Far-ultraviolet Spectra of Metal Halide Complexes

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THE charge-transfer spectra of many metal halide complexes in the visible and ultraviolet have been reported,[1–4] but the region above 45,000 cm.$^{-1}$ remains more or less unexplored. A cogent experimental reason for this neglect has been that many of the complexes of interest require a large excess of free halide to ensure their complete formation in solutions dilute enough for transmission spectroscopy, so that the absorption by the complexes is completely masked by free halide-ion absorption. Further, among the dipolar aprotic solvents which permit formation of, *e.g.*, $NiCl_4^{2-}$, with the minimum halide-ion excess, the large majority absorb appreciably above 40,000 cm.$^{-1}$. As part of a comprehensive investigation of the electric-dipole-allowed transitions of the first transition series tetrahalide complexes, we have devised a method of measuring these spectra up to at least 60,000 cm.$^{-1}$, the first results of which are now reported.

Whereas tetramethylammonium and tetraethylammonium salts of the anions MX_4^{2-} ($M = Mn^{II}$, Co^{II}, N^{II}, Cu^{II}, Zn^{II}, and X = Cl, Br, I) crystallize readily from ethanolic solutions,[5] evaporation of ethanolic solutions of the tetra-n-butylammonium salts leaves the compound in the form of an amorphous gum which is only crystallized with difficulty. Hence if samples of tetra-n-butylammonium salts dissolved in ethanol are placed on silica plates and allowed to evaporate, then transparent films of the salts remain. The latter are homogeneous under the microscope, showing no trace of crystallinity, and have transmission spectra in the near-ultraviolet which correspond precisely, both in energy and relative intensity of the peaks, to those of dilute solutions in CH_2Cl_2 containing a large excess of NBu_4X.[3] Even those anions, such as NiI_4^{2-}, which are particularly susceptible to solvolysis and require the largest excess halide-ion concentration for their complete formation in dilute solution, give, under these conditions, evaporated films whose spectra show no trace of solvolysed impurities.

The Figure shows typical examples of the spectra obtained. The spectrophotometer was a far-ultraviolet version of the Beckmann DK 2A, purged with nitrogen, and the slit-width at 56,000 cm.$^{-1}$ was commonly no greater than 0·15 mm. As with all far-ultraviolet spectra measured in condensed phases, the bands are broad and do not show any vibrational fine structure. Since all the tetrahalide complexes studied, except those of Mn^{II} and Zn^{II}, have bands in the near-ultraviolet whose extinction coefficients are known,[3] the correspondence between the near-ultraviolet bands in solution and in the evaporated films permits approximate extinction coefficients for the new far-ultraviolet bands to be obtained by extrapolation. The Table shows such data for all the complexes, and also includes results for films of tetra-n-butylammonium halides prepared in the same way.

The most important feature of the tetrahalogenozincate(II) spectra is their resemblance to the corresponding halide-ion transitions, which are assigned to terms arising from $np^5(n + 1)s$. The p^5 sub-shell is split by spin-orbit coupling into $^2P_{1/2}$ and $^2P_{3/2}$, which then couple with the $(n + 1)s$ and split again. The four resulting transitions are clearly distinguishable in I^- (see Table). In Br^- only the major splitting is seen, TABLE

Far-ultraviolet spectra of first transition series tetrahalogeno-complexes; (cm.$^{-1}$ × 10^{-3})

	Mn^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Halide
Cl	49·4	51·7 (24,900) 57·1 (26,500)	51·7 (22,500)	53·2 (18,600)	56·7	55·5
Br	46·1 (51·3)	47·4 (31,000) (52·1)	47·2 (22,400) 56·0 (29,700)	48·7 (40,000)	49·2 52·4	47·4 50·8
I		(40·8) 44·1 (16,800)	(39·2) 42·0 (13,400)		40·5 47·0	44·1 (45·9) 51·3 (52·3)

and ζ_{3p} is too small for any splitting to be apparent in Cl^-. From $ZnBr_4^{2-}$ and ZnI_4^{2-} we calculate ζ_{4p}, 2130 cm.$^{-1}$ and ζ_{5p}, 4330 cm.$^{-1}$, compared with 2270 cm.$^{-1}$ and 4800 cm.$^{-1}$ for the halide ions, thus yielding relativistic nephelauxetic ratios[6] 0·94 and 0·90 respectively, as a result of delocalizing the *ligand* electrons over the *metal*. A comparable value for[7] HgI_4^{2-} is 0·85. Among the other tetrahalides, the question is whether the bands in the 45,000—50,000 cm.$^{-1}$ region are also to be assigned as predominantly internal halide transitions or to transitions from one of the deep bonding levels to the partly filled *d*-shell, in the customary[8] numbering of energy levels, $2t_2 \rightarrow 4t_2$. That they are in fact the former follows from (i) their rather small energy variation from one metal to another, compared with the charge-transfer bands in the near-ultraviolet and (ii) that such variation as there is occurs in the opposite sense to the near-ultraviolet bands. (The lowest energy allowed transitions in $CoCl_4^{2-}$, $NiCl_4^{2-}$ and $CuCl_4^{2-}$ occur at 42,650, 35,500, and 24,350 cm.$^{-1}$, respectively.)[3]

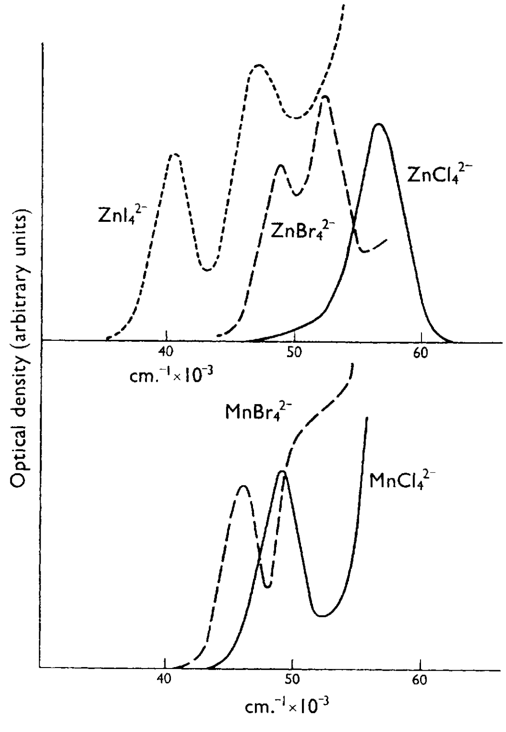

FIGURE. *Ultraviolet absorption spectra of tetrahalogeno-manganate*(II) *and tetrahalogenozincate*(II) *complexes.*

Furthermore the energy of a transition $np \rightarrow (n + 1)s$ increases with increasing effective nuclear charge, and therefore with increasing covalency of the metal–halogen bond, *i.e.*, in the order observed. Identification of these bands as predominantly intra-ligand in character raises a number of points. Thus, the vast majority of molecular-orbital calculations for this type of complex, which use a limited basis set, take no account of the lowest empty ligand orbitals, though they frequently include the metal $4p$. Mixing between, *e.g.*, chlorine $4s$ and copper $4s$ and $4p$ is bound to be considerable, and clearly should be considered in future calculations. There is no reason, in principle, why the type of measurement described in this note should not be extended into the vacuum ultraviolet as far as the internal transitions of the cations permit.

(*Received, June* 19*th*, **1967**; *Com.* 615.)

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