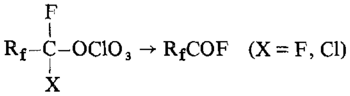
simple polar addition. No examples are known to us in which the alternate adduct is the sole product. Obviously a dominant control is operating but its explanation at this point would be purely speculative.

The overall stability of the perhaloalkyl perchlorates is much superior to that of analogous -OCl compounds.[23] Qualitative tests showed that no decomposition of $CF_3CFClCF_2ClO_4$ occurred on heating in stainless steel at 100° for 72 hr after an initial passivating effect. At 180° complete decomposition in 24 hr produced mainly $CF_3CFClCOF$ with a small amount of COF_2, indicating little carbon–carbon rupture. No decomposition of $ClCF_2CFClClO_4$ was observed after 24 hr at 70° but complete decomposition was found after 72 hr at 100° giving $ClCF_2COF$, $FClO_3$, Cl_2, and O_2. The compound $CF_3CFClCF_2ClO_4$ was insoluble and unaffected by water at ambient temperature.

Alkali metal fluoride catalyzed decomposition of the perchlorates paralleled reported[2,24] reactions of similar fluorosulfate materials. The fluorosulfates produce carbonyl compounds and SO_2F_2 while the perchlorates gave carbonyl compounds and $FClO_3$ or mixtures of $FClO_3$, Cl_2, and O_2. Perchlorates containing $R_fCF_2ClO_4$ structures generated essentially quantitative amounts of $FClO_3$. Perchlorates with $R_fCFClClO_4$ structures gave variable mixtures of $FClO_3$, Cl_2, and O_2. Either type of perchlorate was completely degraded to the respective acid fluoride and was of great assistance in characterizing the perchlorates



$$R_f\text{–}\overset{\displaystyle F}{\underset{\displaystyle X}{C}}\text{–}OClO_3 \rightarrow R_fCOF \quad (X = F, Cl)$$

Reactions of the $R_fCFClClO_4$ compounds did not yield any acid chlorides and therefore some fluorination by the metal fluoride must have occurred before or after the elimination of ClO_3.

Registry No. $CF_3CF{=}CF_2$, 116-15-4; Cl_2O_4, 27218-16-2; $CF_3CFClCF_2ClO_4$, 38126-25-9; $BrClO_4$, 32707-10-1; $CF_3CFBrCF_2ClO_4$, 38126-26-0; $CF_2{=}CFCl$, 79-38-9; $ClCF_2CFClClO_4$, 38126-27-1; $BrCF_2CFClClO_4$, 38217-36-6; C_2F_4, 116-14-3; $ClCF_2CF_2ClO_4$, 38126-28-2; $ClCF{=}CFCl$, 598-88-9; $Cl_2CFCFClClO_4$, 38126-29-3; $CF_2{=}CFCF{=}CF_2$, 685-63-2; 2-chlorotetrafluoropropionyl fluoride, 28627-00-1; $CF_3CFBrCOF$, 6129-62-0; dichlorofluoroacetyl fluoride, 354-18-7; $ClCF_2COF$, 354-27-8; $BrCF_2COF$, 38126-07-7.

Acknowledgment. Support for this work by the Office of Naval Research, Power Branch, is gratefully acknowledged. We are also indebted to Dr. K. O. Christe for helpful discussions and to Dr. R. A. Meyer of the NAR Science Center for the mass cracking patterns.

(23) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.*, 91, 2902 (1969).

(24) M. Lustig and J. K. Ruff, *Inorg. Chem.*, 3, 287 (1964).

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Nuclear Quadrupole Resonance Study of Heavy Transition Metal Pentahalide Dimers, M_2X_{10}[1a]

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Halogen and metal nqr transitions have been measured in a series of heavy transition metal pentahalide dimers M_2X_{10} ($M = {}^{93}Nb, {}^{181}Ta$, W, Re; $X = {}^{35}Cl, {}^{81}Br, {}^{127}I$), in which each molecule contains eight terminal and two bridging halogen atoms. The ^{181}Ta nqr resonances are believed to be the first such resonances detected. From the ^{181}Ta and ^{93}Nb resonances detected in Ta_2X_{10} (X = Cl, Br, I) and Nb_2X_{10} (X = Cl, Br) it was concluded that the coordination about the metal atoms more closely approaches octahedral symmetry as the halogen is varied from Cl to Br to I. In general, terminal halogen atom resonances were found to exhibit small asymmetry parameters and/or positive temperature coefficients ($d\nu/dT$) indicative of M–X π bonding, while bridging halogen atom resonances were found to have large asymmetry parameters and/or negative temperature coefficients. The bridging halogen resonances in these compounds occurred consistently at higher frequencies than the terminal halogen resonances. A trend of increasing halogen resonance frequencies accompanied the increasing covalent character of the M–X bonds as the metal atoms varied from members of group Vb to VIb to VIIb.

Introduction

An important application of nuclear quadrupole resonance (nqr) spectroscopy to the study of the structure of transition metal halide compounds resides in the ability to distinguish between bridging and terminal halogen atom resonances. Buslaev and coworkers have suggested that the sign of the temperature coefficient ($d\nu/dT$) of an nqr transition can be used as a criterion for assigning resonances in the nqr spectrum of a transition metal compound containing both bridging and terminal halogen atoms.[2] Their argument is based in part on their study of the Br nqr spectra of Nb_2Br_{10}, Ta_2Br_{10}, and $NbOBr_3$, in which the terminal Br atoms exhibited positive values, and the bridging Br atoms negative values of $d\nu/dT$. This argument should be applicable to any compound in which one type of halogen atom has the ability to donate electron density, *via* a π interaction, to another atom in the molecule, while the other type of

(1) (a) Presented in part before the Division of Inorganic Chemistry, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972. (b) A portion of a thesis presented by P. A. Edwards to Iowa State University in partial fulfillment of the requirements for the degree Doctor of Philosophy.

(2) Yu. A. Buslaev, E. A. Kravchenko, S. M. Sinitsyna, and G. K. Semin, *Izv. Akad. Nauk SSSR, Ser. Khim*, 12, 2816 (1969).

halogen atom does not have this opportunity. The results reported here not only support and apply the arguments of Buslaev and coworkers but also indicate the valuable information which can be inferred from the nqr data for the metal atoms in these compounds.

Experimental Procedures

Synthesis of Metal Pentahalides. With the exception of W_2Cl_{10} all of the M_2X_{10} compounds were prepared by the reaction of elemental halogen with high-purity metal.[3] The reaction between WCl_6 and $W(CO)_6$ at 100° was used to prepare W_2Cl_{10}.[4] Because of the susceptibility of all of the metal pentahalides to hydrolysis or air oxidation, all samples were handled on the vacuum line or in an inert-atmosphere drybox maintained at a dew point of about −75°.

Several samples were subjected to an annealing procedure to facilitate the detection of resonances. This procedure, very similar to a procedure used for the growing of large single crystals, involved slowly lowering the sample in a sealed, tapered-tip sample tube through a vertically mounted tube furnace. The center of the furnace was set at a temperature conducive to complete sublimation of the material from one end of the sample tube to the other. This annealing procedure was especially suitable for the metal pentahalides studied because the volume of these usually fluffy materials was significantly reduced in the sample tube, thus increasing the filling factor.

Nqr Spectra. Two different spectrometers were used during this study. All resonances were initially detected using a Wilks NQR-1A superregenerative spectrometer, where frequency measurements were made using spectrum-analyzing techniques.[5] In the range 5-50 MHz precise frequency measurements and resolution of closely spaced resonances were made using a wide-line induction spectrometer.[6]

Studies of the temperature dependence of resonances in the range of the Wilks OS-1 and OS-2 oscillators (*ca.* 5-90 MHz) were carried out as previously described.[6] A similar procedure for resonances in the range of the OS-3 oscillator (*ca.* 90-350 MHz) was impossible because of the physical design of the apparatus. A special Pyrex tube with an evacuated jacket was designed to fit inside the sample coils of the OS-3 oscillator and cold nitrogen gas was blown around the sample container which was mounted inside this tube.

Corresponding ^{37}Cl and ^{79}Br resonances were detected for all new ^{35}Cl and ^{81}Br resonances listed in the tables. The values for the ratio of the quadrupole moments for the different isotopes of elements under investigation were obtained from Segel and Barnes.[7]

Assignment of Resonances

Niobium Pentahalides. The experimental results for all of the niobium pentahalides are listed in Table I. It was not possible to reproduce the nqr results of Reddoch[8] in Nb_2Cl_{10} without annealing the sample. The sample of Nb_2Br_{10} used in this study was similarly annealed and the results of Buslaev, *et al.*,[2] were also reproduced. The sample of Nb_2I_{10} was not annealed. The assignment of the ^{93}Nb resonances in Nb_2Br_{10} is clear despite the fact only two of the four possible resonances were detected. Because no signals were detected at higher frequencies, the 9.891- and 7.270-MHz resonances are assigned as the $\pm^7/_2 \leftrightarrow \pm^9/_2$ and $\pm^5/_2 \leftrightarrow \pm^7/_2$ transitions, respectively. This assignment requires the other two allowed transitions for the $I = {}^9/_2$ nucleus to fall in the range 4.5-5.0 MHz, but this could not be verified because those frequencies were below the operating range of our spectrometer systems. The value for the asymmetry parameter (obtained using Cohen's tables),[9] $\eta = 0.40$, also corresponds well to that exhibited by ^{93}Nb in Nb_2Cl_{10}, $\eta = 0.32$. Because the ^{93}Nb resonances in Nb_2Br_{10} are at lower frequencies than those in Nb_2Cl_{10} and because repeated scans from 5 to 20 MHz revealed no resonances in Nb_2I_{10}, it is presumed all ^{93}Nb resonances in Nb_2I_{10} are at frequencies less than 5 MHz. The ^{127}I resonances in Nb_2I_{10} are also easy to assign. Using either the criterion of a positive temperature coefficient indicative of a terminal halogen atom resonance as suggested by Buslaev, *et al.*,[2] or the criterion of a large asymmetry parameter indicative of a bridging halogen atom resonance as found in the group IIIa trihalides,[10,11] the assignment is the same. The resonances at higher frequencies are assigned to the bridging halogen atoms while the resonances at lower frequencies are assigned to the terminal halogen atoms.

Tantalum Pentahalides. The experimental results for all of the tantalum pentahlides are listed in Table II. The room-temperature ^{35}Cl nqr results of Safin, *et al.*,[12] were reproduced and ^{181}Ta resonances were detected using an annealed sample of Ta_2Cl_{10}. The room-temperature Br nqr results of Buslaev, *et al.*,[2] were confirmed using an unannealed sample of Ta_2Br_{10}, but an annealed sample was used for the ^{181}Ta study. Additional Br resonances very close in frequency to those reported by Buslaev, *et al.*,[2] were also detected in the annealed sample. The frequencies of these resonances were not measured because this change of multiplicity of resonances did not change the assignment of the detected resonances. It is, however, a "textbook" demonstration of the impact of subtle crystal effects on the multiplicity of resonances of chemically equivalent nuclei. The sample of Ta_2I_{10} used was not annealed.

To the authors' knowledge the ^{181}Ta resonances listed in Table II are the first nqr resonances reported for this nucleus. Unfortunately, since only two of the three allowed transitions for an $I = {}^7/_2$ nucleus (such as ^{181}Ta) have been detected, the assignment of the resonances as shown in the table is open to question. Scans from 100 to 350 MHz yielded no other resonances in Ta_2Cl_{10} or Ta_2Br_{10} not otherwise accounted for. Other potential assignments require the third transition to be in the frequency range scanned and/or yield values of η much greater than reasonable when compared to values of η exhibited by ^{93}Nb in Nb_2Cl_{10} or Nb_2Br_{10}. In fact, the third transition for ^{181}Ta in Ta_2Br_{10} is required by the assignment shown in the table to fall in the range 300-350 MHz. We have been unable to search at frequencies >300 MHz because of instrumentation problems. We hope in the near future to be able to affirm our assignments by detecting the missing transitions. Because it is hard to conceive of Cl or Br resonances falling in the range of 200 MHz in these compounds, these resonances are interpreted as ^{181}Ta resonances.

The assignment of resonances detected in Ta_2I_{10} is not so clear-cut because the ^{127}I and ^{181}Ta resonances could fall in the same frequency range; thus the assignment shown in Table II should be considered as tentative. One factor used in making the assignment was the observation that in the

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(3) R. R. Smardzewski, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1969.

(4) M. A. Schaefer and R. E. McCarley, to be submitted for publication.

(5) G. E. Peterson and P. M. Bridenbough, *Rev. Sci. Instrum.*, 37, 1081 (1966).

(6) P. A. Edwards, R. E. McCarley, and D. R. Torgeson, *Inorg. Chem.*, 11, 1185 (1972).

(7) S. L. Segel and R. G. Barnes, Report IS-520 (revised), USAEC, Ames, Iowa, 1968.

(8) A. H. Reddoch, Ph.D. Thesis, University of California, Berkeley, Calif., 1959; USAEC Report UCRL-8972.

(9) M. H. Cohen, *Phys. Rev.*, 96, 1278 (1954).

(10) S. L. Segel and R. G. Barnes, *J. Chem. Phys.*, 25, 578 (1956).

(11) G. E. Peterson and P. M. Bridenbough, *J. Chem. Phys.*, 51, 238 (1969).

(12) I. Safin, B. Pavlov, and D. Shtern, *Zavod. Lab.*, 30, 676 (1964).

Table I. Experimental Results for Niobium Pentahalides

Isotope	T, °C	ν_{terminal}, MHz	ν_{bridge}, MHz	ν_{metal}, MHz		Extracted parameters		Ref
				Obsd	Calcd	e^2Qq/h	η	
				Nb_2Cl_{10}				
^{35}Cl	24.5		13.06					8
^{35}Cl	−196		13.28					
^{93}Nb	24.5			ν_1 5.423	5.423	78.08	0.32	
				ν_2 6.062	6.062			
				ν_3 9.561	9.561			
				ν_4 12.903	12.903			
^{93}Nb	−196			ν_1 5.715	5.715	78.26	0.35	
				ν_2 6.052	6.051			
				ν_3 9.547	9.547			
				ν_4 12.913	12.913			
				Nb_2Br_{10}				
^{81}Br	27	50.53	87.96					2
		52.11	88.39					
			89.07					
^{81}Br	−196	49.43	89.37					
		49.95	89.83					
			90.25					
^{93}Nb	~24			ν_3 7.270	7.270	60.01	0.40	This work
				ν_4 9.891	9.891			
				Nb_2I_{10}				
^{127}I	RT[a]	ν_1 49.55	118[b]			Terminal		This work
		ν_1 50.26				327.6	0.14	
		ν_2 96.56	185[b]			323.2	0.15	
		ν_2 97.87				Bridge		
						642	0.48	
^{127}I	−196	ν_1 48.69				Terminal		
		ν_1 49.60	119[b]			313.4	0.18	
		ν_2 93.43	188[b]			314.9	0.22	
		ν_2 93.63				Bridge		
						655	0.47	

[a] Not all data taken at same temperature. [b] Possibly multiple resonances too close together to resolve.

Table II. Experimental Results for Tantalum Pentahalides

Isotope	T, °C	ν_{terminal}, MHz	ν_{bridge}, MHz	ν_{metal}, MHz	Extracted parameters		Ref
					e^2Qq/h	η	
				Ta_2Cl_{10}			
^{35}Cl	20		13.35				12
			13.37				
			13.39				
^{35}Cl	−196	12.30 (mean of doublet)	13.6 (mean of triplet)				
^{181}Ta	RT[a]			ν_1 177.6	1786	0.36	This work
				ν_1 183.0	1795	0.38	
				ν_2 241.4			
				Ta_2Br_{10}			
^{81}Br	27	54.98	90.30				2
		55.30					
		56.59					
^{81}Br	−196	54.18	91.48				
		54.27					
		54.50					
		54.97					
^{181}Ta	RT[a]			ν_1 156.7	1421	0.45	This work
				ν_1 161.1	1436	0.46	
				ν_2 190.0			
				Ta_2I_{10}			
^{127}I	RT[a]	ν_1 71.98	ν_1 123.3		Terminal		This work
		ν_1 72.69			478.0	0.06	
		ν_2 143.4	ν_2 211.6		482.6	0.06	
		ν_2 144.6			Bridge		
					723.2	0.37	
^{181}Ta	RT[a]			ν_1 87.4	861	0.38	
				ν_2 116.3	870	0.37	
				ν_2 117.3			

[a] Not all data taken at same temperature.

group Vb metal pentachlorides and pentabromides, the halogen resonances in the tantalum compounds are all at higher frequencies than in the corresponding niobium compounds. Other factors considered were the temperature dependence of the resonances and the magnitude of the asymmetry parameter implied by each potential assignment. Several assignments were eliminated from consideration because the magnitude of implied asymmetry parameters did not compare well with those observed in less ambiguous cases. As in the cases of Ta_2Cl_{10} and Ta_2Br_{10}, absence of resonances clearly assignable as ν_3 of ^{181}Ta is a matter of concern.

Related Metal Pentahalides. The experimental results for the other related metal pentahalides are listed in Table III. The assignments shown in the table are again based primarily on the sign of the temperature coefficient, $d\nu/dT$. It is interesting to note that the multiplicity of the terminal resonances, for example, varies from compound to compound and appears to bear little correlation to their similar dimeric structure. In the same vein, the lack of terminal halogen nqr data for yet another compound (Mo_2Cl_{10},[13] as in Nb_2Cl_{10} and Ta_2Cl_{10}) continues to defy explanation.

The results for W_2Cl_{10} are not easy to correlate with the dimeric structure of the compound.[14] The detection of three distinct groups of ^{35}Cl resonances does not correlate with the two types of halogen atoms present in the molecule, especially when the number of resonances in each group is considered. Three samples of W_2Cl_{10} were examined for resonances. The first sample, which was annealed, was probably contaminated by the presence of a tungsten oxychloride, as indicated by a W-O stretching band in the region of 900 cm^{-1} in the far-infrared spectrum. The second sample was obtained by removal of the tungsten oxychloride impurity, which was sublimed away from the W_2Cl_{10} almost quantitatively as indicated by the disappearance of the W-O stretching band. This unannealed sample of the purified W_2Cl_{10} and a third, consisting of an unannealed sample of the impure W_2Cl_{10}, exhibited all of the resonances detected in the original sample. Therefore, it is concluded that each of the resonances is "real" and should be considered part of the nqr spectrum of W_2Cl_{10}.

The interpretation of the experimental results for W_2Br_{10} (obtained with a sample in the as-prepared state) is complicated by a different problem. The temperature coefficients of the bridging and terminal halogen atom resonances over the range +30 to −110° are negative and positive, respectively, as expected. However, at −196° the terminal halogen atom resonance splits into two resonances, both of which are at frequencies higher than the room-temperature resonance; *i.e.*, the sign of the temperature coefficient has changed from positive to negative. Such a change in the sign of $d\nu/dT$ is not easy to interpret, particularly without additional frequency measurements made at temperatures between −110 and −196°. This change in sign of $d\nu/dT$ could be indicative of a phase transition or subtle changes in bonding as detected by Barnes and Engardt in $TiBr_4$.[15] Additionally this behavior could be a manifestation of a change in the electronic structure of the compound, which is paramagnetic at room temperature[16] as expected if each W(V) atom has one unpaired electron. However the molecule as a whole could undergo a transition from the $S = 1$ spin state to the $S = 0$ state at low temperature. In this event there is no reason to assume that the field gradients at the Br nuclei in the two states should be the same. Without additional data further speculation as to the actual mechanism leading to the unusual temperature dependence exhibited by the terminal Br atom resonances in W_2Br_{10} would be imprudent.

Table III. Experimental Results for Related Metal Pentahalides

Compd	Isotope	T, °C	ν_{terminal}, MHz	ν_{bridge}, MHz	Sign of $d\nu/dT$	Ref
Mo_2Cl_{10}	^{35}Cl	32		14.085	Negative	13
W_2Cl_{10}	^{35}Cl	~24		14.374	Negative	This work
				14.362		
				14.327		
			12.226		~0	
			9.444		Positive	
			9.371			
			9.254			
W_2Br_{10}	^{81}Br	RT		95.68	Negative[a]	This work
			72.24		Positive[a]	
		−196		96.57		
			75.58			
			76.34			
Re_2Cl_{10}	^{35}Cl	~24		17.318	Negative	This work
				17.104		
				16.387		
				16.312		
			15.891		Positive	
			15.731			
			13.291			
			13.277			
			13.203			
			13.155			

[a] Over the range RT to −110°.

The experimental results for Re_2Cl_{10} appear at first glance to be the easiest to interpret in relation to the known dimeric structure[17] of the compound. The coincidence of ten detected ^{35}Cl resonances and ten Cl atoms per molecule of dimer appears convenient, but the fact that four of these resonances exhibit negative temperature coefficients indicative of bridging halogen atom resonances destroys that convenience. Although both Re_2Cl_{10} and Nb_2Cl_{10} are dimeric and structurally approximated as two octahedra sharing an edge, there are significant differences in their respective structures because the two compounds are not isomorphous. The symmetry of the unit cell of Re_2Cl_{10}, $P2_1/c$, requires the four molecules in the unit cell to be equivalent. The symmetry of each molecule almost contains three mutually perpendicular mirror planes, although no symmetry is required. Thus ten ^{35}Cl resonances, one from each Cl atom in the dimeric unit, would be expected in the nqr spectrum of Re_2Cl_{10}. It is possible that two terminal Cl atoms unexpectedly exhibit negative rather than positive temperature coefficients. In fact, the magnitude of the temperature coefficients associated with the resonances at 16 MHz is approximately half as large as those of the resonances at 17 MHz. The assignment of the resonances at 16 MHz must then be considered as suspect. One factor affecting this behavior may be that crystal effects play a more significant role in the nqr spectrum of Re_2Cl_{10}. The lack of detection of any resonances assignable as ^{185}Re or ^{187}Re transitions is a disappointing aspect of the nqr study of Re_2Cl_{10}.

Interpretation

Interpretation of Metal Resonances. In order to interpret

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(13) T. L. Brown and L. G. Kent, *J. Phys. Chem.*, **74**, 3572 (1970).

(14) P. M. Boorman, N. N. Greenwood, M. A. Hildon, and H. J. Whitfield, *J. Chem. Soc. A*, 2017 (1967).

(15) R. G. Barnes and R. D. Engardt, *J. Chem. Phys.*, **29**, 248 (1958).

(16) B. J. Brisdon, D. H. Edwards, D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc. A*, 1825 (1967).

(17) K. Mucker, G. S. Gordon, and Q. Johnson, *Acta Crystallogr., Sect. B*, **24**, 874 (1968).

the ^{93}Nb and ^{181}Ta data, values for the asymmetry parameter and the quadrupole coupling constant were calculated from the observed resonance frequencies. The values for e^2Qq/h and η (except of those exhibited by Nb in Nb_2Cl_{10}) given in Tables I and II were obtained using Cohen's tables. Values for the effective field gradient (eq), listed in Table IV, were extracted from the quadrupole coupling constant using values for the quadrupole moments of ^{93}Nb and ^{181}Ta, equal to −0.20 and 3.9 barns, respectively, as given by Korol'kov and Makhanek.[18]

The trend toward smaller effective metal field gradients as the halogen is varied from Cl to Br to I is significant. The effective field gradient of the metal atom is a function of the orientation of the six bonding tensors representing the six σ bonds in which the metal is participating. If each of these tensors were of equal magnitude and pointed directly toward the corner of a regular octahedron, the effective field gradient around the metal at the center of that octahedron would be zero *regardless* of the magnitudes of those tensors. The implication of the trend toward smaller values of eq is that the environment around the metal atom more closely approaches octahedral symmetry as the halogen is varied from Cl to Br to I.

A normal-coordinate analysis of M_2X_{10} compounds has been performed in this laboratory.[3] Values for axial, equatorial, and bridging M–X stretching force constants were determined during that study. A quantity of interest in that study was the ratio of the M–X–M bridging to the equatorial M–X terminal stretching force constant. The quantity of interest in interpreting field gradients should not be dependent upon whether the vibration involved is a bridging or terminal vibration; only the magnitudes of the force constants should be germane. Thus the quantity $f_</f_>$ shown in Table IV is the ratio of the smaller to the larger of the two force constants. Significantly, the bridging and terminal force constants become more similar as the halogen is varied from Cl to Br to I. Figure 1 shows a plot of $f_</f_>$ as the ordinate *vs.* eq as the abscissa. This plot clearly demonstrates the correlation between the two quantities and is support for the claim that the metal is more closely approaching octahedral symmetry as the halogen is varied from Cl to Br to I.

Interpretation of Halogen Resonances. The interpretation of the halogen resonances is very difficult for several reasons. Consider, for example, the results for the terminal halogen atoms in Re_2Cl_{10} and W_2Cl_{10}. It appears imprudent to attempt to "interpret" these resonances because it is hard to explain their multiplicities. Consider also the results in Nb_2Cl_{10} and Mo_2Cl_{10}, where the terminal halogen atom resonances have not been detected. Indeed, the fact that no terminal halogen atom resonances were observed is not easily rationalized in view of the fact that strong resonance signals were observed for the bridging Cl atoms and for ^{93}Nb in Nb_2Cl_{10}.

Table IV. Metal Field Gradients and Ratios of Force Constants in M_2X_{10}

Compd	Metal field gradient, esu/cm^3 × 10^{-15}	$f_</f_>$
Nb_2Cl_{10}	5.39	0.380 ± 0.043
Nb_2Br_{10}	4.14	0.563 ± 0.097
Ta_2Cl_{10}	6.32 6.35	0.335 ± 0.012
Ta_2Br_{10}	5.03 5.08	0.511 ± 0.014
Ta_2I_{10}	3.08 3.05	0.825

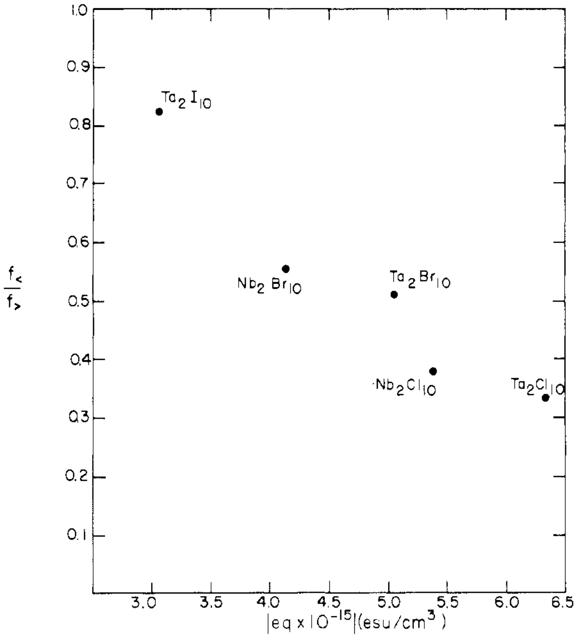

Figure 1. Plot of ratio of force constants *vs.* metal field gradients in M_2X_{10}.

Some general comments about the terminal halogen atom resonances, however, do seem appropriate. To some degree the terminal halogen atoms in these dimeric compounds donate electron density into empty metal d orbitals *via* π bonds.[19] It is the magnitude of this π bonding which is very difficult to estimate. One view, in accord with the suggestions made by Buslaev and coworkers,[2] attributes the positive temperature coefficients ($d\nu/dT$) of the terminal halogen resonances to the attenuation of the π-bonding interactions by thermal population of excited vibrational states. Also the π interaction may be regarded as sufficiently strong that resonances of the terminal halogens are shifted to lower frequencies than those of the bridging halogens in all of these compounds. This behavior can be compared to that observed in the group IIIa metal halide dimers M_2X_6[10,11] where the terminal halogen resonances occur at *higher* frequencies than those of the bridging halogens. Significantly, the group IIIa metal atoms do not have empty d orbitals readily accessible for π bonding with the filled p orbitals of the halogen atoms. Thus the resonance frequencies must be regarded as mainly determined by σ-bonding interactions.

However there is an alternative view, recently expressed by O'Leary,[20] which questions the need to attribute such effects as the positive temperature coefficients of these resonance frequencies to π bonding. According to this view low-frequency lattice vibrational modes may cause the observed effect. Since at present, insufficient evidence has been obtained to assess the relative merits of the alternative views we find the π-bonding argument is still the most convenient framework in which to discuss the results obtained in this work.

Also noteworthy is the general trend toward higher terminal halogen atom resonance frequencies as the metal is changed

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(18) V. S. Korol'kov and A. G. Makhanek, *Opt. Spectrosc. (USSR)*, 12, 87 (1962).

(19) For a discussion of the effect of π bonding on halogen nqr frequencies see E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969, pp 311–321.

(20) G. P. O'Leary, *Phys. Rev. B*, 3, 3075 (1971).

Table V. Interpretation of Bridging Halogen Atom Resonances

Compd	Nucleus	$M\text{-}X_b\text{-}M$ angle, deg	ν_Q, MHz	Calcd parameters			
				e^2Qq/h	η	a^e	$N_t{}^f$
Nb_2Cl_{10}	^{35}Cl	101.3[a]	13.058	24.731	0.588[d]	1.73	7.46
Ta_2Cl_{10}	^{35}Cl	101.3[b]	13.35	25.284	0.588[d]	1.72	7.45
Mo_2Cl_{10}	^{35}Cl	98.6[a]	14.08	27.260	0.449[d]	1.71	7.43
W_2Cl_{10}	^{35}Cl	98.6[b]	14.327	27.739	0.449[d]	1.71	7.42
			14.361	27.805		1.71	7.42
			14.373	27.828		1.71	7.42
Re_2Cl_{10}	^{35}Cl	98.74[a]	17.318	33.495	0.456[d]	1.65	7.30
			17.104	33.081		1.65	7.31
			16.387	31.695		1.67	7.33
			16.312	31.625		1.67	7.34
Nb_2Br_{10}	^{81}Br	101.3[b]	88.39	167.40	0.588[d]	1.69	7.38
Ta_2Br_{10}	^{81}Br	101.3[b]	90.30	171.02	0.588[d]	1.68	7.36
W_2Br_{10}	^{81}Br	98.6[b]	95.68	185.25	0.449[d]	1.67	7.34
Nb_2I_{10}	^{127}I	99[c]	118 185	642	0.48	1.69	7.38
Ta_2I_{10}	^{127}I	97[c]	123.3 211.6	722	0.37	1.65	7.30

[a] Angles as obtained from published crystal structure determinations. [b] Angles assumed on the basis of structure data reported for the related compounds Nb_2Cl_{10}, Mo_2Cl_{10}, or Re_2Cl_{10}. [c] Angles determined from observed nqr asymmetry parameters. [d] Calculated from the M-X-M bond angle shown in column 3. [e] Electron population in each σ-bonding hybrid orbital on the bridging halogen atoms. [f] Total valence electron population on each bridging halogen atom.

from a member of group Vb to VIb to VIIb. For the resonance frequency of a π-bonded terminal halogen atom to increase, the absolute magnitude of the difference between the populations of the σ- and π-bonded orbitals must increase. It is assumed the population of the π-bonding halogen orbitals is only slightly less than 2. Thus, either an increase in the covalency of the M-X σ bond (lowering the σ population on the halogen atom) or a decrease in the covalency of the M-X π bond (raising the π population on the halogen atom) leads to an increase in the absolute magnitude of the difference between the two populations. Both mechanisms are probably operative. First, the electronegativity difference between metal and halogen decreases as the metal is varied from group Vb to VIIb providing a potentially more covalent σ bond. Second, as the metal is varied from group Vb to VIIb the metal d orbitals become more populated with metal electrons thus reducing the ability of the halogen to donate electron density to the metal. These two mechanisms do not appear easily separable.

A little more can be said quantitatively about the bridging halogen atom resonances. The coordinate system and equations used to interpret the bridging halogen atom resonances are as previously published.[6] The values of the atomic coupling constants (e^2Qq_{atm}) used in these computations for ^{35}Cl, ^{81}Br, and ^{127}I, taken from Townes and Schawlow,[21] are 109.7, −643.1, and 2292.8 MHz, respectively. It is possible to predict the $M\text{-}X_b\text{-}M$ angle in the case of ^{127}I-containing compounds because the asymmetry parameter η can be experimentally determined, while, conversely, because η cannot be explicitly determined in the case of ^{35}Cl- and ^{81}Br-containing compounds, known or assumed structural data[3] are used to predict values for η. The results of these numerical calculations are shown in Table V, where the quantity a represents the electron population in each σ-bonding hybrid orbital on the bridging halogen atoms and N_t the total valence electron population on the bridging halogen atom.

Three important conclusions can be drawn from the data presented in the table. First, the $M\text{-}X_b\text{-}M$ angles inferred from experimental results for Nb_2I_{10} and Ta_2I_{10} correspond well to those angles determined by single-crystal X-ray diffraction studies of Nb_2Cl_{10},[22] Mo_2Cl_{10},[23] and Re_2Cl_{10}.[17] All angles whether determined by nqr or X-ray diffraction studies fall in the range 97-102°. This is particularly noteworthy because the angle determined by nqr is most correctly the angle between regions of high electron density arising from the hybrid orbitals and need not necessarily correspond to the angle between internuclear vectors as determined by crystallographic studies. Said differently, the possibility of "bent" or "banana" bonding does exist; but based on the close correlation between nqr and crystallographically determined bond angles, it does not appear necessary to invoke such bonding in these compounds. Second, there appears to be a trend toward smaller $M\text{-}X_b\text{-}M$ angles as the halogen is varied from Cl to Br to I. This is not surprising because the hybridization energy for I is greater than for Cl. Thus, the amount of s character in the hybrid orbitals and in turn the interorbital angle would be expected to decrease in the order shown. Additionally, a larger halogen, such as I, would tend to minimize repulsive interactions between the formally positively charged Nb atoms. In the case of Nb_2Cl_{10} these repulsive interactions lead to a surprisingly large $M\text{-}X_b\text{-}M$ angle because the Nb atoms are situated in positions distorted from octahedral holes with greater M-M distances than would be found if the Nb atoms were in octahedral holes. A larger halogen would lessen these repulsive interactions thus leading to a smaller bridging angle. Third, a general trend toward more covalent $M\text{-}X_b\text{-}M$ binding is apparent both as the atomic number of the metal atom is increased and as the atomic number of the halogen atom is increased. A similar trend was inferred from the terminal halogen atom data.

Registry No. Nb_2Cl_{10}, 17499-28-4; Nb_2Br_{10}, 17633-68-0; Nb_2I_{10}, 26740-66-9; Ta_2Cl_{10}, 17499-29-5; Ta_2Br_{10}, 17786-61-7; Ta_2I_{10}, 26814-38-0; W_2Cl_{10}, 17499-30-8; W_2Br_{10}, 26721-60-8; Mo_2Cl_{10}, 26814-39-1; Re_2Cl_{10}, 26721-61-9; ^{35}Cl, 13981-72-1; ^{81}Br, 14380-59-7; I_2, 7553-56-2; Nb, 7440-03-1; Ta, 7440-25-7.

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(21) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

(22) A. Zalkin and D. E. Sands, *Acta Crystallogr.*, 11, 615 (1958).

(23) D. E. Sands and A. Zalkin, *Acta Crystallogr.*, 12, 723 (1959).