6.2 eV, respectively. The assignment of the final very weak peak VIII is rather uncertain, but we do calculate a $^1T_2$ state of VCl_4^+, 9.3 eV from the ground state, with predominant orbital configuration $8a_1{}^1 10t_2{}^1$, having ~20% of configurations which differ from VCl_4 by one spin orbital.

Conclusions

The ab initio calculations we have described here are successful in interpreting the photoelectron and absorption spectrum of $TiCl_4$. The d–d transition in VCl_4 is well described by the limited configuration interaction calculations we have performed, but the charge-transfer states, where more electron reorganization occurs upon excitation, are calculated to be some 2 eV too high, as we also found in the case of $TiCl_4$. Only a tentative interpretation of the photoelectron spectrum of VCl_4 is possible due to the large number of states of VCl_4^+ which are calculated to contribute to the spectrum. It would appear that in this molecule an interpretation of the photoelectron spectrum in terms of a simple orbital picture is not possible.

Registry No. $TiCl_4$, 7550-45-0; VCl_4, 7632-51-1; VCl_4^+, 57842-82-7.

References and Notes

(1) P. A. Cox, S. Evans, A. Hamnett, and A. F. Orchard, *Chem. Phys. Lett.*, **7**, 414 (1970).

(2) J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Philos. Trans. R. Soc. London, Ser. A*, **268**, 111 (1970).

(3) C. A. L. Becker, C. J. Ballhausen, and I. Trabjerg, *Theor. Chim. Acta*, **13**, 355 (1969).

(4) D. S. Alderdice, *J. Mol. Spectrosc.*, **15**, 509 (1965); C. Dijkgraaf, *Spectrochim. Acta*, **21**, 1419 (1965).

(5) J. P. Dahl and J. H. Johansen, *Theor. Chim. Acta*, **11**, 26 (1968); **14**, 26 (1969).

(6) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

(7) T. Parameswaran and D. E. Ellis *J. Chem. Phys.*, **58**, 2088 (1973).

(8) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(9) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

(10) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965); J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(11) M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **29**, 113 (1975).

(12) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 161 (1951).

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

Oxidative Addition of Hydrohalic Acids to Dimolybdenum(II) Species. Reformulation of $Mo_2X_8^{3-}$ as $Mo_2X_8H^{3-}$

F. ALBERT COTTON* and BARBARA J. KALBACHER

Received August 29, 1975 AIC50644+

Several years ago a series of compounds thought to have the general formula $M^I{}_3Mo_2X_8$ (M^I = K, Rb, Cs; X = Cl, Br) was reported, and the structures of the binuclear anions were described as confacial bioctahedra with one-third of the bridging halogen atoms missing or, alternatively, as pairs of square pyramids sharing a basal edge. We now present evidence that these anions are in fact $Mo_2X_8H^{3-}$ ions with bridging hydrogen atoms and that they result from oxidative addition of HX to intermediates such as $Mo_2X_7(H_2O)^{3-}$. The compounds are diamagnetic. In the case of the chloro species, tritium labeling has demonstrated the presence of the H atoms and the reactions of $Mo_2X_8H^{3-}$ with D^+ or Mo_2X_8D with H^+ generate HD. There is also infrared evidence for the presence of the bridging hydrogen atoms.

Introduction

In 1969 Bennett, Brencic, and Cotton[1] reported that reaction of dimolybdenum tetraacetate with aqueous hydrochloric acid produced, under certain conditions, dinuclear anions which could be precipitated with large alkali cations such as Rb^+ and Cs^+ to give compounds of apparent formula $M^I{}_3Mo_2Cl_8$. An x-ray crystallographic study showed that these were not the desired oxidation products of $Mo_2Cl_8^{4-}$ (i.e., species retaining the same $Cl_4MoMoCl_4$ structure); instead, they were species similar in structure to the $Mo_2Cl_9^{3-}$ ion, but lacking one bridging Cl^- ion. The $Mo_2Cl_8^{3-}$ ion was found at a site of D_{3h} crystallographic symmetry and the occupancy factor for the bridging position was refined to 0.67. It was concluded that the vacancy in one bridging position of each anion was randomly distributed in the crystal as a whole (i.e., that it varied randomly from one unit cell to another). An approximate measurement[1] of the magnetic susceptibility indicated paramagnetism roughly consistent with the existence of one unpaired electron per formula unit, as would be required by the postulated formula. Moreover, the crystal structure analysis excluded the possibility of any other formula, except for the possible presence of one or more hydrogen atoms, a contingency not considered at the time, since the structure and magnetic data appeared perfectly consistent.

More recently, we investigated the analogous bromo compounds[2] and found a structure for $Cs_3Mo_2Br_8$ entirely identical (except for a slight technicality concerning space group symmetry, which is unimportant in the present context) with that of $Rb_3Mo_2Cl_8$. In this case, however, the magnetic susceptibility was not measured until after the structure had been published. It was then found that $Cs_3Mo_2Br_8$ is diamagnetic.[3] The magnetic susceptibility of $Rb_3Mo_2Cl_8$ was then remeasured, using a carefully purified sample. It, too, was found to be diamagnetic.[3]

To reconcile the diamagnetism of these compounds with their structures, only two possibilities appeared to exist: (1) the assumption of strong intermolecular antiferromagnetic interactions, sufficient to put the Néel temperature well above 25 °C; (2) revision of the formulas in the only way consistent with the crystallographic results, namely, by addition of one atom of hydrogen to each formula unit. The first possibility appeared highly improbable and so attention was turned to obtaining direct evidence regarding the latter.

Experimental Section

The cesium salts of $Mo_2Br_8H^{3-}$ and $Mo_2Br_7^{3-}$ and the rubidium and cesium salts of $Mo_2Cl_8H^{3-}$ were prepared according to literature methods.[1,2,5] The deuterated compounds were prepared by reaction of DBr or DCl with $Mo_2(CH_3CO_2)_4$ under the same conditions employed in the preparation of the corresponding hydrido compounds but with longer reaction times.

DBr (47% in D_2O) was purchased from Bio-Rad, Richmond, Calif. Concentrated DCl was obtained from the ICN Co., Irvine, Calif. Tritiated water (250 μCi/ml) was purchased from New England Nuclear Corp., Boston, Mass.

Infrared spectra were obtained on Nujol mulls using either polyethylene film or KBr plates. Spectra were calibrated with polystyrene.

Table I. Infrared Mo-H-Mo and Mo-D-Mo Absorptions (cm^{-1}) for Hydridooctahalodimolybdate(III) Complexes

Compd	Mo-H-Mo	Mo-D-Mo	Compd	Mo-H-Mo	Mo-D-Mo
$Cs_3Mo_2Br_8H$	1245		$Cs_3Mo_2Cl_8H$	1245	
$Cs_3Mo_2Br_8D$		915	$Rb_3Mo_2Cl_8D$		916
$Cs_3Mo_2Br_7·2H_2O$			$Cs_3Mo_2Cl_8D$		904
			$Rb_3Mo_2Cl_8H$	1274	

The mass spectra were obtained at 8 kV referenced to He and H_2.

Tritium Labeling. Tritium-enriched $Rb_3Mo_2Cl_8H$ was dissolved in dimethyl sulfoxide. One milliliter of the resultant solution was added to Aquasol scintillation counting fluid for tritium counting. A control mixture of unlabeled $Rb_3Mo_2Cl_8H$, dimethyl sulfoxide, Aquasol, and a known quantity of ^3H_2O was counted also.

The octabromo system $Cs_3Mo_2Br_8{}^3H$ could not be counted because of its dark color and $Cs_3Mo_2Cl_8{}^3H$ proved to be too insoluble in all solvents except water, with which it reacts.

Results

It is not, in fact, easy to prove or disprove the presence of one hydrogen atom in compounds of such high molecular weights which are also practically insoluble except when they react with the solvent.

The first experiment[4] was to repeat the preparation of "$Cs_3Mo_2Br_8$" under conditions where the uptake of a gas (O_2) or the evolution of a gas (H_2) would be evident. Neither was observed. This appeared to leave, then, only the possibility that the oxidizing agent is HX and, thus, that the overall reaction of $Mo_2(OAc)_4$ to give the isolated products had to be described by eq 1.

$$Mo_2(OAc)_4 + 5HX + 3M^+ + 3X^- = M_3Mo_2X_8H + 4HOAc \qquad (1)$$

The use of tritium labeling was feasible only for $Rb_3Mo_2Cl_8H$. Two independent experiments, where the counting procedure was calibrated with a blank sample prepared from $Rb_3Mo_2Cl_8$ to which a known activity of ^3H_2O had been added, gave the following values for atoms of H per formula unit: 1.12 and 0.818.

Infrared evidence for the presence of bridging hydrogen atoms is presented in Table I, where the frequencies of bands with medium intensities are listed for analogous protium- and deuterium-containing compounds.[15] The observed shifts are in the range of 90–96% of the values expected for an increase in reduced mass by a factor of 2. This indicates that the modes responsible for the bands are nearly pure antisymmetric Mo–H–Mo and Mo–D–Mo stretches in which essentially all of the motion is executed by the H and D atoms.

We have found that $Cs_3Mo_2Br_8H$ reacts slowly with 23% aqueous HBr or with water to liberate hydrogen. From the acid solution an apparently homogeneous brick red precipitate is obtained which appears from analysis to be $Cs_3Mo_2Br_9$ although the analytical data are not precise enough to afford definitive identification. The average of several analyses for percent Br is 53.1 while the theoretical values for $Cs_3Mo_2Br_9$ and $Cs_3Mo_2Br_8H$ are 54.90 and 51.93, respectively. $Cs_3Mo_2Cl_8H$ does not react at an observable rate with aqueous HCl but does react with H_2O to generate H_2. The above observations proved useful in demonstrating that hydrogen is actually present in the $M^I{}_3Mo_2X_8H$ compounds as the following results show.

In the first experiment, a sample of $Cs_3Mo_2Br_8D$ was added to degassed, frozen water. The entire system was then evacuated and allowed to warm to 25 °C. The gas generated was collected and its mass spectrum was recorded. It consisted of 20% H_2, 80% HD, and no detectable quantity of D_2. Ideally, the gas should have been 100% HD according to eq 2.

$$Cs_3Mo_2Br_8D + H^+ + Br^- = Cs_3Mo_2Br_9 + HD \qquad (2)$$

The complete absence of D_2 is consistent with this equation and the presence of D_2 would have been a serious complication. The presence of some H_2 is not, however, surprising when the likelihood of deviations from ideality in the experiment is recognized. The H_2 must arise from H in the sample of $Cs_3Mo_2Br_8D$. CsBr is rather hygroscopic and it was probably the main source of H_2O in the preparation of $Cs_3Mo_2Br_8D$ although small amounts may also have originated in other ingredients of the reaction mixture. When it is recalled (see Experimental Section) that oxidative addition of HBr seems to occur more rapidly than that of DBr, an appreciable increase of the H:D ratio in the product, $Cs_3Mo_2Br_8D$, over that in the reaction medium is to be expected. Thus even a few percent H in the nominally deuterated reagents could lead to some 20% of H in the $Cs_3Mo_2Br_8D$.

In view of the foregoing explanation, it was expected that a much neater experiment would involve the reaction of one of the octahalo systems with D_2O. In a manner analogous to that employed for the bromo compound, $Cs_3Mo_2Cl_8H$ was allowed to react with D_2O. The mass spectrum of the evolved gas showed that it contained 1.6% H_2, 94.7% HD, and 3.6% D_2. Since quantitative work to calibrate the mass spectrum was not performed and the relative peak heights are a function of which peak was used to tune the instrument, it is possible that the actual percentage of D_2 may be lower than 3.6%. On the basis of these results, however, it is impossible to rule out the possibility that solvent exchange of the hydride takes place.

Discussion

In view of the evidence that the species previously believed to be $Mo_2X_8^{3-}$ are in fact $Mo_2X_8H^{3-}$, we now believe that eq 1 represents the overall reaction for their formation from $Mo_2(O_2CCH_3)_4$ and aqueous HX. Moreover, in view of the recent report by Brencic of the isolation of $Cs_3Mo_2Br_7·2H_2O$, it seems probable that eq 1 represents the combined result of two reaction steps

$$Mo_2(O_2CCH_3)_4 + 4HBr + 3Br^- = Mo_2Br_7^{3-} + 4CH_3CO_2H \qquad (1a)$$

$$Mo_2Br_7^{3-} + HBr = Mo_2Br_8H^{3-} \qquad (1b)$$

Reaction 1b is then to be regarded formally as an oxidative addition of HBr to $Mo_2Br_7^{3-}$. Of course, in aqueous solution the HBr is dissociated and the process presumably takes place as two discrete steps, each involving the addition of an ion. While oxidative addition reactions are now very well known to occur at monatomic metal centers, so that the formal oxidation number of a single metal atom increases by +2, this appears to be the first (or at least one of the first) example of oxidative addition to a binuclear complex so that each metal atom has its formal oxidation number increased by +1.

Even when $Cs_3Mo_2Br_7$ is not actually isolated, as Brencic has done, it is seen in all preparations of $Cs_3Mo_2Br_8H$ as an initial, transient purple precipitate which changes to the dark brown $Cs_3Mo_2Br_8H$ product in 45 min or less. The analogous reaction to eq 1b in which DBr is the oxidative addend proceeds much more slowly and approximately 24 h is required for the disappearance of all of the purple intermediate.

The observation of infrared bands due to bridging hydrogen atoms is not new but has been largely confined to trinuclear species with equilateral triangular clusters of metal atoms and a (presumed) bridging hydrogen atom on each edge.[8–10] These bands have been found in the 1100–1300-cm^{-1} range and shift into the 800–900-cm^{-1} range upon deuteration.

More recently, Sacconi and coworkers[11] have reported $M(\mu\text{-}H)_3M$ species (M = Fe, Co) in which the protium compound of iron has a band at 1048 cm^{-1} while the deuterium analogue has a band at 790 cm^{-1}. The shift here is about 5% short of the full amount for a change in reduced mass from 1 to 2. In other dinuclear systems for which infrared data are available, the M–H–M bands appear over a wide range. For

Table II. Structural Comparison of the $Mo_2X_8H^{3-}$ Ions with the $Mo_2X_9{}^{3-}$ Ions[a]

Anion	Mo–Mo, Å	Mag moment	Angles at bridging X atoms, deg	Mo–X-(term), Å	Mo–X-(br), Å	Ref
$Mo_2Cl_9{}^{3-}$	2.665 (1)	~0	65.6 (4)	2.384 (6)	2.487 (12)	13
$Mo_2Cl_8H^{3-}$	2.380 (10)	0	56.8 (9)	2.380 (10)	2.500 (20)	1
$Mo_2Br_9{}^{3-}$	2.816 (9)	>0	64.9 (4)	2.544 (3)	2.624 (5)	13
$Mo_2Br_8H^{3-}$	2.439 (7)	0	54.3 (2)	2.554 (3)	2.672 (5)	2

[a] Numbers in parentheses beneath each parameter are esd's occurring in the least significant digit.

the hydride-bridged dimers, characterized as $[HTi(C_5H_5)_2]_2$ and $[HTi(C_5H_5)(C_5H_4)]_2$, bands are observed at 1450 and 1230 cm^{-1}, respectively.[12] The dimeric chromium system $H_2Cr_2(CO)_{10}{}^-$ exhibits a Raman-active band at 1004 cm^{-1} which is shifted to 705 cm^{-1} upon deuteration.[10] Thus, the bands we assign to bridging protium and deuterium atoms are within the proper range for μ-hydrido and -deuterio systems.

Now that the true identity of the $Mo_2X_8H^{3-}$ anions, with three bridging atoms including hydrogen, is known, a structural comparison of the pairs of $Mo_2X_9{}^{3-}$–$Mo_2X_8H^{3-}$ anions (Table II) is of interest. The data for the $Mo_2X_9{}^{3-}$ ions are taken from the work of Saillant and Wentworth.[13] It is evident that the replacement of one Cl or Br bridge by an H atom enormously increases the strength of the interaction between the metal atoms; in both the chloro and the bromo pairs, the hydrido-bridged species has an Mo–Mo distance some 0.3–0.4 Å shorter than in the species with three halogen bridges, and the angles at the bridging halogen atoms contract considerably (ca. 10°) to some of the lowest values ever recorded for bridging Cl and Br atoms. At the same time the Mo–Cl and Mo–Br distances to the bridging atoms lengthen slightly. The Mo–X distances to terminal X atoms are unchanged, however, in support of the assignment of the same oxidation number, +3, to the Mo atoms in both the $Mo_2X_9{}^{3-}$ and the $Mo_2X_8H^{3-}$ ions.

It seems reasonable to suppose[13] that in the $Mo_2X_9{}^{3-}$ species there exist Mo–Mo bonds, as in the analogous $W_2Cl_9{}^{3-}$ ion, since the central MX_3M bipyramid is significantly flattened relative to the shape expected for the ideal confacial bioctahedron.[14] The zero or near-zero magnetic moments are consistent with M–M bonding. Probably the factor which limits the closeness and strength of the Mo–Mo interaction in the $Mo_2X_9{}^{3-}$ species is the size of the bridging Cl or Br atoms, which impedes the approach of the Mo atoms to each other. When one of the three Cl or Br atoms is replaced by the bridging H atom, this steric factor is reduced and the Mo–Mo interaction can become appreciably closer and stronger.

Acknowledgment. We are grateful to Dr. John McGinley for help in developing the tritium-counting procedure and to Dr. Ronald Grigsby for measuring the mass spectra. We thank Dr. Jack Williams of Argonne National Laboratory for evaluating the possibility of securing unambiguous information from neutron powder patterns. Financial support by the National Science Foundation (Grant No. 33142X) is gratefully acknowledged.

Registry No. $Cs_3Mo_2Br_8H$, 57719-38-7; $Rb_3Mo_2Cl_8H$, 57719-39-8; $Cs_3Mo_2Cl_8H$, 57719-40-1.

References and Notes

(1) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).
(2) F. A. Cotton, B. A. Frenz, and Z. C. Mester, *Acta Crystallogr., Sect. B*, **29**, 1515 (1973).
(3) These measurements were kindly carried out by Dr. Eric Pedersen, Technical University of Denmark, Copenhagen.
(4) This work was done by Dr. Z. C. Mester.
(5) J. V. Brencic, D. Dobcnik, and P. Segedin, *Monatsh. Chem.*, **105**, 944 (1974); *Chem. Abstr.*, **80**, 115441 (1974).
(6) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 2698 (1969).
(7) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 351 (1970).
(8) J. Knight and M. J. Mays, *J. Chem. Soc. A*, 711 (1970).
(9) B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 901 (1970).
(10) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(11) P. Dapporto, S. Midollini and L. Sacconi, *Inorg. Chem.*, **14**, 1643 (1975).
(12) J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, **91**, 7301 (1969); *ibid.*, **92**, 6182 (1970).
(13) R. Saillant, R. B. Jackson, W. E. Streib, K. Folting, and R. A. D. Wentworth, *Inorg. Chem.*, **10**, 1453 (1971); R. Saillant and R. A. D. Wentworth, *ibid.*, **8**, 1226 (1969).
(14) F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972).
(15) We are unable to account with certainty for the earilier failure[1] to detect the infrared bands which we now find. Presumably the samples were not properly prepared or were too dilute.

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19174

Crystal and Molecular Structure of Hexadecamethylbicyclo[3.3.1]nonasilane[1]

WILLIAM STALLINGS and JERRY DONOHUE*

Received March 4, 1975 AIC50160D

The crystal structure of $Si_9(CH_3)_{16}$ was determined by the single-crystal x-ray diffraction technique using data collected from a fully automated diffractometer. The unit cell is monoclinic, space group $P2_1/c$, with $a = 25.952 \pm 0.007$ Å, $b = 10.398 \pm 0.005$ Å, $c = 28.146 \pm 0.009$ Å, and $\beta = 122.32 \pm 0.02°$, and contains eight molecules. The structure was elucidated to determine which isomer of the polysilane backbone had been synthetically prepared. A trial structure was obtained by direct methods and Fourier techniques and refined by full-matrix least squares. The final value of the R index is 0.092. Each independent molecule contains a bicyclo[3.3.1] system, a six-membered polysilane ring in a classical chair conformation, a six-membered polysilane ring, five of whose atoms are roughly coplanar, and an Si–Si–Si bond angle of 120°. Methyl groups bonded to the five coplanar silicon atoms are eclipsed.

Introduction

The synthesis of permethylated, bicyclic, and cage polysilanes has been recently reported by West and Indriksons.[2] Their preparation was accomplished by the reaction

$$(CH_3)_2SiCl_2 + CH_3SiCl_3 + Na(K) \xrightarrow[\text{naphthalene}]{\text{THF}} (CH_3Si)_n((CH_3)_2Si)_m + Na(K)Cl$$

The product mixture was vacuum distilled and products in the