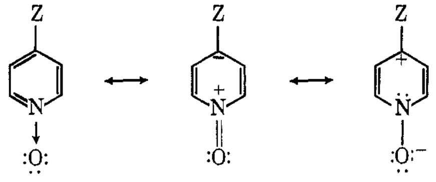
and *cis*-$SnF_4 \cdot 2C_2H_5OH$.[13] The two triplet F^{19} resonances of the $TiF_4 \cdot 2C_2H_5OH$ (d^0) complex are separated by 60 ppm, showing a significant difference in the shielding of the two fluorine environments. The F^{19} spectrum of *cis*-$SnF_4 \cdot 2C_2H_5OH$, where p_π–d_π interaction is reduced by the d^{10} electronic configuration, is second order since the chemical shift between the two types of fluorine is approximately equal to the coupling constant (~1 ppm).

In octahedral complexes there are three metal d orbitals of proper symmetry for π bonding. It is possible, therefore, to make a total of three pure π bonds.[14] In distorted octahedral complexes such as $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$ the three d_π orbitals will, in general, be distributed unequally among the ligands. The ability of N-oxide oxygen to π bond to titanium depends in part upon the *para* substituent. Pyridine 1-oxide can be represented by the three principal resonance structures shown below (Z = H).



A B C

The presence of an activating group such as 4-methoxy would be expected to enhance contributions from structures similar to C, whereas electron-withdrawing groups such as 4-nitro would enhance contributions from structures similar to B. The resonance forms for the $4\text{-}ZC_5H_4NO$ ligands producing the largest downfield shifts in the F^{19} signal are those which show oxygen to ring nitrogen π bonding. The change in the fluorine π donation to the titanium d orbitals could result from competition between the pyridine 1-oxide donor oxygen and fluorine for the available d orbitals of proper symmetry. The more O–N π bonding that exists, the less successfully can the oxygen compete with fluorine for the available metal d orbitals. As fluorine to titanium p_π–d_π donation increases, the F^{19} nmr signal shifts downfield.

D. Coupling Constants.—The F^{19} spin–spin coupling constants of the $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$ complexes are assigned as follows: $J_{\alpha\beta} = 39$ cps, $J_{\alpha\beta'} = 34\text{–}35$ cps, and $J_{\beta\beta'} = 48$ cps. Comparison of the J_{F-F} values of the different complexes shows that the spin–spin interactions are insensitive to the nature of Z. This observation indicates that there is little change in the σ-bond framework as Z is varied. However, the three coupling constants of each complex are quite different from each other. Since the hybridization[15] of the orbitals involved contributes to the magnitude of the coupling constant, it is suggested that there is a significant difference in the various F–Ti–F bond angles.

Acknowledgments.—The financial support of this work by the U. S. Air Force Material Laboratory, RTD, is gratefully acknowledged. The authors wish to thank Mr. Carl Popp for a supply of 4-bromopyridine 1-oxide.

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(13) R. O. Ragsdale and B. B. Stewart, *Proc. Chem. Soc.*, 194 (1964).

(14) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 184–188.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS, AND THE UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA

Far-Infrared Spectra of Metal Atom Cluster Compounds.
I. $Mo_6X_8^{4+}$ Derivatives[1]

BY F. A. COTTON, R. M. WING, AND R. A. ZIMMERMAN

Received May 26, 1966

The infrared spectra of $Mo_6X_8Y_6$ species in which X is Cl or Br and Y is Cl, Br, or I, as well as a few other related species, and also the spectrum of $W_6Cl_{14}^{2-}$ have been recorded. The effect of varying the cations (*e.g.*, $(n\text{-}C_4H_9)_4N^+$, $(C_6H_5)_4N^+$, $(C_6H_5)_4As^+$, Cs^+) has been shown to be negligible. The results have been considered in relation to the selection rules and the empirically established ranges for M–X stretches and X–M–X bends with the result that the observed spectra have been completely assigned with considerable certainty to the various T_{1u} modes. Of particular interest is the conclusion that the Mo–Mo stretching frequency has been identified at ~230 cm^{-1}.

Introduction

Metal atom cluster compounds[2] of the kind which contain metal atoms in low formal oxidation states together with halide ions are a common and important type. The vibrational spectra of such species are expected to be interesting and informative just as for

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(1) Supported by the United States Atomic Energy Commission under Contract At(30-1)-1965.

(2) *Cf.* F. A. Cotton, *Quart. Rev.* (London), **20**, 389 (1966); "McGraw-Hill Yearbook of Science and Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

other classes of molecules, but, since the fundamentals are all of relatively low frequencies (<500 cm^{-1}) and the molecules are all colored, many of them rather intensely so, the chief source of data must be the far-infrared spectra.

Of greatest interest are the vibrations associated primarily with metal–metal bond stretching, but in order to identify these it is necessary to sort out and assign the entire spectrum, which will also contain bands due to metal–halogen stretching and deformation modes.

This paper is the first report of some investigations of this kind. It is primarily concerned with $Mo_6X_8Y_6$ species, in which the X's are the eight bridging halide ions which are intimately associated with the Mo_6 cluster and the Y's (which may be the same as the X's or not) are the labile, nonbridging halide ions which occupy the six centrifugally directed orbitals of the Mo_6 cluster. By studying suitable permutations of X and Y it was hoped that sufficient data for a fairly complete and conclusive assignment of all of the spectra could be obtained. This expectation was realized as will be described below.

Experimental Section

Preparation of Compounds.—Hexamolybdenum dodecachloride, Mo_6Cl_{12}, and hexatungsten dodecachloride, W_6Cl_{12}, were prepared by the method of Sheldon[3] as modified by Cotton and Curtis.[4]

$[(C_2H_5)_4N]_2[Mo_6Cl_8(Cl)_6]$.—$Mo_6Cl_{12}$ was dissolved in a small volume of absolute ethanol. The solution was filtered and the product precipitated by addition of an excess of $(C_2H_5)_4NCl$ in dilute HCl. Alternatively, the Mo_6Cl_{12} was dissolved in a minimum amount of warm 0.1 *N* NaOH, and upon addition of the $(C_2H_5)_4NCl$ + HCl solution the desired product again precipitated. In the same way were prepared similar products in which the cations were Cs, $(C_6H_5)_4As$, and other quaternary ammonium salts. The products were filtered, washed with ethanol, and dried under vacuum at 100° to yield yellow powders.

Anal. Calcd for $C_{16}H_{40}N_2Cl_{14}Mo_6$: C, 14.42; H, 3.03; N, 2.10; Cl, 37.25; Mo, 43.20. Found: C, 14.5; H, 3.16; Cl, 37.6; Mo 41.4.

$[(C_2H_5)_4N]_2[W_6Cl_8(Cl)_6]$.—This was prepared in the same way as the molybdenum compound, using W_6Cl_{12} in place of Mo_6Cl_{12}, to yield a pale green powder.

Anal. Calcd for $C_{16}H_{40}N_2Cl_{14}W_6$: C, 10.33; H, 2.17; N, 1.51; Cl, 26.69; W, 59.31. Found: C, 10.3; H, 2.22; N, 1.51; Cl, 26.0; W, 59.3.

$[(n\text{-}C_4H_9)_4N]_2[Mo_6Cl_8(Br)_6]$.—$Mo_6Cl_{12}$ (1 mmole) was placed in 50 ml of absolute ethanol and 25 ml of HBr (48% solution) added to make the mixture ~4 *M* in HBr. Gentle warming for 1 hr completely dissolved the starting material, and $(n\text{-}C_4H_9)_4NBr$ (4 mmoles) in 20 ml of alcohol was added. Cooling and standing precipitated a yellow-orange crystalline powder, which was collected and washed with alcohol and dried at 100° under vacuum. As an alternative method of preparation the labile chloride ions of Mo_6Cl_{12} were titrated off using $AgBF_4$, followed by addition of NaBr, in excess, to the resulting mixture. Removal of the AgX precipitate by filtration gave a pale yellow solution, to which was added an excess of $(n\text{-}C_4H_9)_4NBr$. The resulting solid was collected and washed with hot methanol to remove the $(n\text{-}C_4H_9)_4NBr$ impurity and yielded a yellow powder, which was dried at 100° under vacuum.

Anal. Calcd for $C_{32}H_{72}N_2Br_6Cl_8Mo_6$: C, 21.07; H, 3.98; N, 1.54; Br, 26.29; Cl, 15.55; Mo, 31.57. Found: C, 21.4; H, 4.07; N, 1.74; Br, 24.8; Cl, 15.9; Mo, 29.8.

$[(n\text{-}C_4H_9)_4N]_2[Mo_6Cl_8(I)_6]$.—This was prepared in the same way as the bromide salt above, using HI or NaI in place of HBr or NaBr.

Anal. Calcd for $C_{32}H_{72}N_2Cl_8I_6Mo_6$: C, 18.25; H, 3.45; N, 1.33; Cl, 13.47; I, 36.16; Mo, 27.34. Found: C, 18.7; H, 3.88; N, 1.35; Cl, 13.5; I, 34.8; Mo, 27.5.

Mo_6Br_{12} and Mo_6I_{12}.—These compounds were prepared by reaction of Mo_6Cl_{12} with fused LiBr and LiI according to Sheldon.[5]

Anal. Calcd for $Br_{12}Mo_6$: Br, 62.50; Mo, 37.50. Found: Br, 60.5; Mo, 36.7. Calcd for $I_{12}Mo_6$: I, 72.50; Mo, 27.50. Found: I, 68.8; Mo, 29.3.

$[(C_2H_5)_4N]_2[Mo_6Br_8(Cl)_6]$.—$Mo_6Br_{12}$ was dissolved in the minimum amount of 0.1 *N* NaOH, and an excess of a hot solution of HCl and $(C_2H_5)_4NCl$ added. The yellow precipitate was digested, collected, washed with a little methanol, and dried at 100° under vacuum.

Anal. Calcd for $C_{16}H_{40}N_2Br_8Cl_6Mo_6$: C, 11.38; H, 2.39; N, 1.66; Br, 37.87; Cl, 12.60; Mo, 34.10. Found: C, 12.3; H, 2.53; N, 2.00; Br, 35.9; Cl, 12.4; Mo, 34.1.

$[(C_2H_5)_4N]_2[Mo_6Br_8(Br)_6]$.—This was prepared in the same way as the preceding chloride compound, using HBr and $(C_2H_5)_4NBr$ in place of HCl and $(C_2H_5)_4NCl$.

Anal. Calcd for $C_{16}H_{40}N_2Br_{14}Mo_6$: C, 9.83; H, 2.06; N, 1.43; Br, 57.23; Mo, 29.45. Found: C, 9.70; H, 2.10; N, 1.60; Br, 56.4; Mo, 29.0.

$[(CH_3)_4N]_2[Mo_6Br_8(I)_6]$.—This was prepared in the same way as the preceding two compounds, using HI and $(CH_3)_4NI$.

Anal. Calcd for $C_8H_{24}N_2Br_8I_6Mo_6$: C, 4.52; H, 1.14; N, 1.32; Br, 30.09; I, 35.84; Mo, 27.09. Found: C, 4.28; H, 1.11; N, 1.29; Br, 28.4; I, 36.7; Mo, 28.1.

Recording of Spectra.—Most of the measurements were made using a Fourier spectrophotometer, Model FS-520, manufactured by the Research and Industrial Instruments Co., London, England. This instrument is a Michelson interferometer. For the range 80–350 cm^{-1}, a beam splitter consisting of a 0.001 in. thick Mylar sheet and a filter consisting of a 0.006 in. thick plate composed of black polyethylene, beryllium oxide, and zinc oxide were used.

Samples were prepared by intimately mixing powdered polyethylene and the powdered solid compound, then pressing and melting the mixture to suspend the solid uniformly in a sheet of clear polyethylene. Typically, 100–200 mg of sample (depending upon its molecular weight) was mixed with 1.0 g of polyethylene and pressed at 10,000–15,000 psi at ~250° to form a disk 0.005 in. thick and 3 in. in diameter.

The direct output of the interferometer, which is a Fourier transform of the absorption spectrum, is obtained on punched tape which is transferred to cards and fed to a program for carrying out the transform to the absorption spectrum on an IBM 7094 computer. The output of this computation is a plot of intensity in arbitrary units scaled to lie in the range 0–100 and thus corresponds to the usual absorption (or transmission) spectrum. The resolution of the instrument can be varied. The spectra recorded in this study have a theoretical resolution of 2.5 cm^{-1}.

The region 500–200 cm^{-1} was also recorded for many though not all compounds, using a Perkin-Elmer Model 621 spectrometer, well flushed with dry nitrogen. Several spectra were also run in the region 80–180 cm^{-1} on a single-beam, nitrogen-flushed Perkin-Elmer Model 301 grating spectrometer.

The main purpose of recording spectra with several instruments was to assure the absence of instrumental artifacts from the spectra which were finally taken to be genuine. In fact, no major feature shown in Figures 1–3 failed to appear in every spectrum recorded.

Results

Representative spectra for the various compounds are displayed in Figures 1–3. There is a certain choppiness

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[3] J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960); 4183 (1963); 1287 (1964).

[4] F. A. Cotton and N. F. Curtis, *Inorg. Chem.*, **4**, 241 (1965).

[5] J. C. Sheldon, *J. Chem. Soc.*, 410 (1962).

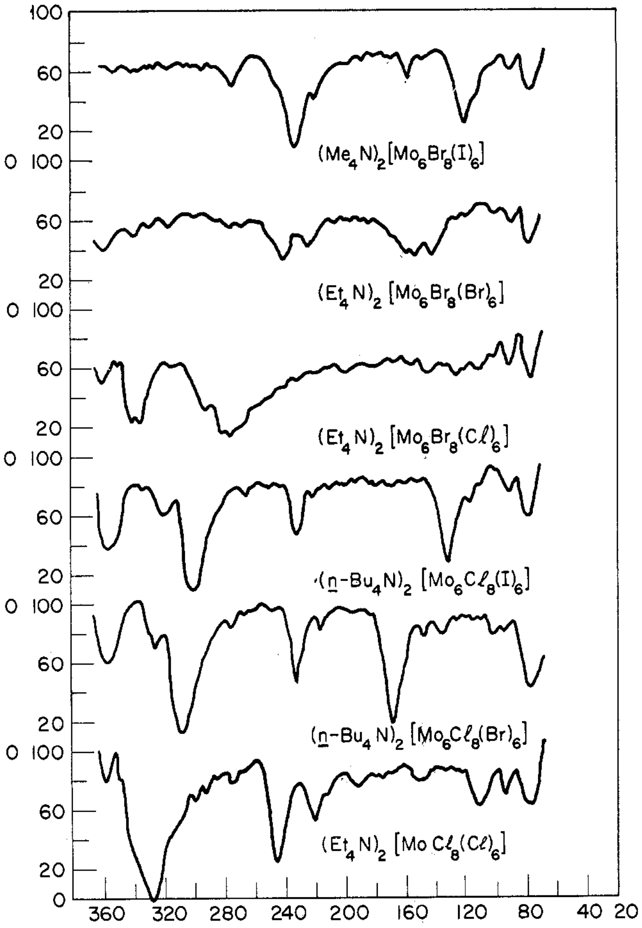

Figure 1.—Spectra of $Mo_6X_8Y_6^{2-}$ ions with X = Cl, Br and Y = Cl, Br, I. The traces shown were all obtained using the interferometer.

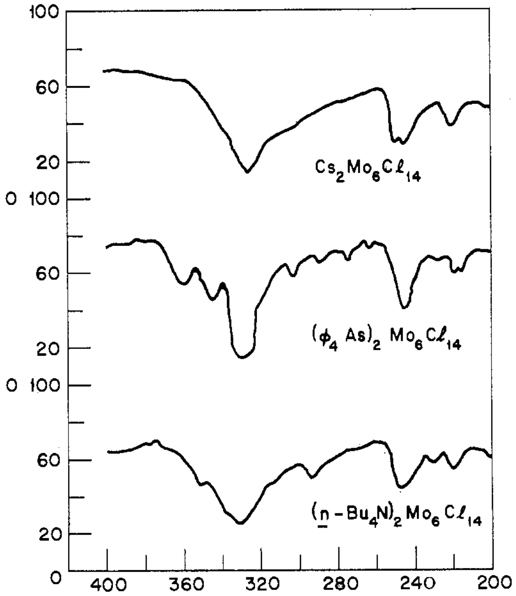

Figure 2.—Spectra of three compounds containing the $Mo_6Cl_{14}^{2-}$ ion with different cations. These were recorded on the Perkin-Elmer 621 spectrometer. They may bef urther compared to the bottom trace in Figure 1.

to the spectra produced by the interferometer due to the incompleteness of the Fourier series and to the point by point mode of recording. Thus, small features in

Figure 3.—Spectra of $W_6Cl_{14}^{2-}$ salts: (a) $[(n\text{-}C_4H_9)_4N]_2W_6Cl_{14}$ recorded on the Perkin-Elmer 621; (b) same compound as (a), recorded on the Perkin-Elmer 301; (c) $[(C_2H_5)_4N]_2W_6Cl_{14}$ recorded on the interferometer.

the spectra must be treated with doubt. However, the well-defined absorption bands are all that need be considered in the interpretations to be made, so this feature is of no practical importance here.

Figure 1 shows mainly how the spectra change as the identity of either X or Y is changed while the other is kept fixed. Figure 2 together with the bottom curve of Figure 1 indicate that the principal spectral features are essentially independent of the specific compound of a given $M_6X_8Y_6^{2-}$ ion which is used and also of the spectrometer used. Figure 3 gives the so far limited data for a tungsten species, namely, $W_6Cl_{14}^{2-}$.

Discussion

Symmetry and Selection Rules.—The $M_6X_8Y_6^{2-}$ species have intrinsic O_h symmetry, though this may be degraded by their environment in crystalline compounds. Figure 4 shows the structure[2] of the $M_6X_8Y_6$ unit. Table I gives the symmetry classes and selection rules for such a molecule, using various kinds of internal coordinates as a basis set for constructing symmetry coordinates. It is seen that there are five T_{1u} modes (T_{1u} being the only symmetry type which is infrared active), of which two are M–X stretches, one is an M–Y stretch, one is an X–M–Y bend (which presumably comes close to being a wagging of the Y atoms), and, finally, one is an M–M stretch.

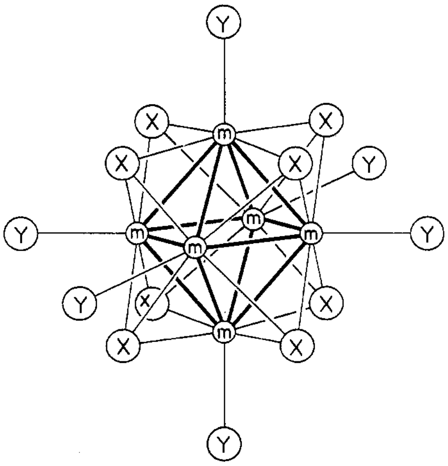

Figure 4.—A drawing showing the structure and labeling of the atoms of an $M_6X_8Y_6^{2-}$ ion.

TABLE I

SELECTION RULES FOR $M_6X_8Y_6^{2-}$ SPECIES

POINT GROUP: O_h

Internal coordinate (no. in parentheses)	No. of modes of each symmetry class									
	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}	A_{1u}	A_{2u}	E_u	T_{1u}	T_{2u}
M–M (12)	1		1		1				1	1
M–X (24)	1		1	1	2		1	1	2	1
M–Y (6)	1		1						1	
X–M–Y (12)				1	1				1	1
Totals (54)	3		3	2	4		1	1	5	3

Assignment of Spectra.—On the basis of existing data for far-infrared spectra of halo complexes[6–9] the following empirical rules, which will be useful here, can be formulated. (1) M–Cl, M–Br, and M–I stretching modes tend to occur in the regions 280–350, 200–240, and 160–190 cm^{-1}, respectively. (2) For a given type of compound, $M_mX_x^n$, the ratios $\nu(\mathrm{Br})/\nu(\mathrm{Cl})$ and $\nu(\mathrm{I})/\nu(\mathrm{Br})$ are typically ~0.70 and ~0.80, respectively, that is, not very different from the square roots of the inverse mass ratios of the halogen atoms. (3) The X–M–X bending (or X wagging) frequencies are in the ranges 90–130, 50–100, and <50 cm^{-1} for X = Cl, Br, and I, respectively.

It should also be noted, as a criterion for assignment, that the weight of evidence suggests that in metal atom cluster compounds generally[2] M–Y type of bonds are longer and weaker than M–X type of bonds (see Figure 4), although the $Mo_6Cl_8^{4+}$ systems which have been studied crystallographically are few and there are no data for the $Mo_6X_8Y_6^{2-}$ species actually studied in this work.

The assignments which have been made are given in Table II. The rationale for these assignments is as follows. We consider first the three ions $Mo_6Cl_8Cl_6^{2-}$, $Mo_6Cl_8Br_6^{2-}$, and $Mo_6Cl_8I_6^{2-}$. In each case there is strong, broad absorption in the region 290–350 cm^{-1}. This can be assigned to the two M–X (X = Cl) stretching modes of the $Mo_6Cl_8^{4+}$ group.[10] The next strongest band in each spectrum occurs at 246, 168, and 132 cm^{-1} in the Cl, Br, and I compounds, respectively. These frequencies and their ratios (0.69, 0.79) clearly show that they are due to the M–Y (Y = Cl, Br, I) mode. The slight downward drift of the M–X absorption can be attributed to the decreasing interaction of the M–X stretches with the M–Y stretches as the frequency of the M–Y stretch moves away. It is important to keep in mind that *all* of the infrared-active modes have the same symmetry and hence are described by a 5 × 5 secular equation in which, in principle, *all* off-diagonal elements are nonzero.

TABLE II

PROPOSED FREQUENCY (CM^{-1}) ASSIGNMENTS IN $M_6X_8Y_6^{2-}$ IONS

			T_{1u} Modes[a]				
M	X	Y	ν_1(M–X)	ν_2(M–X)	ν_3(M–Y)	δ_4(M–Y)	ν_5(M–M)
Mo	Cl	Cl	← 350–310 →		246	110	220
Mo	Cl	Br	← 330–290 →		168	77 (?)	232
Mo	Cl	I	← 325–280 →		132	<70	233
Mo	Br	Cl	← 345–330, 300–260 →			~120	240–260 (?)
Mo	Br	Br	← 270, 250–220 →		130–170	<80	220 (?)
Mo	Br	I	← 274, 250–210 →		120	<80	210–250
W	Cl	Cl	← 320–290 →		224	205 (?)	150 (?)

[a] These are purely qualitative indications of the approximate nature of the normal coordinate. ν denotes a stretching mode; δ denotes a bending or wagging mode.

The M–Y wagging mode seems likely to be responsible for the band at 110 cm^{-1} in $Mo_6Cl_8Cl_6^{2-}$. The analogous modes for $Mo_6Cl_8Br_6^{2-}$ and $Mo_6Cl_8I_6^{2-}$ should be below the range of observation.

We are thus left to account for the bands found at 220, 232, and 233 cm^{-1} in $Mo_6Cl_8Y_6^{2-}$ (Y = Cl, Br, I, respectively) and to find an assignment for the expected T_{1u} Mo–Mo stretching mode. It seems likely that these bands and the required assignment can be matched. The reason for the shift of ν(Mo–Mo) from 220 to ~232 cm^{-1} is again interaction between modes of the same symmetry. In $Mo_6Cl_8Cl_6^{2-}$, the M–Y (Y = Cl) band lies just above (~245 cm^{-1}) the "natural" frequency (~230 cm^{-1}) of the Mo–Mo mode and hence "pushes it down" a little, whereas in the other cases the Mo–Y (Y = Br, I) frequency is well below the Mo–Mo frequency tending to have little influence on the band positions.

Thus, the conclusion we reach regarding the force constant and hence the metal–metal bonding in $Mo_6X_8Y_6^{2-}$ species is that they are not appreciably influenced by changes in the nature of Y.

For the $Mo_6Br_8Y_6^{2-}$ species, the spectra are less well defined and they could probably not, by themselves, be fully interpreted. However, with the foregoing interpretation of the $Mo_6Cl_8Y_6^{2-}$ spectra as a basis, the following interpretation can be made. In these cases, the recognition of extensive interaction and mixing of symmetry coordinations formed from different types of internal coordinates is most important. In $Mo_6Br_8Cl_6^{2-}$, it would appear that ν_1(M–X), ν_2(M–X), and ν_3(M–Y) are thoroughly mixed and account for the absorption in the region 220–320 cm^{-1}. Presumably ν_5(Mo–Mo) is also involved here, perhaps mainly in the tail region, around 240–260 cm^{-1}. There is no well-defined band attributable to δ_4(M–Y) but, compared to the other $Mo_6Br_8Y_6^{2-}$ compounds, $Mo_6Br_8Cl_6^{2-}$ does absorb more intensely in the region of ~120 cm^{-1} where this mode would be expected. It is not clear to us what assignment is appropriate for the absorption at ~340 cm^{-1}.

Turning then to $Mo_6Br_8Br_6^{2-}$, the ν_3(Mo–Y) absorption is now in the region 130–170 cm^{-1}. The reason for its breadth is not clear. This then leaves the ν_1(Mo–X), ν_2(Mo–X), and ν_5(Mo–Mo) absorptions in the region 220–250 cm^{-1} and, perhaps also, as a broad absorption around 270 cm^{-1}. The δ_4(Mo–Y) band is apparently below the range of observation.

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(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 106.

(7) R. J. H. Clark, *Record Chem. Progr.*, **26**, 269 (1965).

(8) T. C. Ray and A. D. Westland, *Inorg. Chem.*, **4**, 1501 (1965).

(9) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).

(10) The possibility that the absorptions occurring at ~355 cm^{-1} in all of the $Mo_6Cl_8Y_6^{2-}$ compounds and more weakly at ~360 cm^{-1} in two of the $Mo_6Br_8Y_6^{2-}$ compounds shown in Figure 1 are also due to ν_1(M–X) and ν_2(M–X) is difficult to rule out conclusively since no other certain explanation of these bands can be given. However, their absence in $Cs_2Mo_6Cl_{14}$, $[(n\text{-}C_4H_9)_4N]_2Mo_6Cl_{14}$, and the $W_6Cl_{14}^{2-}$ spectra has led us to discount them as genuine T_{1u} absorptions of the $M_6X_8Y_6^{2-}$ species.

For $Mo_6Br_8I_6^{2-}$, the absorptions at 274 cm^{-1} and in the range 210–250 cm^{-1} can again be assigned to the ν_1(Mo–X), ν_2(Mo–X), and ν_5(Mo–Mo) modes; that at 120 cm^{-1}, to the ν_3(Mo–Y) mode, with δ_4(Mo–Y) being again out of range. The small peak at 157 cm^{-1} remains unassigned.

Finally, for the $W_6Cl_{14}^{2-}$ spectrum, the following assignments seem certain: ν_1(W–X) and ν_2(W–X) occur at 290–320 cm^{-1} and ν_3(W–Y), at 224 cm^{-1}. δ_4(W–Y) may be occurring at $\sim$105 cm^{-1}, but the reliability of the spectra here is questionable. Finally, in part b of Figure 3, there is some indication of a weak absorption at 150 cm^{-1}. This is approximately where ν_5(W–W) might be expected to occur assuming that only the masses and not the force constants change on going from Mo_6 to W_6.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Tautomeric Changes in Metal Carbonyls. I. π-Cyclopentadienyliron Dicarbonyl Dimer and π-Cyclopentadienylruthenium Dicarbonyl Dimer[1]

BY F. A. COTTON AND G. YAGUPSKY[2]

Received June 9, 1966

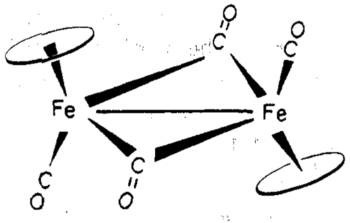
The problem of the structure of π-cyclopentadienyliron dicarbonyl dimer in nonpolar solvents (*e.g.*, C_nH_{2n+2}, CS_2) has been reconsidered. New data and a reanalysis of all data lead to the conclusion that the molecule exists as a doubly bridged dimer in which both C_5H_5 groups lie on one side of the mean plane of the Fe and bridging C atoms and the equivalent terminal CO groups lie on the other side. It is suggested that this structure and the centrosymmetric tautomer which exists in the solid are interconverted *via* a nonbridged structure in which rotation about the Fe–Fe bond can occur. The Ru compound has been carefully studied and the conclusion reached that in nonpolar solvents there is a tautomeric equilibrium between a bridged structure similar to that postulated for the Fe compound and a nonbridged structure of the sort which provides a pathway between the *cis-* and *trans*-bridged structures in the iron case. The precise rotational configuration of the nonbridged structure of the Ru compound could not be established definitely but appears to be *cis* (*i.e.*, eclipsed), rather than *gauche* or staggered, but definitely not *trans*. The prediction is ventured that the osmium homolog of these compounds may exist under all or most conditions entirely in a nonbridged structure.

Introduction

The idea that a metal carbonyl or metal carbonyl derivative of given stoichiometry may exist in tautomeric forms is not new. However, the idea that such tautomerism may be of frequent occurrence perhaps is.

Probably the best characterized tautomeric system is $Co_2(CO)_8$, which has a structure with two bridging CO groups in the crystalline state but exists as a mixture of this and a nonbridged structure in solution.[3,4] Tautomerism also has been suggested[5] for $Co_4(CO)_{12}$. Studies in this laboratory indicate that tautomeric rearrangements and equilibria also occur in other systems, and in this paper we describe studies of $Cp_2Fe_2(CO)_4$ and $Cp_2Ru_2(CO)_4$ (Cp = π-C_5H_5) which show that the existence of such equilibria provides an explanation for the heretofore puzzling infrared spectra of $Cp_2Fe_2(CO)_4$.

The preparation and infrared spectrum of $Cp_2Fe_2(CO)_4$ were first reported[6] in 1955. When X-ray study[7] of the crystalline solid later showed it to have a centrosymmetric structure, I, with two bridging and two terminal CO groups (molecular symmetry,[8] C_{2h}), the interpretation of this spectrum became challenging and controversial.[9,10] Another experimental observation which must be kept in view in these discussions is the dipole moment of about 3.1 D. possessed by $Cp_2Fe_2(CO)_4$ in benzene solution.[11] The work of Stammreich,



I (C_{2h})

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(4) G. Bor, *ibid.*, **19**, 2065 (1963).

(5) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

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(7) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(8) Molecular symmetry assignments in this paper will be made treating the (π-C_5H_5)–M groups as circular cones. A considerable body of data on π-cyclopentadienylmetal carbonyl compounds has shown that, insofar as selection rules for CO stretching modes are concerned, this is a highly satisfactory assumption.

(9) H. Stammreich, G. Wilkinson, and F. A. Cotton, *J. Inorg. Nucl. Chem.*, **9**, 3 (1959).

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(11) E. Weiss, W. Hubel, and R. Merengi, *Chem. Ber.*, **95**, 1155 (1962).