)	H(21)-C(2)-H(22)	106 (4)	110.4 (3)
Cl(2)	88.98 (4)	88.02 (4)	H(22)-C(2)-H(22)'	123 (8)	110.5 (5)
Cl(2)'	179.28 (4)	179.2 (1)	N(1)-C(3)-H(31)	110 (5)	108.4 (3)
Cl(3)	87.04 (4)	86.53 (7)	H(32)	112 (5)	108.4 (3)
H(1)	93 (1)	95.0 (1)	H(33)	101 (4)	108.4 (3)
Cl(2)-Mo(1)-Cl(2)'	91.38 (6)	91.72 (9)	H(31)-C(3)-H(32)	120 (6)	110.4 (3)
Cl(3)	93.56 (4)	94.21 (7)	H(33)	97 (6)	110.4 (3)
H(1)	87 (1)	84.2 (1)	H(32)-C(3)-H(33)	114 (6)	110.8 (3)
Cl(3)-Mo(1)-H(1)	180 (2)	177.8 (2)	N(2)-C(4)-H(41)	110 (4)	108.8 (3)
Mo(1)-Mo(2)-Cl(1)	61.12 (3)	61.44 (6)	H(42)	107 (4)	108.9 (2)
Cl(4)	117.28 (3)	117.46 (7)	H(41)-C(4)-H(42)	98 (4)	110.2 (3)
Cl(5)	131.72 (5)	130.8 (1)	H(42)-C(4)-H(42)'	134 (8)	109.8 (5)
H(1)	48 (2)	49.5 (2)	N(2)-C(5)-H(51)	106 (6)	108.6 (3)
Cl(1)-Mo(2)-Cl(1)'	90.05 (5)	91.64 (8)	H(52)	91 (8)	108.2 (2)
Cl(4)	89.44 (4)	88.65 (4)	H(51)-C(5)-H(52)	79 (8)	110.3 (3)
Cl(4)'	178.34 (4)	178.45 (9)	H(52)-C(5)-H(52)'	157 (15)	111.2 (5)
Cl(5)	86.34 (4)	85.91 (7)	N(2)-C(6)-H(61)	98 (7)	108.1 (3)
H(1)	93 (1)	94.3 (1)	H(62)	102 (5)	109.4 (3)
Cl(4)-Mo(2)-Cl(4)'	91.03 (6)	91.01 (9)	H(63)	100 (5)	109.5 (3)
Cl(5)	95.20 (4)	95.63 (7)	H(61)-C(6)-H(62)	125 (8)	109.2 (3)
H(1)	85 (1)	84.2 (1)	H(63)	107 (8)	110.4 (3)
Cl(5)-Mo(2)-H(1)	179 (2)	179.7 (2)	H(62)-C(6)-H(63)	119 (6)	110.2 (3)
Mo(1)-Cl(1)-Mo(2)	57.19 (2)	56.6 (1)	N(3)-C(7)-H(71)	112 (4)	107.8 (3)
Mo(1)-H(1)-Mo(2)	86 (2)	80.6 (2)	H(72)	110 (4)	108.1 (2)
C(1)-N(1)-C(2)	109.7 (6)	110.9 (2)	H(71)-C(7)-H(72)	106 (4)	110.7 (3)
C(3)	109.2 (4)	109.1 (1)	H(72)-C(7)-H(72)'	113 (7)	111.2 (5)
C(2)-N(1)-C(3)	108.3 (4)	108.7 (1)	N(3)-C(8)-H(81)	85 (11)	108.0 (3)
C(3)-N(1)-C(3)'	112.2 (7)	110.4 (2)	H(82)	101 (4)	108.3 (2)
C(4)-N(2)-C(5)	108.6 (6)	110.1 (2)	H(81)-C(8)-H(82)	120 (4)	110.3 (3)
C(6)	110.5 (4)	109.4 (1)	H(82)-C(8)-H(82)'	118 (7)	111.5 (5)
C(5)-N(2)-C(6)	109.0 (5)	109.0 (1)	N(3)-C(9)-H(91)	110 (4)	108.3 (3)
C(6)-N(2)-C(6)'	109.3 (8)	109.9 (2)	N(3)-C(9)-H(92)	115 (7)	108.5 (3)
C(7)-N(3)-C(8)	107.2 (6)	109.7 (2)	H(93)	102 (5)	108.0 (3)
C(9)	109.0 (4)	109.3 (1)	H(91)-C(9)-H(92)	104 (8)	108.7 (3)
C(8)-N(3)-C(9)	109.7 (5)	109.4 (1)	H(93)	112 (5)	113.1 (3)
C(9)-N(3)-C(9)'	112.0 (9)	109.7 (2)	H(92)-C(9)-H(93)	115 (9)	110.1 (3)
N(1)-C(1)-H(11)	104 (4)	108.1 (3)			
H(12)	111 (4)	107.9 (2)			

[a] Estimated standard deviations are given in parentheses for the least significant digits.

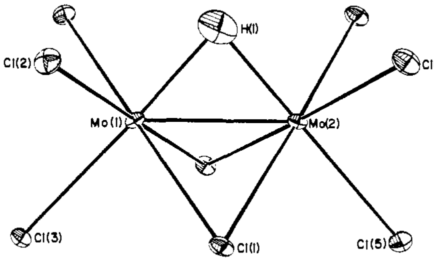

Figure 1. ORTEP drawing of the $Mo_2Cl_8H^{3-}$ ion based upon the results of neutron diffraction analysis. Atoms are represented by ellipsoids of thermal vibration corresponding to 80% probability. Crystallographic mirror plane incorporates both Mo atoms, H(1), Cl(3), and Cl(5).

each of the latter, lie in the mirror plane. All distances and angles within the $N(CH_3)_4^+$ ions are close to ideal values for tetrahedral configurations, thus attesting to the accuracy of the neutron diffraction structure and the lack of disorder. The mean N-C distances by X-ray and neutron diffraction are 1.487 [3] Å and 1.497 [1] Å, respectively. The difference is scarcely significant statistically ($\Delta/\sigma \approx 3$), and both results are in good accord with the sum of standard tetrahedral radii of C and N, viz., 0.77 + 0.70 = 1.47 Å. The C-H distances as determined by X-ray diffraction average 0.98 [2] Å, while the neutron value is 1.088 [2] Å. These values, and the difference between them, are entirely normal for aliphatic C-H bonds. The C-N-C angles range from 108.7° to 110.9° in the neutron determined structure while the H-C-H angles lie in the narrow range 108.7°-113.1°.

Discussion

The present X-ray structure does not differ significantly from the three previous X-ray structures, as can be seen from Table VI. This discussion will therefore focus on comparing the grand average of all X-ray results with the results of the neutron study. Individual bond lengths and angles in the latter can reasonably be averaged according to C_{2v} symmetry and these average values then used in making comparisons with the grand average X-ray values. It is clear from Table VI that for the three kinds of Mo-Cl distances the X-ray and neutron results are in complete agreement. Each of the $|N - X_{av}|$ values for these distances is about equal to its esd. For the Mo-Mo distance the $|N - X_{av}|$ value and its esd are 0.019 (5) Å. From a purely statistical point of view, the neutron value is ca. 0.02 Å shorter than the X-ray value. This may be a real difference in the bond lengths, attributable to the difference in temperature, or it may simply reflect some systematic error. It is, in any case, not of chemical significance at this time.

The important comparison to be made here is between the X-ray and neutron results for the Mo-H distances and the Mo-H-Mo angle. The two are, of course, interdependent, and for a given value of the Mo-Mo bond length are simply related by the equation:

$$r_{\text{Mo-Mo}}/r_{\text{Mo-H}} = 2 \sin (\alpha/2)$$

The neutron results yield a significantly larger value of $r_{\text{Mo-H}}$ than that obtained in any one, or all, of the X-ray determinations

Table VI. Mean Dimensions of the $[\mathrm{Mo_2Cl_8H}]^{3-}$ Ion by X-ray Diffraction (Four Compounds) and Neutron Diffraction[a]

dimens[b]	1[c]	2[c]	3[d]	4	grand av[e]	neutron results indiv	neutron results av	$\lvert N - X_{\mathrm{av}}\rvert$[f]	Δ/σ[g]
Mo–Mo, Å	2.371 (1)	2.384 (1)	2.375 (2)	2.374 (1)	2.376 [3]	2.357 (3)	2.357 (3)	0.019 (5)	4
Mo–H, Å	1.74	1.793 (4)	1.728 (2)	1.75 (5)	1.73 [1]	1.816 (5)	1.823 [7]	0.09 (1)	9
	1.62			1.73 (6)		1.829 (5)			
Mo–H–Mo, deg	89.6 (3)	83.3 (2)	86.8 (1)	85 (2)	86 [1]	80.6 (2)	80.6 (2)	5 (1)	5
Mo–Cl$_{\mathrm{b}}$, Å	2.499 (1)	2.474 (1)	2.466 (3)	2.473 (1)	2.478 [4]	2.480 (2)	2.486 [6]	0.008 (7)	1
	2.494 (1)								
	2.486 (1)	2.473 (1)	2.465 (3)	2.486 (1)		2.492 (2)			
	2.490 (1)								
Mo–Cl$_{\mathrm{t,Cl}}$, Å	2.407 (1)	2.392 (1)	2.393 (2)	2.404 (1)	2,394 [3]	2.409 (2)	2.401 [8]	0.007 (8)	1
	2.386 (1)								
	2.392 (1)	2.404 (1)	2.395 (3)	2.383 (1)		2.393 (2)			
	2.370 (1)								
Mo–Cl$_{\mathrm{t,H}}$, Å	2.504 (1)	2.517 (1)	2.500 (3)	2.490 (2)	2,498 [5]	2.498 (3)	2.490 [8]	0.008 (9)	1
				2.481 (2)		2.481 (3)			

[a] Numbers in brackets are estimated standard deviations 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$_{\mathrm{b}}$ is a bridging chlorine atom. Cl$_{\mathrm{t,Cl}}$ and Cl$_{\mathrm{t,H}}$ are terminal chlorine atoms trans to Cl$_{\mathrm{b}}$ and H, respectively. [c] Reference 7. [d] Reference 6. [e] Averaging all values from all four structures with equal weight for each bond, even those in pairs that are symmetry related. [f] N is the average value by neutron diffraction; X_{av} is the grand average X-ray value. [g] Ratio of $\lvert N - X_{\mathrm{av}}\rvert$ to its esd.

by 0.09 (1) Å. It should be noted that the various individual X-ray studies show good agreement among themselves and their mean value has a variance of only 0.01 Å. The difference between the mean X-ray value and the neutron value may be attributed to a systematic error in the X-ray values of the same kind found in a variety of other X–H bond length determinations. Indeed, comparison of the X-ray and neutron C–H distances in this investigation provides an excellent example of the well-established fact that X-ray diffraction systematically gives C–H distances that are too short by ca. 0.10 Å. This is attributable to the fact that the valence electron density of the hydrogen atom is appreciably skewed toward atom X and there is no other electron density associated with the hydrogen atom. Such an apparent shortening is to be expected regardless of the identity of X and for (nonlinear) bridging as well as terminal hydrogen atoms. There is also a systematic shortening due to thermal motion for terminal X–H bonds. The smaller bond angles of 80.6 (2)° in the neutron-determined structure as compared to 86 [1]° for the X-ray results is in accord with the above relationship between angle and distance.

It is noted that while in this compound the hydrogen bridge is not crystallographically required to be symmetrical, both the X-ray results and (more significantly) the neutron results show it to be so to well within the experimental error using the 3σ criterion.

Finally, with regard to the location of the hydrogen atom, the accurate neutron result can be compared with the estimate made from the vibrational spectrum by Katovič and McCarley.[10] These workers employed a well-known result, summarized by Herzberg years ago,[11a] based on the application of a simple central force field to a bent, symmetrical (C_{2v}) triatomic molecule, whereby the frequencies of the symmetric and antisymmetric Mo–H stretching modes, ν_{s} and ν_{as}, can be used to calculate the angle at the H atom. From this angle, α, and the X-ray value for the Mo–Mo distance, one can, of course, calculate the Mo–H distance using the equation above. This latter relationship is rigorous, but *the equations used to obtain α from ν_{s} and ν_{as} are not.* A simple central force field is only an approximation and all relationships obtained by algebraic manipulations of the secular equation derived therefrom are only approximate. Indeed, Herzberg points out specifically[11b] that in a number of cases quantities which ought to be equal according to this approximate treatment disagree by ca. 25%. Katovič and McCarley obtained values of $\alpha = 77.6°$ and $r_{\mathrm{Mo-H}} = 1.90$ Å by this procedure. These are smaller and larger, respectively, than the neutron results of 80.6 (2)° and 1.823 [7] Å. It should also be noted that their work was done on the cesium and rubidium compounds where the high symmetry and close packing may alter the dimensions of the $[\mathrm{Mo_2X_8H}]^{3-}$ slightly from what they are in the compounds we have examined. With these caveats in mind, it must be said that the vibrational spectroscopy approach has worked remarkably well. It appears to give $r_{\mathrm{Mo-H}}$ values that are slightly high, but only by about 4%. However, the result so obtained was a bit closer than the Mo–H distance obtained by X-ray diffraction, which was 5% too low. However, the error in the X-ray result is an understandable, systematic one that could, in principle, have been anticipated and approximately corrected for.

In any event, to summarize briefly, the neutron diffraction study has now resolved all remaining doubts and inaccuracies concerning the structure of the $[\mathrm{Mo_2Cl_8H}]^{3-}$ ion and given a precise description of the hydrogen bridge arrangement.

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Supplementary Material Available: Tables of structure factors, atomic positional parameters, and anisotropic thermal parameters (33 pages). Ordering information is given on any current masthead page.

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