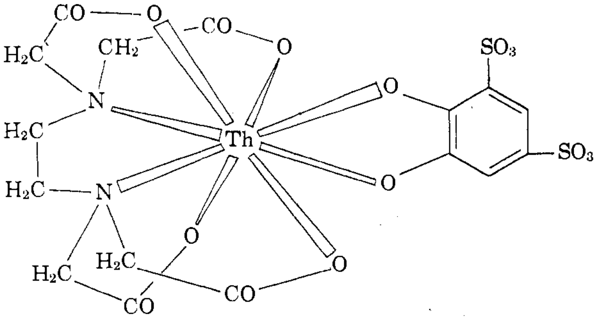
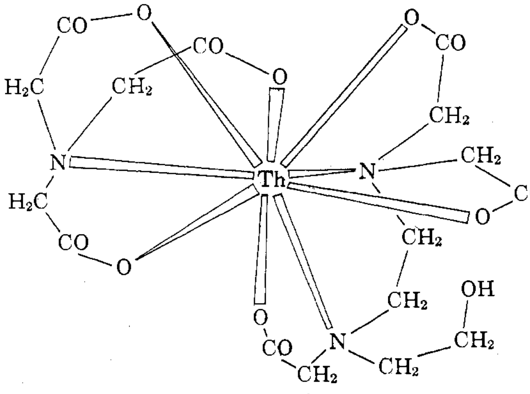
are so high that the mixed ligand is not formed to any detectable extent.

It has been noted in the present investigation that in the great majority of the mixed ligand chelates studied, the Th(IV) ion exhibits a coordination number of eight. Hence, the resulting Th(IV) mixed ligand complex will display a dodecahedron structure similar to that shown by I for the 1:1:1 Th(IV)–EDTA–Tiron complex.



I



II

However, both the 1:1:1 Th–EDTA–IMDA and the 1:1:1 Th–HEDTA–NTA systems indicate the possibility of the expansion of the coordination number of Th(IV) from a value of eight to that of nine Formation of an EDTA–IMDA mixed ligand chelate may be interpreted as involving the displacement of one of the carboxylate groups of EDTA to make way for the three donor groups of IMDA, thus keeping the total coordination of Th(IV) at eight. On the other hand, the relatively high stability constant for the addition of IMDA argues in favor of expansion of the coordination number of Th(IV) to nine. For the NTA–HEDTA mixed ligand chelate, it seems unlikely that one of the carboxylate groups of the pentadentate HEDTA anion is displaced from the coordination sphere of the metal ion, since that would leave one of the amino groups without an adjacent coordinated carboxylate group. Thus, since the nitrilotriacetate anion is probably quadridentate, the NTA–HEDTA mixed ligand chelate would involve nonacoordination of Th(IV) in aqueous solution, as is indicated by II. Although no structural data are available for nonacoordination in solution, the trigonal prism +3 structure chosen[12] seems to offer the greatest reduction in mutual repulsions between the negative carboxylate donor groups of the ligand and a reasonable arrangement of the metal chelate rings.

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[12] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, New York, N. Y., 1962, pp. 98–100.

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Distortions about Six-Coordinate Ferrous Ion[1a]

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The ionic model is used to account for possible tetragonal distortions of ferrous compounds. The near-infrared spectrum of FeF$_2$ is reported and analyzed. It is shown that distortions are not possible when the force constant for distortion is large as for example in the case of FeO. However, it is very likely that distortions of about 0.1 Å. do occur if the force constant is small as in the case of Fe(OH$_2$)$_6^{2+}$.

The consequences of the Jahn–Teller theorem for transition metal chemistry were first investigated by Van Vleck.[2] The Jahn–Teller effect is commonly considered to be difficult to establish. Of it Low[3] says "indeed it seems nearly a property of the Jahn–Teller effect that whenever one tries to find it, it eludes the possibility of being measured." However, the stereochemistry of Cu^{2+} (3d^9) and Mn^{3+} (3d^4) compounds offers the best evidence that Jahn–Teller distortions do occur; references to this work may be found in the very thorough review and topological treatment of the subject by Liehr.[4] These two ions in an octahedral field have orbital degeneracy in the e$_g$, σ antibonding component of the d subshell. It would be very interesting to discover if degeneracy in the t$_{2g}$, π antibonding component would lead to significant distortions. It is commonly assumed that such distortions if detectable at all would be difficult to estab-

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[1] (a) Supported by the National Science Foundation; (b) Alfred P. Sloan Foundation Fellow.

[2] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 72 (1939).

[3] W. Low, *Phys. Rev.*, **109**, 256 (1958).

[4] A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963).

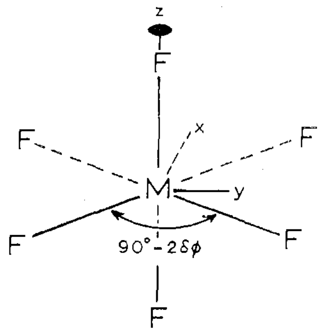

Fig. 1.—The structure of the first coordination sphere of the divalent metal fluorides.

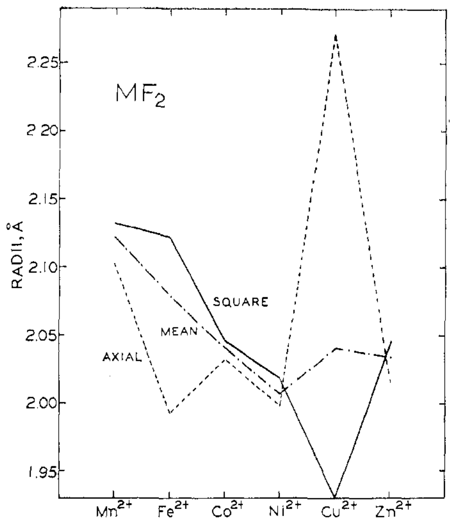

Fig. 2.—The metal–fluoride bond distances for the divalent metal fluorides (see text).

lish. The results of Low and Weger,[3,5,6] who studied the electron spin resonance of Fe^{2+} ($3d^6$) and Co^{2+} ($3d^7$) metal ion sites in cubic MgO crystals, did not conclusively establish the existence of distortions. Furthermore FeO at room temperature is cubic; distortions of antiferromagnets such as FeO below the Néel temperature are not relevant for the present discussion.[7]

The most conclusive evidence for Jahn–Teller distortions is provided by a series of compounds which are isomorphous and which should have very nearly the same structure except for distortions caused by differences in the number of electrons in the d subshell. Such a series is afforded by the fluorides MnF_2, FeF_2, CoF_2, NiF_2, (CuF_2), and ZnF_2. All of these compounds except for CuF_2[8] have the rutile structure.[9,10] The first coordination sphere of the metal ion in this structure is illustrated in Fig. 1; the site symmetry is D_{2h}. In addition to a slight angular distortion from octahedral symmetry the structure exhibits a characteristic axial compression: two fluoride ions are at a distance R_z somewhat shorter than four other fluoride ions at a distance R_{xy}. The CuF_2 structure although not strictly a rutile structure is similar and exhibits a very pronounced axial elongation. In Fig. 2 we plot the values of R_z and R_{xy} as well as the mean, R_{av}, of $^1/_3(R_z + 2R_{xy})$. If the electron distribution in the 3d subshell were spherically symmetric, then the average radii would be expected to lie on a straight line drawn through the points R_{av} for the $3d^5$ and $3d^{10}$ configurations; these hypothetical radii we refer to as R_0. The contraction $R_0 - R_{av}$ has been nicely accounted for by Hush and Pryce[11] in terms of the octahedral crystal field stabilization energy which gives rise to a force tending to contract the first coordination sphere in the totally symmetric "vibrational" mode.

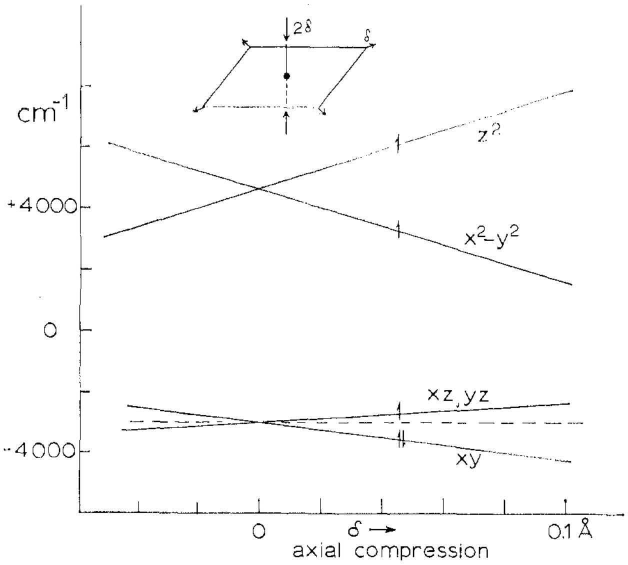

Fig. 3.—The splitting of $^2D(3d^1)$ in a tetragonal field as a function of the tetragonal distortion (note standard choice of coordinates).

In this paper we consider the tetragonal distortions from R_{av} for FeF_2 ($3d^6$). From Fig. 2 we can see that this distortion is quite significant. The sign of the distortion is opposite to that of CuF_2 as is to be expected since an orbitally nondegenerate ground state must result. In the ionic model which we adopt here, this distortion is caused by the tetragonal part of the crystal field potential. Recently a Hückel style molecular orbital treatment has been used to account for distortions of Cu^{2+} compounds.[12] The energy levels calculated for $CuCl_4^{2-}$ were in excellent qualitative agreement with those we measured for $CuBr_4^{2-}$ and calculated in the ionic model.[13] We feel that it is worthwhile to explore further the ionic model because of its simplicity and because, even at this late date in the development of the theory, the model has not been extensively tested for fields other than octahedral as a means of representing energy levels in terms of empirically measured radical parameters.

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(5) W. Low and M. Weger, *Phys. Rev.*, **118**, 1119 (1960).
(6) W. Low and M. Weger, *ibid.*, **118**, 1130 (1960).
(7) J. Kanamori, *J. Appl. Phys.*, **31**, 145 (1960).
(8) C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, **79**, 1049 (1957).
(9) W. Baur, *Naturwissenschaften*, **44**, 349 (1957).
(10) J. W. Stout and R. G. Shulman, *Phys. Rev.*, **118**, 1136 (1960).
(11) N. S. Hush and M. H. L. Pryce, *J. Chem. Phys.*, **26**, 143 (1957); **28**, 244 (1958).
(12) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **2**, 911 (1963).
(13) A. G. Karipides and T. S. Piper, *ibid.*, **1**, 970 (1962).

TABLE I

CRYSTAL FIELD MATRIX ELEMENTS

Element	Coefficients of the parameters ρ_n[a]			
	ρ_2xy	ρ_2z	ρ_4xy	ρ_4z
$(z^2\|V\|z^2)$	-4	$+4$	$+3$	$+4$
$(xy\|V\|xy)$	$+4$	-4	$+{}^1/_2 + {}^{35}/_6 \cos 4\delta\phi$	$+{}^2/_3$
$(x^2 - y^2\|V\|x^2 - y^2)$	$+4$	-4	$+{}^1/_2 - {}^{35}/_6 \cos 4\delta\phi$	$+{}^2/_3$
$(xz\|V\|xz)$	$-2 + 6 \sin 2\delta\phi$	$+2$	$-2 - {}^{10}/_3 \sin 2\delta\phi$	$-{}^8/_3$
$(yz\|V\|yz)$	$-2 - 6 \sin 2\delta\phi$	$+2$	$-2 + {}^{10}/_3 \sin 2\delta\phi$	$-{}^8/_3$
$(xy\|V\|z^2)$	$-4\sqrt{3} \sin 2\delta\phi$	0	$-(5/\sqrt{3}) \sin 2\delta\phi$	0

[a] Factor of $^1/_7$ omitted from each element in table.

Results

The Crystal Field Potential.—The effects of ions beyond the first coordination sphere are neglected. The crystal field matrix was calculated and is given in Table I for the field illustrated in Fig. 1. In this table the radial parameters ρ_n are $eZ\overline{r^n}/R^{n+1}$ where Z is the effective ligand charge, r is the d electron radius, and R is the internuclear metal–ligand distance. It is well known that these parameters are underestimated if $\overline{r^n}$ values are calculated using the best free ion 3d wave functions. We fit the ρ_n to the experimental data. Note that as defined the ρ_n have units of energy.

The Spectrum of FeF$_2$.—We have measured the spectrum of FeF_2 at 25° as a powder and as a polycrystalline mass. There are two well-resolved bands with maxima at 10,660 and 6990 cm.$^{-1}$ and with half-widths of 2500 and 1000 cm.$^{-1}$, respectively. We assign these transitions to the upper levels A_g and B_{1g}, respectively (in D_{2h}). The ground state is probably B_{1g}, although our calculation cannot rule out B_{3g} because of the very large digonal splitting of the tetragonal E_g level.

At this point we have four radial parameters to fit to two pieces of experimental data. For small displacements of the ligands we assume that the radial parameters ρ_n vary as $1/R^{n+1}$. This assumption and the matrix in Table I allow calculation of two radial parameters. In this way we find that $\rho_2(R_{av})$ is 9358 cm.$^{-1}$ and $\rho_4(R_{av})$ is 4598 cm.$^{-1}$, where R_{av} is 2.079 Å.

The Tetragonal Distortion.—We are now in a position to consider the Jahn–Teller effect. It would be ideal to treat the problem of ferrous fluoride for which we have an accurate crystal structure. However, this is a very complex problem as we have no straightforward way to evaluate the force constants of the various modes of distortion of a lattice as complicated as that of rutile. Therefore we choose to consider a simpler example—a gas phase complex with crystal field parameters derived from the spectrum of FeF_2; this complex is allowed to distort tetragonally. Since water has a crystal field very similar to the fluoride ion this example ought to inform us as to how the hexaaquoferrous ion will distort. We consider only axial compression since this is the simplest mode which resolves the orbital degeneracy and since it is observed in ferrous fluoride. The splitting of $^2D(3d^1)$ in such a tetragonal field is given in Fig. 3; the distortion coordinate δ is $^1/_2(R_{av} - R_z)$ or equally well $R_{xy} - R_{av}$. The crystal field potential was expanded in powers of δ and only linear terms were retained. The effect of spin–orbit splitting on the ground state $^5T_2$ (from ^5D of $3d^6$) is illustrated in Fig. 4. We took the spin–orbit coupling constant to be 90% of the free ion value 103 cm.$^{-1}$. We used the spin–orbit matrix of Low and Weger.[5] The unfactored 25×25 matrix retaining only first-order terms in λ but retaining potential terms connecting ^5E_g to $^5T_2$ was solved by computer methods. Finally from results of Fig. 4 we computed the tetragonal stabilization energy of the lowest lying spin–orbit component as a function of δ and added to this the elastic potential energy $^1/_2k\delta^2$ for a variety of force constants k; the resulting net potential energy is plotted in Fig. 5.

Discussion

From Fig. 3 we can readily see that the driving force to distortion, that is, the derivative of the potential with respect to δ, is considerably larger for degeneracy in the e_g level than for degeneracy in the t_{2g} level. The ratio of slopes is about 2.5. Thus with similar complexes of say Fe^{2+}, Cr^{2+}, Cu^{2+} we can expect that the distortion of the d^4 or d^9 complexes will be two or three times as large as that of the d^6 complex. One would be led to the same conclusion in qualitative terms by the molecular orbital model since σ-bonding ought to be stronger than π-bonding.

Now consider the effect of spin–orbit coupling on the energy levels for $3d^6$. Van Vleck[14] has pointed out that the Jahn–Teller matrix element, that is, the derivative of the potential linear in δ, is zero for the ground spin–orbit triplet. This is readily verified in Fig. 4 in that the initial slope of this triplet is zero. However, this small region of zero slope has no significant effect on the net Jahn–Teller plus elastic potential energy curves illustrated in Fig. 5. This we might have anticipated in any case since the spin–orbit coupling constant is quite small. We conclude that the lack of a Jahn–Teller effect in a ferrous compound cannot be ascribed to the spin–orbit splitting of the ground state.

Now let us consider why Jahn–Teller effects are not commonly observed in ferrous compounds. As examples we may cite $KFeF_3$ and cubic ferrous oxide at room temperature. By differentiation of the lattice energy of FeO we can estimate a value of the force constant for the totally symmetric distortion; the result is 14.4 mdynes/Å. The force constant for the tetragonal mode assumed in Fig. 3 and 4 will not be much different from this value. From Fig. 5 we see that for force con-

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(14) J. H. Van Vleck, *Physica*, **26**, 544 (1960).

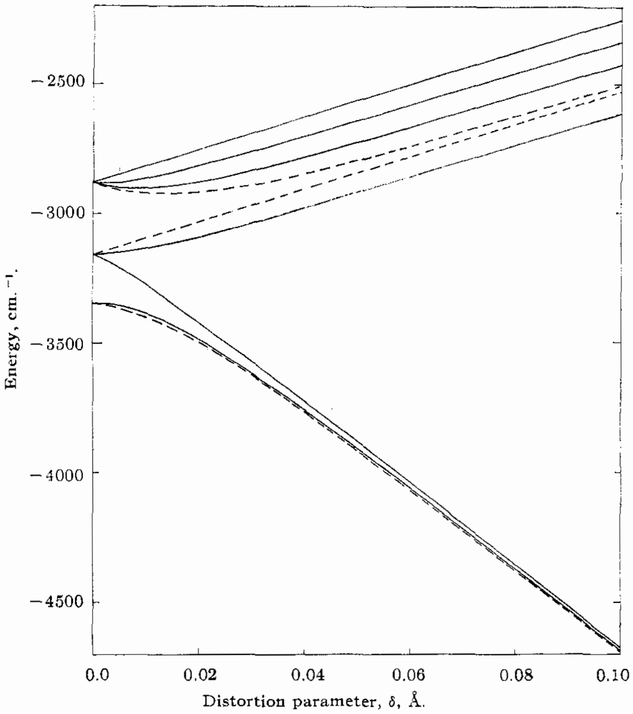

Fig. 4.—The effect of spin-orbit splitting of the $^5T_2$ ground state as a function of the tetragonal distortion. The dashed lines represent nondegenerate states, the solid, doubly degenerate states.

stants greater than about 10 mdynes/Å. the minimum in the potential energy is less than kT at room temperature, about 200 cm.$^{-1}$. Thus thermal averaging of the structure to octahedral symmetry will occur. At lower temperatures the situation is complicated by "antiferromagnetic" distortions. In $KFeF_3$ the resistance to distortion is increased by the lattice energy of the added potassium and fluoride ions.

The absence of distortions about the ferrous ions substituted in cubic MgO[3,5,6] is also explicable in terms of this model. For distortions to occur the ferrous ions would have to do work against the full lattice potential of the crystal since the cations do not cooperate in the distortion.

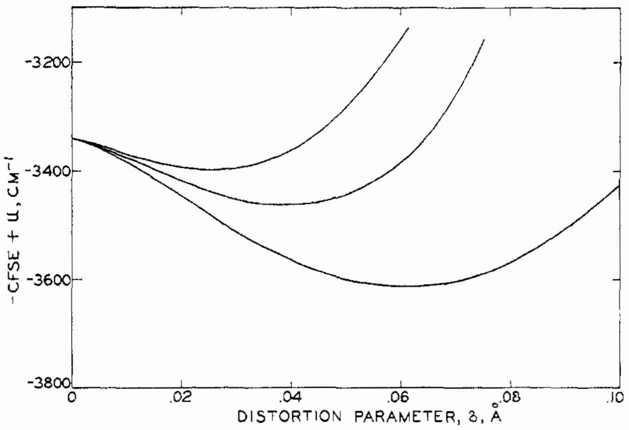

Fig. 5.—Net potential energy (−CFSE + U) as a function of the tetragonal distortion for a variety of force constants. The lower curve is for k = 5 mdynes/Å., the middle curve for 7.5 mdynes/Å., and the top curve for 10 mdynes/Å.

Finally, let us consider the hexaaquoferrous ion. Hush and Pryce[11] have estimated the force constant for the totally symmetric mode to be about 1.12 mdynes/Å. This seems a bit low to us. The force constant for the tetragonal mode is typically about 20% smaller than that of the A_{1g} mode. From a curve such as those shown in Fig. 5 we find that the equilibrium value of δ lies between 0.3 and 0.15 Å. for a force constant between 1 and 2 mdynes/Å. Furthermore, the potential minimum lies well below kT. We conclude that the ferrous ion in aqueous solution should exhibit significant distortion. Crystal structure evidence on this score is meager; it is difficult to sort out distortions due to electronic effects from those of the lattice anions such as SO_4^{2-}. The spectrum of aqueous ferrous ion shows some splitting of the band in the near-infrared,[15] although not as much as the solid fluoride. We believe that a static distortion may account for much if not all of this observed spectral splitting.

[15] F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

Contribution No. 970 from the Central Research Department and Explosives Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Five-Coordinate Stereochemistry

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N.m.r. data for a series of five-coordinate species are presented and discussed in terms of structure and exchange processes. Trigonal bipyramidal geometry prevails in these compounds, at least for the liquid or solution state, and the more electronegative ligands prefer the axial positions. Intramolecular ligand exchange is a common phenomenon in these structures.

In an earlier article,[1] we presented n.m.r. data for a group of substituted phosphorus(V) fluorides. These data were interpreted in terms of trigonal bipyramidal geometry with occupancy of axial sites by the most electronegative ligands. A case was also made for the susceptibility of five-coordinate structures to fast *intramolecular* positional exchange of ligands. We have now completed a further study of five-coordinate

[1] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).