

1188. *A Simple Molecular Orbital Model of Transition-metal Halide Complexes.*

By P. DAY and C. K. JØRGENSEN.

A simple second-order perturbation treatment is applied to the visible and ultraviolet spectra of cupric halide complexes with four, five, and six halogens, and to the tetrachloro- and tetrabromo-complexes of Mn^{II} , Fe^{II} , Fe^{III} , Co^{II} , Ni^{II} , and Cu^{II} . All the cupric halide ligand field spectra can be fitted by a single parameter for each halogen, instead of the two required by a point charge crystal field model. The electron transfer spectra of all the tetrahalides are reported, and compared with the energy differences between the diagonal elements of the metals and halogens as calculated by the model. It is emphasised that two-electron quantities are important in determining the observed electron transfer energies.

THE inadequacy of the electrostatic model as a description of the energy levels in open-shell complex ions is now well documented.^{1,2} Instead of using a first-order perturbation to rationalize the changes brought about in the open shell by a ligand field, a realistic treatment would include the possibility of electron exchange between the metal and ligands, enlarge the basic set of wave-functions of the metal atom to include the ligand orbitals, and examine the degree of metal-ligand mixing by second-order perturbation theory. Molecular orbitals obtained in this way are familiar in discussions of electron transfer spectra, but are still not extensively used in quantitative work on intra-*d*-shell spectra. Undoubtedly, the reason for this is that a full molecular orbital calculation requires a great deal more effort than a crystal field calculation, and the result is a function of many more variables. In the point charge approximation, the *d*-shell splitting, in whatever symmetry field, can be reduced, when spin-orbit interactions are neglected, to functions of two variables only. On the other hand, the fact that the diagonal elements of the effective one-electron operator (the "core field" of the molecule) are steep functions of charge means that a molecular, orbital calculation must start from an assumed charge distribution, use the calculated metal-ligand mixing coefficients to compute overlap populations, and then adjust the diagonal elements and repeat the calculation to self-consistency. We wish to show that a simpler model, within the framework of LCAO-MO theory, can give useful results with very much less labour, and allow comparisons

¹ B. R. Judd, *Proc. Roy. Soc.*, 1957, **241**, A, 414.

² S. Sugano and R. G. Shulman, *Phys. Rev.*, 1963, **130**, 517.

to be made among series of ions and electron transfer energies to be calculated with the same facility as intra-subshell transitions.

One of us has shown³ that the f -orbital energies in lanthanide complexes are explained by the weak effects of σ -antibonding on the partly filled shell, the different angular dependence of such effects producing the observed splittings. We start from the assumption of the Wolfsberg-Helmholz method^{4a} that the non-diagonal element of the molecule's core-field between appropriate linear combinations of orbitals on the central M and the ligands X in MX_N is

$$H_{\text{MX}} = k S_{\text{MX}} (H_{\text{M}} + H_{\text{X}}) / 2 \quad (1)$$

where the constant k is somewhere between 1.6 and 2. S_{MX} is the overlap integral and H_{M} , H_{X} the diagonal elements of the core-field. To estimate the relative amounts of σ -antibonding between the ligands and the orbitals of different symmetry types belonging to the same partly filled shell of M, we separate S_{MX} into a radial and an angular part

$$S_{\text{MX}} = \Xi S_{\text{MX}}^* \quad (2)$$

If the orbitals of the partly filled shell are written

$$\psi_{\text{M}} = N_{\text{M}} \cdot A(x, y, z) \cdot P(r) / r \quad (3)$$

and the ligand σ -function of appropriate symmetry as a product of normalized Kronecker δ -functions

$$\psi(\text{X}_N) = \sum_{i=1}^N N_i \delta(x-x_i) \cdot \delta(y-y_i) \cdot \delta(z-z_i) \quad (4)$$

then the angular parameter Ξ is given by

$$\Xi = N_{\text{M}} \sum_{i=1}^N A(x_i, y_i, z_i) N_i \quad (5)$$

If the effects of covalent bonding are weak, second-order perturbation theory indicates that the relative σ -antibonding effect on different orbitals of the same d - or f -shell is proportional to Ξ^2 . As Ξ^2 is a function only of the geometry of the system, there remains but one freely chosen parameter, the proportionality factor which we shall call σ^* . When second-order perturbation theory is applied to equation (1), (cf. ref. 6, p. 93)

$$\sigma^* \simeq \frac{[(\frac{1}{2}k-1)H_{\text{M}} + \frac{1}{2}k \cdot H_{\text{X}}]^2 (S_{\text{MX}}^*)^2}{H_{\text{M}} - H_{\text{X}}} \quad (6)$$

The Ξ^2 theory is therefore particularly well adapted to studying the energy levels of MX_N for a given M and X as a function of N and the symmetry. The cupric halides, which have already been treated from an electrostatic point of view,⁵ provide a convenient example. We shall also discuss the energy level variations in a series of constant formula type, MX_4^{2-} (where M is Mn, Fe, Co, Ni, or Cu and X is Cl or Br) to illustrate the use of equation (6) for predicting electron-transfer energies when the energy differences in the partly filled shell are known. However, Cotton and Haas,^{4b} recently applied the Wolfsberg-Helmholz method to the purely σ -bonded hexa-ammine complexes of Cr^{III} , Co^{III} , Co^{II} , and Ni^{II} and obtained agreement with the observed Δ values within some 20%. Similar to our treatment, the Madelung-like terms favouring charge separation⁶ were not taken into account, and the central atom charges q reported, between 0.1 and 0.9, seem far too small when compared with data for the nephelauxetic effect.⁷

³ C. K. Jørgensen, R. Pappalardo, and H.-H. Schmidtke, *J. Chem. Phys.*, 1963, **39**, 1422.

⁴ (a) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 1952, **20**, 837; (b) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, **3**, 1004.

⁵ P. Day, *Proc. Chem. Soc.*, 1964, 18; W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 841.

⁶ C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

⁷ C. K. Jørgensen, *Progr. Inorg. Chem.*, 1962, **4**, 73.

The Cupric Halides.—Tetrahalogenocuprate(II) anions are flattened tetrahedra of point symmetry D_{2d} .^{8,9} The co-ordinates of the four halogens are 1: $\chi, 0, \xi$; 2: $0, \chi, -\xi$; 3: $-\chi, 0, \xi$; 4: $0, -\chi, -\xi$; where the unit of length is such that $\chi^2 + \xi^2 = 1$. Using the metal orbitals and ligand combinations in Table 1, we find $\Xi^2(a_1) = 20(\xi^2 - \frac{1}{2}\chi^2)^2$, $\Xi^2(b_2) = 15\chi^4$

TABLE 1.

Central atom (M) and ligand (X_N) orbitals.

MX ₄ (D _{2d})	a_1 : $\sqrt{5}(z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2)$	$(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/2$
	b_2 : $\frac{1}{2}\sqrt{15}(x^2 - y^2)$	$(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$
	e : $\sqrt{15}(xz)$	$\begin{cases} (\sigma_1 - \sigma_3)/\sqrt{2} \\ (\sigma_2 - \sigma_4)/\sqrt{2} \end{cases}$
MX ₅ (D _{3h})	a_1' : $\sqrt{5}(z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2)$	$\begin{cases} (\sigma_1 + \sigma_2)/\sqrt{2} \\ (\sigma_3 + \sigma_4 + \sigma_5)/\sqrt{3} \end{cases}$
	e' : $\sqrt{15}(xy)$	$\begin{cases} (\sigma_4 - \sigma_5)/\sqrt{2} \\ (2\sigma_3 - \sigma_4 - \sigma_5)/\sqrt{6} \end{cases}$
		$(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/2$
MX ₆ (D _{4h})	a_{1g} : $\sqrt{5}(z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2)$	$(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/2$
	b_{1g} : $\frac{1}{2}\sqrt{15}(x^2 - y^2)$	$(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$

and $\Xi^2(e) = 30\chi^2\xi^2$. Note that in a regular tetrahedron, $\chi = \sqrt{2}\xi$ so that $\Xi^2(a_1) = 0$ and $\Xi^2(b_2) = \Xi^2(e) = 20/3$, since $\chi = 1/\sqrt{3}$ and $\xi = \sqrt{2}/\sqrt{3}$.

In the tetrachlorocuprate(II) ion⁸ $\xi/\chi = \tan 28^\circ = 0.532$ and in tetrabromocuprate(II)⁹ $\xi/\chi = \tan 26^\circ = 0.488$, whence χ_{Cl}, ξ_{Cl} are 0.883 and 0.470, and χ_{Br}, ξ_{Br} are 0.899 and 0.439, respectively.

The pentahalogenocuprates(II)¹⁰ are trigonal bipyramids, point group D_{3h} , and we assume (which is not required by the symmetry, though almost the case in practice) that all the bonds have equal lengths. The σ -bonding metal orbitals have a_1' and e' symmetry, with e'' remaining non-bonding in this approximation, and the angular parameters are as previously given, ${}^3\Xi^2(a_1') = 55/4$ and $\Xi^2(e') = 45/8$.

Tetragonally distorted octahedral arrangements of halogens surround the copper atoms in CsCuCl₃,¹¹ CuCl₂,¹¹ and CuBr₂.¹² The metal and ligand orbitals are classified according to the point group D_{4h} in Table 1, and the resulting angular parameters are $5 + 10\chi^4$ and 15 for a_{1g} and b_{1g} , respectively, when the unit of length is such that four ligands are distant one unit, and the other two χ units, from the metal.

Now that the ligands are not equidistant from the metal, it is necessary to consider the variation of σ^* (*i.e.*, of S_{MX}^*) with distance, and to do this we need an approximation to the $3d$ radial function of copper. Watson's analytic Hartree-Fock function for Cu⁰($3d^9 4s^2$) is¹³

$$P(r)/r = r^2(4.006e^{-2.413r} + 45.14e^{-4.706r} + 158.6e^{-8.843r} + 19.57e^{-15.52r}).$$

In the graph of $\log P(r)/r$ against r , the best fitting straight line between 3 and 7 a.u. suggests that $P(r)/r \simeq Ke^{-1.99r}$, that is, the tail of the function is quite well represented as a Slater 1s orbital with, of course, a smaller orbital exponent. If we now replace the $\psi(X_N)$ of equation (4) by a linear combination of $3p\sigma$ or $4p\sigma$ orbitals on each ligand, S_{MX}^* can be estimated from the tables of Slater overlap integrals $S(1s, 3p\sigma)$ and $S(1s, 4p\sigma)$ calculated by Mulliken, Rieke, Orloff, and Orloff.¹⁴ The device of the Kronecker δ -function simply restricts the angular extension of the ligand atoms and avoids the need to consider ligand-ligand overlap integrals.

⁸ L. Helmholz and R. F. Krub, *J. Amer. Chem. Soc.*, 1952, **74**, 1181.

⁹ B. Morosin and E. C. Lingafelter, *Acta Cryst.*, 1959, **13**, 807.

¹⁰ M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1961, **34**, 295.

¹¹ A. F. Wells, *J.*, 1947, 1662, 1670.

¹² L. Helmholz, *J. Amer. Chem. Soc.*, 1947, **69**, 886.

¹³ R. E. Watson, *Phys. Rev.*, 1960, **119**, 1934; Technical Report no. 12, Solid State and Molecular Theory Group, M.I.T. 1960.

¹⁴ R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

With values from ref. 14 for p_{CuCl} , t_{CuCl} as $3.85R$ and -0.01 , and p_{CuBr} , t_{CuBr} as $3.875R$ and -0.016 , the crystallographic data on the cupric halides produces the following values of $(S_{\text{MX}})^2$:

	$R(\text{\AA})$	$S(1s, 3p\sigma)$	$(S_{\text{CuCl}})^2$		$R(\text{\AA})$	$S(1s, 4p\sigma)$	$(S_{\text{CuBr}})^2$
CuCl_4 :	2.22	0.059	0.0035	CuBr_4 :	2.38	0.060	0.00360
CuCl_5 :	2.32	0.050	0.0025	CuBr_5 :	2.46	0.053	0.00281
CuCl_6 : (4)	2.285	0.056	0.00314	CuBr_6 : (4)	2.40	0.059	0.00348
(2)	2.65	0.023	0.00053	(2)	3.18	0	0

In CsCuCl_3 therefore, the overlap integral for the two axial ligands is reduced to 0.41 of that for the equatorial ligands, while in CuBr_2 there is approximately zero overlap with the axial ligands. Thus, χ for CsCuCl_3 is $1.16 \times 0.41 = 0.48$, and $\chi(\text{CuBr}_2)$ is zero, from which it follows that $\Xi^2(a_{1g})$ is 5.5 for the former and 5.0 for the latter. We also see that when χ is unity (*i.e.*, a regular octahedron) $\Xi^2(a_{1g}) = \Xi^2(b_{1g}) = 15$ (e_g in O_h), and combining this with the previous result that $\Xi^2(t_2)$ of T_d is $20/3$, we find that the ratio of octahedral to tetrahedral d -shell splitting is $9/4$, exactly the same as in crystal field theory.

To see whether all the observed bands of the CuX_N can be described by a single parameter we must take account of the difference in internuclear distance by expressing the theoretical energy level differences in units of $\sigma^*/(S_{\text{MX}})^2$. In Table 2 the observed energies are compared

TABLE 2.
Observed and predicted cupric halide ligand field bands.

		X = Cl			X = Br		
		Obs.	Calc. Ξ^2	Calc. $p/c.$ ^e	Obs.	Calc. Ξ^2	Calc. $p/c.$ ^e
		CuX_4^{2-}	${}^2B_2 \rightarrow {}^2B_1$	9.05 ^a	8.6	8.5	8.0 ^b
	${}^2B_2 \rightarrow {}^2A_1$	7.90 ^a	8.1	7.8	7.57 ^b	7.2	7.2
	${}^2B_2 \rightarrow {}^2E$	5.55 ^a	3.8	4.3	4.65 ^c	4.2	4.8
CuX_5^{3-}	${}^2A_1' \rightarrow {}^2E'$	9.5 ^e	9.2	9.5	8.7 ^e	8.7	8.8
	${}^2A_1' \rightarrow {}^2E'$	—	3.8	6.5	—	4.9	6.0
CuX_6^{4-}	${}^2B_{1g} \rightarrow {}^2B_{2g}$	11.8 ^e	12.7	11.6	11.5 ^e	11.8	11.7
	${}^2B_{1g} \rightarrow {}^2A_{1g}$	—	4.7	4.5	—	3.9	3.7

^a J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406.
1962, **1**, 970. ^e P. Day, *Proc. Chem. Soc.*, 1964, 18.

A. G. Karipdes and T. S. Piper, *Inorg. Chem.*,

first with those calculated using a point charge crystal field model with two parameters, and then with the values corresponding to $\sigma^*/(S^*)^2 = 270$ kK (chlorides) and 226 kK (bromides). The fit in both cases is quite good, though the experimental radial parameters reveal the inadequacy of the electrostatic model in a most convincing way. $\langle r^2 \rangle$ is three times bigger than the value calculated with Watson's Hartree-Fock radial function for Cu^{2+} , while $\langle r^4 \rangle$ is no less than twenty times too large. Bearing in mind that the Ξ^2 theory entirely ignores π -bonding, we are encouraged that two $\sigma^*/(S^*)^2$ reproduce the ten observed bands so closely, though even if the theory were accurately true for these compounds, there is no reason why H_{Cu} and H_{X} should be precisely the same in each case, since they are steep functions of the charge distribution.

In order to see whether the fitted parameters represent reasonable charge distributions, we need to know the variation of H_{Cu} and H_{X} with charge. Equation (6) can then be reduced to a function of the single variable n , the fractional positive charge on the copper, which is obviously related *via* the formula type (*e.g.*, CuX_4^{2-}) to the fractional negative charge on the halogen. We will have succeeded if the resulting value of $(H_{\text{Cu}} - H_{\text{X}})$, plus the energy difference between the non-bonding and highest σ -antibonding orbitals is close to the energy of the lowest electron transfer transition.

Valence state ionization potentials have been tabulated by Pritchard and Skinner¹⁵ and

¹⁵ H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 1955, **55**, 745.

more recently by Hinze and Jaffe¹⁶ for the halogens in various states of ionization. Taking care to choose values for the ionization of a $p\sigma$ electron, we fit the transitions $X^{n+} \rightarrow X^{(n+1)+}$ by $-H_{Cl} = I_n(Cl) = 121.4 + 91.5n$ and $-H_{Br} = I_n(Br) = 110.7 + 82.5n$. To estimate the charge dependence of H_{Cu} , we take the energies of the transitions $d^9 \rightarrow d^8$ in Cu^{2+} , Ni^+ , and Co^0 and correct them for the change in spin-pairing energy accompanying the ionization. The latter has the form

$$D[< S(S+1) > - S(S+1)] \quad (7)$$

where $D \simeq 7B = 7(F_2 - 5F_4)$ for d -electrons, and the values of the expression in the square bracket have been tabulated.¹⁷ With this correction, ionizations $(d^9)^{+n} \rightarrow (d^8)^{+(n+1)}$ are represented by $-H_{Cu} = I_n(d^9) = 38.5 + 91.7n + 20.1n^2$. $CuCl_5^{3-}$ being used as an example, when the H 's are substituted back into equation (6), the resulting charge distribution $Cu^{0.19+}Cl^{0.64-}$ predicts the first electron transfer band at 23.9 kK. The reflection spectrum of $Co(NH_3)_6CuCl_5$ diluted in KCl has its first intense band at 25.9 kK. Not only, therefore, does the Ξ^2 theory account for the ligand field bands of all the $CuCl_N$ species in terms of a single freely chosen parameter, but in addition it enables us to make rough predictions of the positions of electron transfer bands. We have therefore used a similar approach to examine the electron transfer spectra of the first-transition series tetrahalide complexes.

Tetrahalide Complexes.—The first part of the discussion concerns only the lowest energy bands in the ultraviolet spectrum. These are commonly assigned to transitions from the p non-bonding set on the halogens of symmetry t_1 into the partly filled d -shell of the metal. Watson's analytic radial functions have once again been fitted by single term Slater I -functions between 3 and 7 a.u. having orbital exponents: Mn, 1.61; Fe, 1.71; Co, 1.80; Ni, 1.90; Cu, 1.99. The figures clearly illustrate the contraction of the d -shell into the core towards the end of the transition series. Since we are using overlap integral tables of Mulliken *et al.* we have followed their recommendations about halogen orbital exponents and used $\mu_{Cl}(3p\sigma) = 2.033$ and $\mu_{Br}(4p\sigma) = 2.054$ rather than attempt to fit the available analytic Hartree-Fock data.

There is no complete set of bond lengths for these ions derived from a single set of compounds. P. Pauling's X -ray studies on the bistetraphenylarsonium tetrachloro-compounds¹⁸ produced a bond length only for the nickel salt (2.27Å), unit-cell dimensions alone being available for the others. The latter are all very similar and show no obvious trends. No doubt they are dominated by the dimensions of the large cation. Powell and Wells,¹⁹ thirty years ago, found $r_{CoCl} = 2.34\text{Å}$ in Cs_3CoCl_5 , and more recently 2.26Å has been given as the Co-Cl distance in Cs_2CoCl_4 .²⁰ 2.28Å is the distance adopted here. The unit-cell dimensions of the series²¹ of isomorphous salts MCl_2 reveal the bond length variation: Mn, 2.58Å; Fe, 2.53Å; Co, 2.51Å; Ni, 2.50Å; Cu, 2.30(4), 2.95(2)Å; Zn, 2.55Å. But if we attempt to apply L. Pauling's²² ionic radius factor 0.95 to convert them into tetrahedral distances the results are too large. Octahedral MCl_6^{4-} ions have been reported²³ for Mn and Fe with distances of 2.51 and 2.30, the latter almost certainly too small. From all the evidence we have therefore chosen the set of distances for MCl_4^{2-} shown in Table 3. 0.16Å is the difference between the observed distances in $CuCl_4^{2-}$ and $CuBr_4^{2-}$, 0.14 the difference between the Pauling radii of Cl^- and Br^- , and 0.15 the difference between the covalent radii. As no other datum is available on bromide bond lengths we have put the bromide distances 0.15Å greater than the chlorides of the same metal. Ligand field splitting parameters for all the tetrahalides have been measured by a number of workers. Those in Table 3 seem to us the most reliable.

¹⁶ J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

¹⁷ C. K. Jørgensen, *Solid State Physics*, 1962, **13**, 375.

¹⁸ P. Pauling, Ph.D. Thesis, Univ. of London, 1959 and personal communication.

¹⁹ H. M. Powell and A. F. Wells, *J.*, 1935, 359.

²⁰ M. A. Porai-Koshits, *Krystallographiya*, 1956, **1**, 291.

²¹ R. G. Wyckoff, "Crystal Structures," Interscience, New York, 2nd edn., 1963, vol. I, p. 268.

²² L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 3rd edn. 1960, p. 538.

²³ "Interatomic Distances," *Chem. Soc. Special Publ.*, no. 1.

TABLE 3.

Data for the molecular orbital calculations on tetrahalides.

(a) Tetrachlorides.

	Mn	Fe	Co	Ni	Cu
t	-0.115	-0.086	-0.060	-0.033	-0.010
p	3.49R	3.584R	3.67R	3.764R	3.85R
$R(\text{\AA})$	2.40	2.30	2.28	2.27	2.22
$[S(1s, 3p\sigma)]^2$	0.00412	0.00492	0.00452	0.00366	0.00347
$\Delta(\text{kk})$	3.6 ^a	4.0 ^a	3.0 ^b	3.6 ^c	—
$0.15\Delta/(S)^2$	131.1	122.0	99.6	147.5	216.2
n	0.285	0.30	0.17	0.215	0.25
$-H_M$	53.8	52.3	48.9	56.7	62.7
$-H_{Cl}$	69.1	68.7	71.7	70.7	69.9
$(J-K)(t_1, t_2)$	65.8	74.5	79.0	81.3	—

(b) Tetrabromides.

	Mn	Fe	Co	Ni	Cu
t	-0.120	-0.090	-0.065	-0.038	-0.015
p	3.51R	3.60R	3.69R	3.78R	3.87R
$R(\text{\AA})$	2.55	2.45	2.43	2.42	2.37
$[S(1s, 4p\sigma)]^2$	0.00384	0.00490	0.00410	0.00372	0.00397
$\Delta(\text{kk})$	3.1 ^a	3.8 ^d	2.85 ^b	3.4 ^c	—
$0.15\Delta/(S)^2$	121.2	116.3	104.3	137.2	206.0
n	0.25	0.26	0.15	0.18	0.20
$-H_M$	50.2	48.8	47.2	53.5	57.6
$-H_{Br}$	64.4	64.1	66.4	65.8	65.4
$(J-K)(t_1, t_2)$	64.5	74.2	80.0	84.9	—

N. B. Allowance has been made for the distortion of CuCl_4^{2-} and CuBr_4^{2-} by the method described in the text.

F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **1962**, **84**, 167; ^b 1961, **83**, 4690; ^c 1961, **83**, 4164. ^d C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nuclear Chem.*, **1963**, **25**, 159.

On the Ξ^2 model we have already shown that, with the e -level non-bonding, Δ is $20\sigma^*/3$, and the function of n , the fractional cation charge, is then $3\Delta/20(S^*)^2$. For the equations relating H_M with n , spin-pairing energies are required and hence Slater–Condon F_k 's for each configuration and state of ionization. They are also essential for our discussion of electron repulsion effects on the electron transfer energies. F_2 and F_4 are accessible from atomic spectra, and their lowering in complexes defines the nephelauxetic ratio. F_0 cannot be found in this way, and unfortunately it is much larger than the other two parameters, so we will try to estimate it from the results of Watson's Hartree–Fock calculations. Using Moore's tables,²⁴ Watson carried out a least-squares fit for F_2 as a function of charge and configuration, and then compared the systematic discrepancy with his theoretical results. The ratio F_2 (least-squares)/ $F_2(H-F)$ increases with both ionic charge and number of d -electrons. He did not perform a least-squares fit for the F_4 's, but on the assumption that they and the (unobservable) F_0 's diverge from the theoretical predictions in the same ratio, representative values can be estimated. Including the spin-pairing correction, we write the dependence of the valence state ionization potential $(d^q)^{n+} \rightarrow (d^{q-1})^{(n+1)+}$ as $a + bn + cn^2$ with the following a, b , and c (in kk):

	$d^5 \rightarrow d^4$	$d^6 \rightarrow d^5$	$d^7 \rightarrow d^6$	$d^8 \rightarrow d^7$	$d^9 \rightarrow d^8$
a	25.7	27.0	34.3	37.1	38.5
b	92.0	78.8	82.6	87.2	91.7
c	23.7	19.4	20.9	20.3	20.1

The most conspicuous effect of including the spin-pairing correction is to remove the hump in the ionization potentials at the half-filled shell.

We are now in a position to set up equations for n , based on equation (6), which yield the diagonal elements shown in Tables 3(a) and 3(b). However, observed electron transfer energies are determined, not only by the difference between the diagonal elements H_M and H_X , but

²⁴ C. Moore, "Atomic Energy Levels", N.B.S. Circular 467, 1949—58.

also by the change in two-electron energy accompanying the transition.²⁵ Thus in MX_4^{2-} , the transition $t_1^6 e^r t_2^{q-r} \rightarrow t_1^5 e^{r+1} t_2^{q-r}$ would have an energy

$$H_{\text{M}}(e) - H_{\text{X}}(t_1) + (J - K)_{dd} \text{ (ground state - excited state)} \\ - (J - K)_{\pi d} \text{ (ground state - excited state)} \quad (8)$$

where the J 's and K 's between molecular orbitals centred on the same atom are expressed as Slater-Condon F_k 's calculated for the pure atomic orbitals, scaled according to the fractional charge obtained from equation (6). In this approximation, the energies of the first electron-transfer bands will be given by the following expressions:

$$\begin{aligned} \text{Cu}^{\text{II}}: {}^2T_2 \rightarrow {}^2T_2: & \quad E(t_2 - t_1) \\ \text{Ni}^{\text{II}}: {}^3T_1 \rightarrow {}^3A_2, E, T_1, T_2: & \quad E(t_2 - t_1) - F_0 + 5F_2 + 24F_4 + J(t_1, t_2) - K(t_1, t_2) \\ \text{Co}^{\text{II}}: {}^4A_2 \rightarrow {}^4T_1: & \quad E(t_2 - t_1) - 2F_0 + 10F_2 + 48F_4 + 2J(t_1, t_2) - 2K(t_1, t_2) \\ \text{Fe}^{\text{II}}: {}^5E \rightarrow {}^5T_2: & \quad E(e - t_1) - 3F_0 + 6F_2 + 117F_4 + 3J(t_1, t_2) - 3K(t_1, t_2) \quad (9) \\ \text{Mn}^{\text{II}}: (1) {}^6A_1 \rightarrow {}^6T_2: & \quad E(e - t_1) - 4F_0 + 14F_2 + 126F_4 + 3J(t_1, t_2) - 3K(t_1, t_2) + J(t_1, e) - K(t_1, e) \\ & (2) {}^6A_1 \rightarrow {}^6T_2: \quad E(t_2 - t_1) - 4F_0 + 14F_2 + 126F_4 + 2J(t_1, t_2) - 2K(t_1, t_2) + 2J(t_1, e) \\ & \quad \quad \quad - 2K(t_1, e) \end{aligned}$$

There is no simple method for estimating the Coulomb and exchange integrals between molecular orbitals on different atoms, and as we wish to preserve the empirical character of our model, the best approach is to use the observed spectra and see whether the resulting $J(\pi, d)$ and $K(\pi, d)$ are of the right order of magnitude. Values of $(J - K)(t_1, t_2)$ obtained in this way are shown at the bottom of Tables 3(a) and 3(b). As expected, they are somewhat smaller than $J(d, d)$ but they increase in a similar way with the number of electrons in the d -shell. To obtain the Mn^{II} result, we have assumed that $(J - K)(t_1, e) = (J - K)(t_1, t_2)$. This is reasonable if the first two electron transfer bands in the spectrum of FeCl_4^- are assigned to $t_1 \rightarrow e$ and $t_1 \rightarrow t_2$, because their energy difference would then be $\Delta + (J - K)(t_1, e) - (J - K)(t_1, t_2)$. Experimentally the difference is 4.35 kK, very close to Δ , so that the two pairs of Coulomb and exchange integrals approximately cancel.

The results show very clearly that $H_{\text{M}} - H_{\text{X}}(+\Delta)$ calculated by the σ -bonding model is always much smaller than the energy of the lowest electron transfer band, and the difference is undoubtedly ascribed to the effect of the Coulomb and exchange integrals in equation (9); it is the factor $q(q-1)/2$ multiplying F_0 and $J(\pi, d)$ which is primarily responsible. Neither is our assumption of no π -bonding very accurate, and its breakdown is illustrated by calculating σ for FeCl_4^- . With $R_{\text{FeCl}} = 2.19 \text{ \AA}$,²⁶ and $(S^*)^2 = 0.00757$, if we take Δ as 5 kK, the fractional charge n is only +0.27, while H_{Fe} and H_{Cl} work out as -52.2 and -92.3 kK. This is clearly an absurd result for, if the electron repulsion correction is slightly larger than in the iso-electronic MnCl_4^{2-} because of the higher charge on the metal, the first electron transfer band is predicted at about 60 kK. However, the empirical Δ is actually a difference between σ^* and π^* orbitals, ($\sigma^* - \pi^*$) rather than just σ^* , so that it might be justifiable that $\Delta\sigma$ is about 10 kK if π -bonding is as important as σ -bonding. With this assumption n rises to +0.54 and H_{Fe} , H_{Cl} are, respectively, -82.7 and -72.0, *i.e.*, the orbital energy of the partly-filled shell is lower than that of the chlorine orbital from which an electron is transferred. $J(d, d) - J(\pi, d)$ must be at least 30 kK though, and the first electron transfer band lies at 27.45 kK.

It is not very likely that a theory based solely on σ -bonding will give any accurate account of the higher electron transfer states. The reason why we are on firmer ground with the first electron transfer state is that it involves the excitation of a non-bonding electron; the next

²⁵ H. B. Gray and C. Hare, *Inorg. Chem.*, 1962, **1**, 363.

²⁶ B. Zaslav and R. E. Rundle, *J. Phys. Chem.*, 1957, **61**, 490.

set of absorption bands is usually said to derive from promotion of electrons which are π - as well as σ -bonding.²⁷ Nevertheless, the Ξ^2 model can be used as a basis for classifying the higher states. To the approximation of the model, a $t_{2\sigma}$ orbital should lie nearly as far below $t_1(nb)$ as $t_2(\sigma^*)$ does above $e(nb)$, *i.e.*, only about 3 kK. However, $J(t_{2\sigma}, t_2\sigma^*)$ is likely to be smaller than $J(t_1\pi, t_2\sigma^*)$ and Madelung-like stabilization of the σ -orbitals by the residual positive charge on the central atom will further increase the energy difference between π - and σ -orbitals, so that the $t_{2\sigma} \rightarrow t_2\sigma^*$ absorption will appear at higher energy. It will also be much more intense, because of the high inherent dipole moment. The tetrahalogenocuprates(II) are the best examples because, with one hole in the d -shell the coefficients of $J(\pi, d)$ and $J(d, d)$ are both zero. Our spectra agree with those of Furlani and Morpurgo.²⁸ The first major band, with its small shoulder, is assigned in D_{2d} to $(a_2 + e) \rightarrow b_2$, the former derived from $t_1(nb)$ and the latter from $t_2(\sigma^*)$. Transitions $a_2 \rightarrow b_2$ in D_{2d} are formally forbidden. The next band, much more intense, is assigned to $(b_2 + e) \rightarrow b_2$ derived from $t_{2\sigma} \rightarrow t_2\sigma^*$ in T_d . Alternatively it might be a component of $e\pi \rightarrow t_2\sigma^*$, but there is then a difficulty in assigning the third band (at 42 kK in CuCl_4^-) to $t_{2\sigma} \rightarrow t_2\sigma^*$ on the grounds of its lower intensity. It is only in the tetrahalides of the more easily reduced metals that the intense second band can be seen. Thus, the energy difference between the second and third bands of FeCl_4^- and FeBr_4^- is close to the difference between the first and second main bands in the tetrahalogenocuprates(II). The first band of the tetrahalogenoferrates(III) comes from $t_1(nb) \rightarrow e(nb)$. Again, shoulders are clearly distinguished on the low-energy side of the most intense bands, but this is not likely to result from a lowering of symmetry in the totally symmetric ground state. Rather, it is related to the phenomenon in the ultraviolet spectra of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ where a shoulder appears below the first electron transfer band with an intensity related to the spin-orbit coupling parameter of the halogen.²⁹ Much of the fine structure in the heavier halide complexes is no doubt also due to the effects of intermediate coupling in the halogen. In the Co^{II} spectra for example, one might note the development from the single chloride band to splittings of 2.2 and 4.0 kK in the bromide and iodide. On the other hand, the distance between the two least intense bands in the Ni^{II} spectra falls from chloride to iodide, though the assignment of even the lowest bands is made difficult by the fact that there are three terms arising from the configuration $t_1^5 e^4 t_2^5$, all accessible from the ground state. Even so, we can identify the $t_{2\sigma} \rightarrow t_2\sigma^*$ transition at 42.95, 37.45, and 26.90 kK in the chloride, bromide, and iodide, respectively. The same transition (or a component of it) appears at 32.95 kK in CoI_4^{2-} . In conclusion, the energy difference between $(nb) \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ is very much smaller than in the $4d$ and $5d$ hexahalides, and the latter transition is correspondingly less intense. This results from the lower formal charge of the central atom and reduced metal-halogen overlap in the $3d$ tetrahalides, which leads in turn to smaller values of Δ .

EXPERIMENTAL

Tetraethylammonium or tetra-*n*-butylammonium salts of the tetrahalides were prepared by the usual methods.³⁰ The ferrous halides must be prepared, and their spectra measured, in the absence of air, as oxidation occurs very readily. No trace of absorption due to FeX_4^- could be detected in the near-ultraviolet spectra.

All the tetrahalides are much more subject to solvolysis than is usually recognized, even in aprotic solvents.³¹ It was found, for example, that even in the presence of 0.8M-iodide, the spectrum of NiI_4^{2-} in CH_3CN was still sensitive to further additions of iodide. A much more weakly co-ordinating solvent, dichloromethane, was therefore used for all spectra except the iodides, where chloroform was employed. 0.2M-Excess of halide then sufficed to form the chlorides and bromides to such an extent that the spectra were no longer sensitive to increasing

²⁷ A. Carrington and D. Schonland, *Mol. Phys.*, 1960, **3**, 331; A. Carrington and C. K. Jørgensen, *ibid.*, 1961, **4**, 395.

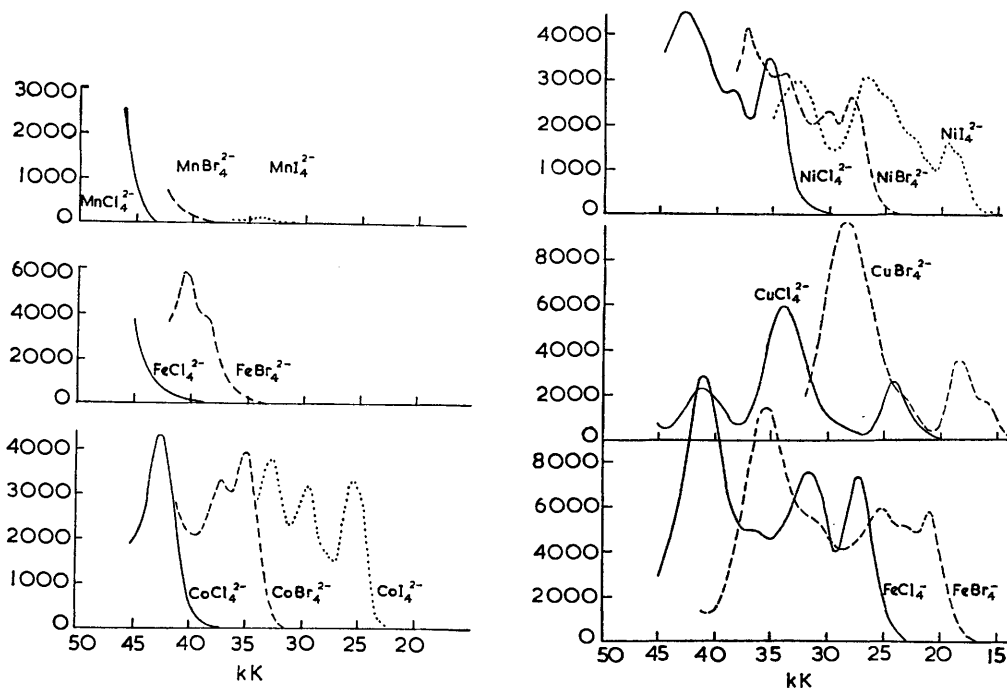
²⁸ C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, 1963, **1**, 103.

²⁹ H. Yamatera, *J. Inorg. Nuclear Chem.*, 1960, **15**, 50.

³⁰ N. S. Gill and R. S. Nyholm, *J.*, 1959, 3997.

³¹ C. P. Nash and M. S. Jenkins, *J. Phys. Chem.*, 1964, **68**, 356.

halide ion concentration. 0.5M-Excess of iodide was used for the tetraiodides. We are therefore confident that none of the peaks or shoulders in the Figure result from solvolyzed species. In every case the wavelength maxima and extinction coefficients of the ligand field spectra were checked against those used in the calculations of Δ (references in Table 3), and the solution was transferred from a 1cm.- or 4cm.- to a 1mm.- cell to measure the ultraviolet spectrum, thus



Electron-transfer spectra of first transition series tetrahalide complexes, measured as tetraethylammonium and tetra-n-butylammonium salts in dichloromethane. Peak positions are given below, followed by molar coefficients in brackets. Inflections are also in brackets.

Mn ^{II} :	Cl	> 46. Br > 41. I > 35
Fe ^{II} :	Cl	45.5(3,840). Br (39); 40.9(6,220)
Fe ^{III} :	Cl	27.45(7,350); 31.80(7,600); (36.8); 41.20(11,900).
	Br	21.20(5,800); (23.6); 25.50(5,960); (31.5); 35.65(10,500).
Co ^{II} :	Cl	42.65(4,320). Br 35.10(3,900); 37.30(3,270).
	I	25.60(3,300); (27.6); 29.60(3,180); 32.95(3,780).
Ni ^{II} :	Cl	35.50(3,440); 38.70(2,630); 42.95(4,370).
	Br	28.30(2,625); 30.25(2,280); 34.10(3,180); 37.45(4,125)
	I	(18.9); 19.65(1,600); (21.8); (23.5); (25.0); 26.90(3,080); 33.10(2,960).
Cu ^{II} :	Cl	(22.3); 24.35 (2,580); (29.6); 34.10(5,900); 41.30(2,280).
	Br	(16.20); 18.60(3,560); (23.5); 28.60(9,650).

eliminating any effects of changing concentration. Agreement with the published visible spectra was excellent, with the sole exception of NiI₄²⁻, where the spectrum reported by Goodgame, Goodgame, and Cotton (ref. *c*, Table 1) appears to be that of a partially solvolyzed species since, on increasing the iodide concentration, the major ligand field band, which they report at 14.03 kK, is replaced by one at 11.90 (ϵ_{\max} , 256) and the first electron transfer band at 18.9 by one at 19.65 (ϵ_{\max} , 1600).

INORGANIC CHEMISTRY LABORATORY, SOUTH PARKS ROAD, OXFORD (P. D.).
 CYANAMID EUROPEAN RESEARCH INSTITUTE, 91 ROUTE DE LA CAPITE,
 COLOGNY, GENEVA, SWITZERLAND.

[Received, August 14th, 1964.]