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Preparation of the New Heteronuclear Hydride-Bridged Anion $MoWCl_8H^{3-}$ and Determination of the Metal–Hydrogen Bond Distance in $Mo_2X_8H^{3-}$ (X = Cl, Br) by Infrared Spectroscopy

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The new heteronuclear compound Cs_3MoWCl_8H has been prepared and shown by x-ray powder diffraction and infrared spectroscopy to have the structure of $Cs_3Mo_2Cl_8H$. The infrared spectra of salts containing the anions $Mo_2X_8H^{3-}$ (X = Cl, Br) and $Mo_2Cl_8D^{3-}$ were redetermined and found to exhibit two bands in the region 1600–1200 cm^{-1} for the hydrides and 1120–890 cm^{-1} for the deuterides. On the basis of band intensities and known geometrical restraints the band of higher frequency was assigned as the symmetric M–H–M stretch and the band of lower frequency as the asymmetric stretch. Using equations relating frequencies of ν(sym) and ν(asym) to the M–H–M bond angle (α) and the known Mo–Mo distances in $Rb_3Mo_2Cl_8H$ and $Cs_3Mo_2Br_8H$, values of d(Mo–H) = 1.90 and 1.93 Å and α = 77.6 and 78.3°, respectively, were determined for the $Mo_2Cl_8H^{3-}$ and $Mo_2Br_8H^{3-}$ anions.

Introduction

In early work on the reactions of dimolybdenum tetraacetate with aqueous hydrochloric acid Bennett, Brencic, and Cotton[2] first reported formation of alkali metal salts containing the $Mo_2Cl_8^{3-}$ anion. Subsequent work, however, elucidated the true formulation of these salts as $M_3Mo_2Cl_8H$ containing the μ-hydrido-di-μ-chloro-hexachlorodimolybdate(III) anions,[3] and the corresponding salt $Cs_3Mo_2Br_8H$ was also reported.[3,4] In the later study the reactions of both the hydride and deuteride derivatives with aqueous acid, the infrared spectra and the magnetic susceptibilites all were found to be consistent with a structure of the anions having a H atom as one of the bridging ligands in the confacial bioctahedral arrangement.

As a result of efforts to prepare new heteronuclear derivatives containing the quadruply bonded MoW^{4+} unit we have examined the reaction of $MoW(O_2CC(CH_3)_3)_4$[5,6] with hydrochloric acid. These reactions have provided salts of the hydrido and deuterio anions $MoWCl_8H^{3-}$ and $MoWCl_8D^{3-}$ and an opportunity to carefully examine the infrared spectra of such species containing bridging H atoms uncomplicated by other ligands which exhibit vibrational frequencies in the M–H region.

Experimental Section

The mixed-metal pivalate $MoW(O_2CC(CH_3)_3)_4$ was prepared and purified as described previously.[6] Salts of $Mo_2Cl_8H^{3-}$, $Mo_2Br_8H^{3-}$, and $Mo_2Cl_8^{3-}$ were prepared according to methods given in the literature.[3,4] A 38% solution of DCl in D_2O was obtained from Stohler Isotope Chemicals. Infrared spectra were measured on a Beckman 4250 spectrometer as Nujol mulls between CsI plates. The accuracy of absorption band frequencies is estimated to be within ±3 cm^{-1}.

Preparation of Cs_3MoWCl_8H. To 30 mL of cold (0 °C) concentrated hydrochloric acid previously saturated with HCl(g) was added 0.50 g of $MoW(O_2CC(CH_3)_3)_4$ followed by cesium chloride (0.70 g) dissolved in 2 mL of water. The reaction mixture was stirred overnight with slow warming to room temperature. The yellow-green precipitate was filtered and washed with several portions of ethanol and finally with ether. In order to remove the last traces of water the compound was dried in vacuo for ca. 12 h at 120 °C. The identical procedure using DCl and D_2O was used to prepare the deuteride Cs_3MoWCl_8D. Anal. Calcd for Cs_3MoWCl_8H: Cs, 41.40; Mo, 9.26; Cl, 29.45. Found: Cs, 41.44; Mo, 9.29; Cl, 29.47.

The same reaction was repeated while maintaining the reaction mixture at 60 °C and the same product was obtained. The compound appeared to be indefinitely stable in air. Comparison of the x-ray powder diffraction photographs of $Cs_3Mo_2Cl_8H$ and Cs_3MoWCl_8H clearly shows that the compounds are isomorphous. From x-ray powder data (Guinier camera, Cu Kα_1 radiation, 1.54050 Å, and film correction with the lines of elemental Si) the following d spacings (Å) were observed (relative intensities in parentheses): 8.60 (4), 6.46 (5), 6.03 (7), 5.06 (3), 4.27 (6), 3.70 (10), 3.56 (3), 3.44 (3), 3.22 (3), 3.02 (7), 2.854 (8), 2.798 (3), 2.570 (6), 2.400 (2), 2.343 (3), 2.284 (2), 2.232 (4), 2.142 (5), 2.028 (3), 1.981 (4), 1.943 (3), 1.850 (7), 1.780 (4), 1.718 (3), 1.595 (2), 1.510 (2), 1.369 (1). From these d spacings the hexagonal lattice parameters a = 7.416 (3) and c = 17.106 (6) Å were computed.

Table I. Infrared Frequencies (cm^{-1}) and Assignments for M–H–M Vibrations of $Mo_2Cl_8H^{3-}$, $MoWCl_8H^{3-}$, and $Mo_2Br_8H^{3-}$

	ν(sym)	ν(asym)	ν(sym)/ ν(asym)
$Cs_3Mo_2Cl_8H$	1553 m[a]	1248 vs[a]	1.244
$Cs_3Mo_2Cl_8D$	1101 m	904 vs	1.218
$Rb_3Mo_2Cl_8H$	1580 m	1270 vs	1.244
$Rb_3Mo_2Cl_8D$	1120 m	920 vs	1.217
Cs_3MoWCl_8H	1575 s	1228 vs	1.283
Cs_3MoWCl_8D	1123 s	890 vs	1.262
$Cs_3Mo_2Br_8H$	1538 m	1259 vs	1.222

[a] Relative intensities: vs, very strong; s, strong; m, medium.

Results and Discussion

A comparison of the infrared spectra and x-ray data of $Cs_3Mo_2Cl_8H$ and Cs_3MoWCl_8H leaves little doubt that these compounds have the same structure. Thus under the mild conditions (0 °C) where reaction of $Mo_2(O_2CCH_3)_4$ leads to formation of $Mo_2Cl_8^{4-}$, e.g., as the K^+ [7] or NH_4^+ [8] salts, the reaction of the heteronuclear dimer $MoW(O_2CC(CH_3)_3)_4$ leads only to formation of $MoWCl_8H^{3-}$ salts. We have so far been unable to obtain derivatives containing the unbridged, quadruply bonded anion $MoWCl_8^{4-}$. This comparison illustrates the greater reactivity of the metal–metal bond in the heteronuclear derivative toward oxidative addition of HCl; i.e., formation of $MoWCl_8H^{3-}$ occurs even at 0 °C whereas a temperature of ca. 60 °C is required for formation of $Mo_2Cl_8H^{3-}$ (as opposed to $Mo_2Cl_8^{4-}$). Similarly, most carboxylate derivatives $Mo_2(O_2CR)_4$ can be handled in air without rapid decomposition whereas $MoW(O_2CC(CH_3)_3)_4$ undergoes rapid oxidation and must be protected from even trace amounts of oxygen.

In the course of examining the infrared spectra of Cs_3MoWCl_8H and Cs_3MoWCl_8D two bands attributable to M–H stretching vibrations were identified. Since only one such band had been previously reported[3] for the salts of $Mo_2X_8H^{3-}$ and $Mo_2X_8D^{3-}$ (X = Cl, Br) the infrared spectra of these compounds were reexamined. A comparison of infrared spectra obtained for salts of $Mo_2Cl_8H^{3-}$ and $MoWCl_8H^{3-}$ and their deuterated derivatives is given in Figure 1. The infrared frequencies are recorded in Table I for compounds which had been rigorously dried in vacuo (10^{-5} Torr) at 120 °C for several hours. In all cases two sharp bands were observed, one of weaker intensity at ca. 1550–1580 cm^{-1} and a stronger one at 1230–1270 cm^{-1} for the hydrides. The corresponding bands

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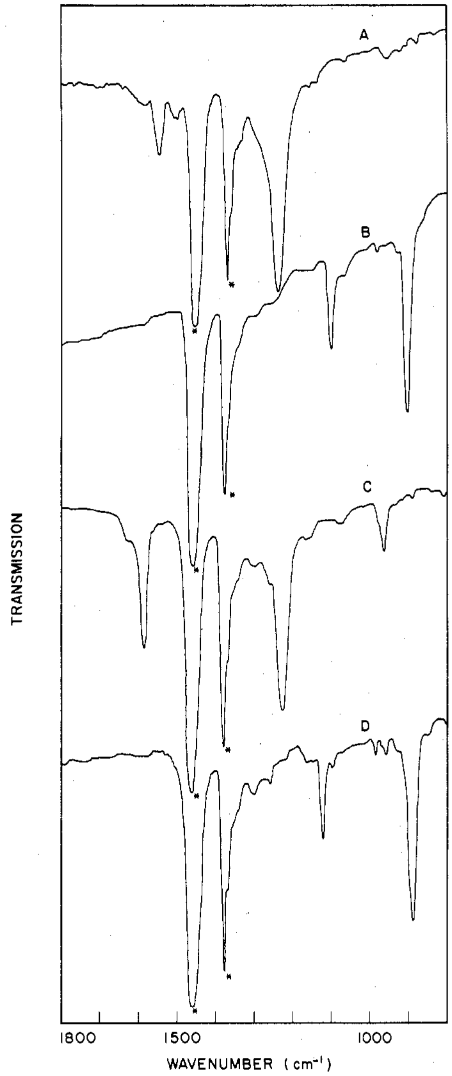

Figure 1. Infrared spectra of Nujol mulls: A, $Cs_3Mo_2Cl_8H$; B, $Cs_3Mo_2Cl_8D$; C, Cs_3MoWCl_8H; D, Cs_3MoWCl_8D. Asterisks indicate bands of Nujol.

were shifted to 1100–1120 and 890–920 cm^{-1}, respectively, for the deuteride derivatives. Additional bands arising from H_2O or D_2O were present in the spectra of compounds which had not been subjected to the rigorous drying procedure. In the earlier study[3] it is possible that the strong band of H_2O at ca. 1600 cm^{-1} obscured the high-frequency Mo–H band which occurs at 1550–1580 cm^{-1} for $Mo_2Cl_8H^{3-}$.

The observation of two M–H stretching bands is consistent with the location of the H atom in one of the bridging positions of the confacial bioctahedral structure. Since the asymmetric M–H–M stretching vibration should lead to the greatest change in dipole moment, this mode should provide the band of greatest intensity. Accordingly the more intense band at lower frequency is assigned as ν(asym), and the band at higher frequency is assigned as ν(sym). These assignments also are consistent with the M–H–M angle being less than 90°. From the known Mo–Mo distance[2] of 1.380 (10) Å in $Rb_3Mo_2Cl_8H$ it can be seen that α, the M–H–M angle, must be less than 90° for any Mo–H bond distance greater than ca. 1.70 Å. In recently reported structures,[9-13] where metal–metal bonds are supported by M–H–M bridging and where the M–H distances have been accurately determined, the bridging M–H distances have generally proven to be greater than 1.7 Å.

Hydrogen stretching vibrations for hydrogen bound to heavy-metal atoms should be relatively mechanically insensitive to vibrations of the nonhydrogen atoms of the molecule since essentially all of the motion is executed by the H atom. Using the observed Mo–H stretching frequencies and the known Mo–Mo distance it is possible to estimate the Mo–H bond distance assuming that the Mo–H–Mo bridge bonding is symmetric. For this purpose we assume that the M–H vibrations are essentially independent of other vibrations of the anion, which because of relative masses of the metal and halogen atoms all occur at very low frequencies compared to stretching vibrations involving hydrogen. Based on this assumption the M–H–M vibrations may be treated as a symmetric three-atom cyclic system HM_2 with C_{2v} symmetry. The M–H–M angle will be designated as α.

In C_{2v} symmetry the three normal vibrations of the HM_2 "molecule" belong to the following representations: M–H–M symmetric stretch, a_1; M–H–M bending (or M–M stretching), a_1; and M–H–M asymmetric stretching, b_1. The associated vibrational frequencies are ν_1, ν_2, and ν_3, respectively. From this it is apparent that the two a_1 modes may interact and in the general case the measured frequencies ν_1 and ν_2 will reflect a contribution from both normal modes. Since there is direct metal–metal bonding, it is more appropriate in the normal-coordinate treatment to choose a central force field which permits the choice of one of the two necessary potential constants as the M–M stretching force constant; the other constant is of course the M–H stretching force constant. In this model the normal-coordinate analysis yields the equations[14]

$$a\nu_3^2 = k_H[M_M^{-1} + M_H^{-1}(1 - \cos\alpha)] \tag{1}$$

$$a(\nu_1^2 + \nu_2^2) = 2k_M M_M^{-1} + k_H[M_M^{-1} + M_H^{-1}(1 + \cos\alpha)] \tag{2}$$

$$a^2\nu_1^2\nu_2^2 = k_H k_M[M_M^{-2}(1 + \cos\alpha) + (M_H M_M)^{-1}(2 + 2\cos\alpha)] \tag{3}$$

where k_H is the M–H stretching force constant, k_M is the M–M stretching force constant, M_M is the atomic weight of the metal, M_H is the atomic weight of hydrogen, and a is a constant which permits the use of frequencies in cm^{-1} for ν_i and gram atomic weights rather than atomic masses for M_M and M_H.

In the present case only the infrared frequencies ν_1 and ν_3 are known. Indeed, as previously shown by Ziegler and Risen[15] in their normal-coordinate analysis of the $W_2Cl_9^{3-}$ ion, the desired metal–metal stretching mode is extensively mixed with the W–Cl–W bridge bending and stretching modes and thus cannot be assigned unambiguously. However, as in the case of $W_2Cl_9^{3-}$,[15] the frequency of this mode (ν_2) is likely to be in the region $\leq$200 cm^{-1}. Because the frequency of ν_2 is small compared to ν_1, it is possible to simplify eq 2. First we note that with $\nu_1 = 1560 \pm 20$ cm^{-1} and $\nu_2 \sim 200$ cm^{-1} the sum $\nu_1^2 + \nu_2^2 \approx \nu_1^2$ within ca. 2%. Secondly, with $M_M \approx 100$ and $M_H = 1$, on the right-hand side of eq 2, we note that $k_M M_M^{-1} \ll k_H[M_M^{-1} + M_H^{-1}(1 + \cos\alpha)]$ for any reasonable values of k_M and k_H. Thus in the case at hand, to a very good approximation

$$a\nu_1^2 = k_H[M_M^{-1} + M_H^{-1}(1 + \cos\alpha)] \tag{4}$$

It is very important to note that this simplification is only possible when the mass difference between atoms in the three-atom system is very large and the middle atom is the light atom.

These relations can then be used to eliminate the need to evaluate k_H by dividing eq 4 by eq 1 and taking the square root[16]

$$\begin{aligned}\nu_1/\nu_3 &= \nu(\text{sym})/\nu(\text{asym})\\ &= [M_M^{-1} + M_H^{-1}(1 + \cos\alpha)]^{1/2}[M_M^{-1} + M_H^{-1}(1 - \cos\alpha)]^{-1/2}\end{aligned} \tag{5}$$

Table II. Comparison of Bond Distances and Angles for Hydride-Bridged Metal-Metal Bonded Species

Species	d(M-M), Å	d(M-H), Å	α(M-H-M), deg	Ref
$[\eta^5\text{-}C_5(CH_3)_5\text{-}RhCl]_2HCl$	2.906 (1)	1.85 (5)	104 (4)	9
$[\eta^5\text{-}C_5(CH_3)_5\text{-}IrCl]_2HCl$	2.903 (1)	1.94 (7)	97 (2)	10
$[H_2W_2(CO)_8]^{2-}$	3.016 (1)	1.86 (6)	108 (5)	12
$[Fe_2H_3(p_3)_2]^{+}$ [a]	2.332 (3)	1.83[c]	79[c]	11
$[Co_2H_3(as_3)_2]^{+}$ [b]	2.377 (8)	1.70[c]	89[c]	11
$H_8Re_2(PEt_2Ph)_4$	2.538 (4)	1.878 (7)[d]	85.0 (3)[d]	13
$Mo_2Cl_8H^{3-}$	2.380 (10)[e]	1.90	77.6	This work
$Mo_2Br_8H^{3-}$	2.439 (7)[f]	1.93	78.3	This work

[a] (p_3) is the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane. [b] (as_3) is the ligand 1,1,1-tris(diphenylarsinomethyl)ethane. [c] Bond distances and angles are averaged for three bridging H atoms and reported with unspecified accuracy. [d] Bond distances and angles determined by neutron diffraction and averaged for four bridging H atoms. [e] Reference 2. [f] Reference 4.

Equation 5 then can be used to evaluate α, the M–H–M bond angle. If the M–M distance is known, as it is in $Rb_3Mo_2Cl_8H$ and $Cs_3Mo_2Br_8H$, the M–H bond distance may be calculated with eq 6.

$$d(\text{M-H}) = d(\text{M-M})[2 \sin (\alpha/2)]^{-1} \tag{6}$$

From the measured frequency ratio $\nu(\text{sym})/\nu(\text{asym}) = 1.244$ and $d(\text{Mo-Mo}) = 2.380$ (10) Å[2] for $Rb_3Mo_2Cl_8H$, we obtain $\alpha = 77.6°$ and $d(\text{M-H}) = 1.90$ Å. Although the observed frequencies in $Cs_3Mo_2Cl_8H$ are lower by ca. 25 cm^{-1} the ratio $\nu(\text{sym})/\nu(\text{asym})$ is unchanged and thus the same value for d(Mo–H) is obtained, provided d(Mo–Mo) remains constant. The corresponding computation using the ratio of frequencies for the deuteride $Rb_3Mo_2Cl_8D$ provides the values $\alpha = 78.6°$ and $d(\text{Mo-H}) = 1.88$ Å in satisfactory agreement with the foregoing values for $Rb_3Mo_2Cl_8H$. The Mo–Mo distance in $Cs_3Mo_2Br_8H$ has been determined as 2.439 (7) Å;[4] from this number and $\nu(\text{sym})/\nu(\text{asym}) = 1.222$ we obtain $\alpha = 78.3°$ and $d(\text{Mo-H}) = 1.93$ Å.

We are unaware of previous application of eq 5 to obtain M–H bond distances in this way and recognize that the values so derived have a small error imposed by the approximations used to derive eq 4 and 5. However, evidence that the error is small is provided by comparing the angle α calculated for $Rb_3Mo_2Cl_8H$ with that for $Rb_3Mo_2Cl_8D$. If the approximations used to simplify eq 2 were not valid, the large decrease in frequency of ν(sym) in the deuteride would cause a large change in mixing of the symmetric a_1 modes and a substantial change in the calculated value of α. The observed difference in angles of 1.0° is only twice that calculated for a maximum error in the ratio $\nu(\text{sym})/\nu(\text{asym})$ caused by an error of 5 cm^{-1} in each of the frequencies. From these considerations we estimate errors in α and d(Mo–H) of ca. 1° and 0.02 Å, respectively. The values of both α and d(Mo–H) obtained here are certainly comparable to those recently determined for hydride bridged, metal–metal bonded transition-metal species as shown in Table II for structures determined by x-ray[9-12] or neutron diffraction.[13] In fact the Mo–H distances and Mo–H–Mo angles determined here may be at least as accurate as the values determined by x-ray diffraction where the esd's average ca. 0.06 Å. Finally the bond parameters determined here are especially valuable; there is little prospect that they could be determined by diffraction methods because the H atoms are statistically disordered among the crystalline sites occupied by the bridging ligands in the $Rb_3Mo_2Cl_8H$ or $Cs_3Mo_2Br_8H$ structures.

Difficulties in the location and assignment of metal–hydrogen bands in the infrared and Raman spectra of compounds with M–H–M bridging have been previously reviewed and discussed by Kaesz and Saillant.[17] Most of the difficulties are avoided in the $M_2X_8H^{3-}$ anions because (1) no other bands from organic or CO ligands occur in the M–H stretching region, (2) there is only one H atom per molecule so only two stretching modes are expected for M–H–M bridged system, and (3) the ions $Mo_2X_8H^{3-}$ have maximum symmetry C_{2v} such that both M–H–M stretching modes are infrared active. Application of the above method to other hydride-bridged systems should be approached carefully since large errors may result in cases where there is likely to be extensive mixing between normal vibrational modes.

This method has not been applied to the new compound Cs_3MoWCl_8H because the Mo–W distance is unknown. Even if the Mo–W distance were known it would be risky to apply the method since the Mo–H–W bonding could be unsymmetrical and/or the Mo–H and W–H force constants could be different. An indication of this is gained by comparing data for the cesium salts. It is notable that the frequency difference, $\nu(\text{sym}) - \nu(\text{asym})$, is larger for $MoWCl_8H^{3-}$ than for $Mo_2Cl_8H^{3-}$, while at the same time ν(sym) is larger and ν(asym) smaller for $MoWCl_8H^{3-}$.

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Registry No. $Cs_3Mo_2Cl_8H$, 57719-40-1; $Cs_3Mo_2Cl_8D$, 65681-90-5; $Rb_3Mo_2Cl_8H$, 57719-39-8; $Rb_3Mo_2Cl_8D$, 65681-89-2; Cs_3MoWCl_8H, 65681-88-1; Cs_3MoWCl_8D, 65681-87-0; $Cs_3Mo_2Br_8H$, 57719-38-7; $MoW(O_2CC(CH_3)_3)_4$, 60511-37-7.

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