# STEREOCHEMISTRY OF IONIC SOLIDS

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## I. Introduction

Once upon a time it was believed that the structures of most binary solid compounds of the metals, other than alloys and related substances, could be described adequately in terms of an ionic model in which metal ions and anions are treated as charged, more or less compressible, spheres. This model leads to a classical electrostatic theory of bonding and is relatively well understood. Naturally, modern developments in valency theory have tended to emphasize those situations in which a simple ionic theory is inadequate and so have occasionally led to the multiplication of hypotheses to explain observations which could just as well be interpreted in terms of an electrostatic theory. This has tended to obscure the fact that the ionic model still forms a satisfactory background to a great part of the theory of the stereochemistry of metal compounds.

In this review we shall emphasize the ionic viewpoint, but not because we are unaware of the importance of covalent bonding. We believe that only after the irrelevance of much that has been presented as qualitative stereochemical evidence for covalency has been appreciated, does the importance of quantitative studies, for example of unpaired electron distributions by paramagnetic resonance experiments, become clear. Our program, then, is to interpret as many features as possible of the stereochemistry of metal compounds from the point of view of an ionic theory; and only incidentally to draw attention to the modifications that are required if the covalent effects (which, to a greater or lesser extent, influence the properties of all compounds) are to be taken into account.

We shall for the most part illustrate our general arguments by examples of typically "ionic" solids; oxides, halides, hydrates, etc. However, it must be appreciated that factors important in determining the structures of ionic solids also decide the stereochemistry of discrete molecules and complex ions. We shall not, therefore, hesitate to discuss the stereochemistry of isolated molecules or complex ions in solution insofar as they are relevant to the general problem of the stereochemistry of metal ions.

## II. Ionic Coordination Polyhedra *(76, 147)*

We first examine the implications of a very much oversimplified ionic theory. We suppose that:

(1) Ions are charged, incompressible, nonpolarizable spheres.

(2) An arrangement of ions of one charge about an ion of the opposite charge is stable only if the central ion is in contact with each of its neighbors. This places a lower limit to the ratio of the radius of the central ion to that of the surrounding ions for each type of coordination polyhedron (Table I). Since positive ions are almost always smaller than the negative ions which accompany them in crystals this restriction means effectively that the coordination number of small metal ions is often limited by the radius ratio rules, while the coordination numbers of anions are rarely limited in this way.

(3) The coordination number is as large as possible, subject to condition (2). Of course, the coordination number may also be restricted by the composition of the substance if it is necessarily present as discrete molecules, for example $TiCl_4$ in the gas phase.

(4) The arrangement of the coordinated groups minimizes the electrostatic repulsion energy between them.

It follows from (4) that an ideal $MX_2$ complex should be linear, for this is the arrangement which maximizes the X-X distance and so minimizes the electrostatic repulsion between X ions. In a similar way the repulsion between X ions in an $MX_3$ complex is minimized if the molecule is planar and the X ions are at the vertices of an equilateral triangle. There are two other cases in which the preferred configuration depends only on symmetry, namely $MX_4$ and $MX_6$ complexes which should adopt regular tetrahedral and regular octahedral structures respectively. These symmetry determined arrangements are illustrated in Fig. 1.

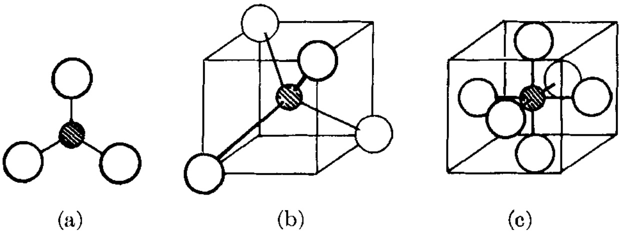


FIG. 1. Symmetry determined coordination polyhedra: (a) planar equilateral triangle, (b) tetrahedron, (c) octahedron.

In all other important cases the optimum configuration is not determined by symmetry alone. Although it is possible to arrange eight equivalent X anions at the vertices of a cube about a central M ion as in Fig. 2a, this is not the configuration which minimizes the electrostatic repulsion energy, for clearly the square antiprism shown in Fig. 2b is more favorable.

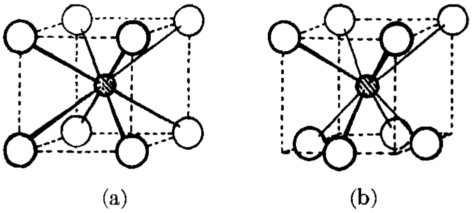


FIG. 2. Possible arrangements for 8-coordination: (a) cube (the CsCl structure), (b) square Archimidean antiprism.

The only configurations of $MX_5$, $MX_7$, and $MX_9$ groups which maintain the equivalence of all MX bonds are the energetically unfavorable planar ones. Some of the configurations which lead to relatively favorable electrostatic energies are illustrated in Fig. 3.

So far we have made use of condition (4) to determine the ideal configuration for each type of $MX_n$ complex. Now we must determine for each coordination number the values of the ratios of the radii $r_M$ and $r_X$ of the M and X ions which are consistent with (2) and (3). Clearly a linear $MX_2$ arrangement (but not a nonlinear one) satisfies (3) for any value of the radius ratio. On the other hand in a planar $MX_3$ complex the M ion would "rattle" inside the triangle of X ions if the ratio $r_M/r_X$ of the two ions were less than 0.155. Thus according to (2) a very small A ion cannot form an $MX_3$ complex with a large X ion, but must instead form an $MX_2$ complex.

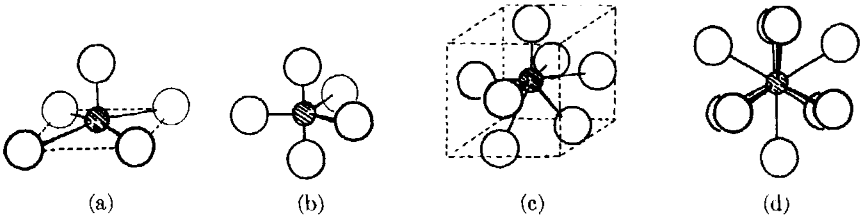


FIG. 3. Some favorable arrangements for $MX_5$, $MX_7$, and $MX_9$ groups: (a) square pyramid (note that the square of ligands is not necessarily coplanar with the metal ion), (b) trigonal bipyramid, (c) octahedron distorted by expanding one face and inserting an extra ligand on the line through its center, (d) trigonal prism with additional ligands on the lines through the centers of the three rectangular faces.

In the same way it follows from (3) that an $MX_3$ complex should only be stable if the radius ratio lies in the range $0.155 \leqslant r_M/r_X \leqslant 0.225$. Proceeding in this way we can derive the ranges of the radius ratio consistent with each type of coordination as shown in Table I.

TABLE I

LIMITING RADIUS RATIOS FOR VARIOUS COORDINATION POLYHEDRA

| Polyhedron | Coordination number | Minimum radius ratio |
|---|---|---|
| Equilateral triangle | 3 | 0.155 |
| Tetrahedron | 4 | 0.225 |
| Trigonal biprism | 5 | 0.414 |
| Square pyramid | 5 | 0.414 |
| Octahedron | 6 | 0.414 |
| Square Archimidean antiprism | 8 | 0.645 |
| Cube | 8 | 0.732 |

The $MX_5$ complex may now be considered in the light of conditions (2) and (3). In a trigonal bipyramid the angle between axial and radial bonds is just 90°, that is the X-X distance is no smaller than in the octahedron. Thus (3) leads us to expect that the octahedron will be preferred to the trigonal pyramid. An exactly similar argument shows that the octahedron will also be preferred to a square prism. Thus, except in isolated molecules or ions, we should not expect to find $MX_5$ arrangements.

This discussion shows that the widespread occurrence of regular tetrahedrally and octahedrally coordinated metal ions calls for no special interpretation in terms of bond hybridization, and so forth. It is rather the other four or six coordinated structures which require explanation; for example, we shall need a special explanation of the widespread occurrence of planar coordination among the compounds containing the $Ni^{++}$, $Pd^{++}$ and $Pt^{++}$ ions.

The arguments from electrostatic theory apply formally only to substances made up from monoatomic ions. However, there is reason to believe that they are qualitatively correct in a much less restricted context. Thus, although it cannot be proved generally and rigorously, it is very plausible that regular octahedral and tetrahedral coordination are the preferred arrangements for the disposition of most dipolar molecules or polyatomic anions around a central positive ion. They are simply the arrangements which place the ligands as far apart as possible, and since ligands usually repel one another they are to be expected if the metal ion behaves as a spherically symmetric charge distribution. Thus the octahedral character of $[Co(NH_3)_6]^{3+}$ no more *implies* covalent binding than does the octahedral environment of $Na^+$ in NaCl. Conversely, the planarity of $[Pt(NH_3)_4]^{++}$ requires comment in just the same way as does the square coplanar environment of $Pt^{++}$ in PtO.

## III. Simple Ionic Compounds

The compounds which according to almost any theory should be the most nearly ionic in character are the alkali halides. It is, therefore, particularly interesting to compare their structures with those predicted by our simple theory. We see in Table II that only the NaCl rocksalt (Fig. 4) and the CsCl structures (Fig. 2a) occur. In the NaCl structure each cation is surrounded by a regular octahedron of anions and each anion by a regular octahedron of cations, and the structure conforms to our deductions about stable coordination polyhedra. On the other hand, the coordination about

TABLE II
RADIUS RATIOS AND CRYSTAL STRUCTURES OF ALKALI HALIDES (*150*). WHERE TWO STRUCTURES ARE LISTED, THE FIRST REPRESENTS THE STABLE MODIFICATION

| | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| F | 0.44[a] | 0.70[a] | 0.98[a] | 1.09[a] | 1.24[a] |
| Cl | 0.33[a] | 0.52[a] | 0.73[a] | 0.82[a,b] | 0.93[b,a] |
| Br | 0.31[a] | 0.49[a] | 0.68[a] | 0.76[a] | 0.87[b] |
| I | 0.28[a] | 0.44[a] | 0.62[a] | 0.69[a] | 0.78[b] |

[a] Rocksalt structure (Fig. 4).

[b] CsCl structure (Fig. 2a).

each ion in the CsCl structure is cubic and so does not correspond to the ideal arrangement for isolated $AB_8$ groups.

A study of a number of other compounds which are generally considered to be among the most completely ionic shows that cubic coordination is not confined to the alkali halides. It occurs, for example, in the fluorite structure in which many ionic $MX_2$ compounds crystallize. On the other hand the isolated $[TaF_8]^{3-}$ group has the square antiprism arrangement (*64*) predicted by the simple theory. This underlines a point of great importance to the understanding of ionic crystal structures, namely, that the requirement that a structure can be extended indefinitely in space imposes severe restrictions on the types of coordination which are possible. Cubic coordination can be extended indefinitely, but it is not possible to form an extended structure in which every ion is surrounded by a square antiprism of ions of the opposite charge. Thus a cubic structure is stable for a crystal as a whole, although it does not provide individual ions with their optimum environments; the stability of individual coordination polyhedra is sacrificed in the interest of long-range order.

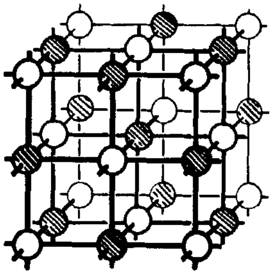


FIG. 4. The rocksalt structure.

To proceed further with our comparison of theory with experiment we require values of the radii of the ions concerned. The values recommended by Pauling (*114*) are given in Table III and a discussion of their derivation in the Appendix.

A comparison of the limiting radius-ratio values given in Table I with the radius ratios of alkali halides in Table II shows that the observed structures are not always as predicted. According to the simple theory, the rocksalt structure should be stable only within the range $0.414 \leqslant r_M/r_X \leqslant 0.732$. Thus LiCl (0.33), LiBr (0.31), and LiI (0.28) should have tetrahedrally coordinated structures, while KF (0.98), RbF (1.09), and CsF (1.24) should have eight or twelve coordinated structures. These disagreements are perhaps not surprising in view of the crudeness of the approximations involved, but more realistic models do not lead immediately to an explanation of the persistence of the rocksalt structure not only in the alkali

TABLE III

CRYSTAL RADII AND UNIVALENT CRYSTAL RADII (IN BRACKETS) OF CERTAIN IONS, AFTER PAULING (*114*). VALUES IN ANGSTROM UNITS

| | | |
|---|---|---|
| $Li^+$ 0.60 | $Be^{++}$ 0.31 [0.44] | $Al^{3+}$ 0.50 [0.72] |
| $Na^+$ 0.95 | $Mg^{++}$ 0.65 [0.82] | $Sc^{3+}$ 0.81 [1.06] |
| $K^+$ 1.33 | $Ca^{++}$ 0.99 [1.18] | $Y^{3+}$ 0.93 [1.20] |
| $Rb^+$ 1.48 | $Sr^{++}$ 1.13 [1.32] | $La^{3+}$ 1.15 [1.39] |
| $Cs^+$ 1.69 | $Ba^{++}$ 1.35 [1.53] | $Ga^{3+}$ 0.62 [0.81] |
| $Cu^+$ 0.96 | $Zn^{++}$ 0.74 [0.88] | $In^{3+}$ 0.81 [1.04] |
| $Ag^+$ 1.26 | $Cd^{++}$ 0.97 [1.14] | $Tl^{3+}$ 0.95 [1.15] |
| $Au^+$ 1.37 | $Hg^{++}$ 1.10 [1.25] | |
| $Ti^{4+}$ 0.68 [0.96] | $F^-$ 1.36 | $O^{--}$ 1.40 [1.76] |
| $Zr^{4+}$ 0.80 [1.09] | $Cl^-$ 1.81 | $S^{--}$ 1.84 [2.19] |
| $Ce^{4+}$ 1.01 [1.27] | $Br^-$ 1.95 | |
| $Ge^{4+}$ 0.53 [0.76] | $I^-$ 2.16 | |
| $Sn^{4+}$ 0.71 [0.96] | | |
| $Pb^{4+}$ 0.84 [1.06] | | |
| | Empirical ionic radii | |
| $Tl^+$ 1.44 | $Mn^{++}$ 0.80 | $Ti^{3+}$ 0.69 |
| | $Fe^{++}$ 0.75 | $V^{3+}$ 0.66 |
| | $Co^{++}$ 0.72 | $Cr^{3+}$ 0.64 |
| | $Ni^{++}$ 0.70 | $Mn^{3+}$ 0.62 |
| | | $Fe^{3+}$ 0.60 |

halides but also in silver halides, including AgF (0.93), and in oxides and sulfides of the alkaline earths, and of many other divalent metal ions, often with radius ratios far outside the predicted limits (Table IV). On the other hand, the CsCl structure is confined under ordinary conditions to CsCl, CsBr, CsI, and the ammonium halides (where it is stabilized by a favorable hydrogen bonding arrangement). Since the Madelung constant for this structure is somewhat greater than for the 6-coordinated (1.763 compared with 1.746), one would certainly expect its more widespread occurrence in compounds with suitable radius ratios than is observed.

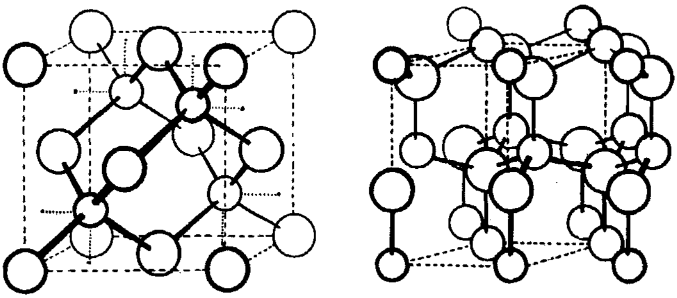
The most important MX structures involving tetrahedral coordination are the cubic ZnS sphalerite (Fig. 5a) and the hexagonal ZnS wurtzite (Fig. 5b) arrangements. It is striking that halides and sulfides of metal ions with $d^5$ and $d^{10}$ shells have a tendency to crystallize in the sphalerite structure; for example, the cuprous halides, AgI, HgS, MnS, CdS, and ZnS. (The last three also occur in the wurtzite modification, as do the oxides of Zn and Be). (See Table V.) Here again, the simple ionic theory fails to account for the facts for (1) the radius ratios of some of these compounds are compatible with a 6-coordinated structure, and (2) interatomic distances calculated from the usual ionic radii (decreased by 5% to com-

TABLE IV

SOME IONIC CRYSTALS WITH THE ROCKSALT STRUCTURE (*150*)

| Compound | M-X (Å) | Ionic radius sum (Å) | $r_M/r_X$ | Compound | M-X (Å) | Ionic radius sum (Å) | $r_M/r_X$ |
|---|---|---|---|---|---|---|---|
| LiF | 2.01 | 1.96 | 0.44 | MgO | 2.10 | 2.05 | 0.46 |
| LiCl | 2.57 | 2.41 | 0.33 | CaO | 2.41 | 2.39 | 0.71 |
| LiBr | 2.75 | 2.55 | 0.31 | SrO | 2.57 | 2.53 | 0.81 |
| LiI | 3.00 | 2.76 | 0.28 | BaO | 2.76 | 2.75 | 0.96 |
| NaF | 2.31 | 2.31 | 0.70 | TiO | 2.12 | — | — |
| NaCl | 2.81 | 2.76 | 0.52 | VO | 2.04 | — | — |
| NaBr | 2.98 | 2.90 | 0.49 | MnO | 2.22 | 2.20 | 0.57 |
| NaI | 3.23 | 3.11 | 0.44 | FeO | 2.16 | 2.15 | 0.53 |
| KF | 2.67 | 2.69 | 0.98 | CoO | 2.13 | 2.12 | 0.51 |
| KCl | 3.14 | 3.14 | 0.73 | NiO | 2.10 | 2.10 | 0.50 |
| KBr | 3.29 | 3.28 | 0.68 | CdO | 2.35 | 2.37 | 0.69 |
| KI | 3.52 | 3.49 | 0.62 | TaO | 2.21 | — | — |
| RbF | 2.82 | 2.84 | 1.09 | | | | |
| RbCl | 3.27 | 3.29 | 0.82 | | | | |
| RbBr | 3.43 | 3.43 | 0.76 | MnS | 2.61 | 2.64 | 0.43 |
| RbI | 3.66 | 3.64 | 0.69 | PbS | 2.96 | — | — |
| CsF | 3.00 | 3.05 | 1.24 | | | | |
| CsCl | 3.51 | 3.50 | 0.93 | | | | |
| AgF | 2.46 | 2.62 | 0.93 | | | | |
| AgCl | 2.77 | 3.07 | 0.70 | | | | |
| AgBr | 2.89 | 3.21 | 0.65 | | | | |

pensate for the change from 6- to 4-coordination) do not agree with the observed distances in a number of cases. The largest discrepancies are observed for compounds of $Cu^+$, $Ag^+$, and $Hg^{++}$, and, as we shall show in a later section, it is just for these cations that deviations from the predictions of the simple ionic picture should be most marked. However a satisfactory and detailed interpretation of these structures is still wanting.



(a) (b)

FIG. 5. Tetrahedrally coordinated MX structures; (a) sphalerite, (b) wurtzite.

TABLE V

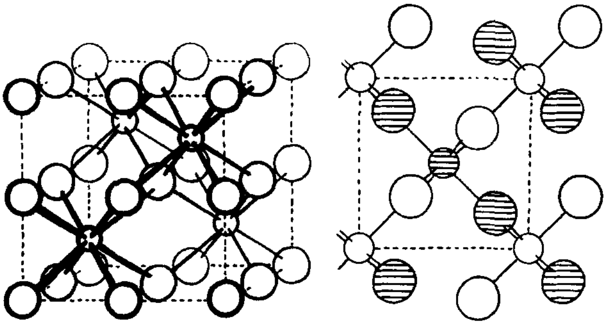
SOME CRYSTALS WITH TETRAHEDRALLY COORDINATED STRUCTURES (*150*)[a]

| Compound | Sphalerite M-X (Å) | Wurtzite M-X (Å) | Ionic radius sum[b] (Å) | $r_M/r_X$ |
|---|---|---|---|---|
| BeO | — | 1.64, 1.65 | 1.62 | 0.22 |
| BeS | 2.10 | — | 2.04 | 0.17 |
| ZnO | — | 1.95, 1.98 | 2.03 | 0.53 |
| ZnS | 2.36 | 2.33, 2.33 | 2.45 | 0.40 |
| CdS | 2.52 | 2.51, 2.53 | 2.67 | 0.53 |
| HgS | 2.53 | — | 2.79 | 0.60 |
| MnS | 2.43 | 2.41, 2.44 | 2.50 | 0.43 |
| CuF | 1.85 | — | 2.20 | 0.71 |
| CuCl | 2.35 | — | 2.63 | 0.53 |
| CuBr | 2.46 | — | 2.76 | 0.49 |
| CuI | 2.62 | — | 2.96 | 0.44 |
| AgI | 2.80 | — | 3.24 | 0.58 |

[a] The interatomic distances in these compounds can be closely reproduced by a special set of covalent radii (*114*, p. 179).

[b] The ionic radius sum has been multiplied by 0.95 to allow for the change from 6- to 4-coordination (see Appendix).

When we turn to ionic solids of the composition $MX_2$ we find that predictions based on the simple ionic model are fulfilled surprisingly well. The two principal structural types are illustrated in Fig. 6. In the fluorite structure, the cation M is surrounded by 8 anions in a cubic arrangement, and the anion X is surrounded by 4 cations at the corners of a tetrahedron. We expect this structure to be stable only for values of the radius ratio greater than 0.73 and in general this is the case. Moreover, the observed M-X



(a) (b)

FIG. 6. Ionic $MX_2$ structures (a) fluorite (b) rutile. In (b) the shaded and unshaded atoms occur in alternate layers separated by about 1.5–1.7 Å.

distances agree well with those calculated from the ionic radii (Table VI). For only one crystal $ZrO_2$ (0.62), is the radius ratio smaller than the required minimum, and it is noteworthy that it adopts the fluorite structure only in an unstable high-temperature modification. The alkali metal oxides, $M_2O$ (except $Cs_2O$), crystallize in the so-called "antifluorite" arrangement, in which the positions of anions and cations are reversed relative to those in the fluorite structure.

TABLE VI
SOME CRYSTALS WITH THE 8-COORDINATED FLUORITE STRUCTURE (*150*)[a]

| Compound | M-X (Å) | Ionic radius sum (Å) | $r_M/r_X$ |
|---|---|---|---|
| $CaF_2$ | 2.36 | 2.35 | 0.87 |
| $SrF_2$ | 2.51 | 2.49 | 0.97 |
| $BaF_2$ | 2.68 | 2.71 | 1.13 |
| $CdF_2$ | 2.33 | 2.33 | 0.84 |
| $PbF_2$ | 2.56 | — | — |
| $HgF_2$ | 2.40 | 2.46 | 0.92 |
| $SrCl_2$ | 3.02 | 2.94 | 0.73 |
| $BaCl_2$ | 3.18 | 3.16 | 0.84 |
| $ThO_2$ | 2.42 | — | — |
| $UO_2$ | 2.37 | — | — |
| $CeO_2$ | 2.34 | 2.41 | 0.72 |
| $PrO_2$ | 2.32 | — | — |
| $HfO_2$ | 2.21 | — | — |
| $ZrO_2$ | 2.19 | 2.20 | 0.62 |

[a] The radius ratios are calculated from the univalent radii (see Appendix and ref. *114*, p. 365).

Fluorides and oxides of composition $MX_2$ adopt the 6-coordinated rutile structure when the radius ratio is less than the critical value, 0.73. Since this structure is tetragonal, the crystal symmetry does not impose a perfectly regular octahedral environment on the metal ions. Nevertheless, the observed deviations are usually quite small (Table VII). The largest deviation from octahedral symmetry occurs in $FeF_2$, where, according to a recent analysis (*9*), four bonds in a plane are significantly longer (0.13 Å) than the remaining two axial bonds. We shall return to this point in a later section. The rutile structure should be unstable if the radius ratio is less than 0.414 and accordingly we find that $GeO_2$ with $r_M/r_X$ on the limit crystallizes also in the tetrahedrally coordinated quartz structure (*150*).

Quite different octahedrally coordinated structures are observed in the bromides, iodides (and some chlorides) of divalent metal ions with suitable radius ratios. In these, the $MX_6$ octahedra are not linked in a three-dimensional network but in two-dimensional sheets, separated from each other only by anion-anion contacts. The halide ions are thus shielded from each other by cations on one side only. This type of structure is incompatible with the simple ionic model but is readily understood in terms of Van der Waals attraction between the large, highly polarizable, anions if it is supposed that the charge on the anions has been greatly reduced by polarization or covalent bonding.

TABLE VII

SOME CRYSTALS WITH THE 6-COORDINATED RUTILE STRUCTURE[a]

| Compound | M-X (Å) | Ionic radius sum (Å) | $r_M/r_X$ |
|---|---|---|---|
| $MnF_2$ (*9*) | 2.13, 2.10 | 2.16 | 0.59 |
| $FeF_2$ (*9*) | 2.12, 1.99 | 2.11 | 0.55 |
| $CoF_2$ (*9*) | 2.05, 2.03 | 2.08 | 0.53 |
| $NiF_2$ (*9*) | 2.02, 1.99 | 2.06 | 0.52 |
| $ZnF_2$ (*9*) | 2.04, 2.02 | 2.10 | 0.54 |
| $MgF_2$ (*8*) | 2.00, 1.98 | 2.01 | 0.48 [0.60] |
| $PdF_2$ (*7*) | 2.16, 2.17 | — | — |
| $TiO_2$ (*8*) | 1.94, 1.99 | 2.08 | 0.49 [0.55] |
| $SnO_2$ (*8*) | 2.05, 2.06 | 2.11 | 0.51 [0.55] |
| $GeO_2$ (*8*) | 1.87, 1.91 | 1.93 | 0.38 [0.43] |

[a] Bracketed values of $r_M/r_X$ are calculated from the univalent radii.

Our review of simple ionic compounds shows that the radius-ratio rules are a useful guide to the stereochemistry of halides and oxides, but that the quantitative predictions are not to be taken too seriously. This is no doubt in part attributable to the crudeness of the model from which the rules are derived, and in part to uncertainties in the values of the ionic radii. There are many examples in which the coordination number increases with increasing radius of the metal ion in closely related compounds; for example, $Mg^{++}$ in $MgF_2$ is 6-coordinated but $CaF_2$ has an 8-coordinated structure. It is in accounting, at least semiquantitatively, for such relations that the radius-ratio rules are most important.

In the simple structures which we have discussed so far the local environment of the central metal ion has been tetrahedral, octahedral, or cubic. We can describe all of these as being of cubic symmetry since they include some or all of the characteristic symmetry elements of a cube. They possess the maximum symmetry compatible with the coordination number and, with the reservations already noted for eightfold coordination, are just those environments which would follow from the properties of the simple ionic model described in the previous section. There are many structures where the symmetry of the local environment of the central metal ion is lower than cubic. We shall discuss some of these in the following sections, and shall usually adopt the view that they correspond to *distortions* from the cubic symmetry which is to be expected from the simple ionic model.

## IV. The Influence of Crystal Fields on Transition-Metal Stereochemistry

In this section we shall develop the electrostatic crystal-field theory to a sufficient extent to give an account of its stereochemical implications particularly with reference to the distortions from cubic symmetry which are characteristic of certain groups of transition-metal compounds. The treatment is not meant to be complete and the reader is referred to the many reviews (*51*, *72*, *97*, *102*, *106*) for detailed references, derivations, qualifications, disputations, and applications.

According to this theory, a transition-metal ion in a compound or complex is supposed to be subjected to an electrostatic field produced by the molecules and ions in its environment, particularly those in its first coordination sphere. Since the ligands which we consider are invariably either negative ions or polar molecules so oriented that their unshared pairs point directly at the metal ion, the field is always roughly equivalent to that due to a set of negative point charges placed about the metal. The electrostatic theory is concerned with the effect of this field on the orbital energies of the metal $d$ electrons.

### A. OCTAHEDRAL COORDINATION

We consider first an octahedral arrangement of negative charges about the metal. The five $d$ orbitals have the forms indicated in Fig. 7, in which the coordinate axes are taken to lie along the bond directions. It is clear that the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals have substantial amplitudes in the bond directions, but that the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals tend to avoid these directions. The energy of an electron in the $d_{z^2}$ or $d_{x^2-y^2}$ orbitals will therefore be raised substantially by the repulsive field of the ligands while the energy of an electron in the $d_{xy}$, $d_{yz}$, or $d_{xz}$ orbitals will be less affected. It is obvious that $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals have an identical environment and hence are degenerate, that is, they have the same energy. And it can be shown by group theory or by direct calculation that the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are also degenerate. Thus the five $d$ orbitals in an octahedral field split into two groups, a lower group of three and an upper group of two, the two groups usually being designated by the labels $t_{2g}$ and $e_g$ respectively (or sometimes by $\gamma_5$ and $\gamma_3$ or by $d_\epsilon$ and $d_\gamma$ respectively). The energy separation between

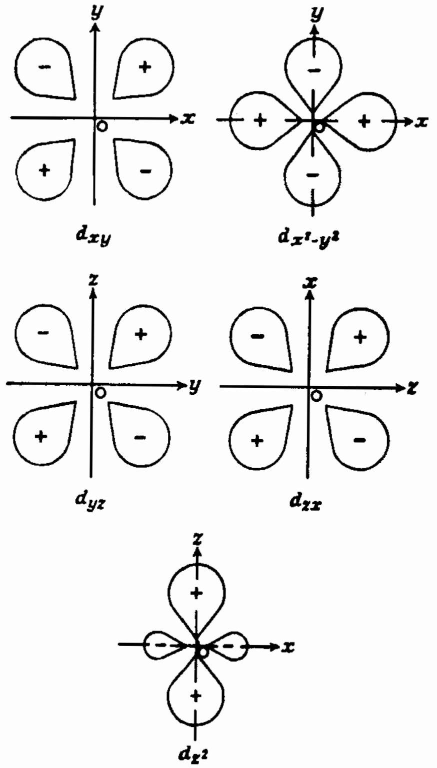


Fig. 7. Cross sections of the five *d* orbitals chosen in real form (*51*, Fig. 1).

the two groups of orbitals is usually designated as $\Delta$, and the energies of the individual orbitals are

$$E(t_{2g}) = -\frac{2}{5}\Delta \qquad \text{and} \qquad E(e_g) = +\frac{3}{5}\Delta$$

referred to the weighted mean energy in the electrostatic field as zero.

We now consider the distribution of electrons on metal ions in octahedral environments. If only one *d* electron is present it must clearly occupy one of the more stable set of $t_{2g}$ orbitals. If more than one *d* electron is present, however, complications may arise for in such cases there are two competing tendencies at work.

(1). The electrons tend, as far as possible, to occupy the more stable $t_{2g}$ orbitals in preference to the less stable $e_g$ orbitals.

(2). The electrons tend to go into different orbitals with their spins parallel, since this results in a lower intra-atomic repulsion energy between them and in a more favorable exchange energy.

With two, or three $d$ electrons present, both of these tendencies can be satisfied simultaneously by placing the electrons in the different $t_{2g}$ orbitals with their spins parallel. For four to seven $d$ electrons there are two favorable arrangements: one which places the maximum number of electrons compatible with the Pauli Principle in the more stable $t_{2g}$ orbitals, and the other which maintains a maximum number of unpaired spins. With more than seven electrons there is again a unique arrangement which gives at the same time the best distribution among the orbitals and the maximum number of unpaired spins. This is illustrated in Table VIII.

In the case that the metal has four to seven $d$ electrons it is clear that a large value of $\Delta$ favors the low-spin configurations for if $\Delta$ is large enough it must finally force the electrons into the $t_{2g}$ orbitals, notwithstanding the opposed tendency to maintain a maximum number of unpaired spins. For this reason the low-spin configurations are often said to correspond to the strong field situation. In a similar way, the exchange forces must dominate and maintain a maximum number of unpaired electrons if $\Delta$ is sufficiently small. High-spin complexes therefore correspond to the weak field limit.

TABLE VIII

*d* ELECTRON ARRANGEMENTS IN OCTAHEDRAL COMPLEXES

| Number of $d$ electrons | High spin (weak field) | | Low spin (strong field) | | Gain in orbital energy in strong field |
|---|---|---|---|---|---|
| | $t_{2g}$ | $e_g$ | $t_{2g}$ | $e_g$ | |
| 1 | ↑ | | ↑ | | 0 |
| 2 | ↑ ↑ | | ↑ ↑ | | 0 |
| 3 | ↑ ↑ ↑ | | ↑ ↑ ↑ | | 0 |
| 4 | ↑ ↑ ↑ | ↑ | ↑↓ ↑ ↑ | | $\Delta$ |
| 5 | ↑ ↑ ↑ | ↑ ↑ | ↑↓ ↑↓ ↑ | | $2\Delta$ |
| 6 | ↑↓ ↑ ↑ | ↑ ↑ | ↑↓ ↑↓ ↑↓ | | $2\Delta$ |
| 7 | ↑↓ ↑↓ ↑ | ↑ ↑ | ↑↓ ↑↓ ↑↓ | ↑ | $\Delta$ |
| 8 | ↑↓ ↑↓ ↑↓ | ↑ ↑ | ↑↓ ↑↓ ↑↓ | ↑ ↑ | 0 |
| 9 | ↑↓ ↑↓ ↑↓ | ↑↓ ↑ | ↑↓ ↑↓ ↑↓ | ↑↓ ↑ | 0 |

The complex $[Co(NH_3)_6]^{3+}$ provides a good example of the strong field case. The ground state is $(t_{2g})^6$ with all $d$ electrons paired and the complex is accordingly diamagnetic. In the case of $[Fe(H_2O)_6]^{++}$, which is formally isoelectronic with $[Co(NH_3)_6]^{3+}$ $\Delta$ is not large enough to break down the tendency of the $d$ electrons to maintain their spins parallel, so that we find a paramagnetism corresponding to four unpaired electrons, that is, the configuration is $(t_{2g})^4(e_g)^2$, as shown in column 2 of Table VIII.

In the purely electrostatic theory which has been presented, covalent bonding between the ligands and the metal ions has not been taken into consideration. It can easily be shown however, that molecular-orbital theory leads to exactly the same kind of splitting of the *d* orbitals, into a lower, nonbonding $t_{2g}$ set of three degenerate orbitals, and an upper, antibonding pair of $e_g$ orbitals. The inclusion of covalent bonding in a more complete theory (ligand field) would only affect the magnitude of the energy separation which is, in any case, usually determined empirically, from analysis of molecular spectral data. It is found from such analyses that $\Delta$ varies somewhat from metal to metal, and also depends on the nature of the ligands. For hydrates and oxides of divalent ions of the first transition-metal series it is in the range 7,500–12,500 $\text{cm}^{-1}$, and for those of the corresponding trivalent ions, in the range 14,000–21,000 $\text{cm}^{-1}$. For compounds of the second and third transition-metal series, $\Delta$ is substantially larger than in the first series. We may also note that the magnitude of pairing energies can also be estimated empirically from atomic spectral data.

## B. THE JAHN-TELLER EFFECT

So far, it has been assumed that the ligands around the metal ion are in a regular octahedral arrangement. We now go on to show that this is *not possible* for certain configurations of the *d* electrons. The theory is essentially that of Jahn and Teller (*68*), but we shall develop it in a qualitative way rather than in the elegant form in which they first presented it. Historically, their ideas were originally applied to the interpretation of the magnetic properties of transition-metal compounds (*137*); the stereochemical applications are much more recent (*35*, *104*).

The physical basis of the Jahn-Teller effect is best illustrated by an example. As we have seen, the ground state of the cupric ion ($d^9$) surrounded by a regular octahedron of ligands would be $(t_{2g})^6(e_g)^3$. The vacancy in the *d* shell can occur either in the $d_{z^2}$ orbital or in the $d_{x^2-y^2}$ orbital, so that the ground state is degenerate. Let us first suppose that the hole is in the $d_{x^2-y^2}$ orbital. In this case the nuclear charge of the ion is more completely shielded in the $z$-direction than in the $x$- and $y$-directions; that is, the atom develops a greater electronegativity in the $xy$-plane than perpendicular to this plane (Fig. 8). It follows from this anisotropic electronegativity that the force acting on the ligands in the $xy$-plane is more strongly attractive than that acting on the ligands in the $z$-direction. Thus if the ligands in the $z$-direction are in equilibrium there will still be an extra attractive force acting on the ligands in the $xy$-plane, which will tend to pull them in to a shorter distance. We see that *in equilibrium* the distance to the ligands in the $xy$-plane must be shorter than that to those along the $z$-axis; that is, four short, and two long bonds are formed. If the hole in the $e_g$ orbitals is in the $\text{d}_{z^2}$ orbital then exactly the opposite result follows, namely that two short bonds to ligands in the $z$-direction and four long bonds in the $xy$-plane are formed.

We have considered the two simplest cases, but it should be remembered that the vacancy in the $d$ shell could also occur in an orbital which was an arbitrary mixture of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals, in which case the distortion would be correspondingly more complicated. It turns out that while it is easy to show that *some distortion must occur,* it is very difficult to be sure which distortion produces the most stable equilibrium configuration. Öpik and Pryce (*103*) have concluded that the configuration with four near neighbors and two distant ones should always be most stable, but Liehr and Ballhausen (*80*) have questioned this conclusion. Experimentally, all but one of the examples studied crystallographically agree with the conclusion of Öpik and Pryce,[1] and it is not yet clear whether the single exception, $K_2CuF_4$ (*18*), is due to an inadequacy of their theory for regular octahedral complexes or to the noncubic environment of the metal ion enforced by the nature of the basic crystal structure, which even in its undistorted form imposes a strongly tetragonal rather than cubic symmetry on the metal.

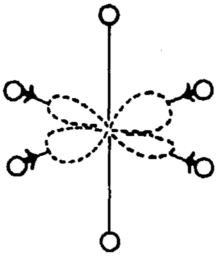


FIG. 8. Anisotropic electronegativity arising in an octahedral complex for a $d^9$ ion with a "hole" in the $d_{x^2-y^2}$ orbital.

There is one important characteristic of the Jahn-Teller mechanism that is independent of detailed models. If the unstable symmetric configuration of an isolated complex has a center of symmetry, this will be preserved in the distorted configuration. This is not necessarily the case with the "near degeneracy instability" to be discussed in later sections.

There is another way of looking at the Jahn-Teller effect in $d^9$ complexes which, while equivalent to the foregoing discussion, throws further light on

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[1] Recent work has shown that the structures of $KCuF_3$ (*39a, 65a*), $RbCuF_3$ (*65a*), and $KCrF_3$ (*39a, 66a*) are tetragonal distortions of the cubic perovskite structure with $c/a < 1$. This new evidence seems to support the conclusions of Liehr and Ballhausen, but a final decision on the matter must be postponed until more detailed results become available.

the principles involved. In Fig. 9 we show the $d$ orbital energy level diagram for a regular octahedral arrangement of ligands, and for an octahedral arrangement slightly distorted in such a way as to produce four shorter bonds in the $xy$-plane and two longer bonds along the $z$-axis. If we have to accommodate nine $d$ electrons in the levels of the undistorted structure the

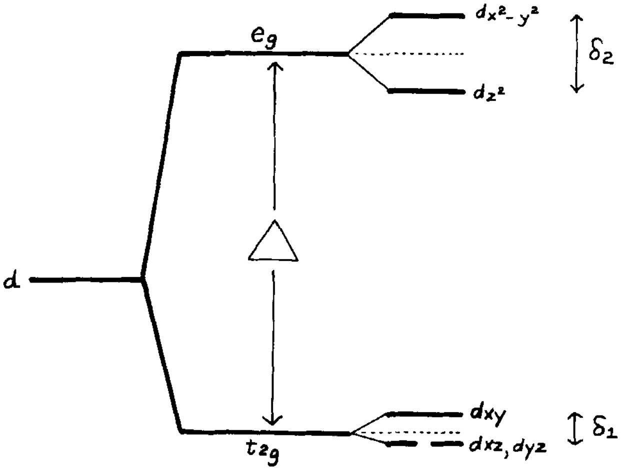

FIG. 9. Splitting of $d$ orbital energy levels in a regular octahedral field and in an octahedral field distorted to produce four shorter bonds in the $xy$-plane and two longer bonds along the $z$-axis.

orbital energy is just $-\frac{3}{5}\Delta$. If, however, we use the levels of the distorted structure, the orbital energy may be lowered to $-\frac{3}{5}\Delta - \frac{1}{2}\delta_2$ by leaving the hole in the $d$ shell in the $d_{x^2-y^2}$ orbital.[1a] Thus the restoring forces which would maintain a regular octahedral environment if the central ion had a filled shell are opposed by forces which tend to distort the octahedron so as to lower the $d$ electron orbital energy. The detailed theory shows that the distorting forces must always prevail.

At this point we can conveniently generalize our arguments to apply to other ions with incomplete $d$ electron shells (*36*, *87*). First, we observe that filled, or half-filled shells of $t_{2g}$ or $e_g$ electrons do not lead to instability. Consider, for example, two electrons with parallel spins in the $e_g$ pair of orbitals. If one electron occupies the $d_{z^2}$ orbital, the other must occupy the $d_{x^2-y^2}$ orbital. Hence the ion is equally shielded in all bond directions and exerts the same attraction on each ligand. In terms of the energy level diagram, one electron would be stabilized by distortion by an amount $\frac{1}{2}\delta_2$ but the energy of the other would be increased by exactly the same

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[1a] A complementary argument applies if the distortion is reversed to give four long and two short bonds.

amount, so that there is no net tendency to distort. We see, therefore, that for the high-spin configurations of $d^3$, $d^5$, $d^8$, and $d^{10}$ and for the low-spin configuration of $d^6$ (Table VIII), a regular octahedral arrangement of ligands is stable against distortion. On the other hand, the high-spin configuration of $d^4$: $(t_{2g})^3(e_g)^1$ and the low-spin configuration of $d^7$: $(t_{2g})^6(e_g)^1$ are similar to the $d^9$ configuration in that they have a degeneracy involving the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals. Consequently, similar distortions of the octahedral environment are to be anticipated.

This leaves for consideration the high-spin configurations $d^1$: $(t_{2g})^1$, $d^2$: $(t_{2g})^2$, $d^6$: $(t_{2g})^4(e_g)^2$, $d^7$: $(t_{2g})^5(e_g)^2$ and the low-spin configurations $d^4$: $(t_{2g})^4$ and $d^5$: $(t_{2g})^5$ which have degeneracies involving the three $t_{2g}$ orbitals. Arguments similar to those already given show that distortions from the regular octahedral environment must again lead to a lowering of the orbital energy. It is evident, however, that for $t_{2g}$ orbital degeneracies, the sense of the distortion corresponding to minimal orbital energy should depend on the number of electrons in the $t_{2g}$ level. Thus, the arrangement with four short and two long bonds leads to the energy level diagram of Fig. 9. For one (or four) $t_{2g}$ electrons the amount of extra stabilization arising from this distortion is $\frac{1}{3}\delta_1$. It is easy to see that for the opposite distortion the corresponding stabilization would be twice as great and hence that ions with $(t_{2g})^1$ or $(t_{2g})^4$ configurations should have two near and four more distant neighbors. For two (or five) $t_{2g}$ electrons the situation is reversed. The preferred environment corresponds to that indicated in Fig. 9 with a stabilization of $\frac{2}{3}\delta_1$ while the opposite distortion produces a lowering of the orbital energy of only $\frac{1}{3}\delta_1$. These conclusions cannot, however, be taken very seriously on account of an important distinction which exists between the $e_g$ and $t_{2g}$ orbitals. As we have already noted, the pair of $e_g$ orbitals point directly at the ligands while the three $t_{2g}$ orbitals point in directions which lie between the ligands. This means that a change from regular to distorted octahedral environment has a much smaller effect on the energies of the $t_{2g}$ orbitals than on those of the $e_g$ orbitals. Thus, although the qualitative considerations outlined above are still valid, the magnitude of $\delta_1$ is quite small compared with that of $\delta_2$. This implies that not only should Jahn-Teller distortions due to $t_{2g}$ degeneracy be much smaller than those due to $e_g$ degeneracy, but also that various factors, particularly spin-orbit coupling, which we have not taken into consideration in this elementary account will have a much greater relative importance and may affect even our qualitative conclusions. Furthermore, there is no good basis for our assumption that Jahn-Teller distortions necessarily lead to tetragonally distorted environments; they might be trigonal. The position, then, is that the Jahn-Teller distortions anticipated for $t_{2g}$ degeneracies are difficult to calculate and are, in any case, small.

There is, perhaps, only one example where an appreciable distortion from octahedral symmetry might be interpreted as a result of $t_{2g}$ degeneracy. As we have seen from Table VII the largest deviation from octahedral symmetry in the transition-metal fluorides with the rutile structure occurs in $FeF_2$, where the $Fe^{++}$ ion is surrounded by 4 $F^-$ at 2.12 Å and by 2 $F^-$ at 1.99 Å (*9*). This is just the kind of distortion which was predicted by the simple theory for the high-spin $d^6$: $(t_{2g})^4(e_g)^2$ configuration of the $Fe^{++}$ ion. On the other hand, the opposite distortion which would be expected in $CoF_2$ does not seem to occur. It has also been suggested that the very small distortions from the rocksalt structure which occur at low temperatures in FeO (*132*) and CoO (*49*) may be attributable to a Jahn-Teller mechanism (*74*). But complex magnetic ordering processes are associated with these transformations (*79*), and the distortions from cubic symmetry must to some extent be due to the anisotropic nature of the interactions between metal ions. Moreover, if the Jahn-Teller mechanism is to be invoked as an explanation of the distortions in FeO and CoO, to what are we to ascribe the very similar distortions which occur also in MnO (*132*) and NiO (*121*), where the Jahn-Teller effect should produce virtually no disturbance of the regular octahedral environment? It would appear that neither theoretical considerations nor the available experimental evidence indicate that the Jahn-Teller effect arising from $t_{2g}$ degeneracies is an important factor in the gross stereochemistry of transition-metal ions, at least of those of the first series.

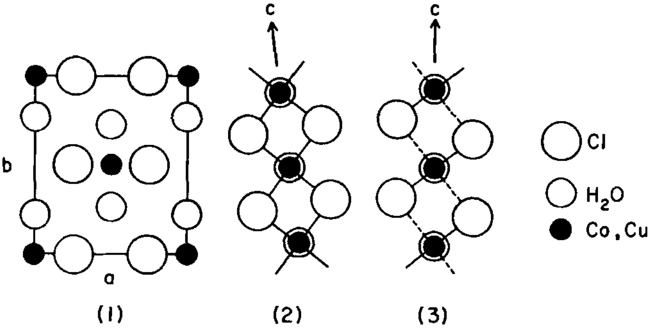


FIG. 10. Comparison of structures of $CoCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$: (1) structures projected down respective *c*-axes, (2) projection of $CoCl_2 \cdot 2H_2O$ chain down *b*-axis, (3) projection of $CuCl_2 \cdot 2H_2O$ chain down *b*-axis (*35*).

The distortions from octahedral symmetry arising from $e_g$ degeneracy are much more important. In the case of cupric compounds, such distortions have been recognized for many years, particularly in their more extreme manifestations, as, for example, in CuO (tenorite) where the $Cu^{++}$ ion is surrounded by $4O^{--}$ anions in a square planar arrangement(*133*).

Square coordination of this kind has been interpreted as a consequence of $dsp^2$ covalent bonding and has been regarded as more or less characteristic of cupric compounds. A review of the environment of the $Cu^{++}$ ion in a number of structures reveals, however, that square coordination is quite rare, that the usual coordination is distorted octahedral, with four short and two long bonds, and that all degrees of distortion can be recognized (*35*). Thus, in compounds containing copper-chlorine bonds, while the short Cu—Cl distances do not vary much from compound to compound (2.26–2.32 A) the long distances vary over a much wider range (2.65–3.05 Å), as is only to be expected from the general manner in which potential energy would vary with internuclear distance. In this context, the square coplanar complexes should be regarded not as representative of a special type of coordination involving a special kind of covalent bonding but simply as the limiting case of the usual distortion from octahedral symmetry with the two distant ligands removed completely. Interatomic distances in some $Cu^{++}X_n$ coordination polyhedra are shown in Table IX.

TABLE IX

INTERATOMIC DISTANCES IN SOME $Cu^{++}X_n$ COORDINATION POLYHEDRA

| Compound | Distances (Å) |
|---|---|
| CuO (*133*) | 4 O at 1.95 (square coplanar) |
| $CuCl_2$ (*146*) | 4 Cl at 2.30, 2 Cl at 2.95 |
| $CuBr_2$ (*60*) | 4 Br at 2.40, 2 Br at 3.18 |
| $CsCuCl_3$ (*145*) | 4 Cl at 2.30, 2 Cl at 2.65 |
| $CuF_2$ (*11*) | 4 F at 1.93, 2 F at 2.27 |
| ($CrF_2$) (*67*) | 4 F at 1.98–2.01, 2 F at 2.43 |
| $K_2CuF_4$ (*78*) | 2 F at 1.95, 4 F at 2.08 |

Cupric fluoride provides an especially interesting case. The cubic fluorite structure which was proposed many years ago has now been shown to be incorrect. The revised structure (*11*) is rutile-like but the environment of the $Cu^{++}$ ions is so strongly deformed from regular octahedral that the crystal symmetry is reduced from tetragonal to only monoclinic. As we have already mentioned, the difluorides of the other transition-metal ions, $Mn^{++}$, $Fe^{++}$, $Co^{++}$, $Ni^{++}$, and $Zn^{++}$, occur in the tetragonal structure with regular or only slightly distorted octahedral environments. The missing member, $CrF_2$, has now been studied (*67*) and found to deviate from the ordinary rutile structure in just the same way as $CuF_2$. In the chromous compound, the coordination consists of $2F^-$ at 1.98, $2F^-$ at 2.01, and $2F^-$ at 2.43 Å.

Copper oxide is the only transition-metal monoxide which does not have the rocksalt structure and the only one for which large deviations from cubic symmetry are predicted, apart from chromous oxide, the structure of which is not established with certainty. Although this compound has been described as crystallizing with the hexagonal wurtzite structure (*86*), the very limited X-ray data which have been obtained are not in good agreement with this. They are, indeed, just as compatible with a tenorite-like structure but are not sufficiently detailed to permit an unequivocal interpretation. It is of interest that in chromous sulfide, the coordination around $Cr^{++}$ is of the distorted octahedral kind with 4 S at 2.43 Å and 2 S at 2.88 Å (*69*).

Very few simple binary compounds of $Mn^{3+}$ are known. The trifluoride is a distorted form of the $VF_3$ transition-metal trifluoride structure with 2 Mn—F at 1.79, 2 Mn—F at 1.91, and 2 Mn—F at 2.09 Å in a distorted octahedral arrangement (*62*). The tendency of $Mn^{3+}$ ions to distort from a regular octahedral environment is best seen in the deviations from cubic symmetry which occur in $M^{++}Mn_2^{3+}O_4$ compounds with the spinel arrangement, but we may note also the distorted octahedral environment which is found in the mineral manganite, $HMnO_2$, where the $Mn^{3+}$ ion has four nearest $O^{--}$ neighbors in a plane at distances of 1.85 and 1.92 Å and two more distant oxygens at 2.30 Å (*23*).

One might well ask at this stage: granted that distortions from regular octahedral coordination do occur in compounds of $Cu^{++}$, $Cr^{++}$, and $Mn^{3+}$, could such distortions not equally well be ascribed to covalent bonding involving $dsp^2$ hybridization on the central ion? To such a question our answer must be a qualified affirmative, for it should be clear that the alternative descriptions of the distribution of electrons in orbitals on the central ion and on the ligands are, in general, complementary rather than in conflict with one another, at least insofar as occupancy of the more stable $t_{2g}$ orbitals is concerned. Both theories agree, moreover, that in a $d^9$ complex with the usual type of distortion, two of the remaining three $d$ electrons occupy the $d_{z^2}$ orbital. A difference arises, however, concerning the placing of the last electron. In the crystal field theory the last electron is placed in the least stable of the $e_g$ orbitals, the $d_{x^2-y^2}$ orbital. In the valence bond theory this electron has to be promoted to a $4p$ orbital, since the remaining $d$ orbital is required for the formation of the set of $dsp^2$ hybrid orbitals. The presence of an unpaired $4p$ electron is, however, incompatible with recent evidence from paramagnetic resonance (*14*, *16*) and optical studies (*13*, *105*) and is, in any case, difficult to reconcile with the marked resistance of $Cu^{++}$ to further oxidation. Thus the valence bond model, in its traditional form, while serving as a basis for the discussion of the stereochemical evidence, is incompatible with many other experimental facts.

Similar deviations from regular octahedral coordination are to be anticipated for $d^7$ ions with the low-spin $(t_{2g})^6(e_g)^1$ configuration. A good example occurs in the low-temperature modification of $NaNiO_2$, where the $Ni^{3+}$ ion has 4 oxide neighbors at 1.95 Å and two more distant at 2.17 Å to complete the octahedron (*38*). The low-spin cobaltous complexes have been divided into two groups, with magnetic moments of 1.7–2.0 B.M. and 2.1–2.9 B.M. respectively. The first group are believed to be octahedral complexes, the second planar (*42*), but detailed X-ray structural evidence is lacking.

So far we have discussed distortions from octahedral symmetry, in which all the ligands could, in principle, be equivalent. While this is the case of interest from the limited point of view of the Jahn-Teller effect, the general arguments apply equally to other systems, for example, $CuCl_2.2$ pyridine or $CuCl_2.2H_2O$. There should, quite generally, be four "more than averagely strong" bonds in a plane and two weaker bonds whenever the $d_{z^2}$ orbital is doubly occupied and the $d_{x^2-y^2}$ orbital singly occupied, whatever the nature of the ligands. Although we cannot follow the arguments here, it should be mentioned that ligand field theory gives some indication about which of the ligands are likely to be attached by short bonds and which by long in a complex of known composition (*35*).

There are, for example, several cases where substitution of $Cu^{++}$ for another divalent ion results in the formation of a related though significantly different structure in which a less symmetrical environment of the cupric ion is attained. The structures of $CoCl_2.2H_2O$ (*134*) and $CuCl_2.2H_2O$ (*54, 88*) are shown diagrammatically in Fig. 10. The two structures are very similar and indeed are virtually identical in projection down their *c*-axes. Both consist of chains running parallel to *c* but in these chains the square coplanar arrangement of the four chlorine atoms about each cobalt atom is

TABLE X

INTERATOMIC DISTANCES IN SOME "MIXED" CUPRIC COORDINATION POLYHEDRA

| Compound | Refs. | Distances (Å) |
|---|---|---|
| $Cu_2(OH)_2CO_3$ | (*148*) | 4 O (OH) at 1.98, 2 O at 2.71<br>4 O (OH) at 2.01, 2 OH at 2.41 |
| $CuCl_2 \cdot 2H_2O$ | (*54, 88*) | $2H_2O$ at 2.01, 2 Cl at 2.31, 2 Cl at 2.98 |
| $K_2CuCl_4 \cdot 2H_2O$ | (*30*) | $2H_2O$ at 2.01, 2 Cl at 2.29, 2 Cl at 2.93 |
| Cu(acetate)$_2 \cdot H_2O$ | (*136*) | 4 O at 1.97, $H_2O$ at 2.20, Cu at 2.64 |
| Cu(formate)$_2$ $4H_2O$ | (*77*) | 4 O at 2.00, 2 $H_2O$ at 2.36 |
| Cu proline $\cdot$ $2H_2O$ | (*90*) | 2 N at 1.99, 2 O at 2.03, $2H_2O$ at 2.52 |
| $CuCl_2 \cdot 2$ pyridine | (*34*) | 2 N at 2.02, 2 Cl at 2.28, 2 Cl at 3.05 |
| $Cu(NH_3)_4 SO_4 \cdot H_2O$ | (*95*) | 4 N at 2.05, $H_2O$ at 2.59, $H_2O$ at 3.37 |
| Cu-dimethylglyoxime | (*43*) | 4 N at 1.94, O at 2.43 |
| $Cu(NH_3)_2 Cl_2$ | (*53*) | 2 N at 1.95, 4 Cl at 2.76 |
| $Cu(NH_3)_2 Br_2$ | (*53*) | 2 N at 2.03, 4 Br at 2.88 |

replaced by a rectangular arrangement in the copper structure. In both cases the water molecules are situated on lines normal to the planes containing the chlorine atoms. A similar relationship holds in the comparison of the structures of cobalt dipyridine dichloride and copper dipyridine dichloride (*34*), which are again virtually identical in one projection but significantly different when the third coordinate is taken into account. Once again the environment of the copper atoms is a distorted version of the more regular environment of the cobalt atoms, with four strong bonds in a plane and with two weaker ones normal to this plane. In Table X we give some interatomic distances in these "mixed" coordination compounds of $Cu^{++}$. Compounds of $Cr^{++}$ have not been so extensively studied, but it is noteworthy that the only other substance known to have the curious dimeric structure of cupric acetate monohydrate is the corresponding chromous compound (*135*).

### C. SQUARE COPLANAR $d^8$ COMPLEXES

We turn now to a slightly different example of a distortion from octahedral symmetry, namely that of $d^8$ ions. We have seen that in an octahedral environment the most stable electronic configuration is $(t_{2g})^6(e_g)^2$ with the spins of the two electrons in the $e_g$ pair of orbitals parallel (triplet state) and that for this configuration the octahedral environment is stable. There is another possible configuration in which the two $e_g$ electrons go into a single orbital with their spins antiparallel. This corresponds to the lowest singlet state which, in a regular octahedral environment, is, of course, less stable than the triplet because of increased Coulombic repulsion between the electrons and a less favorable exchange energy. If the regular octahedron is now distorted so as to form four short and two long bonds, it can be shown by calculation (*92*) that while the energy of the triplet state is unchanged to first approximation, the singlet state splits into two components, one more stable, the other less stable, as shown in Fig. 11. If the distortion is sufficiently large, the lower component of the singlet may become more stable than the triplet, and hence become the ground state. This is the explanation of the occurrence of planar complexes of $d^8$ ions which are invariably diamagnetic.

One can see, in a qualitative way, what has happened by reference to Fig. 9. As $\delta_2$ increases, there is a tendency for both electrons to go into the $d_{z^2}$ orbital, but this can only be done by pairing the spins and is therefore opposed by the unfavorable exchange energy. Thus small distortions do not occur. If, however, the distortion becomes large enough for the orbital stabilization to compensate for the loss of exchange energy the singlet state becomes more stable. The situation is quite different from that which occurs in $d^9$ complexes where the ground state is stabilized by distortions, for then all magnitudes of distortion are possible.

The square coplanar configuration for diamagnetic $d^8$ ions can, of course, be simply interpreted in terms of the formation of four $dsp^2$ hybridized orbitals directed towards the corners of a square. The eight $d$ electrons must accordingly be accommodated in the remaining four $d$ orbitals with paired spins, thus leading to diamagnetism. It is of interest that this argument was first used by Pauling (*113*) in 1931 to *predict* square-coplanar coordination in diamagnetic $Ni^{++}$ complexes before it had been verified experimentally. Since then, conclusive support for the hypothesis has been forthcoming.

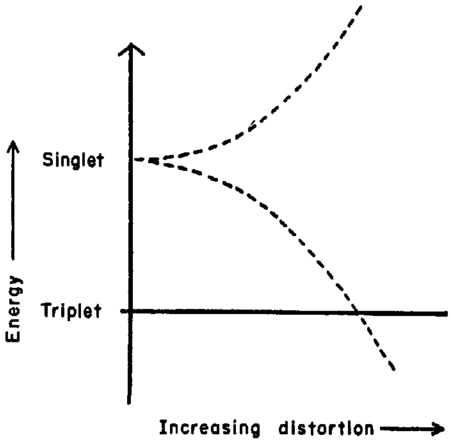


FIG. 11. Energies of $(t_{2g})^6(e_g)^2$ singlet and triplet states as a function of distortion from regular octahedral symmetry.

In $Ni^{++}$ compounds, diamagnetic complexes are not formed with typically "ionic" ligands but only with those which give rise to rather large crystal field splittings (we can refer to such ligands as low-spin or covalent), for example, cyanide ion in the complex ion $[Ni(CN)_4]^{--}$ and the chelating agents dimethylglyoxime, dithiooxalate, etc. In such compounds it is quite common to find isomorphism between the corresponding compounds of $Ni^{++}$, $Pd^{++}$, and $Pt^{++}$.

With ions of the second and third transition series, however, spin-paired complexes are formed with ligands, which according to almost any criteria, would be included among those forming the most ionic compounds. This difference arises because the 4$d$ and 5$d$ orbitals extend to greater radial distances from the metal ion than the 3$d$ orbitals and hence the effect of the ligand field on the splitting of the orbital energies will be greater, and the interelectronic repulsions will be diminished. Both of these effects must increase the tendency of the electrons to go into the lowest available orbitals, and hence must encourage spin pairing. Thus, $Pd^{++}$ is paramagnetic only in the fluoride $PdF_2$ with the octahedrally coordinated rutile structure (*7*), and no paramagnetic $Pt^{++}$ compounds are known. Square coplanar coordination has been found in all the other examples which have been studied; for example, in the oxides PdO and PtO, the sulfides PdS and PtS, the chloride $PdCl_2$, and in a large number of complex ions $[PdCl_4]^{--}$, $[PtCl_4]^{--}$, $[Pt(NH_3)_4]^{++}$, $[Pt(CN)_4]^{--}$, $[Pt(NO_2)_4]^{--}$, etc. (*147*). In one or two cases, for example $Pt(NH_3)_2Br_2$, there is weak residual bonding to complete a distorted octahedral environment (*21*), but this is the exception rather than the rule. As far as is known, all $Au^{3+}$ compounds are diamagnetic, square coplanar complexes. A recent example is represented in $AuCl_3$ which has been shown to consist in the solid state of planar dimeric molecules (*31*). Vapor-density measurements indicate that dimeric molecules must also exist in the gas phase of gold(III) chloride and bromide.

## D. TETRAHEDRAL COORDINATION (*36*)

In the field due to a tetrahedron of negative ions about a positive transition-metal ion, the *d* orbitals are split into a lower doubly degenerate set of *e* orbitals, and an upper triply degenerate set of $t_2$ orbitals. If we take the coordinate axes parallel to the sides of the enclosing cube (Fig. 12), then these two sets comprise the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals, and the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals, respectively. Thus the splitting is just as for the octahedral case, but with the orders of the levels inverted. (A precisely similar splitting occurs with eight ligands at the vertices of a cube.) In the case of a tetrahedral environment, it is the $t_2$ orbitals which interact most strongly with the ligands, so we shall consider only distortions which depend on the degeneracy of these orbitals.

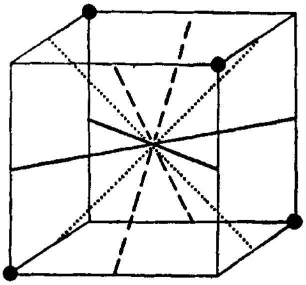


FIG. 12. Showing the symmetrical relationship of the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals which comprise the triply degenerate $t_2$ orbitals in a tetrahedral complex (*36*).

Large distortions from regular tetrahedral symmetry are to be anticipated for the high-spin configurations $(e)^2(t_2)^1$, $(e)^2(t_2)^2$, $(e)^4(t_2)^4$, and $(e)^4(t_2)^5$. The type of distortion which should occur is, as we shall see, different for the $d^3$ and $d^8$ configurations on the one hand, and the $d^4$ and $d^9$ configurations on the other.

To destroy the threefold orbital degeneracy it is quite sufficient to introduce any distortion which removes the cubic symmetry of the complex. For the present, however, we shall consider only tetragonal distortions since rhombohedral distortions, etc., do not seem to have been discovered as yet. In discussing these tetragonal distortions we shall retain the usual crystallographic nomenclature and utilize an orthogonal coordinate system with $a = b \neq c$. If the enclosing cube (Fig. 12) is tetragonally distorted, we must distinguish between two possible cases. (1) $c > a$ involves an elongation of the tetrahedron along one of its fourfold alternating axes; (2) $c < a$ involves a corresponding flattening of the tetrahedron. In both cases, the triply degenerate $t_2$ orbital splits into a singlet and a doublet but which of these lies lower depends on the ratio $c/a$. In the limiting case of (2), $c/a = 0$ the tetrahedron becomes a square in the $xy$-plane. The $d_{xy}$ orbital concentrated in this plane is therefore destabilized: the $d_{xz}$ and $d_{yz}$ orbitals constitute the degenerate doublet which is stabilized. This type of splitting is shown in Fig. 13 from which it is clear that the orbital degeneracy is removed for the $d^4$ and $d^9$ configurations but not for $d^3$ and $d^8$. The opposite distortion, elongation of the tetrahedron ($c/a > 1$) produces just the reverse splitting, that is, the singlet $d_{xy}$ orbital is stabilized and the degenerate pair of orbitals, $d_{xz}$ and $d_{yz}$, are destabilized. This distortion leaves the $d^4$ and $d^9$ systems degenerate but removes the degeneracy of $d^3$ and $d^8$. Thus we expect $d^4$ and $d^9$ systems to flatten, and $d^3$ and $d^8$ systems to elongate.

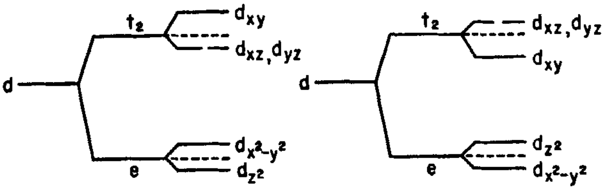
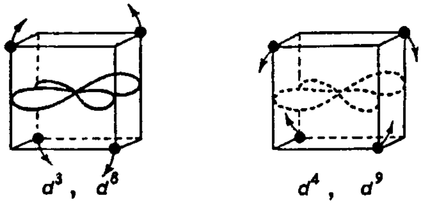


FIG. 13. Splitting of $d$ orbital energy levels in a regular tetrahedral field and in tetragonally distorted fields with $c/a < 1$ (left) and $c/a > 1$ (right). These distortions may be described as flattening or elongation, respectively, of the tetrahedron along an $S_4$ axis (*36*).

Such distortions can be understood very easily by considering the distortions produced by one extra electron ($d^3$ and $d^8$) or one hole ($d^4$ and $d^9$) in a half-filled or filled set of $t_2$ orbitals. The two situations are shown diagrammatically in Fig. 14. The extra $t_2$ electron repels the ligands and so causes elongation of the tetrahedron, while the positive "hole" attracts the ligands and so causes flattening.

It cannot yet be claimed that the experimental evidence for such distortions from tetrahedral coordination is so well established as for the octahedral case, but this is largely attributable to the comparative rarity of structures in which transition-metal ions occur in a tetrahedral environment. There appear to be no examples of tetrahedral coordination about $d^3$ and $d^4$ ions, and only fragmentary information is available for $d^8$ and $d^9$ ions. It may be recalled that tetrahedral coordination was anticipated by Pauling (*114*) for paramagnetic 4-covalent complexes of nickel(II) on the grounds that, since all the $d$ orbitals are occupied by electrons from the metal, the covalent bonding must occur through $sp^3$ hybridized orbitals. It is now known that many formally 4-covalent complexes are, in fact, octahedrally coordinated, with two or more of the ligands shared between pairs of metal atoms, and it is only recently that definite evidence for tetrahedral coordination in such compounds has been obtained. The paramagnetic compound $(Ph_3P)_2NiCl_2$ has been shown by X-ray analysis to be tetrahedral (*139*), in contrast to the diamagnetic $(Et_3P)_2NiBr_2$ which is coplanar (*122*). But since in this compound the ligands are not all equivalent, it is not really relevant to a discussion of distortions from regular tetrahedral symmetry. The $CuCl_4^{--}$ ion however in the compound $Cs_2CuCl_4$ is known to be flattened (*61*) in just the way that the theory would predict while the $CoCl_4^{--}$ ion in the structurally similar $Cs_2CoCl_4$ (*115*) is much more nearly regular. Some other examples of distortions from tetrahedral symmetry occur in $NiCr_2O_4$ and $CuCr_2O_4$, and we shall mention these in our discussion of the spinel structure.



(a) (b)

FIG. 14. Effect of (a) a single electron in the $t_2$ orbital ($T_2$ state), (b) a single hole in the $t_2$ orbital ($T_1$ state) on the stereochemistry of a tetrahedral complex. Only tetragonal distortions are considered (*36*).

Although it is formally possible to have low-spin complexes of $d^3$, $d^4$, $d^5$, and $d^6$ ions, none are known. The reason for this is that the splitting $\Delta$ between the $e$ and $t_2$ levels is much smaller in a tetrahedral than in an octahedral complex. The purely electrostatic theory predicts a ratio of 4/9 between the two cases under equivalent conditions, and the limited spectroscopic evidence for tetrahedrally coordinated complexes in solution and in glasses suggests that this figure is fairly close to the mark. Such a low $\Delta$ would be too small to cause spin pairing for $3d$ electrons, but for $4d$ and *a fortiori* for $5d$ electrons, it seems possible that spin pairing might occur even in tetrahedrally coordinated compounds. This might explain the diamagnetism of the $ReCl_4^-$ (see *45*) ion since the $Re^{3+}$ ions could have the configuration $(e)^4(t_2)^0$.

## E. Octahedral versus Tetrahedral Coordination (*36, 37*)

In addition to the factors which we outlined on p. 2 for assessing the relative stabilities of the various coordination polyhedra, the number of $d$ electrons present in the central ion must also play an important role. Indeed, since transition-metal ions of a given charge have approximately the same ionic radius and differ principally only in the number of $d$ electrons present, we would anticipate that this additional factor would be the determining one in deciding their relative preferences for octahedral and tetrahedral coordination.

TABLE XI

Crystal Field Stabilizations in Terms of $\Delta/10$ for Transition-Metal Ions in Octahedral and Tetrahedral Environments

| Ion | No of $d$-electrons | Octahedral stabilization | Tetrahedral stabilization |
|---|---|---|---|
| $Ti^{3+}$, $V^{4+}$ | 1 | 4 | 6 |
| $Ti^{++}$, $V^{3+}$, $Cr^{4+}$ | 2 | 8 | 12 |
| $V^{++}$, $Cr^{3+}$, $Mn^{4+}$ | 3 | 12 | 8[a] |
| $Cr^{++}$, $Mn^{3+}$, $Fe^{4+}$ | 4 | 6[a] | 4[a] |
| $Mn^{++}$, $Fe^{3+}$, $Co^{4+}$ | 5 | 0 | 0 |
| $Fe^{++}$, $Co^{3+}$, $Ni^{4+}$ | 6 | 4 | 6 |
| $Co^{++}$, $Ni^{3+}$ | 7 | 8 | 12 |
| $Ni^{++}$, $Cu^{3+}$ | 8 | 12 | 8[a] |
| $Cu^{++}$ | 9 | 6[a] | 4[a] |
| $Cu^{+}$, $Zn^{++}$ | 10 | 0 | 0 |

[a] These ions have substantial additional Jahn-Teller stabilizations.

We have shown that for an ion in octahedral coordination, the energies of the $t_{2g}$ and $e_g$ orbitals referred to the mean $d$ orbital energy are $-\frac{2}{5}\Delta^o$ and $+\frac{3}{5}\Delta^o$, respectively. This means that for the electronic configuration $(t_{2g})^m(e_g)^n$ the crystal field stabilization energy is $\Delta^o(4m - 6n)/10$. Similarly, in tetrahedral coordination, the corresponding stabilization for the configuration $(e)^p(t_2)^q$ is $\Delta^t(6p - 4q)/10$, where we remember that $\Delta^t$ is only about 40% of $\Delta^o$ under equivalent conditions. These stabilizations are shown in Table XI for different transition metals. It is clear from the results that $Cr^{3+}$ and $Ni^{++}$ should show the strongest preference for octahedral coordination and that $Mn^{++}$ and $Fe^{3+}$ will have no particular preference insofar as crystal field effects are concerned. We have already mentioned the comparative rareness of high-spin tetrahedral complexes of $Ni^{++}$, which contrasts with the fact that several tetrahedral complexes of $Co^{++}$ are known; for example, the $CoCl_4^{--}$ ion in $Cs_2CoCl_4$ (*115*) and $Cs_3CoCl_5$ (*116*) and the blue complexes of $CoCl_2$ with organic bases (*15, 101*) (the violet complexes have $Co^{++}$ in octahedral coordination). From Table XI we should expect $Co^{++}$ to show a greater preference for tetrahedral coordination than $Ni^{++}$.

In order to make a more critical test of the theory, we must look for a structure in which the transition-metal ion has the possibilities of both octahedral and tetrahedral coordination, and preferably one in which a given transition-metal ion may be exchanged for another without substantial alteration in the atomic arrangement. Such a structure is the spinel arrangement in which a large number of $XY_2O_4$ compounds crystallize, where X is a divalent metal ion and Y is $Al^{3+}$, $Cr^{3+}$, $Mn^{3+}$, $Fe^{3+}$, or $Co^{3+}$. This structure is also of importance in the discussion of distortions from cubic symmetry and we shall now consider it in some detail.

## F. The Structure of Compounds with the Spinel Arrangement

The mineral spinel $MgAl_2O_4$ is the prototype of this structure. The basic framework consists of a cubic close packed arrangement of oxide ions. Such a framework contains both octahedral and tetrahedral interstices. Starting off from any oxygen, we find an octahedral site by moving in a direction parallel to any cube edge to a point halfway to another oxygen. Similarly, a tetrahedral site is found by moving in a direction parallel to any cube diagonal. If all the octahedral sites are occupied by metal ions, we have the rocksalt structure (Fig. 4). If all the tetrahedral sites are occupied we have the fluorite structure (Fig. 6a), and if only every alternate tetrahedral site is occupied we have the sphalerite structure (Fig. 5a). There is a special way of occupying half of the octahedral sites and one-eighth of the tetrahedral sites which gives the spinel structure (Fig. 15). In a "normal" spinel $XY_2O_4$, the trivalent Y ions occupy the octahedral sites, and the divalent X ions the tetrahedral sites. There is also the possibility, however, that half of the Y ions occupy the tetrahedral sites, the remaining half together with the X ions being distributed over the octahedral sites—the so-called "inverted" arrangement. Intermediate arrangements are also possible. If the atomic proportion of the divalent ion occurring in the octahedral sites is expressed as $\delta$, then $\delta = 0$ for a normal spinel

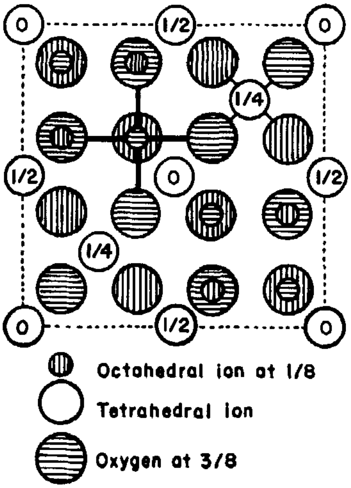


FIG. 15. Arrangement of atoms in the spinel structure. The lower half of the cubic unit cell is shown projected down a cube axis, the heights of the atoms being indicated either by numbers (0, ¼, or ½) or by vertical (⅛) and horizontal (⅜) shading. One octahedron and one tetrahedron are outlined for clarity.

and $\delta = 1$ for an inverse spinel. For completely random distribution of the two kinds of ion between the two kinds of site, $\delta = 0.67$.

As we have mentioned, it is possible to assess the relative tendencies of transition-metal ions to adopt octahedral or tetrahedral coordination from the respective crystal field stabilizations. The results of Table XI could

TABLE XII
CRYSTAL-FIELD STABILIZATIONS (KCAL/MOLE) ESTIMATED FOR TRANSITION-METAL OXIDES

| Ion | Octahedral stabilization | Tetrahedral stabilization | Excess octahedral stabilization |
|---|---|---|---|
| $\mathrm{Mn}^{++}$ | 0 | 0 | 0 |
| $\mathrm{Fe}^{++}$ | 11.9 | 7.9 | 4.0 |
| $\mathrm{Co}^{++}$ | 22.2 | 14.8 | 7.4 |
| $\mathrm{Ni}^{++}$ | 29.2 | 8.6 | 20.6 |
| $\mathrm{Cu}^{++}$ | 21.6 | 6.4 | 15.2 |
| $\mathrm{Ti}^{3+}$ | 20.9 | 14.0 | 6.9 |
| $\mathrm{V}^{3+}$ | 38.3 | 25.5 | 12.8 |
| $\mathrm{Cr}^{3+}$ | 53.7 | 16.0 | 37.7 |
| $\mathrm{Mn}^{3+}$ | 32.4 | 9.6 | 22.8 |
| $\mathrm{Fe}^{3+}$ | 0 | 0 | 0 |

serve as a rough basis for such a theory but it is better to express the crystal field stabilizations in a semiquantitative form by estimating Δ for the individual transition-metal ions in an environment of oxide ions. This can be done from a consideration of the absorption spectra of transition-metal oxides and hydrates (*37*) and the results are given in Table XII. The experimental results on cation distribution in spinels derived from X-ray and neutron diffraction measurements are given in Table XIII and are seen to be in excellent agreement with expectations.

TABLE XIII

EXPERIMENTAL CATION DISTRIBUTIONS AMONG TETRAHEDRAL AND OCTAHEDRAL SITES IN SPINELS (FOR DETAILED REFERENCES SEE *37*).

$\delta = 0$, normal spinel, $M^{++}$ in tetrahedral sites
$\delta = 1$, inverse spinel, $M^{++}$ in octahedral sites
$\delta = 0.67$, random distribution of $M^{++}$ and $M^{3+}$ over tetrahedral and octahedral sites

| | $Mg^{++}$ | $Mn^{++}$ | $Fe^{++}$ | $Co^{++}$ | $Ni^{++}$ | $Cu^{++}$ | $Zn^{++}$ |
|---|---|---|---|---|---|---|---|
| Aluminates | 0 | 0 | 0 | 0 | 0.76 | — | 0 |
| Chromites | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 |
| Ferrites | 0.9 | 0.2 | 1 | 1 | 1 | 1 | 0 |
| Manganites | 0 | 0 | ? | ? | 1 | 0 | 0 |
| Cobaltites | — | — | — | 0 | — | — | 0 |

Thus the ions with the greatest excess octahedral stabilization are $Cr^{3+}$ and $Mn^{3+}$, and in agreement with this we see that all the chromites and manganites (except $NiMn_2O_4$) are normal spinels. For $Fe^{3+}$, on the other hand, there should be no preference, as far as crystal field effects are concerned, for either type of coordination, so that this ion should be displaced from the octahedral sites fairly easily. In agreement with this, all the ferrites except for $ZnFe_2O_4$ are at least partially inverted. Of the divalent ions, the one with the greatest excess octahedral stabilization is $Ni^{++}$, and we see that this is the only divalent ion capable of displacing $Al^{3+}$ or $Mn^{3+}$ from the octahedral sites. The compounds $CoMn_2O_4$ and $FeMn_2O_4$ have been described as having a random distribution of cations over the available sites (*125*) but since electron-transfer reactions (for example, $Co^{++} + Mn^{3+} = Co^{3+} + Mn^{++}$) may occur here it seems doubtful if they are really to be classed as manganites. In contrast to $Mn^{3+}$ ions, $Mn^{++}$ ions should be easily displaced from the octahedral sites.

The ideal spinel structure has cubic symmetry but there are a number of cases where one cube axis becomes longer or shorter than the other two to give a structure with only tetragonal symmetry. Two of these cases have been studied in detail. In $CuFe_2O_4$($c/a = 1.06$), an inverse spinel with $Cu^{++}$ exclusively in the octahedral sites, the tetragonal distortion has been shown (*117*) to be associated with a distortion of these sites from regular octahedral symmetry, in such a way as to surround the metal ion by four nearest neighbors in the *ab*-plane and two more distant neighbors along the *c*-axis. The tetrahedral sites, in which only $Fe^{3+}$ ions occur, retain their regular tetrahedral symmetry. $CuCr_2O_4$ is a normal spinel with $c/a = 0.91$ and here the distortion is associated with a flattening of the oxygen tetrahedron about each $Cu^{++}$ ion so as to make it approach to a square in the *ab*-plane (*118*). We have seen other examples of both of these types of distortion in our account of the stereochemistry of $Cu^{++}$ and have attributed their occurrence to the Jahn-Teller effect.

In the other cases where tetragonal distortions have been observed for spinels, detailed structural evidence is not available. In the absence of such evidence, it is reasonable to suppose that they arise in a similar fashion since, in almost all cases, they occur in compounds for which a large deviation from cubic symmetry would be anticipated as a result of the Jahn-Teller effect. $NiCr_2O_4$, a normal spinel, becomes tetragonal below 310°K. At room temperature, 15° below the transition point, the axial ratio $c/a$ is 1.025 (*85*) and it presumably increases on further lowering of the temperature. We believe that this distortion results from the occurrence of $Ni^{++}$ in tetrahedral coordination and that it consists of an elongation of the oxygen tetrahedra in the direction of a cube axis. We recall that opposite distortions should occur for tetrahedrally coordinated ions with $d^8(Ni^{++})$ and $d^9(Cu^{++})$ and hence the change in $c/a$ from greater to less than unity on passing from $NiCr_2O_4$ to $CuCr_2O_4$ was to be expected.

For the normal spinels $CdMn_2O_4$ (*125*), $Mn_3O_4([Mn^{++}][Mn_2^{3+}]O_4)$ (*120*) $MgMn_2O_4$ and $ZnMn_2O_4$ (*120, 125*), all with $c/a$ ratios greater than unity, the deviations from cubic symmetry are probably associated with the tendency of the $Mn^{3+}$ ion to distort from regular octahedral coordination so as to have four nearest neighbors in a plane and two more distant neighbors in the direction normal to the plane. The random spinels $CoMn_2O_4$ and $FeMn_2O_4$ presumably have sufficient $Mn^{3+}$ ions in octahedral sites to give the same effect. It is more difficult to account for the $c/a$ values of unity reported for normal $CuMn_2O_4$ and inverse $Mn[NiMn]O_4$ (*125*). In both of these cases, the tetrahedral sites should flatten towards a square ($c/a < 1$) while the octahedral sites should distort to give four long and two short bonds ($c/a > 1$). There is a way of distorting the spinel structure to satisfy both of these requirements simultaneously. It consists of displacing every $O^{--}$ ion from its ideal position away from its nearest tetrahedrally coordinated ion in a direction parallel to a diagonal of a given cube face. Such an arrangement has $c/a = 1$, but it is nevertheless only of tetragonal symmetry. It should be possible to detect such a deviation from cubic symmetry from single crystal studies but not, however, from powder samples, and a definite conclusion on the matter must await such evidence.

### G. Concluding Remarks on Jahn-Teller Distortions

This is a convenient point to recall a number of limitations and also a number of further applications of the foregoing discussion:

1. We have neglected spin-orbit coupling, which may well prove to be important particularly in tetrahedrally coordinated compounds.
2. We have been able to predict only that distortions must exist in certain cases and that they maintain the center of symmetry if the metal ion is octahedrally coordinated. We have not been able to specify the details of the distortion which minimizes the energy.
3. We have not considered the role played by cooperative forces in the crystal in trapping the distorted configurations. In an isolated complex the effects which we have discussed lead to the existence of a set of equivalent, distorted configurations. In a $d^9$ complex, for example, a tetragonal distortion could occur about any one of a set of three mutually perpendicular axes. The internal motion of the complex at room temperature would then lead to frequent exchanges between these distorted configurations unless the activation energy for the process were unexpectedly high. In any case, in an assembly of noninteracting molecules, each configuration would be represented an equal number of times. In a *crystalline compound* containing distorting ions regularly arranged on a lattice it is the interaction between the distortions which leads, at sufficiently low temperatures, to the trapping of each distortion in fixed orientation to all the others. Only if this happens can X-ray methods reveal Jahn-Teller distortions, for example, in spinels.
4. We have restricted our discussion to ions in their ground states as this is all that is necessary in stereochemistry. In treating the optical properties of solids, particularly their fluorescence and phosphorescence, it may be anticipated that Jahn-Teller distortions of excited states will be of great importance.

In cubic crystals containing a small amount of a foreign ion such as $Cu^{++}$ or $Ni^{+}$ at low temperatures it is found (*58*) that each metal ion has a distorted environment, but that the tetragonal axis of this environment may have a number of equivalent orientations relative to the crystal as a whole. At higher temperatures the direction of the tetragonal axes changes so very rapidly that each ion experiences on the average a cubic crystal field. Thus impurity ions in a cubic crystal exhibit just the properties expected for isolated complexes, as indeed they should.

## V. Stereochemistry of *B*-Subgroup Ions

### A. IONS WITH $d^{10}$ CLOSED SHELL CONFIGURATIONS (*73, 107*)

In this section we discuss the stereochemistry of *B*-subgroup ions with filled *d* shells. The most striking feature is that in addition to forming tetrahedrally and octahedrally coordinated compounds, these ions exhibit a more or less pronounced tendency to occur in linear environments, for example, $Ag^+$ in the linear cation $[Ag(NH_3)_2]^+$, $Au^+$ in the linearly coordinated infinite chains of AuI, and $Hg^{++}$ in the discrete molecules of $HgCl_2$ which exist in both the gas and crystalline phases. We believe that two influences are at work in determining these structures. One is related to the Jahn-Teller effect, and the other to covalent bonding. We shall discuss them in this order and then consider their relative importance.

We have already shown in a previous section that if a transition-metal ion has an odd number of electrons in the $e_g$ orbitals, then it must necessarily distort a regular octahedral environment in which it is placed. The orbital degeneracy which would occur in the highly symmetrical environment is broken down by a lowering of the symmetry, thus conferring an additional degree of stability to the molecule or complex. We now wish to illustrate an example of a more general but less powerful principle, namely that the existence of low lying excited states often leads to a *tendency* to distort from a highly symmetric environment. If the excited states are sufficiently close in energy to the ground state, then a distortion must occur in a number of important situations.

Consider an ion with the configuration $d^{10}$. The ground state is nondegenerate, $^1S$, but there are also fairly low lying excited states $^3D$ and $^1D$ arising from the configuration $d^9s$.[2] In a cubic environment these states cannot be mixed with the ground state, since neither the $t_{2g}$ orbitals nor the $e_g$ orbitals have the same transformation properties as the *s* orbital. In a tetragonally distorted environment, however, this is no longer true, and the most favorable electronic configuration is then described by $d^{10-\delta}s^{\delta}$. In other words, some of the $^1D$ excited state would be mixed with the ground state. This is most easily seen by considering the separate orbitals. The wave functions for the $d_{z^2}$, $s$, and $(1/\sqrt{2})(d_{z^2} \pm s)$ orbitals are illustrated in Fig. 16.

It is clear that the $(1/\sqrt{2})(d_{z^2} - s)$ orbital is concentrated in the *xy*-plane. If this orbital were occupied, and the $(1/\sqrt{2})(d_{z^2} + s)$ orbital left empty, then the ligands in the *xy*-plane would be repelled more than those along the *z*-axis. A regular octahedron would therefore distort by

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[2] We neglect spin-orbit coupling here, although it would have to be taken into account in quantitative calculations, especially if very heavy ions are concerned.

lengthening the bonds in the $xy$-plane and shortening those in the $z$-direction. Conversely, a distortion of this nature would stabilize the $(1/\sqrt{2})(d_{z^2} - s)$ orbital with respect to both the $(1/\sqrt{2})(d_{z^2} + s)$ and the pure $d_{z^2}$ orbitals. The opposite distortion, that is, one leading to four short bonds and two long ones, would of course make the $(1/\sqrt{2})(d_{z^2} + s)$ orbital more stable than either the $(1/\sqrt{2})(d_{z^2} - s)$ or the $d_{z^2}$ orbital.

Let us first suppose that in a regular octahedral environment the $e_g$ pair of $d$ orbitals and the $s$ orbital are degenerate, and consider what would happen to the lowest singlet state.[3] Since the $d(e_g)$ and $s$ orbitals are degenerate, it requires no intra-atomic reorganization energy to form an arbitrary mixed orbital from them. If the pure $d_{z^2}$ orbital, (together with the other $d$ orbitals), is used there is no tendency to distort, but if the occupied orbital is a linear combination of $s$ and $d$ then the arguments used in the case of the $d^9$ configuration show that distortion must occur with a resulting stabilization of the system. (A theorem related to the Jahn-Teller theorem would apply quite rigorously here, provided that a vibration of appropriate symmetry to mix the two accidentally degenerate orbitals exists.) Thus, either the $(1/\sqrt{2})(d_{z^2} + s)$ orbital would be occupied and we should get four short bonds, or the $(1/\sqrt{2})(d_{z^2} - s)$ orbital would be occupied and we should get two short bonds. There is also the possibility that some other combination of the $d_{z^2}$, $d_{x^2-y^2}$, and $s$ orbitals would be occupied. In this case we should get a distortion to a lower than tetragonal symmetry but always so as to maintain the center of symmetry.

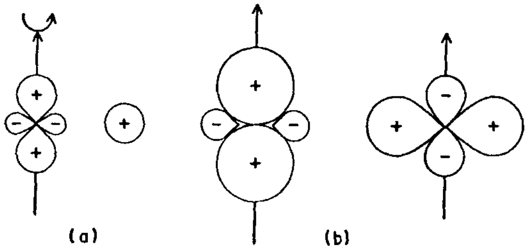

FIG. 16. (a) The $d_{z^2}$ and $s$ orbitals, (b) hybrid orbitals concentrated along the $z$-axis and in the $xy$-plane (*107*, Fig. 2).

Now suppose that the $e_g$ orbitals are more stable than the $s$ orbital by an amount $E_p$. Mixing of the $d_{z^2}$ and $s$ orbitals to give an orbital $\alpha d_{z^2} - (1 - \alpha^2)^{1/2}s$ would still cause a distortion and resultant stabilization of the octahedron, but this would have to be offset by the promotion energy $(1 - \alpha^2)E_p$ required to achieve the mixing. If $E_p$ is sufficiently small then

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[3] We neglect here the fact that in such a system the ground state would in fact be a triplet. This is no longer so, however, if the $d$-$s$ separation is sufficiently large, as it is in all practical cases.

distortion must occur, for we have seen that this is so if $E_p = 0$; that is, if the $d_{z^2}$ and $s$ orbitals are degenerate. Similarly, if $E_p$ is sufficiently large it is clear that little advantage is obtained by mixing the $d_{z^2}$ and $s$ orbitals. Thus it becomes a quantitative question to decide whether any given compound will be stable against distortion or not. Detailed calculations have not been made, but it is an experimental fact that it is just those $d^{10}$ ions which have small $d$-$s$ separations, $Au^+$, $Hg^{++}$, $Ag^+$, and $Cu^+$, which have a strong tendency to give linear complexes (see Table XIV).

TABLE XIV
ENERGIES (EV) OF LOWEST $d^9s$ AND $d^9p$ STATES ABOVE THE $d^{10}$ GROUND STATE (*73*), (*98*)

| | $Cu^+$ | $Zn^{++}$ | $Ag^+$ | $Cd^{++}$ | $Au^+$ | $Hg^{++}$ | $Tl^{3+}$ |
|---|---|---|---|---|---|---|---|
| $d^9s$ | 2.7 | 9.7 | 4.8 | 10.0 | 1.9 | 5.3 | 9.3 |
| $d^9p$ | 8.2 | 17.1 | 9.9 | 17.3 | 7.8 | 14.7 | 18.3 |

The essential difference between the Jahn-Teller effect and the near degeneracy effect which we have just discussed arises because the orbital stabilization is linear in the extent of distortion for the first case (for sufficiently small distortions, at any rate) but quadratic in the second. The restoring forces are always quadratic in the extent of distortion. Thus the Jahn-Teller effect produces a distortion no matter how large the normal restoring forces, while the near degeneracy effect only produces distortion if the quadratic dependence of the stabilization energy on distortion is greater than that of the restoring forces (see Fig. 17).

We turn now to the argument from covalent bonding considerations.[4]

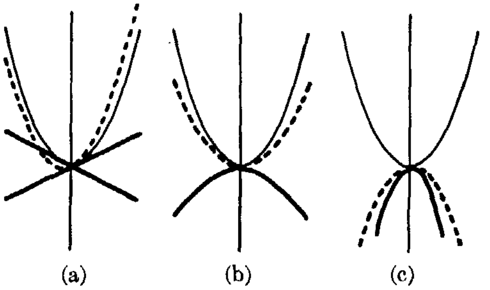

FIG. 17. Potential energy curves for (a) Jahn-Teller distortion, (b) near-degeneracy, small distorting force, and (c) near-degeneracy, large distorting force. The restoring potential is shown as a thin line, the distorting potential as a thick line, the resulting potential as a dashed line.

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[4] This argument seems to have no precise equivalent in an ionic theory so we consider it here.

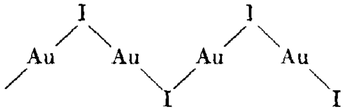
It has been argued (*73*) that the bonds formed by $Hg^{++}$ are more covalent than those formed by $Cd^{++}$ and $Zn^{++}$ because the *s* and *p* orbitals are more stable in the first case. This argument is not good enough as it stands, because an increase in the stability of these orbitals on the metal ion should lead to a uniform increase in bond strength, but not to a reduction in the coordination number. We believe, therefore, that the *s-p separation,* as well as the absolute energies of these orbitals, is important in producing a lowering in the coordination number. If the *s-p* separation were very large we should, from the point of view of a covalent bonding theory, expect discrete MX compounds, insofar as this is allowed by the composition of the substance; for example, in monovalent halides. If the *s-p* separation were small, we should expect high coordination numbers using $sp^3$ or $sp^3d^2$ hybridized orbitals. For intermediate separations, we should expect linear coordination using *sp* orbitals or possibly trigonal coordination using $sp^2$ hybridized orbitals. Thus the greater tendency of $Hg^{++}$, compared with $Cd^{++}$ and $Zn^{++}$, to form linear bonds may be partially attributed to the larger *s-p* separation (by about 2 ev) in $Hg^{++}$. Similar arguments might apply to the other $d^{10}$ ions which form linear complexes.

It seems likely that both the covalent and ionic mechanisms play some part in determining the unusual stereochemistry of these $d^{10}$ ions. The electrostatic arguments do not show whether two or four short bonds are to be anticipated, but analogy with the case of the $Cu^{++}$ ion would suggest the latter. In practice, the other configuration is invariably observed and we are inclined to attribute this to the importance of covalent factors neglected in the ionic theory. On the other hand, there is a drastic change in the *d-s* separation on going from $Zn^{++}$ and $Cd^{++}$ to $Hg^{++}$, which seems more in keeping with the drastic change in typical coordination number than does the comparatively small change in the *s-p* separation. It is not at present possible to decide which effect, if either, is the dominant one.

One must remember too that even if the *tendency* to distort may be largely electrostatic in origin, its *consequences* may include ones that can be understood only in terms of covalent bonding. Once distortion has occurred, for whatever reason, the shorter bonds will certainly be stronger and, in the conventional sense, more covalent. There is, for example, no question that the bonds in the $HgCl_2$ are more covalent than those in $CdCl_2$: the point at issue is rather to establish the reasons why $Hg^{++}$ prefers to form these two more covalent short bonds, and $Cd^{++}$ to form six equivalent, longer, more ionic bonds.

Mixing of the *d* and *s* orbitals in tetrahedrally coordinated $d^{10}$ ions (*108*) can occur only if the symmetry is lowered by an off-center movement of the ion ($T_2$ vibration). In this respect it is interesting that certain unusual features of the X-ray scattering from $Cu^+$ and $Ag^+$ halides can be understood only on the hypothesis that the metal ions have extremely large amplitudes of vibration or, in some cases, if there exist subsidiary potential energy minima displaced from the centers of the coordination tetrahedra (*66*).

We now proceed to discuss the stereochemistry of $d^{10}$ ions in the light of the preceding discussion, beginning with the monovalent ions. The linear coordination about the metal atom in AuI, a structure composed of infinite chains (*144*)



is in contrast to the tetrahedral coordination in CuI and AgI, and establishes the position of $Au^+$ as the ion with the greatest tendency to the formation of linear bonds. At the other end of the scale, the position of $Cu^+$ is established from a comparison of the structures of the complex cyanides $KM^I(CN)_2$. The silver and gold compounds contain discrete linear complexes N—C—M—C—N (*63*), but $KCu(CN)_2$ has an entirely different structure in which the complex anion consists of infinite chains of alternating copper atoms and cyanide groups with the extra cyanide group attached through carbon to each copper atom (*32*). The angle N-Cu-C within a chain is close to tetrahedral and the Cu atom lies about 0.27 Å from the plane of its three nearest neighbors, thus achieving a trigonal pyramidal-like coordination.[4a] In this respect it is interesting that $Cu^+$ readily forms higher complex cyanides $[Cu(CN)_3]^{--}$ and $[Cu(CN)_4]^{3-}$ which are presumably both tetrahedrally coordinated, while $Ag^+$ forms $[Ag(CN)_3]^{--}$ only with difficulty, and $Au^+$ forms only the linear double cyanide. Compounds of $Ag^+$ are known with octahedral (AgF, AgCl, AgBr), tetrahedral (AgI), and linear coordination (AgCN), the coordination number generally decreasing with increase in the electron-donor properties of the attached ligands although with many exceptions. Thus $Ag_2O$, by the usual criteria an ionic substance, has a linear arrangement of oxygen about the silver ions (*149*).

Among the cuprous compounds which have been studied by X-ray methods, linear coordination is quite rare but it does occur in cuprite, $Cu_2O$ (*100*), which is isostructural with argentous oxide, and in cuprous chromite (*33*) and ferrite (*127*). In these three linearly coordinated oxide structures,

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[4a] The coordination about $Cu^+$ in $KCu(CN)_2$ may be described as trigonal (*32*) with 2 C at 1.92 Å and 1 N at 2.05 Å. There is, however, an extra C, belonging to a different chain, at 2.68 Å near the apex of the tetrahedron defined by the three nearest neighbors.

the Cu-O distances are appreciably shorter than the sum of the ionic radii. The only other example of linear coordination in a cuprous compound occurs in the cuprous diazoaminobenzene derivative. This molecule has been shown (*22*) to be dimerized in the solid state, with formation of the eight-membered ring shown in Fig. 18.

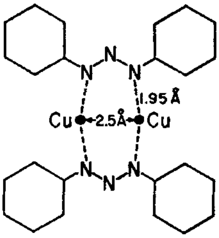


FIG. 18. Drawing of the diazoaminobenzene:copper complex.

Of the divalent $d^{10}$ ions, $Zn^{++}$ and $Cd^{++}$ are invariably found in highly symmetrical environments with coordination number 4 or 6, and it is only $Hg^{++}$ which shows a tendency towards linear coordination. The most ionic compound, $HgF_2$, has the 8-coordinated fluorite structure (Table VI), compatible with the rather large ionic radius (1.10 Å) which has been assigned to the $Hg^{++}$ ion. In crystals of $HgCl_2$ (*18, 47*), $HgBr_2$ (*140*), and the yellow modification of $HgI_2$ (*46*), the $Hg^{++}$ ions are surrounded by six halide groups in a much distorted octahedral arrangement with two coaxial bonds much shorter than the other four. This type of coordination seems to be quite common among mercuric compounds: it occurs also in the complex halides $NH_4HgCl_3$ (*55*) and $K_2HgCl_4.H_2O$ (*89*) and in $HgCl_2$.2 pyridine (*48*) (the last is almost isostructural with $CoCl_2$.2 pyridine and $CuCl_2$.2 pyridine (*34*) but the distortion of the octahedral environment is even more extreme). In all of these compounds the distortion from octahedral coordination has gone so far that discrete $HgX_2$ molecules, similar to those which occur in the gas phase (*50*), may be said to exist in the crystals. Such discrete molecules also occur in the complex of $HgCl_2$ with 1:4 dioxane (*57*) but here there are only two (rather than four) more distant oxygen neighbors. In the red, low-temperature form of the iodide (*10*) the $Hg^{++}$ ions are, however, in tetrahedral coordination and no discrete molecules can be recognized.

The recently determined structure of mercuric oxide has two short collinear Hg-O bonds and two much weaker bonds at right angles (*6*). The sulfide is dimorphic. One form has the tetrahedrally coordinated sphalerite structure (Table V): the other, cinnabar (*5*), contains infinite chains like those of the oxide. Here, however, the packing of the chains is different and is such as to complete a very distorted octahedral environment about the metal. An unusual structure has been reported for the compound $2HgCl_2.HgO$ (*123*), containing trichlormercury oxonium cations with $C_3$ symmetry: the O-Hg-Cl angle is 175°, close to linear.

It is seen that $d^{10}$ ions exhibit a considerable variety in their coordination potentialities, from octahedral and tetrahedral with little or no distortion from regularity, to highly distorted linear coordination. The ions with large *d-s* separations seem to be immune from distortion, but the tendency to distortion does not always run parallel with the *d-s* separations of the different ions. If this were the sole determining factor we should expect $Ag^+$ to show a smaller tendency to linear coordination than $Cu^+$, whereas the contrary is sometimes the case. The importance of covalent bonding is indicated by the increased tendency to linear coordination with increase in the electron-donor properties of the ligands, for a given metal ion. Here again, however, the correlation is only very rough, and there are many exceptions. Finally, the frequent occurrence of polymorphic forms with different coordinations would suggest that the balance between the various factors that are involved may be very sensitive to a number of environmental features which we have neglected in our discussion.

## B. THE "INERT" PAIR

It is well known that the presence of pairs of unshared electrons in the valency orbitals of an atom affects the stereochemistry of the molecule in which it occurs. This is equally evident from the nonplanarity of molecules such as $NH_3$ and $PH_3$ and from the irregular coordination often found about $Sn^{++}$ or $Pb^{++}$ ions. As in the case of many stereochemical facts, interpretations of the influence of the unshared pair can be given either from the electrostatic or from the covalent point of view. Here we restrict our discussion to the most "ionic" compounds of the metals and hence use the electrostatic approach which is then more appropriate. We leave for other publications detailed discussions of the *quantitative* importance of covalency.

Let us first consider the structure of tetragonal (red) lead monoxide from the conventional viewpoint. The $Pb^{++}$ ion has the environment illustrated in Fig. 19 with four nearest neighbors (2.30 Å) forming a square

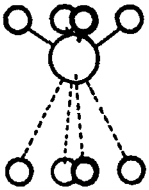


FIG. 19. Environment of $Pb^{++}$ ion in red PbO.

on one side of the metal ion and four more distant neighbors (4.3 Å) completing a much distorted cube (*24*, *99*). It is usually supposed that the "inert" pair occupies an *sp* hybridized orbital pointing away from the four near neighbors and that it is electrostatic repulsion between the unsymmetrically distributed lone pair electrons and the ligands which accounts for the characteristic deviation from cubic symmetry.

Almost all theories agree that the deviation from cubic symmetry of the environment is associated with a nonspherical charge distribution of the unshared pair. We take this for granted and enquire in more detail about the relation of the electronic properties of the metal ion and the nature of the anion to the extent of distortion (*110*). Our arguments follow closely those already outlined for the problem of the distortions associated with $d^{10}$ ions.

Ions with an outer, doubly occupied *s* orbital, such as $Tl^+$ and $Pb^{++}$, differ from all other filled shell ions in that they have a *low lying* excited configuration . . . $(ns)^1(np)^1$, obtained by promoting an electron from the occupied *s* to the unoccupied *p* orbital (6*s*-6*p*) in the case of $Tl^+$ and $Pb^{++}$. The important $^1P$ state of this excited configuration is 7.4 ev above the ground state in the case of $Tl^+$, for example. Since the *s* orbital is spherically symmetrical while the *p* orbital changes sign on reflection in the origin, only antisymmetric vibrations can mix them together. When the octahedron distorts in one of the ways shown in Fig. 20 the stabilization accompanying *sp* mixing tends to counteract the normal forces which hold the octahedron in its regular configuration. An exactly analogous argument holds for distortions from regular cubic coordination. If the *s*-*p* separation is sufficiently small then the regular environment must be unstable. However, it may require low temperatures to reveal the nature of the distortions, for at high temperatures the distortions at different sites may not be ordered in which case the crystal, as a whole, would behave as if it were cubic.[5]

It should be noted that these distortions are sharply distinguished from those predicted for $d^{10}$ ions in that they lead to environments *without a*

[5] "It's your move" said the Queen.

"Oh dear" answered Alice. "But I don't know where to move. One move seems just as good as another and I really cannot make up my mind which is best."

"When I say it's your move, you've got to move whether you like it or not." Alice looked at the board and tried to concentrate on the game but no matter how hard she tried all the moves seemed exactly equivalent. "Take her away and give her a cold compress" cried the Queen angrily—"she won't play properly and she's spoiling the game for me."

She turned to Alice and explained, in a kinder tone, "It's for your own good, my dear. You're looking a little feverish but once you've cooled down you'll be much more cooperative and make just the same move as everyone else. Then I'll be the winner!" (See *126*).

*center of symmetry.* It is the nature of the low lying excited states which dictates the nature of the characteristic distortions, and these are quite different for $d^{10}$ and $d^{10}s^2$ ions.

In our discussion of the stereochemistry of "inert" pair ions we shall restrict ourselves to compounds which have structures that may reasonably be regarded as distortions of simple ionic ones. It must be emphasized that a large number of otherwise relevant compounds do not fall into this category although the environment of the metal nearly always lacks a center of symmetry. For example, the high-temperature modifications of the oxides $As_2O_3$ and $Sb_2O_3$, like the vapor phases of these compounds, contain discrete $M_4O_6$ molecules (*1*) with the characteristic cage structure of $P_4O_6$ (*52*, *94*). On the other hand, as we have seen, no discrete PbO molecules can be recognized in the structure of red PbO, which can be regarded as a distortion of the typically ionic CsCl structure. Exactly the same structure is found for the "inert" pair oxide, SnO (*99*).

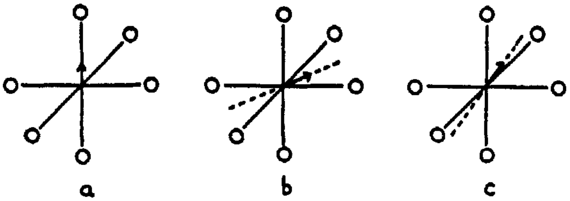


FIG. 20. Distortions from octahedral coordination preserving (a) a fourfold axis, (b) a twofold axis, (c) a threefold axis.

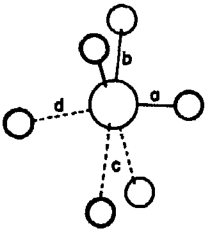


FIG. 21. Environment of the metal ion in GeS and SnS. The interatomic distances are, for GeS and SnS respectively (a) 2.47, 2.68, (b) two: 2.64, 2.62, (c) two: 2.91, 3.27, and (d) 3.00, 3.39 Å.

In the same way, the structures of GeS (*151*) and SnS (*65*) can be regarded as distortions of the rocksalt structure. The deviations from octahedral coordination are not quite the same but are very similar in that in both compounds the metal ion is much closer to three of its neighbors than to the other three (Fig. 21). Another kind of deviation from octahedral coordination is found in TlF which also possesses a distorted rocksalt structure. The early structure determination in which the $Tl^+$ ion was at the *center* of a distorted octahedron has now been shown to be incorrect. In the revised structure (*56*) each metal ion has five nearest neighbors and one more distant. In TlI (*59*), InBr (*129*), and InI (*71*) this kind of distortion has become more extreme: there are only five neighbors, one corner of the octahedron being unoccupied (Fig. 22). TlCl and TlBr, on the other hand, appear to have the undistorted CsCl structure at ordinary temperatures (*150*). A 5-coordinated structure, based on a distorted octahedron but with one corner missing also occurs in complex salts of the type $M^+SbF_4$ and $M_2{}^+SbF_5$ (*39*).

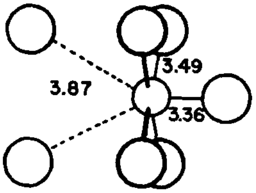


FIG. 22. Environment of the $Tl^+$ ion in TlI. Regarded as either 5- or 7-coordination the distortion from an octahedron can be clearly recognized (distances in Angstrom units).

Pronounced off-center distortions of a rather different kind occur in tetragonal $PbTiO_3$ (*124*) and orthorhombic $PbZrO_3$ (*70*). Both crystals have deformed perovskite structures. In the ideal cubic structure (Fig. 23) each $Pb^{++}$ ion would be in cubic closest packing with 12 oxygen neighbors, but in the titanate the $Pb^{++}$ ion moves by 0.5 Å from its ideal position to give four nearest neighbors (2.53 Å) arranged in a similar fashion as in red PbO, four more distant ones (2.80 Å), and four very distant ones (3.20 A). In the zirconate there is also a large displacement of the $Pb^{++}$ ion, but this time along a threefold axis of the cube, to give three nearest neighbors (2.55 Å) at the corners of a rather flat trigonal pyramid, with six more dis-

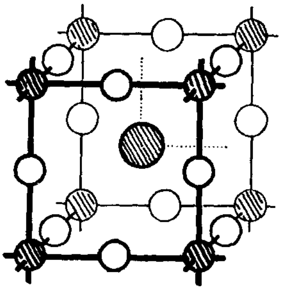


FIG. 23. The cubic perovskite ($ABO_3$) structure. The small B ion is octahedrally surrounded by oxygens, the large A ion is in cubic closest packing with 12 oxygen neighbors. Removal of the large A ion gives the $ReO_3$ structure.

tant and three very distant neighbors. It must be emphasized that in these compounds, the $Ti^{4+}$ and $Zr^{4+}$ ions also undergo considerable displacements from the centers of their surrounding oxygen octahedra. The nature of these is discussed in the next section.

Extreme forms of the trigonal distortion shown in $PbZrO_3$ occur in orthorhombic (yellow) PbO and in $Pb_3O_4$ (*26*). In both of these compounds, the environment of the $Pb^{++}$ ions is best described as 3-coordinated, based on tetrahedral coordination but with one corner missing, and with a rather indefinite number of next nearest neighbors. The short Pb-O distances are about 2.24 Å. A very similar 3-coordinated arrangement of oxygens about the $Sb^{3+}$ ion occurs in compounds of the type $M^{++}Sb_2O_4$ (isostructural with $Pb_3O_4$) and also in the low-temperature modification of $Sb_2O_3$, and about the $Bi^{3+}$ ion in $Bi_2O_3$ (*26*). These structures, however, can scarcely be regarded as distortions of simple "ionic" ones and are perhaps better considered in the usual way, as involving covalent bonding, with the "inert" pair pointing away from the other ligands. But although the approach from distortion of regular ionic packing may be misleading if taken too seriously, it does enable us to recognize the intermediate stages in the transition from high-coordinated, regular, ionic environments to low-coordinated, unsymmetrical, covalent ones.

The low-coordination structures, so characteristic of the oxygen compounds of $Pb^{++}$, do not seem to occur in the halides. At least two modifications of $PbF_2$ are known to occur, one with the 8-coordinated cubic fluorite structure, the other, held in common with $PbCl_2$, $PbBr_2$, $BaCl_2$, $BaBr_2$, etc., with the metal ions in 9-coordination as in Fig. 3d. Interatomic distances are not known with precision for any of these compounds and it may also be mentioned that the evidence for the plane of symmetry in this structure cannot be regarded as convincing by modern criteria. The interatomic distances reported for the fluoride (*25*) make five Pb-F bonds (2.50 Å) shorter than the other four (2.85 Å): for the chloride (*17*), one distance is 2.67 Å, two are about 2.90 Å, and the other six are greater than 3 Å. The iodide is also dimorphic (*150*), occurring with the $CdI_2$ and $CdCl_2$ structures, in both of which the metal ions are presumably octahedrally coordinated. Thus the "inert" pair does not seem to play such an important role in determining the structures of the halides, as it does for the oxides.

It is possible, making use of known values of ionic polarizabilities, to calculate semiquantitatively the extent to which polarization stabilizes the distorted structures (*110*). The stabilization energy, like the restoring potential, increases quadratically with the extent of the distortion and is of the same order of magnitude. Particularly interesting is the $R^{-6}$ dependence of the stabilization on the interatomic distance $R$, for this suggests that the small anions $F^-$ and $O^{--}$ should lead to particularly pronounced stereochemical effects. This is in contrast to the predictions of a purely covalent model of the distortion mechanism, which would lead to larger distortions in, say, sulfides than in oxides. It is, therefore, particularly interesting that "metallic" PbS has the rocksalt structure but that both forms of PbO are strongly distorted. Similarly, TlCl has a cubic structure but TlF is distorted. On the other hand, one would certainly expect a much more pronounced "inert" pair distortion in $PbF_2$ than probably occurs, particularly in the low-temperature $PbCl_2$-like modification.

## VI. Small Ion Distortions and "Rattling" (*109*)

Up till now, the distortions from cubic symmetry that we have discussed have all been attributed to various features of the electronic structure of the metal ion which lack spherical symmetry and which hence lead to more or less strongly directional electrostatic interactions with the environment. In other words, these deviations from ideal ionic packing result from the breakdown, in a number of cases, of the assumption made on p. 2 that ions can be regarded as *spheres.*

We now consider a quite different type of distortion, a good example of which occurs in the structure of vanadium pentoxide, $V_2O_5$ (*27*). The environment of the $V^{5+}$ ion is illustrated in Fig. 24. Each $V^{5+}$ ion has five oxide neighbors in a trigonal bipyramid-like arrangement at distances ranging from 1.54 to 2.02 Å. At the very great distance of 2.81 Å from the $V^{5+}$ ion occurs a sixth oxide neighbor which can be regarded as completing a very distorted octahedron. Clearly, none of the electronic factors previously introduced can play any important role in this very marked off-center displacement which, although rather extreme, is typical of a whole class of distortions to be found in the higher oxides of transition metals.

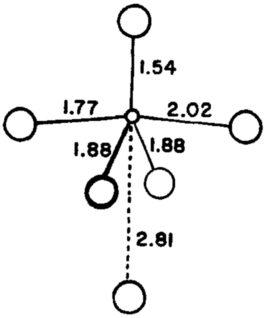


FIG. 24. Environment of the $V^{5+}$ ion in vanadium pentoxide (distances in angstrom units).

We believe that this class of distortions has its origin in the breakdown of other assumptions of the elementary ionic theory, namely, that ions are incompressible and that an arrangement of ions of one charge about an ion of opposite charge is stable only if the central ion makes simultaneous contact with each of its neighbors. We shall see that if we relax these restrictions we do not necessarily predict a sharp transition from octahedral to tetrahedral coordination at the limiting ratio, 0.414. On the contrary, a more realistic consideration of the potential energy of aggregates of ions shows that a slowly developing instability of the octahedral structure with respect to the tetrahedral may occur as the size of the central cation decreases. This instability leads successively to a loosening of the central cation at the center of its surrounding octahedron, to off-center displacements characteristic of ferroelectric and antiferroelectric substances, and finally to such large distortions that the coordination of the central ion becomes fivefold or tetrahedral. According to this view, 5-coordinated structures do not necessarily indicate a curious bonding tendency of the metal ion but merely represent a stage in the gradual transition from 6-coordinated to 4-coordinated structures.

We suppose that a cation M is surrounded by a regular octahedral arrangement of oxide ions which, for the moment, may be regarded as fixed, as they would be if they formed part of a close-packed array. The cations can then be imagined as occupying the octahedral interstices of such a close-packed oxide structure. If the cation is sufficiently large (Fig. 25a), it will be subjected to compression by the fixed environment of oxide ions, and the potential energy diagram describing the motion of M away from its central position is of the type shown, for any direction of displacement.

On the other hand, if the cation is sufficiently small, it is no longer compressed. For small displacements, its potential energy depends solely on Coulombic forces, and only for large displacements do the repulsion forces come into play. The potential energy diagram is of the form shown in Fig. 25b, and the symmetrical configuration is now one of maximum potential energy. (Obviously, if the dimensions of the oxide octahedron become very large, an MO molecule and five oxide ions is more stable than the set of widely separated ions.)

Somewhere between these two extremes there must be a radius of the metal ion for which the potential energy curve is *flat* for small displacements from the center of the octahedron (Fig. 25c). We call the corresponding interionic distance the *maximum contact distance* $L_0$, for insofar as analogies with classical particles are permissible, the flatness of the potential energy curve may be said to correspond to contact between compressible spheres. If the interionic distance increases the metal ion becomes free to "rattle": if it is decreased the metal ion is subjected to compression. Note too that the maximum contact distance does not correspond to the sum of the ionic radii as usually defined (see Appendix).

Our assumption that the anions are fixed and form part of a rigid extended framework within whose octahedral interstices the cations are free to move is not, of course, very realistic except, perhaps, when the anions form a close-packed arrangement. For some other structures it would seem equally plausible (or implausible) to assume that the cations were rigid and that the anion environment could be distorted, though only in such a way as to make an extended framework possible. Neither of these models is in any sense complete but they are distinct in that they may lead to rather different kinds of distortion. If the anions are fixed, then the distorted structure *must* lack a center of symmetry. If they are free to move to any extent, the distorted structure may or may not be centrosymmetric. In fact, most of the higher oxides of transition-metal ions do have structures based on close-packed, or nearly close-packed anion arrangements so that off-center displacements of the metal ion are the rule, while symmetric collapsing of the coordination polyhedron is found much less frequently, if at all.

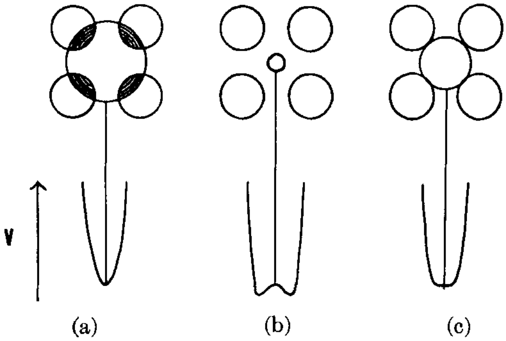
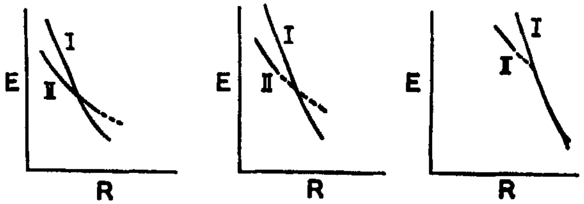


FIG. 25. Variation of potential energy with displacement of a metal ion from the center of a fixed oxide octahedron (for clarity shown in two dimensions): (a) large ion, (b) small ion, (c) ion of intermediate size.

Some comments on distortions from cubic eightfold coordinated oxide structures are of interest in this connection. Hafnium dioxide, $HfO_2$, has the 8-coordinated fluorite structure (see Table VI), while $ZrO_2$ only adopts this structure in an unstable high-temperature modification. In the stable, room-temperature modification, baddeleyite, the coordination is only sevenfold but can still be regarded as derived from a cube with four oxygens at the base and one at one of the upper corners, the remaining two being at the midpoints of the cube edges between the unoccupied corners (*87a*). Alternatively the Zr atom may be regarded as occupying the common apex of a tetragonal and of a trigonal pyramid, so oriented that one atom of the oxygen square is directly opposite another of the oxygen triangle. The Zr-O distances range from 2.04 to 2.26 Å. A quite different kind of distortion from a cube occurs in zircon, $ZrSiO_4$. Here (*78a*), the symmetry of the Zr environment has been reduced from cubic to only $\bar{4}2m$ ($D_{2d}$), and the cube collapses into two tetrahedra rotated 90° with respect to each other, one flattened (Zr-O, 2.15 Å), the other elongated (Zr-O, 2.29 Å). We see that when the size of the central ion is reduced beyond the point at which cubic coordination becomes unstable, we do not necessarily get octahedral coordination but rather distorted cubic environments which, at least in the two examples mentioned, lack a center of symmetry.



(a) (b) (c)

FIG. 26. Potential energy diagrams showing possible types of transition from octahedral (II) to tetrahedral (I) coordination; —, stable; - - -, unstable. (a) Transformation from stable octahedral to stable tetrahedral coordination, (b) development of unstable octahedral coordination before transition to stable tetrahedral coordination, (c) unstable octahedral coordination changing continuously to tetrahedral coordination (*109*).

We now consider the consequences of continuously reducing the size of the central cation in an octahedrally coordinated structure. First, there may be another structure, perhaps quite unrelated and involving tetrahedral or other coordination, which becomes stable relative to the octahedral structure before the latter becomes unstable with respect to small displacements, that is, before the maximum contact distance is reached. In this case there is a sudden change from regular octahedral to regular tetrahedral coordination, as shown in Fig. 26a. The oxides of the divalent transition-metal ions have structures in accord with this model, for, in the absence of Jahn-Teller effects, they are either octahedrally or tetrahedrally coordinated.

Another possibility is that instability with respect to small distortions occurs before any tetrahedrally coordinated structure becomes stable relative to the octahedral one. In this case, Fig. 26b, we have a range of metal radii for which the structure is neither regular octahedral nor regular tetrahedral, but, rather, distorted octahedral. At high enough temperatures, the metal ions will generally be distributed at random over offcenter sites if the distortion is small, but at lower temperatures cooperative interactions between the ions will lead to a structure involving a definite arrangement of displaced metal ions in almost regular octahedral coordination. The ferroelectric and antiferroelectric oxides with distorted perovskite or $ReO_3$ structures belong to this class. We may carry this argument further by supposing that extensive distortion is possible before a tetrahedral structure becomes stable. Then, just as for ions with a pair of *s*-electrons, the distorted environments will correspond to a coordination number of less than six, possibly with a sufficient number of more distant neighbors to complete a very distorted environment, as for example, in $V_2O_5$.

Finally, there is the possibility that a sufficiently distorted octahedral structure may be able to go over continuously into a tetrahedral structure, as shown in Fig. 26c. An example of this is seen in the $MO_3$ oxides. $WO_3$ has a structure (*2*) which is only a slight distortion of the cubic $ReO_3$ type (see Fig. 23) in which the metal ions occur in the octahedral interstices of a nearly close-packed array of oxide ions. In $MoO_3$, the distortion from the ideal structure has increased. Although the coordination can still be described as octahedral, one oxygen is much more distant than the other five, giving a square pyramidal arrangement of nearest neighbors (*4*). In $CrO_3$ (*28*) the distortion has become extreme. The structure contains chains $-CrO_2-O-CrO_2-O-CrO_2-$ in which each $Cr^{6+}$ ion is tetrahedrally coordinated, but the chains are arranged in such a way that there are two very distant neighbors (3.10 Å) completing a very distorted octahedral environment.

$WO_3$, $MoO_3$, and $CrO_3$, therefore, illustrate three stages in the transition from octahedral to tetrahedral stereochemistry: slightly distorted, strongly distorted, and, finally, tetrahedral with two scarcely recognizable additional ligands.

Since instability to distortions increases as the "size" of the metal ion becomes smaller, it is possible to arrange the various ions of high valency in approximate order of "size" from a comparison of the crystal structures of their oxides. We shall not carry out this analysis in detail but shall draw attention to a number of important features.

The very largest ions will be 8-coordinated and indeed $ThO_2$, $CeO_2$, $PrO_2$, $UO_2$, $HfO_2$, $NpO_2$, $PuO_2$, and $AmO_2$ occur with the regular fluorite structure (*150*). For $ZrO_2$, as already mentioned, the stable crystal modification is only 7-coordinated (*87a*) but in the mineral zircon, $ZrSiO_4$, the $Zr^{4+}$ ions are again in distorted 8-coordination (*12*, *78a*, *138*). We may suppose that $Zr^{4+}$ is the smallest of the above mentioned tetravalent ions. Next come those ions whose dioxides have the 6-coordinated rutile structure, $PbO_2$, $NbO_2$, $OsO_2$, $RuO_2$, $SnO_2$, $IrO_2$, $TaO_2$, $TiO_2$, and $GeO_2$ (see Table VII and ref. *150*). In the last two members, the oxygen-oxygen distances are such that large anion-anion repulsions must come into play, and the octahedron cannot contract any further. This suggests that $Ti^{4+}$

(and $Ge^{4+}$) have $L$ close to $L_0$ for the 6-coordinated rutile structure. The metal-oxygen distances have been determined in both $TiO_2$ and $GeO_2$ with good accuracy (*9*). In both compounds the octahedra are not far from regular; Ti-O, 1.94 Å (four), 1.99 Å (twice); Ge-O, 1.87 Å (four), 1.91 Å (twice). The shortest O-O distances are 2.52 and 2.40 Å respectively.

That $Ti^{4+}$ is close to the critical size is much more convincingly shown by the occurrence of this ion in a large number of oxide ferroelectrics of the general formula $A^{++}TiO_3$. At high enough temperatures, these compounds are cubic with the perovskite structure (regular octahedral coordination), but, on lowering the temperature, transitions to ferroelectric distorted structures, characterized by offcenter displacements of the $Ti^{4+}$ ion, occur. In tetragonal $BaTiO_3$, the displacement is along a fourfold axis of the octahedron, the Ti-O distances being 1.87, 2.00 (four), and 2.17 Å (*44*). At lower temperatures, a rhombohedrally distorted structure occurs, the displacement of the $Ti^{4+}$ ion being now presumably along the threefold axis (*96*). In tetragonal $PbTiO_3$, the displacement of the $Ti^{4+}$ ion is even greater than in the barium compound, the distances being 1.78, 1.98 (four), and 2.38 Å (*124*). Here a large complementary displacement of the $Pb^{++}$ ion also takes place to give the metal ion four nearest neighbors, the arrangement being square pyramidal as in PbO (see Section V.B).

The structure of $VO_2$ is closely related to that of $TiO_2$. It is a monoclinic distorted rutile-like structure in which the $V^{4+}$ ion has moved away from the center of the surrounding octahedron, approximately along a threefold axis, to give three short bonds, 1.86, 1.87, and 1.76 Å, and three long ones, 2.01, 2.03, and 2.05 Å (*3*). The displacement is thus similar to that which probably occurs in the rhombohedrally distorted perovskites. A distortion something like that in tetragonally distorted perovskites occurs in hydrated vanadium dioxide, $V_2O_4.2H_2O$ in which there is one V-O bond of 1.65 Å, much shorter than any other (*41*). The structures of $MoO_2$, $WO_2$, $TcO_2$, and $ReO_2$ are closely related to that of $VO_2$ (*91*). These facts suggest that $V^{4+}$, $Mo^{4+}$, $W^{4+}$, $Tc^{4+}$, and $Re^{4+}$ have radii considerably smaller than the critical contact radius for an oxide octahedron. The possibility that the distortions are attributable to a Jahn-Teller effect can be discounted since this should always produce an arrangement distorted in such a way as to preserve a center of symmetry, contrary to the observed displacements of the metal ions from the center of their surrounding octahedra. Nevertheless, some sort of bonding interaction between metal ions, involving the use of the *d* electrons, cannot be excluded, and in order to contrast the crystal chemistry of $Ti^{4+}$ with that of smaller metal ions without introducing complications due to the presence of *d* electrons, one is obliged to go to $V^{5+}$ and $Cr^{6+}$.

Pentavalent vanadium occurs in a variety of different oxide environments, and may be 4-, 5-, or 6-coordinated. Isolated $VO_4$ tetrahedra occur in the orthovanadates, for example, in $BiVO_4$ (*119*) and in $CrVO_4$ (*19*). In the metavanadates, $NaVO_3$ (*128*) and $KVO_3$ (*40*), chains of tetrahedra joined by corners are found. In $KVO_3.H_2O$, the $V^{5+}$ ion is in an almost exactly trigonal bipyramidal environment (*29*). In $V_2O_5$, as we have seen, the vanadium ion is again 5-coordinated but with a further distant oxide neighbor to complete a much distorted octahedron. The compound $NaV_6O_{15}$ contains $V^{5+}$ ions in two different types of distorted octahedral environments (*143*). In one type the V-O distances vary from 1.57 to 2.33 Å, in the second type the distortion is more extreme, one V-O bond being 2.68 Å so that the ion can be considered to be 5-coordinated. We have already drawn attention to the gradually increasing departure from ideal ionic packing which takes place as we go from $WO_3$, through $MoO_3$, to $CrO_3$. A rather similar relationship exists between the structures of $NaTaO_3$, $NaNbO_3$, and $NaVO_3$. While the compounds of the heavier elements are ferroelectrics based on the perovskite structure, the vanadate is a tetrahedrally coordinated structure. Pentavalent niobium and tantalum appear to have octahedral coordination, often distorted, in all of their oxide compounds. Those of the composition, $A^+NbO_3$, $A^+TaO_3$, have perovskite-like structures (*142*), those of the composition $A^{++}Nb_2O_6$, $A^{++}Ta_2O_6$ have the niobite structure (*20*). In niobite itself, $(Fe,Mn)Nb_2O_6$, the $Nb^{5+}$ ion is in octahedral coordination but is displaced from the center towards one of its neighbors to form one rather short bond, 1.86 Å, the other five contacts being from 2.04 to 2.12 Å (*131*). Compounds of the formula $A^{3+}NbO_4$, $A^{3+}TaO_4$ have a rutile-like structure, with the two kinds of metal ion randomly distributed over the octahedral sites (*20*).

It would seem that $W^{6+}$ and $Mo^{6+}$ ions are able to occur in both tetrahedral and octahedral (usually deformed) coordination. Although most of the simple tungstates and molybdates have structures based on tetrahedral coordination the series $Ca_3WO_6$, $Sr_3WO_6$, $Ba_3WO_6$, and a number of related molybdates possess octahedrally coordinated (possibly deformed) structures (*130*). The more complex para-, meta-, and poly-acid salts (*81, 82, 83*) and the heteropoly-acids (*75*) are also octahedrally coordinated. Sodium dimolybdate $Na_2Mo_2O_7$ (and the isostructural ditungstate) contains highly distorted $MoO_6$ octahedra and $MoO_4$ tetrahedra (*84*).

These selected examples, and a number of others, suggest that for the transition-metal ions with empty *d* shells, the contact radius decreases (and instability to distortion increases) in the approximate order $Hf^{4+}$, $Zr^{4+}$, $Ti^{4+}$, $Ta^{5+}$, $Nb^{5+}$, $W^{6+}$, $Mo^{6+}$, $V^{5+}$, $Cr^{6+}$, $Mn^{7+}$ (Table XV). Ferroelectrics are largely restricted to compounds containing the group of ions of intermediate size, $Ti^{4+}$, $Ta^{5+}$, $Nb^{5+}$, $W^{6+}$. We can see, in a qualitative way, why this should be so. Larger ions are too stable in regular octahedral environ-

TABLE XV
COORDINATION POLYHEDRA IN OXIDES OF TRANSITION-METAL IONS WITH INERT GAS CONFIGURATIONS

| Ion | Pauling ionic radius (Å) | Coordination | Examples |
|---|---|---|---|
| $Hf^{4+}$ | — | Cubic | $HfO_2$ |
| $Zr^{4+}$ | 0.80 | Cubic | $ZrO_2$ (>1600°C) |
| | | Distorted cubic | $ZrO_2$, $ZrSiO_4$ |
| | | Octahedral | $BaZrO_3$ |
| $Ti^{4+}$ | 0.68 | Octahedral | $TiO_2$, $BaTiO_3$ (>120°) |
| | | Distorted octahedral | $BaTiO_3$ |
| $Ta^{5+}$ | — | Octahedral | $NaTaO_3$ (>475°) |
| | | Distorted octahedral | $NaTaO_3$ |
| $Nb^{5+}$ | 0.70 | Octahedral | $NaNbO_3$ (>640°) |
| | | Distorted octahedral | $FeNb_2O_6$, $NaNbO_3$ |
| $W^{6+}$ | — | Distorted octahedral | $WO_3$ |
| | | Tetrahedral | $CaWO_4$ |
| $Mo^{6+}$ | 0.62 | Distorted octahedral (Square pyramidal +1 distant) | $MoO_3$ |
| | | Tetrahedral | $CaMoO_4$ |
| $V^{5+}$ | 0.59 | Very distorted octahedral (3 near + 3 distant) | $VO_2$ |
| | | Trigonal bipyramid (+1 distant) | $V_2O_5$ |
| | | Trigonal pyramid | $KVO_3 \cdot H_2O$ |
| | | Tetrahedral | $NaVO_3$ |
| $Cr^{6+}$ | 0.52 | Tetrahedral (+2 distant) | $CrO_3$ |
| | | Tetrahedral | $BaCrO_4$ |
| $Mn^{7+}$ | 0.46 | Tetrahedral | $KMnO_4$ |

The simple ionic theory predicts transition from octahedral to tetrahedral oxide environment at $r_M \sim 0.58$ Å, assuming $r_O^{--} = 1.40$ Å.

ments, while smaller ions form structures which are so strongly distorted that no phase transition occurs below the melting point, and, if the structure is polar, the field required to reverse the polarization cannot be attained. We must emphasize, too, that the idea of a critical ionic radius at which "rattling" of metal ions within their oxide environments begins is part of the Mason and Mathias theory of ferroelectricity (*93*).

## VII. Conclusions

We have seen that many characteristic features of metal ion stereochemistry which involve the occurrence of ions in sites of unexpectedly low symmetry can be explained without recourse to detailed arguments about the nature of the chemical bonding. We have emphasized particularly that ions with incomplete *d* electron shells may intrinsically have less than spherical symmetry. In such cases the electronic structure may be incompatible with the existence of a cubic environment about the metal ion.

In a rather similar way ions which have all their electrons in closed shells may nevertheless show a strong tendency to occur in distorted environments if there exist sufficiently low lying excited states. Essentially the electronic distribution is then so easily distorted that the ion becomes less than spherically symmetrical once it is brought into contact with ions of the opposite charge. The distortion of the electronic cloud corresponds to a simple polarization in the case of $(ns)^2$ ions, and hence the environment must lack a center of symmetry if it is to produce an appreciable stabilization energy. With $d^{10}$ ions the nature of the polarization is different (quadrupole polarization) and a quite different environment is required.

In addition to these effects of the electronic properties of the free ions on stereochemistry we have also discussed the effect of ionic size somewhat more fully than is usual. Again we find that certain distortions from cubic symmetry can be understood qualitatively in terms of the properties of ions without detailed consideration of covalency.

In every case we have emphasized that the distortions are not without effect on the covalent character of the bonds involved. We have tried to show that the *tendency* to distortion could often have an electrostatic origin, and hence that other than stereochemical arguments must be used in determining the degree of covalency both in distorted and in undistorted complexes. Such methods include the study of antiferromagnetic interaction, nuclear magnetic resonance spectra, and paramagnetic resonance spectra.

For convenience we have usually supposed environments of less than cubic symmetry to arise by distortion from fully cubic ones. This is particularly useful when the distortions are small, but inadequate if the deviations from cubic symmetry are very large. Even in the latter case our general principles should apply, for example, centrosymmetrical environments should be common for $d^9$ and $d^{10}$ ions but not for $s^2$ ions. The justification for our approach is that it provides a useful bridge between cubic and other structures which enables the cause of the unusual stereochemistry to be more easily discerned.

Finally we note that once the various types of characteristic distortions have been recognized, predictions of new properties can be made. For example, oxides of $s^2$ ions should form mixed crystals with oxides of transition metals in sufficiently high valencies, since, for different reasons, they are both susceptible to antisymmetric distortion. This seems to be the case.

Again, cubically coordinated $Tl^+$ salts should be particularly susceptible to polarization by applied fields; that is, they should have anomalously large dielectric constants.

## VIII. Appendix: Ionic Radii

Of the several systems of "ionic" radii which have been proposed to account for the approximately additive relationships which exist between the observed interatomic distances in ionic crystals, the one which has come into most general use is that of Pauling (*111*, *114*). This is not, as is variously supposed, either a set of empirical radii derived purely from the experimental data which it is, in turn, supposed to reproduce, or one which has been derived purely from theoretical considerations. It is a semiempirical system in the sense that from a very limited set of experimental data, certain relationships are derived using approximate theories of atomic and crystal structure, which adequately account for a much wider set of data.

Since no precise physical significance can be attached to the concept of atomic or ionic radius (the electronic wave functions approach zero asymptotically), the radii to be assigned are those which reproduce the equilibrium interatomic distances in ionic crystals. These distances depend on the balance between the attractive and repulsive forces, and thus not only on the electron distributions of the ions but also on the crystal structure and the radius ratios. Pauling assumes that the relative sizes of a pair of isoelectronic ions are inversely proportional to the effective nuclear charges operating on the outmost electron shell; that is

$$r_1 = C_n/(Z - S),$$

and divides the experimental interatomic separation in this ratio. The quantity $C_n$ is a constant for a given isoelectronic sequence, depending only on the total quantum number of the outmost electrons; $Z$ is the atomic number; and $S$ is a screening constant. For neon-like ions, $S$ is 4.52 and hence the effective nuclear charges for $Na^+$ and $F^-$ are $6.48e$ and $4.48e$ respectively. We now have

$$\frac{r_1(Na^+)}{r_1(F^-)} = \frac{4.48}{6.48},$$

$$r_1(Na^+) + r_1(F^-) = 2.31 \text{ Å},$$

and hence $r_1(Na^+) = 0.95$ Å and $r_1(F^-) = 1.36$ Å. From the observed interatomic distances—Na-F, 2.31 Å; K-Cl, 3.14 Å; Rb-Br, 3.43 Å; Cs-I[6], 3.85 Å—the effective radii of the singly charged ions are calculated and

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[6] This value is that observed in CsI reduced by 2.7% to give the value for 6-coordination, assuming $n = 12$ (see p. 56).

the constants $C_n$ are then used to derive a set of "univalent radii" for multiply charged ions with inert gas configurations. These "univalent radii" are "the radii which multivalent ions would possess if they were to retain their electron distribution but enter into Coulomb attraction as if they were univalent." They do not, as they stand, reproduce observed interatomic distances. In order to convert them into crystal radii we have to take into account the effect of the ionic charge on the equilibrium distance. From the Born equation we have

$$V = -\frac{Ae^2z^2}{R} + \frac{Be^2}{R^n},$$

where $V$ is the potential energy; $A$, the Madelung constant; and $B$, the Born coefficient.

Hence,

$$\frac{dV}{dR} = \frac{Ae^2z^2}{R^2} - \frac{nBe^2}{R^{n+1}}.$$

At equilibrium $dV/dR = 0$ and $R_z = (nB/Az^2)^{1/(n-1)}$. If the ions were to enter into Coulomb attraction *as if* they were monovalent, with the repulsion coefficient unchanged, the equilibrium interatomic distance would be

$$R_1 = (nB/A)^{1/(n-1)}$$

corresponding to addition of univalent radii, and hence

$$R_z = R_1/z^{2/(n-1)}.$$

Approximate values of $n$ are known for various types of ions and are used to calculate the crystal radii of Table III.[7]

Since the ionic radii of Table III have been obtained with reference to the NaCl type of structure as standard, it is not to be expected that they should apply to other types without corrections to take into account possible variation of $A$ and $B$. For two different structures with Madelung constants $A_1$ and $A_2$, and repulsion coefficients $B_1$ and $B_2$ we have

$$\frac{R_2}{R_1} = \left(\frac{A_1B_2}{A_2B_1}\right)^{1/(n-1)}.$$

If it is now assumed that $B_1$ and $B_2$ are proportional to the respective coordination numbers for the two structures, we can virtually ignore the ratio $A_1/A_2$ which is always close to unity and write

$$\frac{R_2}{R_1} = \left(\frac{B_2}{B_1}\right)^{1/(n-1)}.$$

---

[7] The "ionic radius" assigned to $Li^+$ (0.60 Å) is obtained from a further experimental quantity, namely the observed Li-O distance in $Li_2O$ (2.00 Å) from which the calculated ionic radius of $O^{--}$ (1.40 Å) is subtracted.

Thus, for a change in coordination number from 6 to 8 and for $n = 9$, the standard ionic radius must be multiplied by $(8/6)^{1/8} = 1.036$. For a change from 6 to 4, the corresponding factor is 0.950.

In the derivation of these ionic radii, it has been assumed that the repulsion coefficient $B$ depends only on the coordination number; that is, on the number of anion-cation contacts, but if the radius ratio is close to or less than the lower limit, anion-anion contact occurs and the additional Born repulsion will lead to equilibrium with the attractive Coulomb forces at a larger distance than that given by the sum of the ionic radii. This phenomenon of "double repulsion" is shown (see tabulation) by the lithium halides especially. In a more detailed treatment, Pauling (*112*, *114*) has used a modified form of the Born expression for the lattice energy considered now not as a function of the cation-anion distance alone, but taking into account also the dependence of the Born repulsion energy on anion-anion and cation-cation distances. The equilibrium value of $R$ now depends not only on the magnitudes of the ionic radii but also on the radius ratio

| | LiF | LiCl | LiBr | LiI |
|---|---|---|---|---|
| Sum of ionic radii (Å) | 1.96 | 2.41 | 2.55 | 2.76 |
| Observed distance (Å) | 2.01 | 2.57 | 2.75 | 3.02 |
| Radius ratio $r_M/r_X$ | 0.44 | 0.33 | 0.31 | 0.28 |

$$R_0 = (r_{m^+} + r_{x^-})F\left(\frac{r_{m^+}}{r_{x^-}}\right),$$

where $F$ is a rather complicated function of the radius ratio. Pauling has evaluated this function for the NaCl structure, and has shown that it compensates exactly for the deviations from strict additivity in the alkali halide series.

For crystals in which the charge of the anion and cation are unequal it is more appropriate to use the univalent radii for estimating the radius ratio. This is because the stabilities of the various coordination polyhedra depend on the relative magnitudes of cation-anion and anion-anion repulsions. For calculating the absolute distances between multiply-charged ions in such crystals, it is sufficient to use the direct sum of the crystal radii without correction (see ref. *114*, p. 365).

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