The relatively weak bands observed in the 500–450-$cm^{-1}$ region are assigned to the $T_{1u}$ metal–nitrogen (M–N) stretching vibrations which are split in the solid state owing to the low-site symmetry of the metal atom in the crystal.[9] There appears to be evidence for hydrogen bonding between the N–H of the ammine complex ions and anions such as halogens. It is noted that the relatively weak M–N stretching vibrations are significantly shifted, intensified, and sharpened on going from the $M^{III}(NH_3)_6Cl_3$ compound to the corresponding pentachlorocuprate(II) complex. This may indicate that complexing the $M^{III}(NH_3)_6^{3+}$ ion (where $M^{III}$ = Cr, Co, Rh, or Ru) in a compound of type $M^{III}(NH_3)_6CuCl_5$ decreases the broadening of the M–N stretching vibration which results from hydrogen bonding in compounds of type $M^{III}(NH_3)_6Cl_3$.

The bands observed in the 340–270-$cm^{-1}$ region are assigned to the $NM^{III}N$ deformation vibration. The resolution of these bands is considerably improved for the pentachlorocuprate(II) complexes. The $CuCl_5^{3-}$ ion has two fundamental species $A_1'$ and $E'$, respectively. The selection rules for $D_{3h}$ show that both of these are Raman active since $A_1'$ and $E'$ are both contained in $\Gamma_\alpha$ but that only the $E'$ fundamental is infrared active since $\Gamma_t$ contains $E'$ but not $A_1'$.

The $Cu(II)\cdots Cl$ $E'$ stretching vibration observed at 273 $cm^{-1}$ ($\Delta = 30$) is clearly resolved in the $Co(NH_3)_6CuCl_5$ complex only. The tail of the $N\cdots M^{III}\cdots N$ bending modes for the $Cr(NH_3)_6^{3+}$, $Rh(NH_3)_6^{3+}$, and $Ru(NH_3)_6^{3+}$ cations extends into the 280–270-$cm^{-1}$ region. As a result, in the corresponding pentachlorocuprate(II) complexes the $Cu(II)\cdots Cl$ stretching vibration is observed only as a strong shoulder to one side of the stronger $N\cdots M^{III}\cdots N$ deformation. The appearance of a single band at closely similar frequencies in this region is good evidence that the $CuCl_5^{3-}$ ion has the same symmetry in all the metal hexaammine complexes.

For the complex formulated as $dienH_3CuCl_5$, however, the presence of the $CuCl_5^{3-}$ ion could not be demonstrated unambiguously since the infrared spectrum, although similar to those of the corresponding metal hexaammine complexes, was not sufficiently well resolved. The observed absorption maxima have not, therefore, been included in Table III.

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# Fluorine-19 Nuclear Magnetic Resonance Study of Mixed Adducts of Titanium Tetrafluoride

BY DANIEL S. DYER AND RONALD O. RAGSDALE

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A new $TiF_4\cdot 2$(donor) complex in which the two donor molecules are nonidentical is reported. $TiF_4\cdot 2CH_3C(O)N(CH_3)_2$ was found to undergo exchange reactions in which one of the N,N-dimethylacetamide molecules is replaced by a *para*-substituted pyridine 1-oxide. Seven complexes of general formula $TiF_4\cdot CH_3C(O)N(CH_3)_2$,4-$ZC_5H_4NO$, where Z represents a *para*-substituent, were studied by $F^{19}$ nmr. The chemical shifts were correlated with appropriate Hammett substituent constants.

## Introduction

The behavior of titanium tetrafluoride toward a variety of organic donor molecules has been described.[1] Monofunctional donors coordinating through oxygen form octahedral complexes of the type $TiF_4\cdot 2$(donor), reflecting the tendency of titanium to achieve sixfold coordination. Nmr data showed that in these complexes the donor molecules coordinate at positions *cis* to each other.[1,2] In this paper a new $TiF_4\cdot 2D$ (D = donor) complex is reported in which the two donor molecules in the octahedron are nonidentical. A series of $TiF_4\cdot D,D'$ complexes was studied, where D is N,N-dimethylacetamide (DMA) and D′ is a *para*-substituted pyridine 1-oxide. The compounds investigated have the general formula $TiF_4\cdot DMA$,4-$ZC_5H_4NO$, where Z represents $CH_3O$, $CH_3$, H, Cl, Br, $CH_3OC(O)$, and $NO_2$. The structure of these complexes was established by a study of the nuclear magnetic resonance spectra.

## Experimental Section

**Materials.**—Practical grade chloroacetonitrile and N,N-dimethylacetamide were purified by standard literature procedures. Titanium tetrafluoride obtained from Allied Chemical Corp. was used without further purification. $TiF_4\cdot 2DMA$ was prepared by the method of Muetterties.[1] All pyridine 1-oxides except 4-chloro- and 4-bromopyridine 1-oxides and methyl pyridine-4-carboxylate 1-oxide were obtained from Aldrich Chemical Co. Pyridine 1-oxide was purified by vacuum sublimation. 4-Methoxypyridine 1-oxide was purified by recrystalliza-

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(1) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).
(2) R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).

tion from an acetone–ether solvent. The remaining commercial pyridine 1-oxides were used with no further purification. 4-Chloro- and 4-bromopyridine 1-oxides were prepared from the 4-nitro compound by the method of Ochiai.[3] Methyl pyridine-4-carboxylate 1-oxide was prepared from methyl isonicotinate.[4]

**Preparation of $TiF_4\cdot(CH_3)_2NC(O)CH_3$,4-$ZC_5H_4NO$ Solutions.**—Weighed samples of the respective substituted pyridine 1-oxides were added to $TiF_4\cdot$2DMA–$ClCH_2CN$ solutions of known concentration. The usual concentration for nmr measurements was approximately 1 *M* for each reactant.

**Instrumental Data.**—The fluorine nmr spectra were obtained with a Varian A 56/60A high-resolution spectrometer equipped with a V-6057 variable-temperature accessory. The spectra were calibrated in ppm displacements from the upfield triplet of internal $TiF_4\cdot$2DMA. The chemical shifts of the two $F^{19}$ spin–spin triplets of $TiF_4\cdot$2DMA in chloroacetonitrile were measured with respect to internal primary standard trichlorofluoromethane.

## Results

The $F^{19}$ nmr spectra of the $TiF_4\cdot$2DMA,4-$ZC_5H_4NO$ solutions gave conclusive evidence for the formation of a new octahedral $TiF_4\cdot$2D complex. $TiF_4\cdot$2DMA was shown to undergo exchange reactions in which one of the N,N-dimethylacetamide molecules is replaced by a *para*-substituted pyridine 1-oxide. Nuclear magnetic resonance data for the $TiF_4$ complexes are given in Table I.

TABLE I

$F^{19}$ CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS FOR $TiF_4\cdot(CH_3)_2NC(O)CH_3$,4-$ZC_5H_4NO$ COMPLEXES IN CHLOROACETONITRILE AT −40°

| Substituent | Chemical shifts,[a] ppm | | | F–F coupling constants,[b] cps | | |
|---|---|---|---|---|---|---|
| Z | $\delta F_{\alpha}{}^{c}$ | $\delta F_{\beta}{}^{d}$ | $\delta F_{\beta}{}^{d}$ | $J_{\alpha\beta'}$ | $J_{\alpha\beta}$ | $J_{\beta\beta'}$ |
| $CH_3O$ | +1.7 | −19.2 | −39.4 | 35 | 39 | 48 |
| $CH_3$ | +0.6 | −25.2 | −41.3 | 35 | 39 | 48 |
| H | −0.5 | −28.9 | −42.3 | 35 | 39 | 48 |
| Cl | −0.9 | −32.6 | −42.7 | 34 | 39 | 48 |
| Br | −1.1 | −33.5 | −42.5 | 34 | 39 | 48 |
| $CH_3OC(O)$ | −2.2 | −39.4 | −44.3 | 34 | 39 | 48 |
| $NO_2$ | −3.7 | −46.6 | | 34 | 39 | ... |

[a] Recorded at 56.4 Mc/sec relative to the upfield triplet of internal $TiF_4\cdot 2CH_3C(O)N(CH_3)_2$. [b] Accuracy for the coupling constants is ±1 cps. [c] ±0.1 ppm. [d] ±0.5 ppm.

The $F^{19}$ spectrum of $TiF_4\cdot$2DMA in chloroacetonitrile at −40° consists of two 1:2:1 triplets of equal intensity, showing that the two donor molecules are *cis* to each other. Upon addition of a *para*-substituted pyridine 1-oxide to the solution, the $TiF_4\cdot$2DMA triplets decrease in intensity, and new $F^{19}$ resonances appear. In each case, except for the 4-nitropyridine 1-oxide complex, the new fluorine resonances consist of a doublet of doublets and two doublets of 1:2:1 triplets. The doublet of doublets has twice the area of either of the doublets of triplets. The spectra are shown diagrammatically in Figure 1.

These spectra are typical of an $A_2MX$ system and clearly indicate a structure in which there are two equivalent and two nonequivalent fluorine atoms. The only structure consistent with the data is a $TiF_4\cdot$2D complex in which two nonidentical donor molecules occupy positions *cis* to each other in the octahedron.

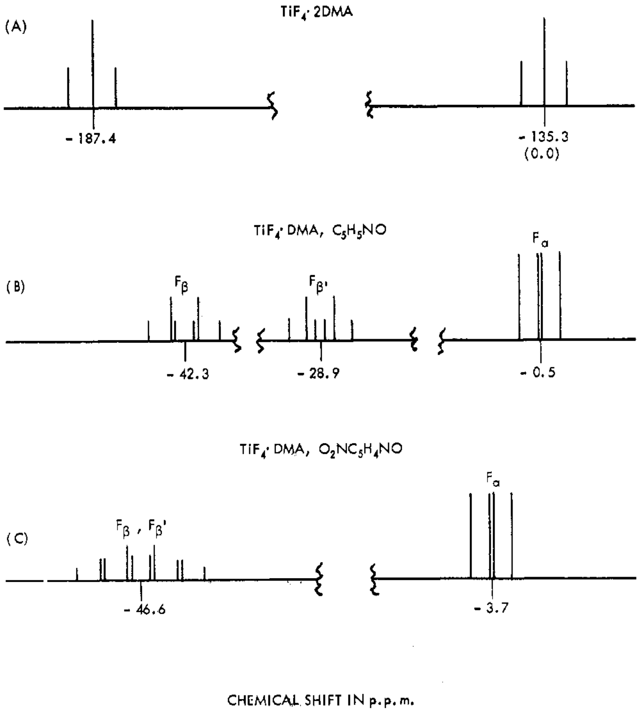
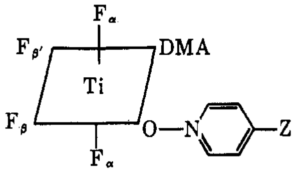


Figure 1.—Diagrammatic representation of some of the $F^{19}$ nmr signals observed at −40°: (A) $TiF_4\cdot$2DMA in chloroacetonitrile ($CFCl_3$ internal reference); (B) $TiF_4\cdot DMA,C_5H_5NO$ in chloroacetonitrile (all $TiF_4\cdot$DMA,4-$ZC_5H_4NO$ chemical shifts are relative to the upfield triplet of internal $TiF_4\cdot$2DMA); (C) $TiF_4\cdot DMA,O_2NC_5H_4NO$ in chloroacetonitrile.



The spectra of the $TiF_4\cdot$2DMA solutions to which 4-nitropyridine 1-oxide was added are typical of an $A_2XY$ system. In this case the chemical shift between $F_\beta$ and $F_{\beta'}$ is of the same order of magnitude as the corresponding spin–spin coupling constant, and the portion of the spectrum due to these two fluorines is second order.

## Discussion

**A. Analyzing the Spectra.**—The upfield doublet of doublets is due to the two equivalent fluorines ($F_\alpha$) which are *cis* to both of the donor molecules. The resonance of these two fluorines is split into a doublet of doublets by the two nonequivalent *trans*-fluorines, $F_\beta$ and $F_{\beta'}$ (see Figure 2). The downfield peaks are due to the latter fluorines. Each of these two principal resonances is split into a triplet by the *cis*-fluorines and each of the triplets is further split into a doublet of triplets by the other nonequivalent *trans*-fluorine, $F_\beta$ or $F_{\beta'}$. This helps to establish the previous assignment[2] of the downfield triplet in the $F^{19}$ spectrum of the $TiF_4\cdot$2ROH complex to the fluorines which bear a *trans* relationship to the alcohols.

In Figure 3 the chemical shifts of the three types of fluorines are plotted against the appropriate Hammett

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(3) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(4) A. R. Katritzky, *J. Chem. Soc.*, 2404 (1956).

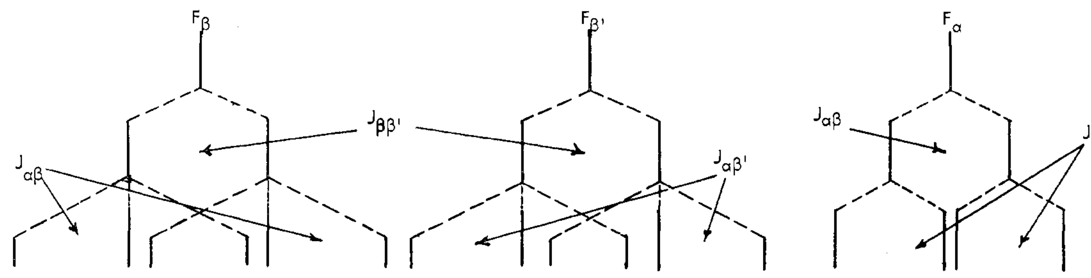

Figure 2.—Analysis of coupling between the three nonequivalent fluorine environments of $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$.

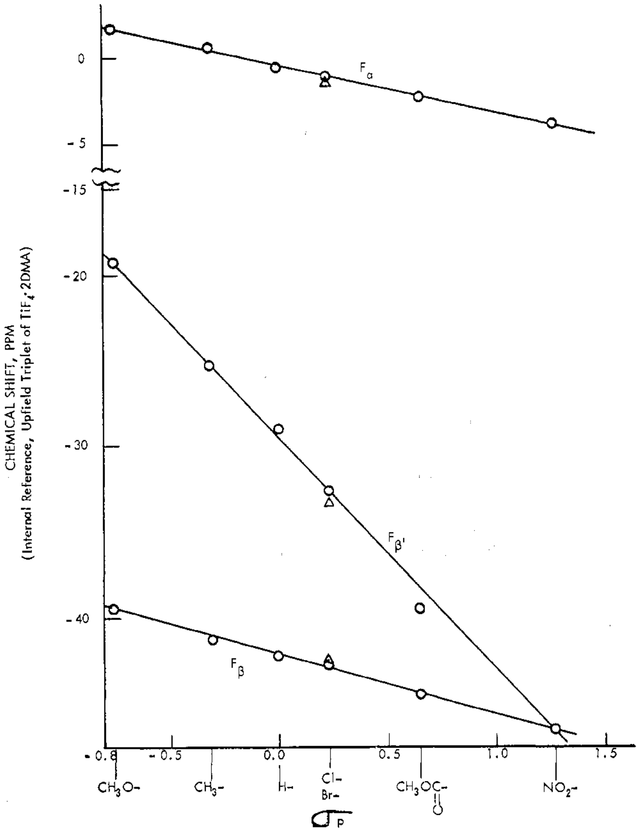

Figure 3.—Correlation plot of the chemical shifts for $F_\alpha$, $F_\beta$, and $F_{\beta'}$ *vs.* the appropriate Hammett substituent parameters.

σ constants.[5,6] It can be seen that the upfield multiplet, $F_\alpha$, is influenced less by the *para* substituent, Z, than either of the downfield resonances. Since Z has relatively little influence on these two equivalent fluorines which are *cis* to the two donor molecules, the downfield set of triplets, also little influenced by Z, is assigned to the fluorine, $F_\beta$, which has a *cis* relationship to the pyridine 1-oxide. The upfield set of triplets, the resonance influenced most by the *para* substituent, is assigned to the fluorine, $F_{\beta'}$, which is *trans* to the pyridine 1-oxide.

**B. Exchange Processes.**—The $F^{19}$ spectra of the $TiF_4 \cdot D,D'$ complexes are temperature dependent. On warming a solution, the fine structure of the spectrum is lost, and the peaks broaden and then collapse into a single resonance. Recooling reversibly yields the low-temperature $F^{19}$ spectrum. These observations indicate that the fluorine nuclei in different environments in the $TiF_4 \cdot 2D$ complexes are changing places with one another.

Temperature effects which were observed in the spectra of the $TiF_4 \cdot 2D$ solutions were attributed to a rapid base (donor molecule) exchange.[1] The replacement of N,N-dimethylacetamide by a 4-substituted pyridine 1-oxide in the $TiF_4 \cdot 2DMA$ complex confirms base exchange. Equilibrium seems to be established in the time necessary to prepare the solutions. Coalescence of all peaks into a single resonance at high temperature (~100°) suggests a fast interconversion between $TiF_4 \cdot 2DMA$ and $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$. Since nucleophilic displacement reactions are generally not observed in solutions of transition metal octahedral complexes,[7] an exchange mechanism involving preliminary ligand dissociation is favored.

$$TiF_4 \cdot 2DMA \rightleftarrows TiF_4 \cdot DMA + DMA$$

$$TiF_4 \cdot DMA + 4\text{-}ZC_5H_4NO \rightleftarrows TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$$

In some solutions additional low-intensity $F^{19}$ resonances which may be due to $TiF_4 \cdot 2(4\text{-}ZC_5H_4NO)$ formed by a similar mechanism were observed.

**C. Chemical Shifts.**—It is of interest to study the effect of substituent Z upon the $F^{19}$ chemical shifts. When the chemical shifts for the *cis-* and *trans*-fluorines are plotted *vs.* the Hammett substituent parameters (Figure 3), a linear correlation is obtained for each type of fluorine. In some series of compounds, $C^{13}$,[8,9] $F^{19}$,[10] and $N^{15}$ [11,12] chemical shifts have been shown to be linearly related to the π-orbital electron densities of the atoms under consideration. In particular, fluorine shielding in the *para*-substituted fluorobenzenes is very sensitive to perturbations induced in the fluorine atom π-charge density by the distant *para* substituent.[10] It is suggested that the large perturbation produced by the substituent Z in the shielding of the fluorine, $F_{\beta'}$, *trans* to $4\text{-}ZC_5H_4NO$ in the $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$ complex is transmitted through the titanium d orbitals by a π mechanism. The progressive downfield shift in the spectra as the *para* substituent becomes more electron attracting is brought about by an increase in the relative amount of fluorine π donation to the titanium d orbitals.

Evidence that $p_\pi$-$d_\pi$ interaction is responsible for the chemical shifts in the $TiF_4$ complexes can be found by comparison of the $F^{19}$ nmr data for $TiF_4 \cdot C_2H_5OH^2$

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(5) H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

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(7) R. G. Pearson, D. N. Edington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

(8) P. C. Lauterbur, *ibid.*, **83**, 1838 (1961).

(9) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

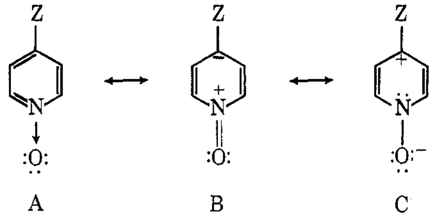
(10) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(11) E. L. Wagner, *J. Chem. Phys.*, **43**, 2728 (1965).

(12) J. E. Kent and E. L. Wagner, *ibid.*, **44**, 3530 (1966).

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 $p_\pi$–$d_\pi$ 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 $\pi$ bonding. It is possible, therefore, to make a total of three pure $\pi$ bonds.[14] In distorted octahedral complexes such as $TiF_4 \cdot DMA,4\text{-}ZC_5H_4NO$ the three $d_\pi$ orbitals will, in general, be distributed unequally among the ligands. The ability of N-oxide oxygen to $\pi$ 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).



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 $\pi$ bonding. The change in the fluorine $\pi$ 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 $\pi$ bonding that exists, the less successfully can the oxygen compete with fluorine for the available metal d orbitals. As fluorine to titanium $p_\pi$–$d_\pi$ 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, $J_{\alpha\beta'}$ = 34–35 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 $\sigma$-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.

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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

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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.