222. *The Infrared Spectra of Some Tetrahedral Inorganic Complex Halides.*

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The infrared spectra of twenty-nine compounds containing inorganic "tetrahedral" metal halides have been examined in the region 200—450 cm.$^{-1}$ in microcrystalline mulls. One of the infrared-active $t_2(\nu_3)$ fundamentals has been observed in all cases, the M^{III} and M^{II} chloride absorptions being at about 380 and 290 cm.$^{-1}$, respectively, while the corresponding bromide absorptions occur at about 290 and 220 cm.$^{-1}$, respectively. From bands observed at $\sim$600 cm.$^{-1}$ for the compound Cs_3CoCl_5, the totally symmetric frequency $a_1(\nu_1)$ has been assigned and some tentative force constants have been derived for the tetrachlorocobaltate anion.

The question how accurately many of the transition-metal halide complexes of the form MX_4^{n-} correspond to regular tetrahedral structures has been of great interest when checking some of the predictions of crystal- and ligand-field theories, as well as when ascertaining the effect of degenerate electronic states on the structure of the complexes (*i.e.*, the Jahn–Teller effect). The one infrared-active frequency which can be determined with not too elaborate spectrometers is the higher of the two t_2 species (usually designated ν_3) and it seemed that the structure of this band might indeed give some information on these matters.

To eliminate any possibility that the observed absorption was due to the cationic part of the complex, as many spectra as possible were recorded with both the tetraethylammonium and the methyltriphenylarsonium cation, and, in addition, four compounds have been studied as their cæsium salts. The results are given in Table 1. The only previous results for this type of complex anion are concerned with the Raman spectra of solutions believed to contain $[ZnX_4]^{2-}$ ions.[1] The ν_3 vibration was not found for the $[ZnCl_4]^{2-}$ ion, but that for the $[ZnBr_4]^{2-}$ ion was located at 210 cm.$^{-1}$.

Table 1.

Metal–halogen stretching frequencies in tetrahedral complex anions.

MX_4^{2-}	$[Et_4N]^+$	$[Ph_3MeAs]^+$	Cs^+
$ZnCl_4^{2-}$	273s, 281m	262s, 283m, 291sh	285m, 292s *
$ZnBr_4^{2-}$	203s, 207m	215s, 223m	
$CuCl_4^{2-}$	247m, 268s, 289sh	283s	256m, 288s †
$CuBr_4^{2-}$	222s, br, 248sh	222s	
$NiCl_4^{2-}$	285s, br	275s, 295m ‡	
$NiBr_4^{2-}$	224s, br	217s, 228m	
$CoCl_4^{2-}$	281sh, 300s	284s, 299m, 308sh	310s § Cs_3CoCl_5, 309s ¶
$CoBr_4^{2-}$	227s	222s, 230m, 237sh	
$FeCl_4^{2-}$	282s	272s, 286m, 298sh	
$FeBr_4^{2-}$	216s		
$MnCl_4^{2-}$	282s	272s, 284m, 294sh	
$MnBr_4^{2-}$	216s	214s, 223m	
$FeCl_4^{-}$	378s		
$FeBr_4^{-}$	290s		

Crystal structures: * Brehler, *Z. Krist.*, 1957, **109**, 68. † Helmholz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176. ‡ Pauling, personal communication. § Poraĭ-Koshits, *Kristallografiya*, 1956, **1**, 291. ¶ Powell and Wells, *J.*, 1935, 359.

The metal–chlorine spectra obtained may be divided into two classes: those which have a single sharp peak and those which have two (or more) absorption maxima

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[1] Woodward, *Trans. Faraday Soc.*, 1958, **54**, 1271; Delwaulle, *Compt. rend.*, 1955, **240**, 2132; Godnev and Aleksandrovskaya, *Optics and Spectroscopy*, 1961, **10**, 14.

or shoulders. In the former category are the compounds Cs_3CoCl_5, Cs_2CoCl_4, $[NEt_4]FeCl_4$, $[NEt_4]_2FeCl_4$, $[NEt_4]_2MnCl_4$, and $[Ph_3MeAs]_2CuCl_4$. The spectrum of methyltriphenylarsonium chloride contains three maxima, at 341, 333, and 318 cm.$^{-1}$. The spectra of the copper complexes also contain these maxima, practically unchanged in position, but the spectra of all other methyltriphenylarsonium complexes appear only to contain the central maximum derived from the cation at 322 cm.$^{-1}$. The metal–bromine stretching frequencies are single in all but the zinc and copper complexes with the tetraethylammonium cation. Tetraethylammonium chloride and cæsium chloride themselves do not absorb in this region of the spectrum.

Discussion.—The crystal structures of only a few of these compounds are available, these being indicated in Table 1. It might have been expected that the t_2 vibration would be split in the crystal from either or both of two possible sources. First, any deviations from perfectly tetrahedral symmetry remove the triple degeneracy; and, secondly, the next nearest (and other) neighbour interactions in the crystal which, together with the primary co-ordination sphere, decide the site symmetry of the ion will again cause removal of the degeneracy in all but very special crystallographic cases. The compound Cs_3CoCl_5 has been crystallographically investigated and the $CoCl_4$ " nucleus " is usually described as " tetrahedral." [2] However, this statement was originally made to emphasise that the cobalt is not five-co-ordinated in this compound, as the formula suggests, and it was not intended to imply that the angles are 109° 28′. Indeed, the angles are close to 106° and 118° [3] (D_{2d} symmetry with two pairs of equal angles, each angle in the pair being related by a crystallographic plane of symmetry), so that the complex cannot truly be described as " tetrahedral " but is, instead, tetragonally distorted. The $CoCl_4$ nucleus in the compound Cs_2CoCl_4 has, in addition to the tetragonal distortion, a small rhombic distortion which leaves two angles equal but changes the others by a degree or so.[4] Thus, the fact that the spectra of these two compounds are identical within experimental error is, in itself, not surprising; but that the absorption should consist of a single sharp band is surprising, since a t_2 vibration splits in a tetragonally distorted molecule to give two vibrations which are both infrared-active [5] (B_2 and E of D_{2d}); both of these should be seen in a randomly oriented mull. No evidence of splitting has been found in these two compounds and, although it seems difficult to conclude that the two frequencies are accidentally degenerate, no other explanation can be advanced at the moment since it seems impossible that the splitting should be so large as to displace the band out of the range studied. That the matter is not completely simple is shown by the fact that the compound Cs_2ZnCl_4 shows a splitting of 7 cm.$^{-1}$ despite the fact that it is isostructural [6] with the cobalt analogue.

The methyltriphenylarsonium–copper complexes are the only ones which apparently possess a single metal–halogen stretching frequency and, while they are isomorphous with each other, they are not isomorphous with the other metal–halide complexes of this cation. Thus it appears that the $CuCl_4$ nucleus could be either perfectly tetrahedral or perfectly square-planar. The former arrangement seems the more likely when the spectrum of the compound Cs_2CuCl_4 is taken into account, for this compound is known from *X*-ray single-crystal analyses [7] to contain tetragonally distorted tetrahedra which result in a 28 cm.$^{-1}$ split in ν_3. The probability that a square-planar molecule has one of is infrared-active frequencies in exactly this position seems to be low. A conclusion about the exact stereochemistry of the $CuCl_4^{2-}$ anion in this complex must await either a study of its

[2] Powell and Wells, *J.*, 1935, 359.

[3] Mason, personal communication.

[4] Poraĭ-Koshits, *Kristallografiya*, 1956, **1**, 291.

[5] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., Princeton, New Jersey, 1945.

[6] Brehler, *Z. Krist.*, 1957, **109**, 68.

[7] Helmholz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

magnetic moment (1·95 B.M. at room temperature) over a temperature range, or an *X*-ray study.

Recently, the preparation of the compound Cs_3NiCl_5 was announced [8] and it will be interesting to see how the infrared spectrum of this compound compares with that of the cobalt complex, particularly in view of the fact that the *X*-ray single-crystal structure of the complex $[Ph_3MeAs]_2NiCl_4$ has just been completed.[9] Though the diffraction results show this complex anion to be regularly tetrahedral, to within experimental error, the crystal environment of the ion [9] only has symmetry 3, not $\bar{4}3m$, and thus a raising of the degeneracy of the t_2 vibration could be expected, as indeed is found (Table 1).

It would have been desirable to obtain a complete set of frequencies for each species studied, but this is difficult because most of the compounds are strongly coloured so that their Raman spectra are not readily obtainable and, also, the lower of the t_2 frequencies is not expected [5] to be much >100 cm.$^{-1}$. However, certain bands observed in an allied investigation [10] make some tentative assignments possible. Large single crystals of the compound Cs_3CoCl_5 show weak bands in the region of 600 cm.$^{-1}$, *viz.*, 627, 613, and 585 cm.$^{-1}$. The band at 628 cm.$^{-1}$ has been assigned as $2\nu_3$, and that at 585 cm.$^{-1}$ as $\nu_1 + \nu_3$, leading to $\nu_1 = 276$ cm.$^{-1}$, *i.e.*, a reasonable value considering the magnitude of ν_3 (cf. titanium, germanium, and stannic tetrachloride [5]).

TABLE 2.

	Frequencies				V.F.F.		C.F.F.		
	ν_1	ν_2	ν_3	ν_4	k	$k\delta/l^2$	k_1	k_2	k'
$CoCl_4^{2-}$	276	71	309	98	1·59	0·035	0·11	1·14	−0·03
$CoCl_4^{2-}$	276	77	309	104	1·59	0·042	0·12	1·12	−0·01
$TiCl_4$	386	120	495	141	3·11	0·100	0·23	2·19	−0·07

V.F.F. = Valence-force-field approximation. C.F.F. = Central-force-field approximation. Force constants × 10^5 dynes/cm.

Further, many of the tetraethylammonium complexes of the MCl_4^{2-} anion possess a weak band at ~380 cm.$^{-1}$ (*e.g.*, zinc 385 cm.$^{-1}$, iron 364 cm.$^{-1}$, manganese 382 cm.$^{-1}$). If this band is a regular feature of the spectrum of the MCl_4^{2-} ion, it may be assigned either as $\nu_2 + \nu_3$, leading to $\nu_2 \sim 71$ cm.$^{-1}$, or as $\nu_1 + \nu_4$, leading to $\nu_4 \sim 104$ cm.$^{-1}$. Both these possibilities seem reasonable. The identification of three frequencies allows the fourth to be calculated by using either the valence-force-field or the central-force-field approximation, since the former involves two parameters and the latter three. The missing frequency has been calculated by using one of the redundant equations of the valence-force-field method, and the force constants have been calculated on both models by using the two sets of frequencies. The results are given in Table 2, together with the analogous values for titanium tetrachloride.

Both approximations yield force constants which are only between one-half and one-third of the corresponding values for titanium tetrachloride. It is not suggested that these values are accurate, but simply that they are of the correct order of magnitude. More refined calculations are not justified at this stage. If, alternatively, the band at ~380 cm.$^{-1}$ is assigned as $\nu_3 + \nu_4$, values for the force constants are obtained which are about one-half of those given above. The initial assignments are, however, preferred on intensity grounds.

One other possible assignment is based upon the appearance of weak bands at 415 and 412 cm.$^{-1}$ in the spectra of the $MnBr_2^{2-}$ and the $FeBr_4^{2-}$ ion, respectively. If these bands arise from a combination of the ν_1 and ν_3 vibrations, the reasonable values of 199 and 196 cm.$^{-1}$ are obtained for the ν_1 vibrations.

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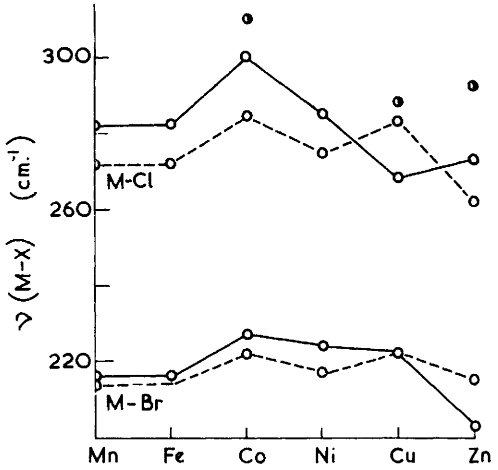
[8] Iberson, Gut, and Gruen, *J. Phys. Chem.*, 1962, **66**, 65.
[9] Pauling, personal communication.
[10] Clark, Dunn, and Stoneman, unpublished work.

The ratio of the metal–bromine to metal–chlorine stretching frequencies is almost constant, independently of the metal and of the cation (0·75—0·78). To treat the halogens as isotopes[5] would give $\nu_3(\mathrm{Br}).\nu_4(\mathrm{Br})/\nu_3(\mathrm{Cl}).\nu_4(\mathrm{Cl}) = 0{\cdot}61$, and, by coincidence, the experimental value of $\nu_3(\mathrm{Br})/\nu_3(\mathrm{Cl})$ is approximately the square root of this value. All tetrahedral bromide : chloride ratios from carbon to tin as "metal" lie[5] in the range 0·9—0·7.

A plot of the metal–halogen stretching frequency against the central metal is given in the Figure. We comment only that the frequencies for a particular series appear to reach a maximum value for the cobalt species ($d_\gamma{}^4 d_\epsilon{}^3$) which have maximum tetrahedral ligand-field stabilization.



Metal–halogen stretching frequencies in tetrahedral $MX_4{}^{2-}$ anions.

◑ Cæsium complexes.
——— Tetraethylammonium complexes.
– – – – Methyltriphenylarsonium complexes.

Experimental.—The infrared spectra were recorded with a Grubb-Parsons double-beam grating spectrophotometer, type D.M.2, serial number 28, over the range 200—450 cm.$^{-1}$ at 25°. The instrument was calibrated by reference to the spectrum of water vapour in this region.[11]

The compounds were prepared by standard methods,[12] and their infrared spectra obtained for Nujol mulls supported between Polythene discs. Absorption due to the Polythene is weak (it occurs only below 228 cm.$^{-1}$ and could be compensated) and did not interfere with the assignment of the metal–halogen stretching frequencies.

The compounds of the type $[\mathrm{Ph_3MeAs}]_2\mathrm{MX_4}$ are all isomorphous, except the copper derivatives, which are themselves isomorphous. The manganese, iron, nickel, and zinc compounds of the type $[\mathrm{N(Et)_4}]_2\mathrm{MCl_4}$ are isomorphous but have a slightly different *X*-ray powder pattern from that of the cobalt and from that of the copper derivatives. For the corresponding bromides, the cobalt, nickel, copper, and zinc compounds have one powder pattern, while the manganese and iron compounds have a second, slightly different one. All four types of powder pattern for the tetraethylammonium series of compounds are, however, closely similar.

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[11] Randall, Dennison, Ginsburg, and Weber, *Phys. Rev.*, 1937, **52**, 160.
[12] Gill, Nyholm, and Pauling, *Nature*, 1958, **182**, 168; Gill and Nyholm, *J.*, 1959, 3997.