26. *The Low-frequency Infrared Spectra of Some Complex Halides of Zinc, Cadmium, and Mercury.*

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Metal–chlorine and –bromine infrared stretching frequencies are reported for a variety of complex halides of zinc, cadmium, and mercury, and for several alkyl- and aryl-mercury halides, including some perfluoro-derivatives. There is no clear relation between ν(M–X) and the type of ligand, but frequencies tend to be relatively high in complexes of chelating ligands. Stretching frequencies involving bridging chlorine atoms are considered to be below 200 cm.$^{-1}$ and were not observed. Cadmium–chlorine are lower than mercury–chlorine stretching frequencies in analogous compounds, and it is suggested that in several of the examined cadmium complexes, L_2CdCl_2, the metal has a distorted-octahedral rather than a tetrahedral environment. Some boronium salts are described which probably contain bridged $(M_2Cl_6)^{2-}$ anions (M = Zn or Cd).

INFRARED spectra, in the 200—400 cm.$^{-1}$ region in which absorptions due to metal–chlorine and metal–bromine stretching vibrations commonly occur, have been reported for a series of tetrahedral complexes $MX_4{}^{2-}$ (M = Mn, Fe, Co, Ni, Cu, or Zn) [1] and for an extensive series of MX_4, MX_5, and MX_6 anions.[2] These absorptions are generally strong and the spectra are relatively simple. They should, therefore, be of considerable diagnostic value, and have, indeed, already been applied to problems in the co-ordination chemistry of tin [3] and some elements of Group VIII.[4]

The value of spectra in this region depends on the availability of data indicating the range of metal–halogen stretching frequencies, and the extent of their dependence on the co-ordination environment of the metal. The aim of the present work is to provide such data for zinc, cadmium, and mercury complexes. Bands due to metal–halogen vibrations could easily be distinguished from those due to the other co-ordinated ligands, for example, by comparing the chloride, bromide and iodide of a given series.

Zinc.—Data for thirteen complexes containing the $ZnCl_2$ group and eleven containing the $ZnBr_2$ group are given in Table 1, together with data for Cs_2ZnBr_4 and a complex containing $[ZnCl_3]^-$ or $[Zn_2Cl_6]^{2-}$ ions. The first point of interest is the small change in ν(Zn–X) on passing from the anions $ZnX_4{}^{2-}$ to the neutral complexes L_2ZnX_2. For Cs_2ZnCl_4, ν(Zn–Cl) is at 285 and 292 cm.$^{-1}$, and is at similar frequencies for $(Et_4N)_2ZnCl_4$ and $(Ph_3MeAs)_2ZnCl_4$.[1] These are near the lower part of, but inside, the range 277—345 cm.$^{-1}$ observed for the neutral complexes. For some tin(IV) complexes,[3] ν(Sn–Cl) is in much the same region for $SnCl_6{}^{2-}$ anions (310) as for the complexes py_2SnCl_4 (324) and $bipySnCl_4$ (327 and 280 cm.$^{-1}$). In the neutral zinc bromide complexes, ν(Zn–Br) tends

[1] Clark and Dunn, *J.*, 1963, 1198.
[2] Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.
[3] Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514; Beattie and McQuillan, *J.*, 1963, 1519.
[4] Coates and Parkin, *J.*, 1963, 421.

to be significantly higher than in salts containing $ZnBr_4^{2-}$ ions. Thus $\nu(Zn-Br)$ is at 203 and 207 cm.$^{-1}$ for $(Et_4N)_2ZnBr_4$, 215 and 223 cm.$^{-1}$ for both $(Ph_3MeAs)_2ZnBr_4$[1] and Cs_2ZnBr_4, but apart from the complexes $(NH_3)_2ZnBr_2$ and $(PEt_3)_2ZnBr_2$ in which $\nu(Zn-Br)$ appeared as an unresolved broad band at 210 and 221 cm.$^{-1}$, the higher of the two frequencies observed in the spectra of the neutral complexes was in the range 230—265 cm.$^{-1}$, the lower in the range 198—256 cm.$^{-1}$.

Secondly, two bands due to metal–halogen stretching were observed in nearly all the complexes examined, as would be expected for symmetric and antisymmetric vibrations. The appearance of two bands in the spectra of ZnX_4^{2-} ions has been considered in terms of departure from exact tetrahedral symmetry in the crystalline state.[1] It is curious that the difference between the two Zn–X frequencies varies so much in the neutral

TABLE 1.

Metal–halogen infrared absorption frequencies (cm.$^{-1}$) of some zinc complexes.

Complex	M. p.	Zn (%) Found	Zn (%) Required	$\nu(Zn-X)$
$(NH_3)_2ZnCl_2$ *	Dec. 210—240°, lit.[5] dec. 200°	38·7	38·4	298s, 285s
$(NHEt_2)_2ZnCl_2$	54—55°, lit.[6] †	31·6	31·2	296s
Py_2ZnCl_2	204—206°, lit.[7]	22·2	22·2	330s, 297s
$(Me_2N \cdot CH_2-)_2ZnCl_2$	177°	25·7	25·9	334s, 312s
$BipyZnCl_2$	>360°, lit.[8] †	22·5	22·4	331s, 323sh
$1,10\text{-PhenanZnCl}_2$	>360°	20·65	20·8	324s, 314s
$TerpyridylZnCl_2$	>360°, lit.[9]	—	—	288s, 279s
$(PEt_3)_2ZnCl_2$	97—98°, lit.[10] †	17·4	17·6	294s, 277s
$(PMe_2Ph)_2ZnCl_2$	118—119°	15·9	15·9	305s, 283s
$(p\text{-}Me_2N \cdot C_6H_4 \cdot PMe_2)_2ZnCl_2$	152—153°, lit.[11] 151·5—152	—	—	305s, 289s
$(PPh_3)_2ZnCl_2$	295°, lit.[12] 209°	9·88	9·9	322s, 299s
$(PPh_2 \cdot CH_2-)_2ZnCl_2$	290—291°	12·3	12·2	315s, 292s
$(EtS \cdot CH_2-)_2ZnCl_2$	95—96°	23·1	22·8	345s, 308s
$(BipyBPh_2)ZnCl_3$	ca. 365°	13·2	13·3	334s, 301s, 238s, 225s
Cs_2ZnBr_4 ‡	—, lit.[13]	10·04	10·12	223m, sh, 215s
$(NH_3)_2ZnBr_2$	Dec. 235—255°, lit.[14] †	25·1	25·2	210s (broad)
Py_2ZnBr_2	220—222°, lit.[15] †	17·2	17·1	257s, 222 (doubtful)
$(Me_2N \cdot CH_2-)_2ZnBr_2$	178°	18·9	19·15	263s, 233s
$BipyZnBr_2$	>360°	17·1	17·1	263s, 256sh
$1,10\text{-PhenanZnBr}_2$	>360°	16·1	16·1	264s, 232s
$(PEt_3)_2ZnBr_2$	130°	14·1	14·2	221s (broad)
$(PMe_2Ph)_2ZnBr_2$	119°	13·1	13·0	239s, 209m
$(p\text{-}Me_2N \cdot C_6H_4 \cdot PMe_2)_2ZnBr_2$	143°, lit.[11] 146°	—	—	230s, 198m
$(PPh_3)_2ZnBr_2$	223°, lit.[12] 220—221°	—	—	235s, 202m
$(PPh_2 \cdot CH_2-)_2ZnBr_2$	287°	10·5	10·5	243s, 209m
$(EtS \cdot CH_2-)_2ZnBr_2$	123°	17·4	17·4	265s, 229m
$(BipyBPh_2)_2ZnBr_4$	260°	6·49	6·37	217m, 209s
$(BipyBPh_2)ZnBr_3$	334—335°	10·32	10·44	253s, 209s

* Tetrahedral crystal structure, MacGillavry and Bijvoet, *Z. Krist.*, 1936, **94**, 249.   † No m. p. given in reference cited.   ‡ Distorted tetrahedral structure, Morosin and Lingafelter, *Acta Cryst.*, 1959, **12**, 744.

complexes, from 33 cm.$^{-1}$ for the chlorides and 36 cm.$^{-1}$ for the bromides down to a broad and presumably unresolved doublet in three compounds.

Thirdly, there does not appear to be any clear pattern relating $\nu(Zn-X)$ to the type of

[5] Block, Florentine, Simkin, and Barth-Wehrenalp, *J. Inorg. Nucl. Chem.*, 1962, **24**, 371.
[6] Hatfield and Yoke, *Inorg. Chem.*, 1962, **2**, 475.
[7] Lang, *Ber.*, 1888, **21**, 1578.
[8] Jaeger and van Dijk, *Z. anorg. Chem.*, 1936, **227**, 273.
[9] Morgan and Burstall, *J.*, 1937, 1649.
[10] Schmelz, Hill, and Curran, *J. Phys. Chem.*, 1961, **65**, 1273.
[11] Cass, Coates, and Hayter, *J.*, 1955, 4007.
[12] Reppe and Schweckendiek, *Annalen*, 1948, **560**, 104.
[13] Morosin and Lingafelter, *Acta Cryst.*, 1959, **12**, 744.
[14] Biltz and Messerknecht, *Z. anorg. Chem.*, 1923, **129**, 161.
[15] Varet, *Compt. rend.*, 1891, **112**, 622.

donor in the complexes, apart from a tendency for the higher frequencies to be associated with chelating ligands, and donors causing high ν(Zn–Cl) also appear to cause high ν(Zn–Br) and *vice versa*. The terpyridyl complex is an exception in that the two Zn–Cl frequencies were near the lower end of the observed range, though in view of its unusual stereo-chemistry [16] and the probability that the $ZnCl_2$ group carries a rather bigger negative charge due to co-ordination with three nitrogen atoms it is perhaps surprising that the frequencies fall within the range of the tetrahedral complexes. The boronium complexes are discussed below, together with those of cadmium and mercury.

Cadmium.—Octahedral complexes of cadmium are very commonly formed, and many compounds whose empirical formula might suggest 4-co-ordination in fact contain 6-co-ordinate cadmium, *e.g.*, $(NH_3)_2CdCl_2$ which has a polymeric structure [17] built from chains of octahedra with shared edges. Similarly the bispyridine complex, py_2CdCl_2, is iso-morphous with its cobalt(II) analogue in which the metal atoms have a distorted octahedral environment.[18] Cadmium is also surrounded by six chlorine atoms in NH_4CdCl_3 [19] and in the salts $(NH_4)_4CdCl_6$ and K_4CdCl_6.[20] No bands that could be due to ν(Cd–Cl) were observed in the spectra of any of these complexes, so ν(Cd–Cl) appears to be at frequencies less than 200 cm.[-1] when the chlorine is in either a terminal or a bridging position in an octahedral cadmium complex.

In contrast, bands evidently due to cadmium–chlorine stretching were observed in the spectra of all complexes examined which contained chelate ligands and of only three that did not. These bands, listed in Table 2, varied in intensity to a much greater extent than those of similar zinc complexes.

No *X*-ray structural determination is available for any of the complexes listed in Table 2, except for the terpyridyl complex which is isomorphous with its trigonal biprismatic 5-co-ordinate zinc analogue.[16] The band due to ν(Cd–Cl) in $(Et_4N)_2CdCl_4$,[2]

TABLE 2.

Metal–halogen infrared absorption frequencies (cm.[-1]) of some cadmium complexes.

Complex	M. p.	Cd (%)		ν(Cd–X)
		Found	Required	
$(Me_2N\cdot CH_2-)_2CdCl_2$	Dec. 240°	37·4	37·6	228w, 222w
BipyCdCl$_2$	>360°, lit.[8] †	33·4	33·1	228w
1,10-PhenanCdCl$_2$	>360°	31·1	30·9	227m, 213m
TerpyridylCdCl$_2$	>360°, lit.[9] †	—	—	269s, 250s
$(BipyBPh_2)CdCl_3$	333°	20·75	20·8	271s, 224w
$(PMe_2Ph)CdCl_2$	254—259°, lit.[11] 302—304° (decomp.)	35·05	35·0	233s
p-$Me_2N\cdot C_6H_4PMe_2CdCl_2$	220—221° lit.[11] 215—217°	—	—	245s
$(PPh_2\cdot CH_2-)_2CdCl_2$	265—266°	19·4	19·3	270s, 258sh
$(EtS\cdot CH_2-)_2CdCl_2$	dec. 140°	33·9	33·7	223w
$(PPh_2\cdot CH_2-)_2CdBr_2$	285—286°	16·9	16·8	~195s

† No m. p. given in literature cited.

presumably containing tetrahedral $CdCl_4{}^{2-}$ anions, is at 260 cm.[-1]. The cadmium–chlorine absorptions of the terpyridyl complex are in this region, as are those of the chelating phosphine complex $(PPh_2\cdot CH_2-)_2CdCl_2$, and we feel confident that the latter consists of individual molecules of complex in the crystalline state. The same is probably true of the corresponding bromide complex, as only in this instance was an absorption observed that could be due to ν(Cd–Br); in all other cases ν(Cd–Br) must be well below 200 cm.[-1].

The low frequencies and low intensities of cadmium–chlorine absorptions in the other complexes which might appear, from their empirical formulæ, to contain tetrahedrally co-ordinated cadmium, raise a suspicion that there may be interaction between the

[16] Corbridge and Cox, *J.*, 1956, 594.
[17] MacGillavry and Bijvoet, *Z. Krist.*, 1936, **94**, 231.
[18] Dunitz, *Acta Cryst.*, 1959, **10**, 307.
[19] Brasseur and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2886.
[20] Bergerhoff and Smitz-Dumont, *Z. anorg. Chem.*, 1956, **284**, 10.

chlorine atoms of one unit and the cadmium atom of another. This is equivalent to suggesting that these complexes, $(Me_2N \cdot CH_2-)_2CdCl_2$, bipy$CdCl_2$, phenan$CdCl_2$ and $(EtS \cdot CH_2-)_2CdCl_2$, have distorted octahedral structures; this is reasonable in view of the known tendency of cadmium to be 6-co-ordinate.

Various complexes, R_3P(or R_3As)$CdBr_2$(or I_2), have been described, which are dimeric in solution, and $[(Et_3P)CdBr_2]_2$ is dimeric in the solid state.[21] Analogous cadmium chloride complexes are not so readily prepared, but the spectra of two such compounds examined, $(PMe_2Ph)CdCl_2$ and $(p\text{-}Me_2N \cdot C_6H_4 \cdot PMe_2)CdCl_2$, are consistent with their also having chlorine-bridged dimeric structures on the basis that the single strong band observed is due to terminal ν(Cd–Cl) and that absorption due to bridging chlorine is below 200 cm.$^{-1}$. This is reasonable since the infrared-active absorptions due to bridging chlorine in Al_2Cl_6 (as gas) [22] are much lower, 301 (calc.) and 420 cm.$^{-1}$, than those due to terminal chlorine, 484 and 625 cm.$^{-1}$. Similarly the Raman-active terminal frequencies are higher than the bridging frequencies.

Mercury.—Crystalline mercury(II) chloride absorbs at 375 cm.$^{-1}$, in fair agreement with a previously reported value,[23] 373 cm.$^{-1}$. The metal is virtually 2-co-ordinate,[24] having two chlorine atoms at 2·25 Å, two at 3·34 Å, and two more at 3·63 Å. The environment of mercury in $HgBr_2$, which has a single strong band at 249 cm.$^{-1}$, is rather similar.[25] Mercury–chlorine and –bromine absorptions are at lower frequencies than these in all other compounds examined.

In the complex $CsHgCl_3$, the mercury is octahedrally co-ordinated, with two chlorine atoms at 2·29 Å and four at 2·70 Å; a strong band was observed at 320 cm.$^{-1}$, and one of medium intensity at 284 cm.$^{-1}$. An unresolved broad band, centred at 304 cm.$^{-1}$, was observed for K_2HgCl_4,H_2O, which has a similar structure [26] with two chlorine atoms at 2·29 Å, two at 2·92 Å, and two at 3·13 Å. The spectrum of NH_4HgCl_3, in which the metal has two chlorine atoms at 2·34 Å [27] and four at 2·96 Å, was similar, with an unresolved broad band centred at 309 cm.$^{-1}$.

The spectrum of the bispyridine complex, py_2HgCl_2, in the 20—50 μ region was particularly interesting since, apart from a single band at 418 cm.$^{-1}$ where co-ordinated pyridine commonly absorbs,[28] no band was observed. Our complex was prepared as described by Grdenić *et al.*,[29] who reported that the mercury has two chlorine atoms at 2·34 Å, two nitrogen atoms at 2·60 Å, and two more chlorine atoms at 3·25 Å. Grdenić *et al.* regard the structure as containing discrete $HgCl_2$ molecules with pyridine of crystallization held together by longer Hg$\cdots$Cl contacts. This description does not seem consistent with the absence of infrared bands in the 300 cm.$^{-1}$ region. On the other hand, Dunitz [30] regards the structure as similar to that of py_2CuCl_2, in which the metal has a distorted octahedral environment. The infrared result provides evidence that all the chlorine atoms in the mercury complex should be regarded as being in bridging rather than in terminal positions, in other words supporting the view that the complex is a polymer held together by bridging chlorine rather as in py_2CoCl_2 and py_2CuCl_2. We expect absorptions due to bridging chlorine to be at frequencies below 200 cm.$^{-1}$, as they are in cadmium complexes.

Data on mercury complexes, in which the metal may be expected to have a tetrahedral environment, are given in Table 3.

[21] Evans, Mann, Peiser, and Purdie, *J.*, 1940, 1209.
[22] Klemperer, *J. Chem. Phys.*, 1956, **24**, 353.
[23] Miller, Carlson, Bentley, and Jones, *Spectrochim. Acta*, 1960, **16**, 135.
[24] Grdenić, *Arkiv Kemi*, 1950, **2**, 14.
[25] Verweel and Bijvoet, *Z. Krist.*, 1931, **77**, 122.
[26] Zvonkova, Samodurova, and Vorontsova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **102**, 1115.
[27] Harmsen, *Z. Krist.*, 1938, **100**, 208.
[28] Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79; Gill, Nyholm, Barclay, Christie, and Pauling, *ibid.*, p. 88.
[29] Grdenić and Kristanovic, *Arkiv Kemi*, 1955, **27**, 143.
[30] Dunitz, *Acta Cryst.*, 1957, **10**, 307.

TABLE 3.

Metal–halogen infrared absorption frequencies (cm.$^{-1}$) of some mercury complexes.

Complex	M. p.	Hg (%) Found	Hg (%) Required	ν(Hg–X)
(Me$_2$N·CH$_2$–)$_2$HgCl$_2$	164°	51·65	51·8	289s, 277s
BipyHgCl$_2$	306—310°	47·3	46·9	273s (broad)
1,10-PhenanHgCl$_2$	>360°	44·8	44·4	279s *
[(PMe$_2$Ph)HgCl$_2$]$_2$	179°, lit.[11] 168—169°	48·7	49·0	305s
[(p-Me$_2$N·C$_6$H$_4$PMe$_2$)HgCl$_2$]$_2$...	235°, lit.[11] 233—235°	—	—	307s
(PPh$_3$HgCl$_2$)$_2$	308—312°, lit.[21] 306—309°	—	—	289s
(PPh$_2$·CH$_2$–)$_2$(HgCl$_2$)$_2$	272—273°	42·35	42·6	292s, 279s
(AsEt$_3$HgCl$_2$)$_2$	163°, lit.[21] 163°	—	—	285s (broad)
(AsEt$_3$)$_2$(HgCl$_2$)$_3$	114°	51·6	51·9	342s, 292s (broad)
(AsPh$_3$HgCl$_2$)$_2$	258°, lit.[21] 251—253°	—	—	290s
(EtS·CH$_2$–)$_2$HgCl$_2$	97—98°, lit.[31] 99—100°	47·8	47·6	288s, 249m
(TeBu$_2$^{n}HgCl$_2$)$_2$	97—98°	39·2	39·1	299s
(BipyBPh$_2$)HgCl$_3$	314°	31·8	32·0	283s
(Me$_2$N·CH$_2$–)$_2$HgBr$_2$	165°	42·4	42·1	213s, 208sh
BipyHgBr$_2$	286—289°	39·0	38·8	Not observed
1,10-PhenanHgBr$_2$	355—360°	36·85	37·1	211s, 205sh
[(p-Me$_2$N·C$_6$H$_4$·PMe$_2$)HgBr$_2$]$_2$	200—202°, lit.[11] 201—204°	—	—	214s (broad)
(EtS·CH$_2$–)$_2$HgBr$_2$	110—111°	39·0	39·3	204s (broad)

* A band at lower frequency is obscured by ligand vibrations.

Mercury differs from zinc and cadmium in that ν(Hg–Cl) in its neutral chloride complexes is in all cases considerably higher than in the anion HgCl$_4$$^{2-}$. Where two frequencies are observed, the upper one is in the range 279—292 cm.$^{-1}$, single bands being at 273—307 cm.$^{-1}$, and the lower component of a pair 249—279 cm.$^{-1}$. The symmetrical stretching frequency [32] of the HgCl$_4$$^{2-}$ ion is at 269 cm.$^{-1}$, the unsymmetrical frequency [2] being at 228 cm.$^{-1}$.

Where observed, mercury–bromine stretching frequencies were near the limit of our spectrometer and were not observed for bipyHgBr$_2$, (PPh$_3$)$_2$HgBr$_2$, (PPh$_3$HgBr$_2$)$_2$, (AsPh$_3$HgBr$_2$)$_2$, and (PPh$_2$·CH$_2$–)$_2$HgBr$_2$.

Complexes of the type LHgX$_2$ are normally dimeric with a halogen bridge,[21] and in the spectra of such complexes we observed a single band, clearly due to a terminal Hg–Cl group, and we conclude, as we did for bridged cadmium complexes, that bridging mercury–chlorine stretching frequencies are below 200 cm.$^{-1}$. The complex (AsEt$_3$)$_2$(HgCl$_2$)$_3$ fits this pattern if it has a structure similar to that of the bromide (AsEt$_3$)$_2$(HgBr$_2$)$_3$ which contains HgBr$_2$ and (AsEt$_3$HgBr$_2$)$_2$ molecules;[21] the band at 342 cm.$^{-1}$ evidently is due to the HgCl$_2$ group, that at 292 cm.$^{-1}$ to terminal Hg–Cl in the dimer, and the bridging frequencies are not observed.

The 1,2-bisdiphenylphosphinoethane complexes call for comment. Attempts were made to prepare these for comparison with complexes with chelate nitrogen atoms, *e.g.*, (Me$_2$N·CH$_2$–)$_2$HgCl$_2$. Though a complex (Ph$_2$P·CH$_2$–)$_2$HgBr$_2$ was prepared, no mercury–bromine band was observed, and attempts to prepare the analogous chloride yielded a compound (Ph$_2$P·CH$_2$–)$_2$(HgCl$_2$)$_2$. We do not know the structure of this and the situation is further complicated by the presence of a band at 350 cm.$^{-1}$. Such a band is found in the spectra of all complexes containing this ligand, and in this instance it could possibly coincide with the antisymmetrical stretching absorption of free HgCl$_2$ [compare ν(Hg–Cl) at 342 cm.$^{-1}$ for HgCl$_2$ in the triethylarsine complex discussed above].

The spectra of alkyl- and aryl-mercury chlorides and bromides all contain, as expected, a single band due to mercury–halogen stretching. This band is always strong in the spectra of chlorides, and considerably weaker in those of bromides, and the frequencies (Table 4) are in the region between those found in the spectra of tetrahedral complexes and those of HgCl$_2$ and HgBr$_2$.

[31] Shostakovskii, Prilezhaeva, and Uvarova, *Izvest. Akad. Nauk S.S.S.R.*, 1954, 526.
[32] Roffe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

TABLE 4.

Metal–halogen infrared absorption frequencies (cm.$^{-1}$) for some two-co-ordinate mercury halides.

Halide	ν(Hg–Cl)	Halide	ν(Hg–Br)
HgCl$_2$	375s	HgBr$_2$	249s
MeHgCl	315s	MeHgBr	214w
EtHgCl	314s	EtHgBr	209w
Pr^{n}HgCl	322s	Pr^{n}HgBr	214w
Bu^{n}HgCl	316s	Bu^{n}HgBr	246m
CH$_2$:CH·HgCl	323s	CH$_2$:CH·HgBr	216m
PhC:C·HgCl	345s		
CCl$_3$HgCl	335s	CCl$_3$·HgBr	238s
PhHgCl	331s	PhHgBr	214m
p-CH$_3$·C$_6$H$_4$·HgCl	325s	p-CH$_3$·C$_6$H$_4$·HgBr	246m
p-CF$_3$·C$_6$H$_4$·HgCl	324s	p-CF$_3$·C$_6$H$_4$·HgBr	230m
p-Cl·C$_6$H$_4$·HgCl	330s		
p-Me$_2$N·C$_6$H$_4$·HgCl	323s	p-Me$_2$N·C$_6$H$_4$·HgBr	233m
[O(HgCl)$_3$]Cl	350s, 334s, 328sh		

Except for the ethynyl [33] and the trigonal oxonium derivative [34] the mercury–chlorine stretching frequencies lie in the range 314—331 cm.$^{-1}$, and there is no apparent relation to the character of the organic group. In the arylmercury series ν(Hg–Cl) varies only between 323 and 331 cm.$^{-1}$. Mercury–bromine stretching frequencies vary rather more, and the high value of ν(Hg–Br) in n-butyl- and p-tolyl-mercury bromide is remarkable, being nearly the same as in HgBr$_2$.

Results relating to some trifluoromethyl- [35] and pentafluorophenyl-mercury [36] compounds are given in Table 5.

TABLE 5.

Principal low-frequency infrared bands (cm.$^{-1}$) of some perfluoromercury derivatives, R$_F$·HgX.

Compound	ν(Hg–CF$_3$)	ν(Hg–X)	C$_6$F$_5$ vibrations
CF$_3$HgCl	252m	327, 339vs	—
CF$_3$HgBr	270s	233m	—
CF$_3$HgI	255s	—	—
C$_6$F$_5$HgMe	—	549w	221m, 278m, 310m, 358s
C$_6$F$_5$HgCl	—	344s	230m, 312w, 362s, 379s
C$_6$F$_5$HgBr	—	246s	223s, 281w, 310m, 360s
(C$_6$F$_5$)$_2$Hg	—	—	226sh, 231s, 279s, 310s, 357s, 368s, 375sh

The spectra of the pentafluorophenylmercury compounds all contain a characteristic pattern due to the C$_6$F$_5$ group, that of (C$_6$F$_5$)$_2$Hg differing only in that the lowest-frequency band is split into two and the 360-cm.$^{-1}$ band is split into three components. The mercury–halogen frequencies fall within, but near the upper part of, the ranges of Table 4.

Bipyridyldiphenylboronium Salts.—Since other work on these was in progress in the laboratory we took the opportunity of preparing the following salts containing this rather large cation and zinc, cadmium, and mercury halogeno-anions: B$^+$ZnCl$_3^-$, B$^+$ZnBr$_3^-$, B$_2$$^{2+}$ZnBr$_4$$^{2-}$, B$^+$CdCl$_3^-$, B$^+$CdBr$_3^-$, B$^+$HgCl$_3^-$, and B$^+$HgBr$_3^-$ (B = bipyBPh$_2$). Only in one instance did we succeed in preparing a salt containing the MX$_4$$^{2-}$ anion. The salts of empirical formula B$^+$MX$_3^-$ could contain three-co-ordinate anions or, more probably, binuclear anions such as Zn$_2$Cl$_6$$^{2-}$ with two bridging halogen atoms. The spectra of the chloride and iodide, [bipyBPh$_2$]X, contain many bands of low intensity in the 200—400 cm.$^{-1}$ region, so the four strong bands at 334, 301, 238, and 225 cm.$^{-1}$ observed in the

[33] Dessy, Budde, and Woodruff, *J. Amer. Chem. Soc.*, 1962, **84**, 1172.
[34] Ščavničar and Grdenić, *Acta Cryst.*, 1955, **8**, 275.
[35] Emeléus and Haszeldine, *J.*, 1949, 2948.
[36] Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367; Coe, Stephens, and Tatlow, *J.*, 1962, 3227.

spectrum of the complex BZnCl$_3$ are difficult to reconcile with the presence of a mononuclear anion. We suggest the bands at 334 and 301 cm.$^{-1}$ are associated with terminal Zn–Cl stretching, and the lower-frequency bands with bridging chlorine. In the spectrum of the bromide BZnBr$_3$, the bands at 253 and 209 cm.$^{-1}$ would be due to terminal Zn–Br stretching, and we would expect the bridging modes to be well below 200 cm.$^{-1}$. For the cadmium complex the bands at 271 and 224 cm.$^{-1}$ may be explained on the same basis, but the single band at 283 cm.$^{-1}$ in the spectrum of the mercury complex is surprising.

<h2 style="text-align:center">EXPERIMENTAL</h2>

M. p.s, analyses, and references are included in Tables 1—3. The following notes refer to new compounds or difficulties encountered in the preparation of previously described compounds.

NNN'N'-Tetramethylethylenediamine complexes crystallized from ethanol containing equimolar quantities of the diamine and the anhydrous halide, as colourless needles (ZnCl$_2$), plates (ZnBr$_2$), fine needles (CdCl$_2$ and CdBr$_2$), needles (HgCl$_2$), and rosettes (HgBr$_2$). *2,2'-Bipyridyl* and *1,10-phenanthroline complexes* were precipitated from dilute ethanolic solution and washed with much ethanol; bipyZnCl$_2$ and bipyZnBr$_2$ were recrystallized from nitrobenzene in which they were very sparingly soluble.

An ethanolic solution of zinc chloride and dimethylphenylphosphine (2 mol.) was cautiously diluted with water and allowed to remain for ~3 hr., during which *dichlorobisdimethylphenylphosphinezinc*, (PMe$_2$Ph)$_2$ZnCl$_2$, separated as large plates. The *bromide*, similarly prepared, crystallized when the ethanolic solution was kept at 0°

Though dichlorobistriphenylphosphinezinc has been described,[12] no preparative details have been given. Attempted preparation from ethanolic solution resulted only in crystallization of triphenylphosphine, but the complex slowly crystallized after anhydrous zinc chloride in ether had been added to the phosphine (2 mol.) in dry benzene. The complex shrank and became opaque from ~250° and melted at 295° (lit.,[12] m. p. 209°). The complex was also prepared by the method given [37] for its nickel(II) analogue, *viz.*, boiling a mixture of zinc chloride in glacial acetic acid with the phosphine (2 mol.) in butan-1-ol for 2 hr. The large colourless crystals thus obtained began to melt at 208° and gave a clear liquid at ~300°. The bromide was similarly prepared.

Dichloro-1,2-bisdiphenylphosphinoethanezinc, (PPh$_2$·CH$_2$–)$_2$ZnCl$_2$, crystallized when hot ethanolic solutions of zinc chloride and the diphosphine (1 mol.) were mixed. The *dibromocomplex* was similarly prepared from zinc bromide in methanol and the diphosphine in propan-1-ol. The *cadmium chloride* and *cadmium bromide analogues* crystallized as needles when the hot ethanolic cadmium halide was mixed with hot propanolic diphosphine (1 mol.). The *mercury chloride complex*, (PPh$_2$·CH$_2$–)$_2$(HgCl$_2$)$_2$ crystallized from hot acetone solutions of the halide and the diphosphine (1 mol.) (Found: C, 33·2; H, 2·7; Hg, 42·35. C$_{26}$H$_{24}$Cl$_4$Hg$_2$P$_2$ requires C, 33·2; H, 2·6; Hg, 42·6%). The *bromo-complex*, (PPh$_2$·CH$_2$–)$_2$HgBr$_2$, crystallized from acetone.

Dichloro-(1,2-diethylthioethane)zinc, (EtS·CH$_2$–)$_2$ZnCl$_2$, was prepared from the disulphide (1 mol.) and anhydrous zinc chloride in ether with rigorous exclusion of moisture. The *dibromozinc* and the *dichloro-cadmium complexes* also crystallized from ether. The zinc and cadmium complexes were very sensitive to moisture. The analogous *dichloro-* and *dibromo-mercury complexes* readily crystallized from ethanol.

The triethylarsine–mercury chloride complex, (AsEt$_3$)$_2$(HgCl$_2$)$_3$, was obtained when triethylarsine (2·3 g.) was shaken with mercury chloride (7·8 g., 0·5 mol.) in water (250 c.c.) and the resulting white flocculent precipitate was separated; it crystallized from methanol as colourless needles, m. p. 114°.

Bipyridyldiphenylboronium Salts.—Slow crystallization from ethanol containing bipyridyldiphenylboronium chloride [38] (2 mol.) and zinc chloride yielded *bipyridyldiphenylboronium trichlorozincate*, [bipyBPh$_2$][ZnCl$_3$], as colourless needles. The use of a larger excess of boronium chloride did not result in crystallization of a tetrachlorozincate. A similar method yielded *bipyridyldiphenylboronium tetrabromozincate*, [bipy BPh$_2$]$_2$ZnBr$_4$, as colourless plates, but

[37] Browning, Davies, Morgan, Sutton, and Venanzi, *J.*, 1961, 4816.
[38] Davidson and French, *J.*, 1962, 3364.

recrystallization of this from an ethanolic solution of zinc bromide gave colourless feathery needles of *bipyridyldiphenylboronium tribromozincate*, [bipyBPh$_2$][ZnBr$_3$].

Bipyridyldiphenylboronium trichlorocadmate, [bipyBPh$_2$][CdCl$_3$], and the *tribromocadmate*, m. p. 315—316° (Found: Cd, 16·8. C$_{22}$H$_{18}$BBr$_3$CdN$_2$ requires Cd, 16·75%), were similarly prepared as colourless plates (from ethanol).

Bipyridyldiphenylboronium trichloromercurate, [bipy BPh$_2$][HgCl$_3$], and the *tribromomercurate*, m. p. 275° (Found: Hg, 26·3. C$_{22}$H$_{18}$BBr$_3$HgN$_2$ requires Hg, 26·3%), were precipitated from ethanol.

Organomercury Halides.—These were prepared by methods already described. The following appear not to have been reported previously: p-*dimethylaminophenylmercury bromide*, m. p. 195—200° (from acetone) (Found: Hg, 49·7. C$_8$H$_{10}$BrHgN requires Hg, 50·0%), p-*trifluoromethylphenylmercury chloride*, m. p. 257° (from ethanol) (Found: Hg, 52·7. C$_7$H$_4$ClF$_3$Hg requires Hg, 52·6%), p-*trifluoromethylphenylmercury bromide*, m. p. 254° (from ethanol) (Found: Hg, 47·04. C$_7$H$_4$BrF$_3$Hg requires Hg, 47·13%).

Pentafluorophenylmercury chloride was prepared by a method similar to that described for the bromide.[36] Bispentafluorophenylmercury (0·54 g.) was boiled with mercuric chloride (0·40 g., 1 mol.) in ethanol (50 c.c.). After removal of the solvent under reduced pressure the residue crystallized from carbon tetrachloride as colourless plates, m. p. 164—165° (Found: Cl, 8·7; F, 23·8. C$_6$ClF$_5$Hg requires Cl, 8·8; F, 23·6%).

Spectra.—Infrared spectra were measured with a Grubb-Parsons double-beam grating spectrometer (DB3/DM2), with a 200-line per cm. grating, swept with dry air; the calibration was checked against part of the rotational spectrum of water vapour, the instrument being used as a single-beam one.[39] Specimens were mounted as Nujol mulls between cæsium iodide discs, halogen exchange being avoided by placing thin Polythene sheets between the mulls and the cæsium iodide.

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[39] Randall, Dennison, Ginsburg, and Weber, *Phys. Rev.*, 1937, **52**, 160.