Calculation of Pseudo-Lattice Energies and the Estimation of Metal–Ligand Bond Energies in Some Tetrahedral Tetrachlorometallate(II) Complexes[1a]

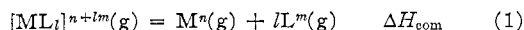By A. B. BLAKE AND F. A. COTTON[1b]

A method of calculating the pseudo-lattice energy, that is, the energy required to separate a crystalline compound containing complex ions into gaseous species so that the complex ions remain intact, is described in detail. The feasibility of the method depends on the availability of an efficient program for machine computation of Madelung energies; such a program is described. It is shown how the pseudo-lattice energy may be used together with experimentally accessible thermodynamic data to calculate the complexation or ligation energy, *i.e.*, the energy released when a gaseous complex ion is formed from a gaseous metal ion and gaseous ligands. The entire procedure is illustrated for the complex ions $[CoCl_4]^{2-}$, $[CuCl_4]^{2-}$, and $[ZnCl_4]^{2-}$, and in the case of $[CoCl_4]^{2-}$ a valuable check is provided by the acceptable agreement between the results obtained using Cs_2CoCl_4 and Cs_3CoCl_5. The significance of the energies of complexation in relation to problems of ligand field stabilization and bond character are briefly discussed.

Introduction

It has been shown[2] that enthalpies of complexation or ligation, that is, the enthalpies, ΔH_{com}, of reactions of the type

$$[ML_l]^{n+lm}(g) = M^n(g) + lL^m(g) \qquad \Delta H_{com} \qquad (1)$$

could be evaluated by setting up a thermodynamic cycle which involves a term called the *pseudo-lattice energy*. The latter is the energy required to separate a crystalline compound containing complex ions into gaseous species in which all complex ions remain intact in the gas. Results were presented for a series of reactions of the type

$$[M(NH_3)_6]^{2+}(g) = M^{2+}(g) + 6NH_3(g)$$
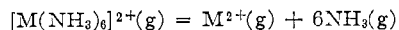
as well as some other similar ones.

It should be noted that this method appears to be the only one capable of providing the fundamentally important complexation energies, ΔH_{com}, themselves, rather than some quantity which is the sum of ΔH_{com} and one or more others which cannot themselves be easily measured or calculated. For example, it is fairly easy in a great many cases to determine from readily accessible experimental data the enthalpy of dissolving gaseous cations and anions into an aqueous solution of a ligand. From this datum, however, one can obtain only a quantity which is the sum of ΔH_{com}, the hydration energy of the gaseous complex ion and the hydration energy of the counter-ion. Since there is no certain method of separately measuring or calculating the two hydration energies, or their sum, ΔH_{com} alone cannot be extracted from the experimental datum.

In their excellent survey of the thermodynamic consequences of inner-orbital splittings, George and McClure[3] pointed out that despite the advantage of having ΔH_{com} values, the above method for obtaining them was limited in applicability by (1) a lack of data on the heats of formation of the crystalline complex compounds and

(2) the difficulty of calculating the pseudo-lattice energies for structures more complicated than the cubic ones considered in ref. 2.
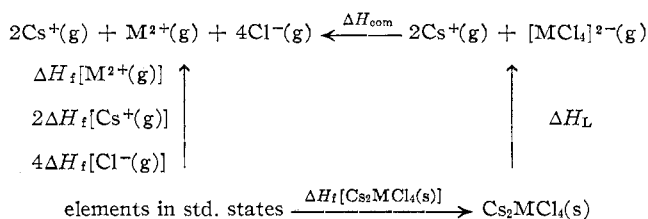
The first of these limitations is relatively unimportant, since quite straightforward calorimetric measurements of only moderate accuracy will provide the necessary heats of formation, as illustrated, for example, by the measurements reported here, and more extensive ones to be reported in another paper from this laboratory.[4] A major purpose of this paper is to show how, with the availability of fast digital computers, the second limitation also becomes inconsequential. This is because programs can be written for rapid computation of Madelung energies of any arbitrary array of ions, however little symmetry it may have. In this paper we shall treat the general theory of computing pseudo-lattice energies and illustrate the method in the cases of Cs_2CoCl_4, Cs_2CuCl_4, and Cs_2ZnCl_4, which have structures for which no Madelung constant can be written analytically. The enthalpies of the processes

$$[MCl_4]^{2-}(g) = M^{2+}(g) + 4Cl^-(g) \qquad (2)$$
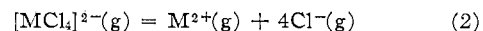
will be reported and discussed. The digital computer program used for computation of the Madelung energies will also be described (see the Appendix).

Procedure

The thermodynamic cycle to be utilized is

$$2Cs^+(g) + M^{2+}(g) + 4Cl^-(g) \xleftarrow{\Delta H_{com}} 2Cs^+(g) + [MCl_4]^{2-}(g)$$

$\Delta H_f[M^{2+}(g)]$ ↑

$2\Delta H_f[Cs^+(g)]$ ↑ ΔH_L

$4\Delta H_f[Cl^-(g)]$

elements in std. states $\xrightarrow{\Delta H_f[Cs_2MCl_4(s)]}$ $Cs_2MCl_4(s)$

This provides the thermochemical equation

$$\Delta H_{com} + \Delta H_L = \Delta H_f[M^{2+}(g)] + 2\Delta H_f[Cs^+(g)] + 4\Delta H_f[Cl^-(g)] - \Delta H_f[Cs_2MCl_4(s)] \qquad (3)$$

(1) (a) Supported by the United States Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation.
(2) F. A. Cotton, *Acta Chem. Scand.*, **10**, 1520 (1956).
(3) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).
(4) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, submitted for publication.

The values of the first three terms on the right side of eq. 3 may be found in the literature. $\Delta H_f[M^{2+}(g)]$ values are given in Table IXA of ref. 3 and the other two quantities are given in the NBS tables.[5] The heats of formation of the three Cs_2MCl_4 compounds were determined by the method of ref. 4; pertinent details are given in the Experimental section and in Table IV. The pseudo-lattice energies were calculated in the manner described in the following section. Table I records

TABLE I
THERMODYNAMIC DATA FOR EQUATION 3, IN KCAL./MOLE

	Co	Cu	Zn
$\Delta H_f[M^{2+}(g)]$	681.2	732.3	664.7
$2\Delta H_f[Cs^+(g)]$	220.2	220.2	220.2
$4\Delta H_f[Cl^-(g)]$	−241.2	−241.2	−241.2
$-\Delta H_f[Cs_2MCl_4(s)]$	294.7	263.5	323.5
$\Delta H_{com} + \Delta H_L$	954.9	974.8	967.2
ΔH_L	329 ± 2	333 ± 2	329 ± 2
ΔH_{com}	625 ± 2	642 ± 2	638 ± 2

the values of all the quantities occurring in eq. 3 for each of the three systems under consideration.

Computation of Pseudo-Lattice Energies.—We assume that ΔH_L can be estimated with the necessary accuracy by considering only those contributions[6]

$$-\Delta H_L = U_M + U_D + U_R + U_Z \qquad (4)$$

specified in eq. 4, in which all quantities are at 0°K. Correction of ΔH_L to the room-temperature value will be discussed later. U_M is the Madelung energy, *i.e.*, the sum of all pairwise coulombic interaction energies. U_D represents the total attraction energy due to dispersion forces (van der Waals or London energy). U_R is the repulsion energy. U_Z is the zero-point vibrational energy. It should now be emphasized that from the definition of ΔH_L, the first three terms on the right-hand side of eq. 4 refer exclusively to interactions between atoms which do not lie within the same complex ion.

Evaluation of U_M.—We define U_M in the following way

$$U_M = U_M^T(\rho^0,\tau^0,q,u) - U_M^I(\tau^0,q,u) \qquad (5)$$

U_M^T is the complete lattice sum taken over all atoms in the crystal. It is a function of the following four parameters:

q, representing the net (integral or fractional) charges on the atoms. In the present case we take q_{Cs} to be fixed at +1, but q_{Cl} and q_{Co} may vary subject only to the limitation $4q_{Cl} + q_{Co} = -2$.

τ^0, representing the set of equilibrium interatomic distances between all pairs of atoms within one complex ion as it exists in the crystal.

ρ^0, representing the set of equilibrium interatomic distances between all pairs of atoms not both lying within one complex ion.

u, a scale factor by which we can measure the expansion or contraction of the crystal in such a way that all the interatomic distances (ρ and τ) change by the same fraction as the scale factor changes. Thus, all distances remain in fixed ratios, but their magnitudes are given by the expressions

$$\rho_{ij} = u\rho^0{}_{ij} \qquad (6)$$
$$\tau_{ij} = u\tau^0{}_{ij}$$

U_M^I is a partial lattice sum extending only over pairs of atoms both lying within one complex ion.

Disregarding the proportionality constant required before each summation to put results in kcal./mole, we may then write

$$U_M^T = \sum_{i>j} \sum_j \frac{q_iq_j}{u\rho^0{}_{ij}} + \sum_{k>l} \sum_l \frac{q_kq_l}{u\tau^0{}_{kl}}$$

$$U_M^I = \sum_{k>l} \sum_l \frac{q_kq_l}{u\tau^0{}_{kl}}$$

whence

$$U_M = \sum_\rho \frac{q_iq_j}{u\rho^0{}_{ij}} = \frac{M}{u} = \frac{M^T - M^I}{u} \qquad (7)$$

Using the computer program described in the Appendix, M^T, M^I, and hence M can be calculated with little effort for any crystal of known structure (*i.e.*, known atom coordinates) and for any desired values of the fractional charges on the atoms.

Evaluation of U_D.—The treatment here parallels that used for the Madelung energy. Thus we write

$$U_D = U_D^T(\rho^0,\tau^0,u) - U_D^I(\tau^0,u) \qquad (8)$$

where we make the approximation of neglecting any dependence of dispersion energy on the distribution of fractional charges over the atoms in the complex ion. Now, explicitly, we have for the U_D term

$$U_D^T = -\sum_\rho \frac{C_{ij}}{(u\rho^0{}_{ij})^6} - \sum_\tau \frac{C_{ij}}{(u\tau^0{}_{ij})_s} \qquad (9)$$

and

$$U_D^I = -\sum_\tau \frac{C_{ij}}{(u\tau^0{}_{ij})^6} \qquad (10)$$

where the C_{ij} are of six types only, *viz.*, C_{CsCs}, C_{CsCl}, C_{ClCl}, C_{MM}, C_{MCl}, and C_{MCs}. For computational purposes it therefore proved simplest to regroup the terms in the sums constituting U_D^T into six separate sums of the type

$$-\sum_\rho \frac{C_{AB}}{(u\rho^0{}_{ij})^6} = -\frac{C_{AB}}{u^6} \sum_\rho \frac{1}{(\rho^0{}_{ij})^6} = \frac{C}{u^6} \qquad (11)$$

A Fortran computer program was then written to calculate sums over r^{-6}, the input being the atom positions in the unit cell. The series were terminated upon reaching a term which was less than a certain predetermined fraction of the sum.[7] The sums over $(\tau^0{}_{ij})^{-6}$

(5) "Selected Values of Chemical Thermodynamic Properties," U. S. Department of Commerce, National Bureau of Standards, Circular 500, Washington, D. C., 1961.

(6) A good background for the present discussion will be found in F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter 2.

(7) The correctness and accuracy of this program were checked by using it to compute van der Waals energies for NaCl and CsCl. The results agreed satisfactorily with those previously obtained using analytical expressions by Jones and Ingham.[8]

(8) J. E. Jones and A. E. Ingham, *Proc. Roy. Soc.* (London), **A107**, 636 (1925).

appearing in the $U_D{}^I$ term are of course few and easily evaluated by hand. These were subtracted from the complete lattice sum over r^{-6}. The C_{AB} values were chosen in the following way. Three of them were taken from the literature[9]

$$C_{CsCs} = C_{ClCl} = 129 \times 10^{-60} \text{ erg-cm.}^6$$

$$C_{CsCl} = 152 \times 10^{-60} \text{ erg-cm.}^6$$

None of the three C_{AB} values involving the metals M could be found in the literature. Assuming them all to be 140×10^{-60} erg-cm.^{6}, the total contribution of the terms involving them is only 4 kcal./mole. The above estimate is not likely to be in error by more than $\pm 50 \times 10^{-60}$ erg-cm.^{6}, thus introducing an error of less than 0.5 kcal./mole into the final result because of the form of eq. 15. It was not, therefore, considered worthwhile to attempt any more refined estimates of C_{MM}, C_{MCl}, and C_{MCs}.

Evaluation of U_R.—We have elected to use an expression of the Born type rather than the more rigorous Born–Mayer exponential type. This is justified in view of the relatively low level of accuracy ($\pm \sim 3$ kcal./mole) to which we are restricted by other approximations and uncertainties. Thus we write

$$U_R = \sum_\rho \frac{B_{ij}}{(u\rho^0{}_{ij})^n} = \frac{B}{u^n} \qquad (12)$$

The summation is over only those interatomic distances which are not internal to one complex ion. In order to eliminate B, we follow the well known procedure of differentiating the expression for the pseudo-lattice energy, *viz.*

$$-\Delta H_L = \frac{M}{u} + \frac{C}{u^6} + \frac{B}{u^n} + U_Z \qquad (13)$$

with respect to internuclear distances as measured by the scale factor, u, and equating the result to zero as the condition of equilibrium, thus obtaining

$$-\frac{M}{u^2} - 6\frac{C}{u^7} - n\frac{B}{u^{n+1}} = 0 \qquad (14)$$

Solving this equation for B in terms of M and C and inserting the result in eq. 13 we obtain the final equation for computation of the pseudo-lattice energy

$$-\Delta H_L = M\left(1 - \frac{1}{n}\right) + C\left(1 - \frac{6}{n}\right) + U_Z \qquad (15)$$

Since the repulsive energy being considered arises from interactions among cesium ions and chlorine ions only, it is correct to assign to n, the repulsion exponent, a value of 10, *i.e.*, that which has been shown[6] to be appropriate for CsCl.

U_Z and Correction to 300°K.—Estimating the Debye maximum frequency, ν_{max}, to be 100–200 cm.$^{-1}$, and using the relation $U_Z = (^9/_4)nNh\nu_{max}$, in which N is Avogadro's number, h is the Planck constant, and n, the number of atoms per formula unit, is taken as 3 for $Cs_2[MCl_4]$, we obtain $0.5 < U_Z < 1.0$ kcal./mole. We have therefore taken 1 kcal./mole as the value of U_Z in all of the Cs_2MCl_4 compounds.

In order to obtain the value of $-\Delta H_L$ at 300°K.

(9) J. E. Mayer, *J. Chem. Phys.*, **1**, 270, 327 (1933).

from that at 0°K. it is necessary to add to it the quantity

$$\int_0^{300} C_p[\text{Cs}_2\text{MCl}_4(\text{d})]\text{d}T - 2\int_0^{300} C_p[\text{Cs}^+(\text{g})]\text{d}T - \int_0^{300} C_p[\text{MCl}_4{}^{2-}(\text{g})]\text{d}T$$

The value of the first integral was roughly estimated as 7 ± 1 kcal./mole. The entropy of $Cs_2MCl_4(s)$ at 300°K. was estimated to be 50 ± 10 e.u., exclusive of that due to internal vibrations of the $MCl_4{}^{2-}$ ion, and a set of Debye functions was selected to fit this entropy; from these functions the integral was evaluated. The second and third terms were estimated by standard statistical mechanical methods (treating the complex ion as vibrationless, however), giving for their sum 6 ± 0.5 kcal./mole. Thus the net correction to $-\Delta H_L$ is ~ 1 kcal./mole.

Results

The results of the computations for Cs_2CoCl_4, Cs_2CuCl_4, and Cs_2ZnCl_4 are summarized in Table II. In each case the calculation of M has been made for eight different charge distributions in the complex ion. The results for Cs_2CuCl_4 are plotted in Fig. 1. It can be

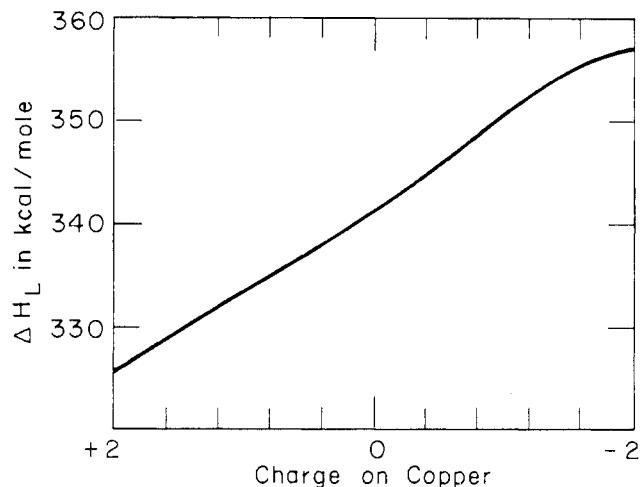Fig. 1.—The variation of the pseudo-lattice energy of Cs_2CuCl_4 with charge distribution in the $[CuCl_4]^{2-}$ ion.

seen that the dependence of ΔH_L upon charge distribution is linear within the significance of the numbers and also that the total range of variation is fairly large, *viz.*, ~ 30 kcal./mole. For use in calculation of ΔH_{com} we have selected values of ΔH_L corresponding to a charge on the metal of 0.5 ± 0.25. This choice is, of course, to some extent arbitrary, but seems in reasonable accord with inferences which may be drawn from various lines of experimental[10,11] evidence and theoretical[12,13] considerations.

(10) K. Kubo, *et al.*, *J. Am. Chem. Soc.*, **83**, 4526 (1961).

(11) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).

(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 163.

(13) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 172.

TABLE II

CALCULATED PSEUDO-LATTICE ENERGIES OF Cs_2CuCl_4 AND Cs_2CoCl_4 FOR VARIOUS CHARGE DISTRIBUTIONS IN THE ANIONS

M	Charges on		$-M,$[a] kcal./mole	$-C,$[a] kcal./mole	$-U_Z,$ kcal./mole	Heat capacity corr., kcal./mole	ΔH_L at 300°, kcal./mole
	M	Cl					
Cu	+2	−1	348.4	31.3	−1.0	−1.0	326.1
	+1.6	−0.9	351.5	31.3	−1.0	−1.0	328.8
	+1.2	−0.8	354.7	31.3	−1.0	−1.0	331.7
	+0.8	−0.7	358.1	31.3	−1.0	−1.0	334.8
	+0.4	−0.6	361.7	31.3	−1.0	−1.0	338.0
	0	−0.5	365.5	31.3	−1.0	−1.0	341.4
	−1.2	−0.2	378.0	31.3	−1.0	−1.0	352.7
	−2.0	0	383.6	31.3	−1.0	−1.0	357.7
Co	+2	−1.0	342.5	27.5	−1.0	−1.0	317.2
	+1.6	−0.9	346.0	27.5	−1.0	−1.0	321.4
	+1.2	−0.8	349.5	27.5	−1.0	−1.0	323.5
	+0.8	−0.7	353.2	27.5	−1.0	−1.0	326.9
	+0.4	−0.6	356.9	27.5	−1.0	−1.0	330.2
	0.0	−0.5	360.6	27.5	−1.0	−1.0	333.5
	−1.2	−0.2	372.4	27.5	−1.0	−1.0	344.2
	−2.0	0.0	378.3	27.5	−1.0	−1.0	349.5

[a] Crystal structure data taken from the following sources: Cs_2CoCl_4, M. A. Porai-Koshits, *Kristallografia*, **1**, 291 (1956); Cs_2ZnCl_4, B. Brehler, *Z. Krist.*, **109**, 68 (1957), reported to be isomorphous with the Co compound—X-Ray powder pictures of the two compounds, taken in this laboratory, are indistinguishable and unit cell dimensions differ by less than 0.005 Å.; Cs_2CuCl_4, B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961).

In the case of the $[CoCl_4]^{2-}$ ion it has been possible to make a severe test of the validity of the procedure and of the numerical correctness of the result. This is because the $[CoCl_4]^{2-}$ ion also occurs in another suitable compound with a different but known structure, namely, Cs_3CoCl_5, which consists of $3Cs^+$, Cl^-, and $[CoCl_4]^{2-}$ ions.[14]

For Cs_3CoCl_5 the results of the lattice energy calculation are collected in Table III. Now it is easily shown that the value of $\Delta H_{com} + \Delta H_L$ obtained from Cs_3CoCl_5 should be equal to that obtained from Cs_2CoCl_4 augmented by the quantity

$$\Delta H_f[Cs^+(g)] + \Delta H_f[Cl^-(g)] +$$
$$\Delta H_f[Cs_2CoCl_4(s)] - \Delta H_f[Cs_3CoCl_5(s)]$$

We have measured the heat of formation of $Cs_3CoCl_5(s)$ and obtained a value of 399.2 kcal./mole. Using this value, together with others from Table I, we obtain for $\Delta H_{com} + \Delta H_L$ for Cs_3CoCl_5 a value of 1110.2 kcal./mole. From Table III we interpolate a value of ΔH_L for a charge of $+1/2$ on cobalt of 503 ± 10 kcal./mole. Thus, the value for ΔH_{com} obtained from Cs_3CoCl_5 is 607 ± 10 kcal./mole, which is to be compared with the value of 625 ± 2 obtained from Cs_2CoCl_4.

The discrepancy of 18 ± 12 kcal./mole, where the limits quoted are based only on the range of uncertainty in selection of the charge distribution, is perhaps larger than would be expected. Several factors may be considered in explanation. First, although we have proposed a charge distribution in the $[MCl_4]^{2-}$ complexes which places a charge of +0.5 ± 0.25 on M, it must be admitted that this is scarcely more than an educated guess; it is not impossible that it is a very

(14) The structure was originally reported by H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935). Recently, however, it has been re-examined by Dr. R. Mason of Imperial College, London (private communication, to be published), who obtains somewhat different and much more reliable atomic coordinates. Mason's results were used in this work.

TABLE III

CALCULATED PSEUDO-LATTICE ENERGY OF Cs_3CoCl_5 FOR VARIOUS CHARGE DISTRIBUTIONS IN $[CoCl_4]^{2-}$

Charges on		$-M,$ kcal./mole	$-C,$ kcal./mole	$-U_Z,$ kcal./mole	Heat capacity corr., kcal./mole	ΔH_L at 300°, kcal./mole
Co	Cl					
1.6	−0.9	606.3	41.7	−1.0	−1.0	560.4
1.2	−0.8	578.3	41.7	−1.0	−1.0	535.2
0.8	−0.7	555.6	41.7	−1.0	−1.0	514.7
0.4	−0.6	538.2	41.7	−1.0	−1.0	499.1
0.0	−0.5	526.1	41.7	−1.0	−1.0	488.2

poor one. If, for example, a charge of zero is assigned to cobalt, the discrepancy is only 7 kcal./mole, which is certainly acceptable. Quite generally, the selection of the correct charge distribution within polyatomic ions constitutes the most vexing difficulty in the entire pseudo-lattice energy treatment, because there is no straightforward way to estimate charge distribution from any experimental data (so far as we know) and theoretical estimates based on, say, molecular orbital calculations would be tedious in any event and of quite uncertain reliability. Fortunately, in many cases, e.g., the Cs_2MCl_4 salts treated here, the results are not extremely sensitive to the charge distribution over a very broad range (for q_{Cu} from 0.0 to +1.0 the spread is only 8 kcal./mole).

It is also possible, however, that at least part of the discrepancy in the results obtained for $CoCl_4^{2-}$ is real. In Cs_3CoCl_5 the $CoCl_4^{-2}$ ion is considerably more and differently distorted (D_{2d} symmetry, all Co–Cl equal, angles 106° (2) and 111° (4)) than in Cs_2CoCl_4.

A separate pseudo-lattice energy calculation for Cs_2ZnCl_4 was not required because the positional parameters of the atoms in this compound are evidently almost identical with those of corresponding atoms in Cs_2CoCl_4 (see footnote to Table II).

Inorganic Chemistry

Discussion

The major emphasis in this paper is on examination of the premises and derivation of general equations for the computation of pseudo-lattice energies and on the presentation of a satisfactory procedure for the actual performance of such computations. There have, in the past, been several attempts to compute Madelung energies of substances containing polyatomic ions but because of computational limitations they have usually assumed the charge on a complex anion (or cation) to be entirely localized on the central atom[2,15] or, alternatively, used only the extreme ionic distribution of charge[16] (*e.g.*, treated NO_3^- as N^{6+} and $3O^{2-}$). In one simple case, namely, that of linear, symmetrical triatomic ions (*e.g.*, N_3^-, F_2H^-), expressions have been derived for a charge distribution correction.[17] However, analytical treatments of this kind are not in general practicable for more complicated polyatomic ions, and a method such as ours, based upon machine computation of the total lattice sum for a variety of preselected charge distributions, seems to be the best general solution to the problem.

In the present paper, we report results only for systems in which the atoms were selected to allow relatively unambiguous choices, based on precedents, for the repulsion exponent and the factors C occurring in the dispersion energy expressions. It should be pointed out that there are many complex ions of interest which crystallize only with polyatomic counter-ions. In such cases criteria for selection of the above-mentioned parameters will have to be developed. However, because of the low sensitivity of the pseudo-lattice energies to the magnitudes of n and C in eq. 15 this should not prove to be an insuperable difficulty in more general application of the sort of treatment reported here, provided results of only moderate precision (say ± 10 kcal./mole) are desired.

With regard to the specific results obtained for the $[MCl_4]^{2-}$ ions, a few comments may be made. First of all, it may be noted that, although ligand field stabilization energies may play some role in making tetrahedral complexes of some ions more stable than those of others,[4] their importance in the over-all energy of complexation is slight. Thus for the $[MCl_4]^{2-}$ ions in the series with M = Fe, Co, Ni, and Cu, these stabilization energies are ~10 kcal./mole[4] and are thus only ~1.5% of the entire ΔH_{com}.

Although there is now a great deal of experimental data to show that the bonds in complexes in general[18] and in $[CoX_4]^{2-}$ species in particular[19] have considerable covalent character, this is not evident from en-

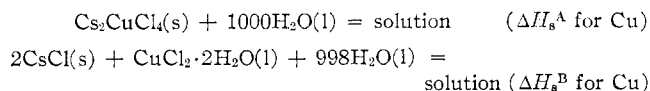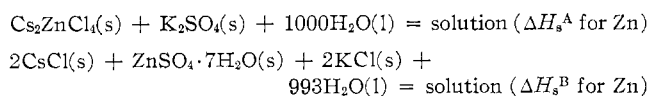ergetic considerations alone. Thus the magnitude of ΔH_{com} calculated by treating $[CoCl_4]^{2-}$ as an array of four charges, $-e$, tetrahedrally arranged about a charge $+2e$, with the distance between opposite charges equal to the mean observed Co–Cl distance in Cs_2CoCl_4, is 652.3 kcal./mole. If one further assumes that for real Co^{2+} and Cl^- ions a repulsive energy of 5–10% of the total attractive energy should also be considered[20] we estimate ΔH_{com} to be 587–622 kcal./mole for purely "ionic" metal–ligand bonds, whereas the value of ΔH_{com} estimated from experimental data is ~616 kcal./mole. We thus conclude that energetic considerations alone cannot be used as a criterion of bond type. This may actually have some advantage in that rough estimates of bond energies may be obtainable by assuming pure ionic bonds even though this is unrealistic. Naturally, it cannot be asserted that this is generally so on the basis only of the one example discussed.

Experimental

Apparatus.—The heats of solution were measured with the twin-chamber calorimeter to be described.[4] The heat absorbed or evolved was balanced by a directly measured quantity of electrical energy supplied to a heating coil in either the solution or reference chamber, to nullify the temperature difference produced by the solute. All experiments were at an initial temperature of $25 \pm 0.1°$.

Materials.—CsCl of 99.9% purity was obtained from Fairmount Chemical Company. $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $ZnSO_4 \cdot 7H_2O$, KCl, and K_2SO_4 were Mallinckrodt A.R. grade. The zinc sulfate was kept in a desiccator over water saturated with KNO_3 and NH_4Cl. Cs_2CoCl_4 was prepared by slow evaporation of an aqueous solution of cesium chloride and cobalt chloride (2:1) and analyzed electrolytically for Co. *Anal.* Calcd.: Co, 12.63. Found: Co, 12.80. Cs_2ZnCl_4 was prepared by mixing solutions of cesium chloride (1 *M*) and zinc chloride (0.5 *M*) in hot 6 *M* aqueous HCl and cooling the solution. Cs_2CuCl_4 was prepared by dissolving 6 g. of $CuCl_2 \cdot 2H_2O$ and 25 g. of CsCl in 50 ml. of hot water, filtering the solution, and evaporating it to 25 ml. on a steam bath, with occasional stirring. After cooling, the golden yellow needles were filtered and dried for 1 hr. at 130°. $CsCoCl_3$ was obtained by evaporating a solution made from 6 g. of $CoCl_2 \cdot 6H_2O$, 25 g. of CsCl, and 50 ml. of water to 25 ml., allowing it to stand about 4 hr., and then filtering off the crystals and drying them several hours at 130°.

Results and Treatment of Data.—The entire approach is analogous to that outlined in ref. 4. Experimental data collected were for the reactions

$Cs_2ZnCl_4(s) + K_2SO_4(s) + 1000H_2O(l) = $ solution (ΔH_s^A for Zn)

$2CsCl(s) + ZnSO_4 \cdot 7H_2O(s) + 2KCl(s) +$
$\qquad\qquad 993H_2O(l) = $ solution (ΔH_s^B for Zn)

$Cs_2CuCl_4(s) + 1000H_2O(l) = $ solution $\qquad(\Delta H_s^A$ for Cu)

$2CsCl(s) + CuCl_2 \cdot 2H_2O(l) + 998H_2O(l) =$
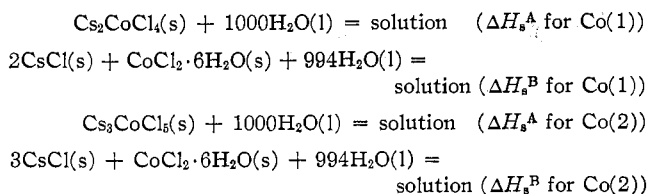$\qquad\qquad\qquad$ solution (ΔH_s^B for Cu)

(15) A. P. Altshuler, *J. Chem. Phys.*, **23**, 1561 (1955).

(16) For a detailed and authoritative discussion of these older calculations (and much other general information on lattice energy calculations), see T. C. Waddington, *Advan. Inorg. Chem. Radiochem.*, **1**, 157 (1959).

(17) P. Gray and T. C. Waddington, *Proc. Roy. Soc.* (London), **A235**, 481 (1956). We have used our method to recalculate their results for KN_3, as a check on both methods. The results agree within 1 kcal./mole.

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Course," Interscience Publishers, New York, N. Y., 1962, pp. 590–596.

(19) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(20) In this connection, it is pertinent to comment on Ballhausen's contention[21] that an electrostatic picture of metal–ligand bonding can be ruled out *a priori* because "we know from Earnshaw's theorem of electrostatics that no system of charges can be in stable equilibrium while at rest." This is true in a limited sense, but is not relevant to a model in which we assume that the forces of attraction between the metal ion and the ligands (as well as part of the repulsive force between ligands of like charge) are purely electrostatic, but in which we also introduce noncoulombic repulsive forces of unspecified origin. This is a model quite analogous to the one commonly used to treat "ionic" solids such as NaCl. We believe the relevant question is whether *this* model, which does *not* violate Earnshaw's theorem, is tenable as far as energetics are concerned, and it is to this question that our discussion here is addressed.

(21) Reference 12, p. 152.

$Cs_2CoCl_4(s) + 1000H_2O(l) = $ solution $(\Delta H_s{}^A$ for $Co(1))$

$2CsCl(s) + CoCl_2 \cdot 6H_2O(s) + 994H_2O(l) = $
$$\text{solution } (\Delta H_s{}^B \text{ for } Co(1))$$

$Cs_3CoCl_5(s) + 1000H_2O(l) = $ solution $(\Delta H_s{}^A$ for $Co(2))$

$3CsCl(s) + CoCl_2 \cdot 6H_2O(s) + 994H_2O(l) = $
$$\text{solution } (\Delta H_s{}^B \text{ for } Co(2))$$

The results are recorded in Table IV. When used together with other data obtained from ref. 5, these data permit us to calculate the standard enthalpies of formation of the Cs_2MCl_4 compounds and Cs_3CoCl_5.

Appendix

Machine Computation of Madelung Energies

A Fortran-coded program has been written[22] for calculating the electrostatic (Madelung) part of the cohesive energy of an ionic crystal on the IBM 709/7090 computer system. The program is based upon the method of Ewald[23] and utilizes Bertaut's device[24] of representing the ions as symmetric gaussian charge distributions of variable distention. Provision is also

(22) The valuable assistance and advice of Mr. J. P. Wright are acknowledged.

(23) P. P. Ewald, *Ann. Physik*, **64**, 253 (1921).

(24) E. F. Bertaut, *J. phys. radium*, **13**, 499 (1952).

TABLE IV
MEASURED ENTHALPIES[a] OF THE SOLUTION PROCESSES[b]

Metal ion	$\Delta H_s{}^A$, kcal./mole	$\Delta H_s{}^B$, kcal./mole
Zn	13.8	20.0
Cu	3.8	3.7
Co(1)	−0.3	11.1
Co(2)	4.8	15.1

[a] All values are the averages of the results of two or more concordant measurements. Mean deviations are all less than ±0.05 kcal./mole. [b] See Experimental section for chemical equations of the processes.

made for checking the degree of convergence of the series in the manner suggested by Templeton.[25]

The input data required are the unit cell parameters (edges in Å. to four decimal places and cosines of angles to four decimal places), the fractional coordinates (to four decimal places) of all atoms of a given kind in the unit cell, and the charges (to two decimal places) of each kind of atom. The machine time required on the 7090 to compute each of the M values used in this work was ~ 1.2 min.

An outline of the theory, directions for using the program, and a Fortran deck may be obtained by addressing requests to F. A. C.

(25) D. Templeton, *J. Chem. Phys.*, **23**, 1629 (1955).

An LCAO–MO Study of Static Distortions of Transition Metal Complexes

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The one-electron-LCAO method in which all valence orbitals are included has provided a semiquantitative basis for "Jahn–Teller" distortions in VCl_4, $CuCl_4^{-2}$, $NiCl_4^{-2}$, CuF_6^{-4}, and for the spectra of these ions.

Introduction

The dynamic,[1] *i.e.*, vibronic, Jahn–Teller[2] effect in transition metal complexes has received recent attention, but little even semiquantitative basis has been provided for the supposedly simpler static effect.[3,4] The problem is one of molecular conformation, for which the recent application of a molecular-orbital (MO) one-electron LCAO method has shown some success.[5] All valence orbitals are used in this method,

(1) W. Moffitt and W. Thorson, *Phys. Rev.*, **108**, 1251 (1957); A. D. Liehr, *J. Phys. Chem.*, **64**, 43 (1960); A. D. Liehr, *Ann. Rev. Phys. Chem.*, **13**, 41 (1962); A. D. Liehr, *J. Phys. Chem.*, **67**, 389, 471 (1963).

(2) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937); H. A. Jahn, *ibid.*, **A164**, 117 (1938).

(3) "It is a great merit of the Jahn–Teller effect that it disappears when not needed," J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).

(4) U. Öpik and H. M. L. Pryce, *Proc. Roy. Soc.* (London), **A238**, 425 (1957); L. E. Orgel and J. D. Dunitz, *Nature*, **179**, 462 (1957).

(5) L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963); T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 846 (1963).

but nuclear repulsions are ignored because they are simulated[5] by over-estimated antibonding electronic interactions.[6] Also explicit and detailed electron-electron repulsion terms are included only in an average way. Therefore, the results described here are mostly confined to V(IV) and Cu(II) systems in which one electron or one hole occurs, respectively, and hence the one-electron approximation also describes the complete electronic states of complexes of these ions rather well. Some extension is made to Ni(II) and Co(II) high-spin systems, containing two and three unpaired electrons, respectively. In particular, the VCl_4 molecule and the $CuCl_4^{-2}$, $NiCl_4^{-2}$, and CuF_6^{-4} ions are treated here as typical of this class of species in which a semiquantitative basis is desirable for the magnitudes of static Jahn–Teller distortions.

(6) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1963, p. 106.