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

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

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

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

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.

TABLE IV

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

Metal ion	ΔH_s^A, kcal./mole	ΔH_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.

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 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.

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

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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, 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.

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(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).

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Procedure

The study consists of carrying out consecutive LCAO–MO calculations for a given molecule, with various choices of the bond angles and/or bond lengths. The object is to find the geometry at which an energy, defined as the sum of the energies of the occupied MO's, is a minimum. In most cases an absolute minimization with respect to geometry is impractical, and only the bond angles, for example, will be varied. A correctly defined total energy would consist of the orbital energy sum mentioned above, in which the electron-repulsion terms are subtracted (because they are counted twice in the orbital energy sum[6]) and the nuclear repulsion terms are added. The neglect of the nuclear repulsion energy in the simple LCAO–MO scheme implies the assumption that the difference of such repulsions and the electron repulsions is nearly a constant over the ranges of molecular geometry being considered. If this assumption is valid, the resulting total energy will have its maximum and minimum values at the same geometries as does the correctly defined total energy, although the numerical values of the two "energies" will in general be different. In fact, use of the LCAO–MO scheme,[7] which in essence is an extension of the familiar Hückel π-electron theory for aromatic systems, leads to bond energies[5,7] that are systematically almost twice too large.

The atomic orbitals used in this study are characterized by Slater exponents and Coulomb integrals (Table I). The exponents for the V (3d) and Cu (3d) orbitals were estimated from the exponents of basis functions for V^{+4} and Cu^{+2} atomic SCF wave functions,[8] while those for the V (4s, 4p), Cu (4s, 4p), F (2s, 2p), and Cl (3s, 3p) orbitals were obtained by application of the standard Slater rules[9] to the species V^{+4} ($4s^1$), Cu^{+2} ($3d^8 4s^1$), F^{-1}, and Cl^0, respectively. The Cl^0 Slater-rule exponent is not greatly different from an average of the exponents for the two p-type basis functions with the largest coefficients in the 3p AO of an SCF Cl^{-1} wave function.[10] The Coulomb integrals were estimated from reported[11] valence state ionization potentials (F and Cl), atomic SCF one-electron energies[8] (V and Cu), and atomic ionization potentials[12] (V and Cu).

VCl_4.—Perhaps the most interesting reason that the electron diffraction study[13] of VCl_4 was undertaken was the possibility that the single d-electron might produce a molecular distortion. A regular tetrahedral structure, however, was found in which V–Cl is 2.03 ± 0.02 Å. Furthermore, the Cl···Cl peak in the radial distribution curve showed no clear evidence that the bending modes of the molecule are anomalously large, but the use of visual estimates of intensities would not allow detection of excess vibrations of only a few degrees. The T_d symmetry indicates a ^2E ground electronic state, which could be split into $^2A_1$ and $^2B_1$ states by distortion into tetragonal D_{2d}. Thus this tetragonal distortion should produce a more stable state, whereas a trigonal distortion would not.

Table I

Atomic Orbital Parameters

	Vanadium	Copper	Chlorine	Fluorine
	Slater exponents			
s	1.55	1.35	2.03	2.42
p	1.55	1.35	2.03	2.42
d	2.70	2.41	...	...
	Coulomb integrals, e.v.			
s	−8.0	−8.0	−22.0	−31.4
p	−6.0	−6.0	−13.0	−17.4
d	−12.0 −10.0	−10.0	...	...

A recent application[14] of the crystal field method to VCl_4 has yielded, by contrast with the electron diffraction results, a stable elongated structure of symmetry D_{2d} in which at temperatures below 200° the ClVCl bond angles are predicted to be approximately 103.5 and 112.5°. The stabilization of this structure relative to the tetrahedral one is 0.7 kcal./mole.

The results of the present study are shown, for the parameters of Table I, in Table II. These LCAO–MO results were obtained for various bond angles, but the observed bond distance of 2.03 Å. was assumed throughout. Either with or without the inclusion of 4s and 4p orbitals of V, the results indicate only two very shallow

Table II

θ^a	E, e.v.[b]	Charge,[c] V	State
	VCl_4 without 4s,4p		
180°[d]	−506.477	+1.381	^2E
140°	−509.582	0.716	$^2A_1(^2E)$
118°	−510.708	.671	$^2A_1(^2E)$
112°	−510.787	.664	$^2A_1(^2E)$
110°[e]	−510.790	.663	$^2A_1(^2E)$
109.45°[f]	−510.788	.662	^2E
108°[e]	−510.790	.664	$^2B_1(^2E)$
106°	−510.781	.666	$^2B_1(^2E)$
100°	−510.660	.676	$^2B_1(^2E)$
80°	−508.232	.450	$^2B_1(^2E)$
	VCl_4 with 4s,4p[g]		
114°	−505.734	+1.554	$^2A_1(^2E)$
112°	−505.753	1.552	$^2A_1(^2E)$
110°[e]	−505.757	1.551	$^2A_1(^2E)$
109.45°[f]	−505.756	1.551	^2E
108°[e]	−505.757	1.551	$^2B_1(^2E)$
106°	−505.742	1.553	$^2B_1(^2E)$

[a] $\angle Cl_1$–V–Cl_2, where Cl_1 and Cl_2 are related by principal C_2 axis. [b] Coulomb integral 3d = −12.0 e.v. [c] For charge definition, see ref. 5. [d] Symmetry D_{4h}. [e] Position of an energy minimum. [f] Symmetry T_d. [g] Coulomb integral 3d = −10.0 e.v.

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(7) For LCAO–MO studies of boron–carbon–hydrogen systems, see R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); *ibid.*, **37**, 2872 (1962).

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minima, depressed from the energy of the tetrahedral structure by only about 0.001 e.v. = 0.023 kcal./mole. The molecular distortion from tetrahedral geometry at the minimum corresponds only to a change in the ClVCl angle by about 1°. For the compressed bisphenoidal geometry the ground state is $^2A_1$, and for the elongated geometry it is $^2B_1$. No significant change occurred in these results when the Coulomb integral of the 3d orbital of V is varied from -12.0 to -10.0 e.v. Of course, no static distortion is to be expected from these minima, which stabilize the distorted form by less than vibrational energies.

Vibrational spectra for the VCl_4 molecule have been reported recently[15] from a Raman study of a CCl_4 solution and from an infrared study of the liquid, the vapor, and a CCl_4 solution. No evidence was found of any influence by the Jahn–Teller effect on the ground-state vibrational spectra. Furthermore, the frequency of the ϵ-symmetry bending mode was not less than that for the non-Jahn–Teller molecule[11] $TiCl_4$, as might have been expected, but, in fact, was found to be slightly greater (128 cm.$^{-1}$ for VCl_4, 120 cm.$^{-1}$ for $TiCl_4$). However, another study[16] of the VCl_4 vapor-phase infrared spectrum gives a somewhat lower value of 112 cm.$^{-1}$ for the frequency of the ϵ-symmetry mode.

$CuCl_4^{-2}$.—If we assume, incorrectly, that $CuCl_4^{-2}$ is tetrahedral, the ground electronic state of the configuration $e^4t_2^5$ is $^2T_2$. First-order spin-orbit coupling[17] splits this state into a low-lying spinor (space plus spin) doublet of symmetry $E''(\Gamma_7)$ and a higher spinor quartet of symmetry $U'(\Gamma_8)$ which has no first-order Zeeman interaction. The amount of this splitting is $(^3/_2)\zeta$, where the one-electron parameter ζ for Cu(3d) is equal to $-\lambda$ for a one-hole system for which $S = {}^1/_2$. If we choose the value[12] of λ for the free Cu^{+2} ion, the splitting $(^3/_2)\zeta$ is 1240 cm.$^{-1}$ = 3.5 kcal./mole. Therefore, relative to the unsplit $^2T_2$ state, the ground-state doublet has a spin-orbit stabilization of $\zeta = 2.3$ kcal./mole. The usual reduction of ζ from the free ion value when complexes are formed may be estimated, but nevertheless the orbital degeneracy even of tetrahedral $CuCl_4^{-2}$ is removed by spin-orbit coupling without recourse to distortion from T_d symmetry.

However, the $CuCl_4^{-2}$ ion in Cs_2CuCl_4 is known[18] to have bond angles ClCuCl of 118 and 104°, to have symmetry C_s, and very nearly to have symmetry D_{2d}. The distortion from T_d symmetry is toward a flattened bisphenoid. This distortion, which corresponds to an ϵ mode of vibration, lifts partly or completely the degeneracy of the $^2T_2$ state. An examination of the effect of this distortion on $CuCl_4^{-2}$, in which Cu–Cl is taken at the observed distance of 2.2 Å., is shown in Table III. As noted above for VCl_4 two minima were found, but by contrast some of the minima for $CuCl_4^{-2}$ are deep and strongly dependent on whether the 4s and 4p orbitals of Cu are included (Fig. 1 and 2). This dependence may be expected at the extreme right of a transition series where 4s and 4p are relatively closer in energy to the valence levels. When 4s and 4p orbitals of Cu are omitted one finds the unbelievable results that minima of -19.9 and -2.1 kcal./mole occur (relative to the energy of the T_d structure) at bond angles of 160° (compressed) and 100° (elongated), respectively, and also that the D_{4h} structure is more stable than the T_d structure by 19.0 kcal./mole. However, the inclusion of 4s and 4p orbitals leads to a $^2B_2$ state in a compressed bisphenoid with ClCuCl = 120° at an energy of -4.6 kcal./mole relative to that of the T_d structure, and to a ^2E state spatially degenerate, which is in an elongated bisphenoid with ClCuCl = 100° at an energy of -0.2 kcal./mole relative to that of the T_d structure. Also, fortunately, the T_d structure

TABLE III

θ^a	E, e.v.	Q (Cu)^e	State
	$CuCl_4^{-2}$ (D_{2d}) without 4s,4p		
180°^{b}	-573.60	$+1.69$	$^2B_2$
160°^{c}	-573.64	1.70	$^2B_2$
140°	-573.56	1.73	$^2B_2$
120°	-573.14	1.78	$^2B_2$
109.45°^{d}	-572.77	1.80	$^2T_2$
100°^{c}	-572.86	1.79	^2E
80°	-571.34	1.74	^2E
	$CuCl_4^{-2}$ (D_{2d}) with 4s,4p		
180°^{b}	-577.18	$+0.89$	$^2B_2$
160°	-577.86	.84	$^2B_2$
140°	-578.55	.82	$^2B_2$
120°^{c}	-578.64	.82	$^2B_2$
109.45°^{d}	-578.44	.83	$^2T_2$
100°^{c}	-578.45	.83	^2E
80°	-576.72	.87	^2E

[a] $\angle Cl_1$–Cu–Cl_2 where Cl_1 and Cl_2 are related by the principal C_2 axis. [b] Symmetry D_{4h}. [c] Position of an energy minimum. [d] Symmetry T_d. [e] For definition of the atomic charge Q, see ref. 5.

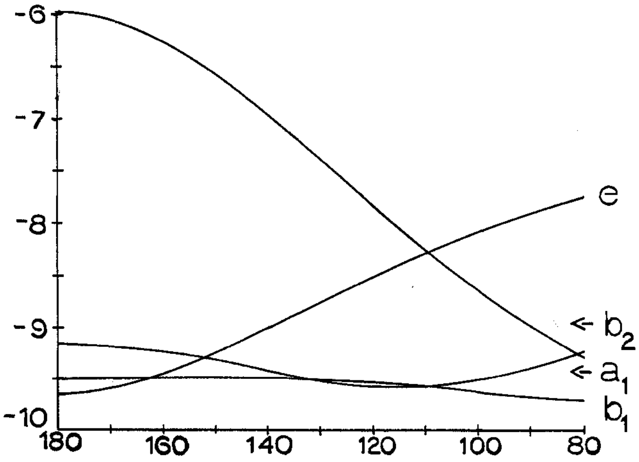

Fig. 1.—Energies (e.v.) of primarily d MO's *vs.* bond angle for the $CuCl_4^{-2}$ ion (D_{2d}), without Cu (4s) and Cu (4p) orbitals. Symmetries D_{4h} and T_d occur at angles of 180 and 109.45°, respectively, while the minima in the total orbital energy (sum of energies of occupied MO's, including the mostly-ligand MO's not shown here) occur at angles of 160 and 100°, respectively.

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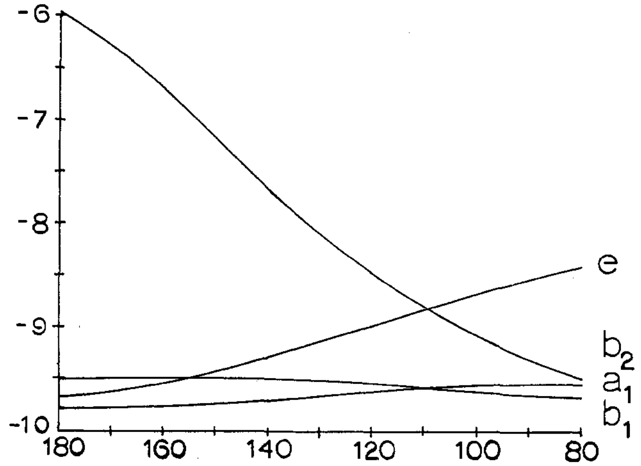

Fig. 2.—Energies (e.v.) of primarily d MO's *vs.* bond angle for the $CuCl_4^{-2}$ ion (D_{2d}), with Cu (4s) and Cu (4p) orbitals. The minima in the total orbital energy (see legend of Fig. 1) occur at angles of 120 and 100°, respectively.

is more stable than the D_{4h} structure by 27.6 kcal./mole. We have therefore included the 4s and 4p orbitals of Cu in all of the other calculations involving Cu(II). The individual orbital energies, shown in Fig. 1 and 2, indicate that when 4s and 4p of Cu are included the $d_{x^2-y^2}$ energy drops much more steeply as the angle decreases, while the d_{xz}, d_{yz} energy rises much less sharply, thus shifting the minimum of the total energy (sum of occupied MO energies, including the primarily ligand MO's not shown in Fig. 1 and 2) toward that of the T_d structure. Also, the d_{z^2} orbital is lowest in energy in all compressed structures. The coordinate system is chosen so that in the group D_{4h} the z^2 orbital transforms as a_{1g}, $x^2 - y^2$ as b_{1g}, xz and yz as e_g, and xy as b_{2g}. Thus the t_2 representation of T_d is spanned by $x^2 - y^2$, xz, and yz, while e is spanned by xy and z^2. The 4s orbital then mixes with z^2 in D_{4h} and D_{2d}, but not in T_d; x, y, z mix with $x^2 - y^2$, xz, yz in T_d; and x, y mix with xz, yz and z mixes with $x^2 - y^2$ in D_{2d}. The shifting of the position of the energy minimum toward the T_d geometry upon inclusion of Cu (4s) and Cu (4p) orbitals then arises primarily from Cu (4p) mixing in the noncentrosymmetric structure. The importance of π-bonding was tested by calculations for a hypothetical CuH_4^{-2} in which the ligands have only 1s orbitals. Two minima occurred at essentially the same bond angles as for $CuCl_4^{-2}$, suggesting that π-bonding is not important in determining the position of the energy minima in the $CuCl_4^{-2}$ ion.

Trigonally distorted $CuCl_4^{-2}$ (C_{3v}) was also considered with a constant Cu–Cl distance. The results shown in Table IV indicate a $^2A_1$ term for a compressed trigonal pyramid, with three bond angles of 105° and an energy relative to the T_d structure of -0.30 e.v. $= -0.7$ kcal./mole. The elongated geometry (^2E state) has a very shallow minimum, with an energy of only -0.01 e.v. $= -0.2$ kcal./mole. The trigonal distortion mixes 4s and $4p_z$ with z^2, and x, y, with xz, yz and with $x^2 - y^2$, xy (the coordinate system is chosen with z as the threefold axis).

Table IV

$CuCl_4^{-2}$ (C_{3v})

θ[a]	E, e.v.	Q (Cu)[d]	State
90°	-577.71	$+0.86$	$^2A_1$
95°	-578.15	.85	$^2A_1$
100°	-578.38	.84	$^2A_1$
105°[b]	-578.47	.83	$^2A_1$
109.45°[c]	-578.44	.83	$^2T_2$
111°[b]	-578.45	.83	^2E
113°	-578.44	.83	^2E
115°	-578.41	.84	^2E
120°	-578.22	.85	^2E
125°	-577.74	.87	^2E
130°	-576.67	.90	^2E

[a] ∠ Cl–Cu–C_{axial}. [b] Position of an energy minimum. [c] Symmetry T_d. [d] For definition of the atomic charge Q, see ref. 5.

In summary of all of these calculations on $CuCl_4^{-2}$, we note that the most stable geometry is the observed tetragonally compressed (D_{2d}) structure, with a stabilization energy which is at least twice the spin-orbit stabilization of the tetrahedral form. This distorted structure has been considered in an electrostatic treatment[19] as resulting from a balance of ligand–ligand repulsions, favoring the symmetry T_d, and the crystal-field stabilization favoring D_{4h}. The interpretation given here for the distortions is similar, but with the crystal-field splittings and ligand–ligand repulsions arising formally from covalency (overlap) effects.[3]

$NiCl_4^{-2}$ and $CoCl_4^{-2}$.—As the semiquantitative results of this study are not greatly sensitive to small changes in either the metal–ligand distances, the orbital exponents, or the Coulomb integrals, the MO energies for $CuCl_4^{-2}$ (with 4s and 4p AO's) were used to consider the ground-state geometries of the high-spin $CoCl_4^{-2}$ (d^7) and $NiCl_4^{-2}$ (d^8) ions. If the ions are of symmetry T_d, the ground states (neglecting spin-orbit coupling) are $^4A_2$ and $^3T_1$, respectively. The ion $CoCl_4^{-2}$ has a nearly tetrahedral structure[20] of D_{2d} symmetry (slightly compressed along an S_4 axis) in Cs_3CoCl_5; however, the X-ray data are poor, and the ion might well be slightly elongated in this particular crystal. The ion $NiCl_4^{-2}$ has C_{3v} symmetry[21] in $((C_6H_5)_3CH_3As)_2NiCl_4$ but the details of the structure do not appear to have been published. Since distortions of a complex in a crystal may arise from packing considerations, care must be exercised in attributing a given distortion to the "Jahn–Teller" effect. It is certainly expected that an isolated $CoCl_4^{-2}$ ion would have T_d symmetry (the $^4A_2$ state is not spatially degenerate) and that an isolated $NiCl_4^{-2}$ ion would be nearly, but not exactly, tetrahedral (the $^3T_1$ state is spatially degenerate). Indeed, the energy minima are found to occur for a structure of T_d symmetry for $CoCl_4^{-2}$ and

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(19) G. Felsenfeld, *Proc. Roy. Soc.* (London), **A236**, 506 (1956).

(20) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935); for the structure of the $CoCl_4^{-2}$ ion in Cs_2CoCl_4, with Co^{+2} site-symmetry C_s (nearly D_{2d}, compressed), see M. A. Porai-Koshits, *Trudy Inst. Krist. Akad. Nauk SSSR*, **10**, **117** (1954), and *Kristallografiya*, **1**, 291 (1956); also see G. N. Tschenko and Z. G. Pinsker, *Dokl. Akad. Nauk SSSR*, **100**, 913 (1955).

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TABLE V

CuF_6^{-4}, D_{4h}

2Cu–F, Å.	4Cu–F, Å.	E, e.v.	Q (Cu)[a]	Q (2F)	Q (4F)	State
2.72	1.70	−1085.84	+1.99	−1.00	−1.00	$^2B_{1g}$
2.52	1.80	−1089.06	+1.98	−1.00	−1.00	$^2B_{1g}$
2.32	1.90	−1090.75	+1.99	−1.00	−1.00	$^2B_{1g}$
2.12[b]	2.00	−1091.18	+2.00	−1.01	−1.00	$^2B_{1g}$
2.04[c]	2.04	−1091.00	+2.01	−0.99	−1.01	^2E_g
1.95[b]	2.08	−1091.12	+2.00	−0.99	−1.01	$^2A_{1g}$
1.72	2.20	−1090.42	+1.97	−0.98	−1.00	$^2A_{1g}$
1.52	2.30	−1087.77	+1.94	−0.96	−1.00	$^2A_{1g}$
1.32	2.40	−1081.30	+1.91	−0.95	−1.00	$^2A_{1g}$

[a] For definition of the atomic charge Q, see ref. 5. [b] Position of an energy minimum. [c] Symmetry O_h.

for both elongated and compressed structures of both D_{2d} and C_{3v} symmetries for $NiCl_4^{-2}$. The positions of the $NiCl_4^{-2}$ minima are essentially identical with those for $CuCl_4^{-2}$; however, it is the elongated structures (maximum stabilization energies of 3.4 and 0.7 kcal./mole for D_{2d} and C_{3v} structures, respectively) that are important for a nearly tetrahedral d^8 system, for the compressed structures correspond to ^3E states still spatially degenerate.

First-order spin-orbit coupling within the $^3T_1$ state of tetrahedral $NiCl_4^{-2}$ could stabilize that structure, but the lowest level would be expected to have a spin-orbit energy less than a value of −1.8 kcal./mole (the magnitude is the one-electron parameter ζ_{3d}) estimated from the free ion Ni^{+2} spin-orbit energy[12] (it should be noted that the ground level of $NiCl_4^{-2}$ is a nondegenerate $J = 0$ level, like the $J = 0$ level of the ^3P term of p^2). Finally, a more thorough treatment of the trigonal distortions of $NiCl_4^{-2}$ (and of $CuCl_4^{-2}$) should include variation of metal–ligand distances as well as the variation of bond angles considered here.

CuF_6^{-4}.—Similar calculations were made for CuF_6^{-4}, with a ^2E ground term in O_h symmetry. In this ion, a tetragonal distortion can lift the spatial degeneracy, but a trigonal distortion cannot, and there is no first-order spin-orbit coupling. The average bond length was assumed constant and taken as 2.04 Å., the average of the observed distances in CuF_2[22] and K_2CuF_4.[23] The results (Table V) indicate two minima, a compressed octahedron (state symmetry $^2A_{1g}$) with 2Cu–F = 1.95 Å. and 4Cu–F = 2.08 Å., and an elongated octahedron (state symmetry $^2B_{1g}$) with 2Cu–F = 2.12 Å. and 4Cu–F = 2.00 Å. The energies relative to the O_h structure are −2.8 and −4.2 kcal./mole, respectively, corresponding to the observed distortions in K_2CuF_4 and CuF_2. Since the complex has D_{4h} symmetry and thus an inversion center, the primarily 3d orbitals have no 4p character, but the a_{1g} orbital does contain about 1% 4s character at the minima, measured in terms of the sum of squares of coefficients, plus one-half of appropriate overlap terms. It should be remembered that the d-orbitals span a_{1g}, b_{1g}, b_{2g}, and e_g representations of D_{4h}.

Spectra.—As the V(IV) and Cu(II) systems are single-electron or single-hole systems, we can consider the one-electron functions as representing total electronic states to a good approximation. The tetrahedral and lower symmetry d-orbital splittings (Table VI) should then correspond to observed absorption bands, if distortions (and hence splittings) of the excited states can be taken to be those appropriate to the ground-state equilibrium geometry. However, the explicit consideration of vibrational effects in the ground state might easily lead to spectral splittings corresponding to excited state splittings appropriate to a nonequilibrium ground-state geometry. This would be particularly true in centrosymmetric systems, where vibrational coupling permits many otherwise-forbidden electric dipole transitions. True "Jahn–Teller" effects in the excited states,[1] namely, the appearance of uni-quantal progressions in an asymmetric vibrational mode, are not considered here. The transition energies are then defined here as simply differences of the one-electron MO energies. While the

TABLE VI

ONE-ELECTRON EXCITATION ENERGIES FOR MINIMA

System	Transition	Energy, cm.$^{-1}$	Polarization[a]
VCl_4,[b] D_{2d}			
Compressed	$a_1 \rightarrow b_1$	32	Forbidden
	$a_1 \rightarrow e$	9,850	$\perp$
	$a_1 \rightarrow b_2$	10,100	$\parallel$
Elongated	$b_1 \rightarrow a_1$	81	Forbidden
	$b_1 \rightarrow b_2$	9,450	Forbidden
	$b_1 \rightarrow e$	10,250	$\perp$
$CuCl_4^{-2}$, D_{2d}			
Compressed	$e \rightarrow b_2$	3,880	$\perp$
	$b_1 \rightarrow b_2$	8,550	Forbidden
	$a_1 \rightarrow b_2$	9,120	$\parallel$
Elongated	$b_2 \rightarrow e$	3,140	$\perp$
	$a_1 \rightarrow e$	7,000	$\perp$
	$b_1 \rightarrow e$	7,550	$\perp$
$CuCl_4^{-2}$, C_{3v}			
Compressed	$e \rightarrow a_1$	807	$\perp$
	$e \rightarrow a_1$	6,850	$\perp$
Elongated	$a_1 \rightarrow e$	320	$\perp$
	$e \rightarrow e$	6,290	$\parallel$, $\perp$
CuF_6^{-4}, D_{4h}			
Compressed	$b_{1g} \rightarrow a_{1g}$	5,170	Forbidden
	$e_g \rightarrow a_{1g}$	14,500	Forbidden
	$b_{2g} \rightarrow a_{1g}$	15,200	Forbidden
Elongated	$a_{1g} \rightarrow b_{1g}$	4,600	Forbidden
	$b_{2g} \rightarrow b_{1g}$	14,000	Forbidden
	$e_g \rightarrow b_{1g}$	14,400	Forbidden

[a] Based on electric dipole selection rules. [b] Without V (4s) and V (4p), with 3d Coulomb integral = −12.0 e.v.

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(22) C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, **79**, 1049 (1957).
(23) K. Knox, *J. Chem. Phys.*, **30**, 991 (1959).

simple LCAO–MO method, which neglects nuclear repulsions, leads[5,7] to bond energies almost twice too large, one-electron excitation energies and ionization energies[24] are more nearly of the correct magnitude. This is a result of the exact cancellation of nuclear repulsions and the approximate cancellation in one-electron or one-hole systems of the also-neglected explicit electron repulsions when the energies of two states of a molecule are subtracted. It is assumed again that the nuclear positions are unchanged[25] upon electronic excitation.

Spectral splittings result primarily from excited state splittings in d^1 systems and ground state splittings in d^9 systems (Table VI), as a typical one-electron ground state is an orbital which interacts weakly with the ligands and hence is an orbital whose energy is only slightly affected by their displacements, while the one-hole ground state is an orbital which interacts strongly with the ligands and is greatly affected by their displacements. The behavior of the excited states is then the opposite of that of the ground states, with energies of one-electron systems being more sensitive to ligand displacements than energies of one-hole systems. A physical reason is thus given for the negligibly small distortion[26] of the VCl_4 ground state relative to distortions of Cu(II) ground states.

Early studies[27] of the VCl_4 electronic spectrum revealed a 9000 cm.$^{-1}$ transition, with a molar extinction coefficient of 110, which is undoubtedly[28] a crystal-field transition. More recently three components have been reported,[16] with maxima at 6600, 7850, and 9250 cm.$^{-1}$, the splittings being attributed to Jahn–Teller distortions of the excited $^2T_2$ state. As with the $^2T_2$ ground state of the $CuCl_4^{-2}$ ion, both tetragonal and trigonal distortions of this excited $^2T_2$ state should be considered. No more will be said, however, in view of the remarks made in the first part of this section.

In the spectrum of the $CuCl_4^{-2}$ ion, taken here to be of D_{2d} symmetry (compressed), we can consider not only the d–d transitions, but also the charge-transfer bands. For example, the following one-electron transitions from mostly ligand MO's to mostly Cu (3d) MO's are allowed by the electric-dipole selection rules for the group D_{2d} (the list gives the energy in units of 10^3 cm.$^{-1}$, the one-electron oscillator strength,[29,30] and the polarization relative to the S_4 axis)

$$e \rightarrow b_2,\ 35.1,\ 4.3 \times 10^{-2},\ \perp$$
$$a_1 \rightarrow b_2,\ 38.3,\ 2.0 \times 10^{-2},\ \parallel$$
$$e \rightarrow b_2,\ 38.7,\ 1.2 \times 10^{-3},\ \perp$$
$$e \rightarrow b_2,\ 40.7,\ 8.7 \times 10^{-2},\ \perp$$
$$a \rightarrow b_2,\ 43.0,\ 7.3 \times 10^{-2},\ \parallel$$

The corresponding energies and oscillator strengths for the allowed crystal-field transitions of $CuCl_4^{-2}$ (Table VI) are

$$e \rightarrow b_2,\ 3.9,\ 3.9 \times 10^{-4},\ \perp$$
$$a_1 \rightarrow b_2,\ 8.6,\ 7.9 \times 10^{-4},\ \parallel$$

Recent studies[31] of the optical spectrum of the $CuCl_4^{-2}$ ion in various solvents indicate a broad d–d band at 8500 cm.$^{-1}$ (log ϵ 2.08), with broad charge-transfer bands at 25,000 cm.$^{-1}$ (log ϵ 3.5), 34,000 cm.$^{-1}$ (log ϵ 3.8), and 41,000 cm.$^{-1}$ (log ϵ 3.4), all having typical half-widths (at half-height) of 1500 cm.$^{-1}$. The bands are quite similar to those observed[32] in the crystal spectrum of Cs_2CuCl_4, which revealed broad charge transfer bands at 22,000 ($\parallel$) and 23,000 cm.$^{-1}$ ($\perp$). These results correspond to approximate oscillator strengths[33] of 1.6 × 10^{-3} for the d–d band and 4.0, 8.7, and 3.4 (each × 10^{-2}), respectively, for the charge-transfer bands. The calculated energies and oscillator strengths are, of course, approximate, as are the oscillator strengths estimated from the observed spectrum, but they are not inconsistent with the observation of three *broad* charge-transfer bands, although the energy scaling is somewhat off (a better choice of Cl Coulomb integrals relative to those of Cu could perhaps have been made). The calculated strength of the d–d transition is about one-half the observed value, this transition being allowed even in T_d symmetry (there is approximately 7% 4p character in the t_2 primarily 3d MO's, measured[5] in terms of sums of squares of coefficients plus one-half of appropriate overlap contributions). Finally, it should be noted that the calculated oscillator strengths for transitions from an e-orbital are the values for each, not both, orbitals of an e-pair.

Spectral studies[34] of the $CuBr_4^{-2}$ ion in Cs_2CuBr_4 indicate band maxima at 8000 ($\parallel$ to S_4 axis) and 7570 cm.$^{-1}$ ($\perp$). The ion is a flattened bisphenoid[35] of symmetry C_s (nearly D_{2d}), the distortion being greater[34] (average polar angle is 64°) than for Cs_2CuCl_4 (59°) and much greater than for Cs_2ZnBr_4[36] (56°), the polar angle for a tetrahedron being 54.7°. LCAO–MO

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[24] SCF eigenvalues are identical with ionization potentials if electronic and nuclear rearrangements are ignored; see T. Koopmans, *Physica*, **1**, 104 (1933).

[25] Nuclear positions are usually unchanged during an electronic transition; see J. Franck, *Trans. Faraday Soc.*, **21**, 536 (1925), and E. U. Condon, *Phys. Rev.*, **32**, 858 (1928).

[26] It was pointed out by R. Hoffman that since the calculated VCl_4 stabilization energy is only 0.001 e.v. out of a total orbital energy of approximately −500 e.v. (about 2 p.p.m.), some criterion for the *numerical* accuracy of the LCAO–MO computer program should be established. This has not been done, although the energy results given here are certainly reproducible to at least 1 p.p.m.

[27] A. G. Whittaker and D. M. Yost, *J. Chem. Phys.*, **17**, 188 (1949).

[28] L. E. Orgel, *ibid.*, **23**, 1004 (1955).

[29] The oscillator strengths are calculated in an approximation which assumes that all off-diagonal two-center matrix elements of the electric dipole operator r correspond to a vector directed to the mid-point of the two centers (exact for AO's identical except for position). This approximation, which enables the transition moments (off-diagonal matrix elements of r) to be expressed in terms of the MO coefficients and the AO overlap integrals, is identical with that made in the population analysis scheme used to obtain atomic charges, which divides the overlap contributions equally between the two AO's involved.

[30] See R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959, p. 215.

[31] C. Furlani and G. Morpurgo, *Theoret. chim. Acta* (Berlin), **1**, 102 (1963).

[32] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **27**, 436 (1954); for a discussion of the $CuCl_4^{-2}$ spectrum, see C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **29**, 4 (1954).

[33] See C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 92.

[34] A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962).

[35] B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960).

[36] B. Morosin and E. C. Lingafelter, *ibid.*, **12**, 744 (1959).

spectral assignments taken from those for $CuCl_4^{-2}$ (Table VI) are identical with the crystal field assignments[34] for the $CuBr_4^{-2}$ ion.

Summary.—It is concluded that the semi-empirical LCAO–MO scheme can be used to give a semiquantitative measure of the ground-state distortions and spectral splittings of transition metal complexes, especially one-electron and one-hole systems. It should be kept in mind that an observed distortion in a crystal does not necessarily result from the so-called Jahn–Teller effect, but may result from packing considerations, such as those giving rise to the trigonal distortion of the $V(OH_2)_6^{+3}$ ion in vanadium alum, which does not appear[3] to arise from Jahn–Teller considerations, even though the ion is in a spatially degenerate $^3T_{1g}$ state if octahedral.[37]

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[37] NOTE ADDED IN PROOF.—For new studies of the $NiCl_4^{-2}$ solution spectrum, see N. K. Hamer, *Mol. Phys.*, **6**, 257 (1963). For recent remarks on the VCl_4 electronic and vibrational spectra, see E. L. Grubb, F. A. Blankenship, and R. L. Belford, *J. Phys. Chem.*, **67**, 1562 (1963), and E. L. Grubb and R. L. Belford, *J. Chem. Phys.*, **39**, 244 (1963). A private communication from R. B. Johannesen informs us that electron paramagnetic resonance studies suggest that the VCl_4 molecule may be distorted in a solid solution of VCl_4 in $TiCl_4$, but the amount of the distortion is not clear. Finally, for optical spectra of Cu^{+2} in Cs_2ZnCl_4, see D. M. Gruen and R. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

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The Kinetics of the Oxidation of Iron(II) and its Substituted *tris*-(1,10-Phenanthroline) Complexes by Cerium(IV)[1,2]

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The kinetics of the oxidation of iron(II) and a number of its substituted tris-(1,10-phenanthroline) complexes by cerium(IV) have been investigated in sulfuric acid using a rapid-mixing and flow technique. The free energies of activation for the latter reactions were found to be related to their standard free energy changes. The rate constant for the oxidation of tris-(1,10-phenanthroline)-iron(II) by cerium(IV) increased with increasing sulfuric acid concentration. The second-order rate constant for the $Fe(phen)_3^{2+}$–Ce(IV) reaction in 0.50 F H_2SO_4 is 1.42×10^5 F^{-1} sec.$^{-1}$ at 25.0° with an activation energy of 6.5 kcal. mole^{-1}. The corresponding quantities for the Fe(II)–Ce(IV) reaction are 1.3×10^6 F^{-1} sec.$^{-1}$ and 9.5 kcal. mole^{-1}, respectively. The results are discussed in terms of the Marcus theory of electron-transfer reactions.

There are several examples of linear free energy relationships in electron-transfer reactions.[3–5] For instance, the free energies of activation for the oxidation of ferrous ions by a variety of substituted tris-(1,10-phenanthroline) complexes of iron(III) are linearly related to their standard free energy changes.[5] Such linear free energy relationships are predicted by the Marcus theory of electron-transfer reactions.[6,7]

In order to obtain additional information concerning the relationship between the rates and the free energy changes of oxidation–reduction reactions we have studied the kinetics of the oxidation of iron(II) and a number of its substituted tris-(1,10-phenanthroline) complexes by cerium(IV) in 0.50 F H_2SO_4. These studies include reactions with larger standard free energy changes than the Fe^{2+}–$Fe(phen)_3^{3+}$ studies. The results are examined in the light of the Marcus equations[8]

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \qquad (1)$$

or

$$\Delta G_{12}^* = 0.50\Delta G_1^* + 0.50\Delta G_2^* + 0.50\Delta G_{12}^\circ - 1.15\,RT \log f \qquad (2)$$

where

$$\log f = (\log K_{12})^2/4 \log (k_1 k_2/Z^2) \qquad (3)$$

In the above expressions k_{12} is the rate constant for the oxidation–reduction reaction, for example, the Fe^{2+}–$Fe(phen)_3^{3+}$ reaction, and K_{12} is the equilibrium constant for the same reaction. The rate constants k_1 and k_2 refer to the corresponding electron exchange reactions; in this instance the Fe^{2+}–Fe^{3+} and $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ exchange reactions. ΔG^* and ΔG° are the appropriate free energies of activation and standard free energy changes, respectively, and Z is the collision frequency of two uncharged molecules in solution. It is assumed to have a value of 10^{11} l. mole^{-1} sec.$^{-1}$. The above equations are applicable to outer-sphere electron-trans-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Based in part on the Ph.D. Thesis submitted by G. Dulz to Columbia University, New York, N. Y., 1962.

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[6] R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

[7] R. A. Marcus, *Can. J. Chem.*, **37**, 155 (1959).

[8] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).