

843. *Stereochemistry of Metals of the B Sub-groups. Part I. Ions with Filled d-Electron Shells.*

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The tendency of Hg^{++} , Au^+ , Ag^+ , and Cu^+ to form compounds in which the metal is attached to only two ligands is attributed to d - s mixing rather than to the special stability of sp -hybrid bonds.

SIMPLE theories of the structures of ionic crystals which treat the component ions as charged, non-polarisable spheres almost inevitably conclude that the most stable arrangements of anions about a given cation has high symmetry.¹ In particular, regular tetrahedral and octahedral environments are predicted to be most stable for tetra- and hexa-co-ordinated cations respectively. These are the most common arrangements encountered in inorganic stereochemistry.

The case of octa-co-ordination is more complicated, for the commonly occurring arrangement of anions at the vertices of a cube is predicted to be unstable relative to their disposition at the vertices of a square antiprism, at least for an isolated XY_8 group. Presumably it is the difficulty of combining these antiprisms into a structure extended in space that prevents their common occurrence in binary compounds. The TaF_8^{3-} ion does have the square-antiprism structure and, although it has been suggested that d^4sp^3

¹ Wells, "Structural Inorganic Chemistry," 2nd edn., Oxford Univ. Press, 1950.

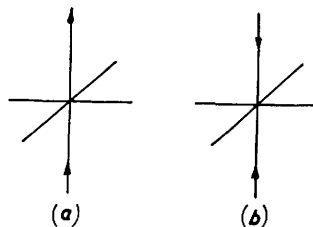
bonding is involved,² there is no reason to suppose that the observed stereochemistry is a consequence of anything other than the electrostatic repulsion between fluoride ions.

There are at least four large groups of related compounds which contain metal ions in environments of less than cubic symmetry. We have dealt with transition-metal compounds^{3a} containing ions such as Cu^{++} , Cr^{++} , and Ni^{++} and with the oxides of the A subgroup such as MoO_3 and BaTiO_3 .^{3b} In this and another paper⁴ we investigate a different group of ions, those either with a filled d^{10} shell or with an inert pair of s electrons. The instability of the octahedral and cubic environments for these ions in certain of their compounds is due to the energies and electronic configurations of their lowest excited states.

General Theory.—A similar environment might be expected for d^{10} ions and A subgroup closed-shell ions in analogous compounds. There is indeed as close a resemblance between the stereochemistry, for example of the Zn^{++} and the Mg^{++} ions as can be expected in view of their different sizes. However, ions such as Au^+ and Hg^{++} strongly tend to form compounds of low co-ordination number, particularly linear XY_2 complexes.

Jørgensen pointed out that the tendency of d^{10} ions to form linear complexes is strongly correlated with the energies of the excited states of the configurations $(n-1)d^9ns$ and $(n-1)d^9np$ above the $(n-1)d^{10}$ ground state.⁵ In Table I we reproduce Jørgensen's

FIG. 1.
 (a) One component of an antisymmetric T_{1u} vibration.
 (b) A symmetrical displacement which can mix d and s orbitals. (This is not the component of a normal mode.)



data for a number of d^{10} ions. Clearly the Au^+ , Hg^{++} , and Cu^+ ions which have the greatest tendency to form linear complexes are those with the lowest d^9s excited states. It has been suggested that the stability of the linear configuration for these ions is due to the formation of covalent sp bonds between the metal ions and the two ligands. We now re-examine and modify this point of view.

Consider the stability of a d^{10} cation at the centre of a regular octahedron of negative ions. An antisymmetric displacement of two or more anions as shown in Fig. 1a removes the centre of symmetry of the environment of the cation and so produces an electric field which can mix together d and p orbitals but not d and s orbitals. The electron configuration is thus changed from d^{10} to $d^{10-\delta}p^\delta$. But a symmetric displacement of anions as shown in Fig. 1b can mix together d and s orbitals but not d and p orbitals to give a configuration $d^{10-\delta}s^\delta$. If the stabilisation due to mixing brought about by either class of distortion is sufficiently large it will more than compensate for the energy lost in distorting the otherwise electrostatically stable regular octahedron and so lead to instability. Since it is the $d-s$ rather than $d-p$ separation that is exceptionally small for certain d^{10} ions we should expect symmetric distortions to be more important. We now make plausible that for any assumed regular octahedral complex there must be a range of $d-s$ (or $d-p$) separations which lead to instability.

The d_{z^2} and s orbitals shown in Fig. 2a can be mixed together (hybridised) to give two new orbitals as shown in Fig. 2b. If the two electrons which occupy the d_{z^2} orbital

² See Gillespie and Nyholm, "Progress in Stereochemistry," Butterworths, London, 1958, Vol. 2, for references.

³ (a) Dunitz and Orgel, *J. Phys. Chem. Solids*, 1957, **3**, 20, and references therein; (b) Orgel, *Discuss. Faraday Soc.*, 1958, in the press.

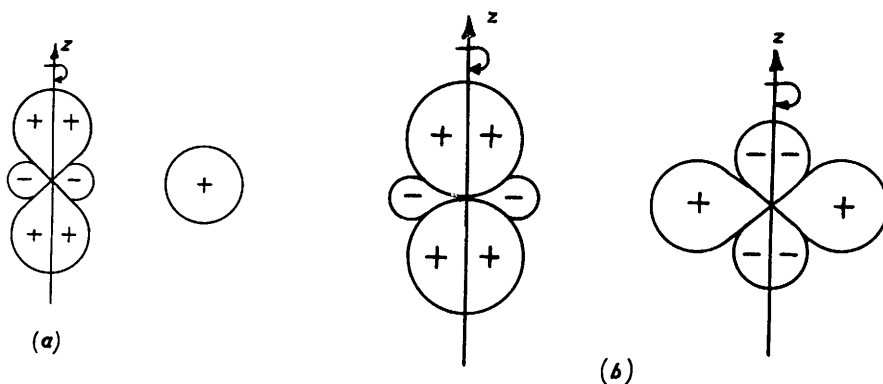
⁴ Orgel, unpublished work.

⁵ Jørgensen, Thesis, Copenhagen, 1957.

of the free ion are put into the $(1/\sqrt{2})(d_{z^2} + s)$ orbital the atom develops a strong electronegativity in the x - and y -directions, while if the $(1/\sqrt{2})(d_{z^2} - s)$ orbital is occupied the opposite is true. If the d_{z^2} and s orbitals are initially degenerate the stable configuration of the octahedron must necessarily be distorted, since d - s mixing can occur without expenditure of energy in the regular octahedral configuration and, in view of the strongly directional electronegativity of the atom, a subsequent distortion of the octahedron must lead to stabilisation. If the d and s orbitals are not degenerate then the expenditure of energy required to produce d - s mixing is proportional to the d - s separation, and so it is mainly this quantity which determines whether the regular octahedral configuration is stable or not. Clearly for any given octahedral environment there must be a range of d - s separations which lead to instability.*

Structural Evidence.—The structural evidence of ions with filled d shells shows that the Zn^{++} and Cd^{++} ions occur in normal tetrahedral or octahedral environments. On the

FIG. 2.

(a) The d_{z^2} and s orbitals.(b) Hybrid orbitals concentrated along the z axis and in the x - y plane.

other hand the Au^+ and Hg^{++} ions are frequently encountered as discrete XY_2 groups, or in environments based on octahedral co-ordination but strongly distorted in such a way as to maintain a centre of symmetry.

Typical distorted octahedral environments occur in HgS (distorted $NaCl$ structure¹), in a variety of halides,¹ in amines,¹ and in $Hg(\text{pyridine})_2Cl_2$.⁸ Linear co-ordination is found for $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ and in Cu_2O and Ag_2O .¹ In HgO there are two short collinear Hg - O bonds and two much weaker bonds at right angles.⁹ Studies of complexes in solution also indicate that twofold co-ordinated complexes are particularly stable, for example, $AgCl_2^-$,¹⁰ $Hg(OH)_2$, and $In(OH)_2^+$.¹¹

Nature of the Bonding.—We attribute the differences in the stereochemistry of Zn^{++} and Cd^{++} on the one hand and Cu^+ , Ag^+ , Au^+ , Hg^{++} , and perhaps Tl^{+++} on the other to the

* These arguments can be made precise along lines very similar to those used in treatments of the Jahn-Teller distortions.^{6,7} It then appears that the stabilisation of the distorted octahedral environment by d - s mixing is determined by the ratio of the matrix element between the s and d orbitals of the potential produced by a distortion of the environment to the d - s separation. This stabilisation can be expanded in powers of the displacement along the normal co-ordinate corresponding to the E_g stretching vibration. If the quadratic term in this expansion exceeds the restoring term due to other interactions the octahedral configuration is unstable. The existence of a range of d - s separations for which the regular octahedral environment is unstable can thus be established.

⁶ Jahn and Teller, *Proc. Roy. Soc.*, 1937, *A*, **161**, 220.

⁷ Longuet-Higgins, Öpik, Pryce, and Sack, *Proc. Roy. Soc.*, 1958, *A*, **244**, 1, and references therein.

⁸ Grđenić and Krstanović, *Archiv Kem.*, 1955, **27**, 143.

⁹ Aurivillius, *Acta Chem. Scand.*, 1956, **10**, 852.

¹⁰ Stability Constants, Part II, Chemical Society Special Publication No. 7, 1958.

¹¹ Basolo and Pearson, "The Kinetics of Inorganic Reactions," Wiley, New York, 1958.

much smaller d - s separations in the latter group. Only for these ions can the stabilisation due to d - s mixing compensate for the loss of energy which normally results from a small co-ordination number.

Although a purely electrostatic account of these ions has been given, covalent bonding must clearly be important in such compounds as $\text{Hg}(\text{CH}_3)_2$ or $\text{Tl}(\text{CH}_3)_2^+$ and also in HgCl_2 , HgBr_2 , etc. To account for the correlations between the stability of these linear compounds and the d - s separation we must, in a covalent-bonding theory, suppose that instead of forming sp hybrids the central ion uses one p orbital and one d - s orbital. The extra stability of linear compounds of Hg^{++} , etc., is largely due to d - s mixing although we do not exclude the possibility that sp hybridisation of the kind normally postulated occurs here as in other linear triatomic molecules.

TABLE 1. Energies (cm.^{-1}) of lowest d^9 s and d^9p states above the d^{10} ground state.

	Cu^+	Zn^{++}	Ag^+	Cd^{++}	Au^+	Hg^{++}	Tl^{+++}
$nd^9(n+1)s$	21,928	78,105	39,164	80,463	15,039	42,862	75,052
$nd^9(n+1)p$	66,418	137,876	80,173	139,042	63,052	118,616	147,635

TABLE 2. Ionisation potentials and s - p separations of Zn, Cd, and Hg.

	1st I.P. (ev)	2nd I.P. (ev)	$E(s-p)$ of M^+ (cm.^{-1})
Zn	9.39	18.0	49,000
Cd	8.99	16.9	45,800
Hg	10.44	18.8	57,600

Since this view differs from that usually expressed, we shall consider the alternative hypothesis of sp hybridisation in more detail. The greater stability of the s -orbital in Hg than in, say, Zn is seen clearly from Tables 1 and 2 which show that the sum of the first two ionisation potentials of Hg is almost 2 ev greater than the corresponding sum for Zn. However this alone, while it would account for a greater stability of Hg^{++} than of Zn^{++} compounds, does not account for the unusual stereochemistry of the Hg^{++} ion. To understand the latter we must look at the $6s$ - $6p$ separation rather than at the absolute energies of the s orbitals, for it is that separation which determines the relative stabilities of sp and sp^3 hybrids. Now the s - p separation is about 1 ev greater in Hg than in Zn and in Hg^+ than in Zn^+ . While this could certainly influence the stereochemistry it hardly seems large enough compared with the total energy of the s and p orbitals to account for the great differences between the two elements. The d - s separation on the other hand is almost halved between Zn^{++} and Hg^{++} and this is more likely to have a drastic influence on the co-ordination.

While we have been able to rationalise the stereochemistry of Hg^{++} compounds, etc., in terms of a simple theory we must point out that this theory is not predictive in one sense—it is not possible to say *a priori* whether an arrangement with two electrons in the $(1/\sqrt{2})(d-s)$ orbital and two short bonds or with the electrons in the $(1/\sqrt{2})(d+s)$ orbital and four short bonds is more stable. Experimentally two bonds always seem to be shorter in compounds containing the Hg^{++} ion, presumably because of some preference for sp -hybrid bond formation.

Conclusions.—We have discussed the d^{10} ions in some detail in order to emphasise points of interest to the more important problem of the stereochemistry of ions with inert pairs. (1) Ionic crystals of high symmetry are likely to be unstable to those distortions which mix together filled and unfilled orbitals of similar energy. (2) The distortions can be understood in terms of electrostatic interactions, but this does not disprove the occurrence of a measure of covalent bonding. Distortions from cubic symmetry are not diagnostic of bond type. (3) While simple theoretical arguments define the symmetry class of displacements which stabilise d^{10} ions, they do not pick out one unique distortion, for the displacements invariably correspond to degenerate vibrations. The actual co-ordination in any particular compound is determined in part by the finer details of the forces between the ions within a complex and in part by packing considerations in the

crystal. (4) The extent of the distortion can have any magnitude from a relatively small one to one which effectively removes some ions from the co-ordination group. In extremely distorted environments it may be better to consider the resulting structure in its own right rather than as derived from a more symmetric structure.

The d - s mixing postulated is capable of experimental investigation by nuclear magnetic and quadrupole resonance experiments. We have shown¹² that interconfigurational mixing leads to paramagnetic terms in the chemical screening constants for d^{10} and $d^{10}s^2$ ions and that sp mixing accounts for the observed chemical shifts in Pb^{++} compounds. Comparable studies on d^{10} ions should enable the extent of d - s mixing to be estimated.

Mixing of d and s orbitals in tetrahedrally co-ordinated compounds by distortion of the regular cubic environment is also to be expected. The phase transitions in and a number of unusual features of the X -ray scattering from the halides of Cu^+ and Ag^+ will be discussed elsewhere.

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¹² Orgel, *Mol. Physics*, 1958, in the press.
