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Stereochemistry of Discrete Eight-Coördination.[1] I. Basic Analysis[1]

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An ordered pattern having useful predictive capacity for discrete eight-coördination is obtained by interweaving helpful bits of theory with accurate stereochemical data from X-ray studies[2] utilizing full three-dimensional analysis. The most sweeping conclusion of this "phenomenological theory" is that the energetics of direct bonding interaction must differ so little for the dodecahedral ($Mo(CN)_8^{-4}$-type) and square antiprismatic configurations (Fig. 1 and 2) that the choice between them is determined, usually or always, by other factors. The detailed shape of the coördination group of a real complex is never that of the hard sphere model, but is rather that which makes the ligand repulsive energy from closed-shell interactions a (constrained) minimum; the most favorable dodecahedral and antiprismatic shapes (Table I) accomplish this equally well. For a tetrakis-bidentate chelate it appears (1) that differences in the closed-shell repulsive energy for competing stereoisomers may run easily to 5 kcal./mole, (2) that minimization of internal coulombic repulsions takes precedence when the complex is charged. Stereoisomerism in the M(IV) β-diketo chelates, $M(X_2)_4$, is discussed in detail. Increasing complication, *e.g.*, mixing of ligands, multidentate character, usually is better served by dodecahedral coördination. The $Mo(CN)_8^{-4}$ ion receives special attention.

Introduction

In view of the outstanding simplicity which characterizes a stereochemistry based upon the geometry of a regular polyhedron, it may be deemed unfortunate that superior stereochemical relations for discrete complexes are provided only by those regular polyhedra having triangular faces. Owing nothing to the cube, the stereochemistry of discrete eight-coördination is based upon less symmetrical polyhedra which are identifiable in crystals by means of X-ray diffraction analysis. Progress in this field has been relatively slow, largely because the complexity of the typical structural problem virtually demands the full power of three-dimensional analysis if stereochemical data having the requisite qualitative certainty and quantitative accuracy are to be obtained. Rather efficient procedures for such three-dimensional analysis, and the results obtained thereby for the tetrakisacetylacetonyl[3] and tetrakisoxalato complexes[4] of zirconium(IV) and hafnium(IV), are described in the accompanying papers; other chemical types of discrete eight-coördination complexes are to be treated in subsequent reports.

Two configurations first observed more than 20 years ago dominate the stereochemistry of discrete eight-coördination. The classic chemical exemplar of eight-coördination, the stable $Mo(CN)_8^{-4}$ ion (with which $W(CN)_8^{-4}$ is isostructural), has the eight bonds from the central atom directed toward the vertices of a dodecahedron with triangular faces[5] (Fig. 1). The TaF_8^{-3} ion (in the sodium salt) assumes the more obvious square antiprismatic configuration, a decahedron having eight triangular and two square faces[6] (Fig. 2). One other configuration of possible stereochemical merit, an undecahedron with one rectangular and ten triangular faces, is derivable[5] from a trigonal prism by adding two ligands along normals to two of the rectangular faces. Although subsequently accorded major theoretical status by Kimball,[7] no experimental evidence for the

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(1) Supported by the U. S. Army Research Office (Durham), the National Science Foundation, and the Advanced Research Projects Agency. We thank also the Staff of the Cornell Computing Center, Mr. Richard C. Lesser, Director.

(2) Two of these (ref. 3 and 4) are reported simultaneously with this paper. We thank G. L. Glen, E. Willstadter, and T. A. Hamor, for permission to quote structural data from forthcoming papers (III, IV, V).

(3) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(4) G. L. Glen, J. V. Silverton, and J. L. Hoard, *ibid.*, **2**, 250 (1963); *Cf.*, J. L. Hoard, G. L. Glen, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 4293 (1961).

(5) J. L. Hoard and H. H. Nordsieck, *ibid.*, **61**, 2853 (1939).

(6) J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *ibid.*, **76**, 3820 (1954). First presented at Sixth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbus, Ohio, Dec., 1941.

(7) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940), whose suggestively inaccurate term "face-centered prism" for this polyhedron was taken to mean the configuration derived from the trigonal prism by adding two ligands along normals to the triangular faces. *Cf.*, L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943); T. D. O'Brien in J. C. Bailar, Jr., "Chemistry of the Coördination Compounds," ACS Monograph No. 131, Reinhold Publishing Corp., New York, N. Y., 1956. This last configuration is sterically so obviously inferior to the cube as scarcely to merit consideration.

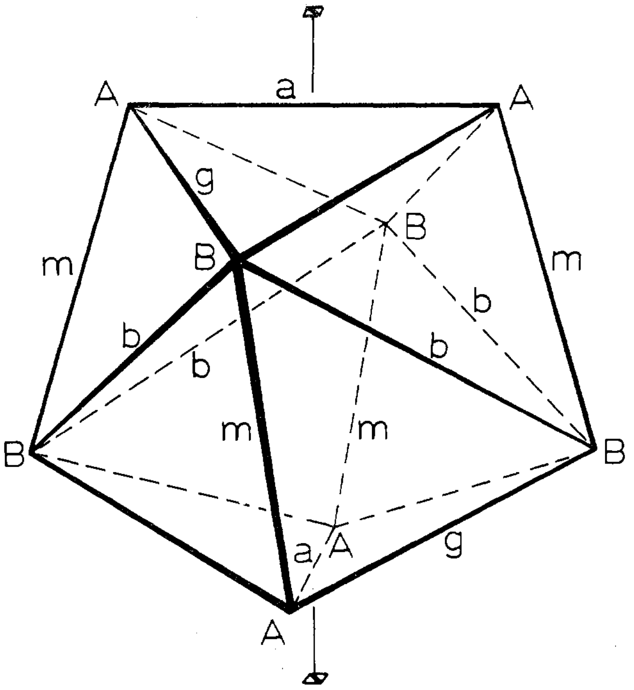

Fig. 1.—The D_{2d}-$\bar{4}2m$ dodecahedron. Equivalent trapezoids, BAAB, lie in the mutually orthogonal mirror planes and interlock in agreement with $\bar{4}$. The labeling of vertices (ligand sites) and of edges of the polyhedron shows how these sort into symmetry equivalent groups; *e.g.*, the 18 edges are distributed among four classes: $a(2)$, $b(4)$, $m(4)$, and $g(8)$. The polyhedron center (the site of the central atom M) is the point of intersection of three mutually orthogonal symmetry axes, the unique $\bar{4}$ and a pair of twofold axes. Each of these latter passes through the mid-points of two opposed b edges.

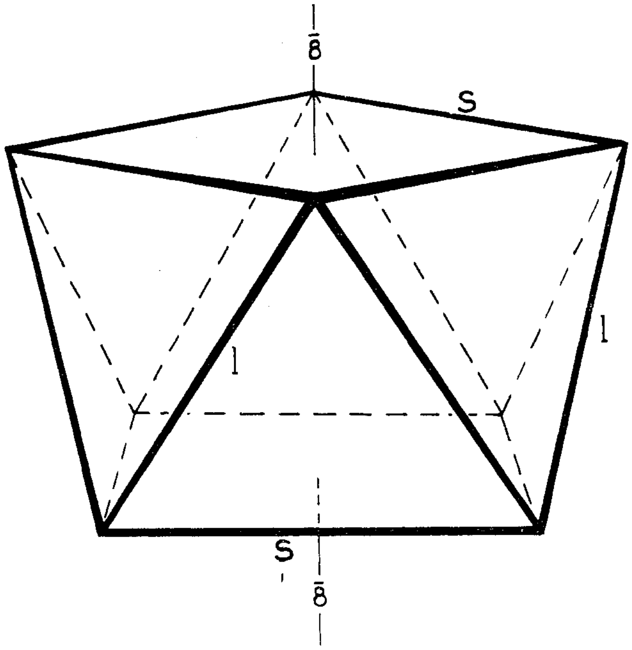

Fig. 2.—The D_{4d}-$\bar{8}2m$ antiprism. All vertices (sites of ligands A) are equivalent. The 16 edges divide equally between two symmetry types, s and l. The polyhedron center (site of the central atom M) is the point of intersection of the unique $\bar{8}$ axis and 4 twofold axes. Each of these latter passes through the mid-points of two opposed l edges. The figure has also four mirror planes. Only the symmetry of a subgroup of D_{4d} (D_{2d} is *not* one of these) can be required in a crystal.

existence of a discrete complex in this highly polar configuration (point group symmetry, C_{2v}-mm2) has ever been obtained.

Appraisal of the relative merits of the $Mo(CN)_8^{-4}$ dodecahedron and the square antiprism as coördination polyhedra should take into account contributions to the energy of each from (1) direct interaction of the central atom with its ligands, (2) mutual repulsions of ligands, (3) the perturbation introduced when nonbonding electrons are present in the valence shell of the central atom, and (4) the constraints imposed when other than monodentate ligands are employed. The structural data suggest, we believe, that the direct bonding interactions are so nearly equal for the two configurations that other considerations suffice to account for the existing (and apparently growing) preponderance of confirmed dodecahedral structures. Not being regular polyhedra, the detailed shapes assumed by the inner coördination groups are dependent upon the several factors cited. It is primarily in this connection that the influence of ligand repulsions from closed-shell interactions is recognizable in the structural data. Coulombic contributions to the repulsive energy, although rather insensitive to moderate variations in shape parameters, may determine the selection of configuration for a highly charged bidentate chelate.

Analysis of the Principal Factors Influencing Configuration

In the dodecahedral $Mo(CN)_8^{-4}$ configuration, the ligands are located at the corners of two trapezoids lying in mutually perpendicular mirror planes which intersect in the $\bar{4}$ axis (Fig. 1). The full symmetry, D_{2d}-$\bar{4}2m$, allows unequal bond lengths M–A and M–B (even though A and B are chemically identical) in two "disphenoidal" sets of four, and of unequal edge lengths, a, m, g, and b; these permissive features turn out to be utilized as a matter of course. The shape of a dodecahedron ($\bar{4}2m$) is specified by three parameters, *e.g.*, the angles θ_A, θ_B which the bonds M–A, M–B make with the unique axis, and the ratio of the bond lengths. The shape of the square antiprism of maximum symmetry D_{4d}-$\bar{8}2m$ (Fig. 2), is determined by either the ratio l/s of the two permitted edge lengths or the angle θ made by a bond M–A with the $\bar{8}$-axis. Because $\bar{8}2m$ is not a crystallographic point group at least one additional shape parameter always must be determined in a crystal.

In the hard sphere idealizations of these MX_8 configurations the dodecahedron has M–A = M–B, $g = m = a$, $b = 1.250a$, while the antiprism has $l = s$. Taking the repulsive energy from closed-shell interactions between ligands as $k\Sigma R_{ij}^{-n}$, with summation over all (28) separations R_{ij} of ligand pairings, the repulsive energies of the two idealized configurations (for the same bond distance) come out equal for $n = 6$. This computational procedure, unrealistic in that it ignores shielding by the central atom of non-contiguous ligands, still favors the antiprism by 0.6% in the repulsive energy for $n = 7$, the expected value[8] for the Born exponent in the usual case of neon-shell ligands. The much more effective shielding provided in the dodecahedron seems to be more than sufficient (*vide infra*) to erase the apparent advantage enjoyed by the antiprism for $n = 7$. We note further that (1) steric stability of the cube relative to the other configurations demands $n \ll 1$, (2) any contribution from coulombic repulsions ($n = 1$) between ligands carrying net charges is smallest for the dodecahedron (but by only 0.083%).

An estimate of the interaction parameter k for neon-shell ligands is obtained by applying Pauling's treatment[8] of double repulsion in the alkali halogenides to the specific case of the sodium fluoride crystal with $n = 7$. Using the relative values of the specific interaction parameters derived by Pauling and the radius ratio $r+/r- = 0.70$, we obtain $k = 3400$ kcal. $(\text{Å.})^7$ mole^{-1}. The corresponding repulsive energy for a discrete complex of mean M–X bond distance d can be written as $U_r = kfd^{-7}$, wherein $f = d^7\Sigma R_{ij}^{-7}$. The geometrical factor f, a constant for a regular polyhedron, is dependent upon shape parameters for the eight-coördination polyhedra of interest; for either of these latter a near minimum value of f turns out to be about 4.1. Taking $d = 2.200$ Å., a value of subsequent interest for ZrO_8 polyhedra, we obtain $U_r = 56$ kcal./mole of complexes or 7 kcal./mole of Zr–O bonds. The net (*i.e.*, thermochemical) Zr–O bond energy probably lies within the range[9] 50–65 kcal./mole, about 7–9 times the estimated ligand repulsive energy. By way of further comparison we note that a regular octahedral MO_6 group having $U_r = (6)(7)$ kcal./mole corresponds to $d = 1.889$ Å., about the bond distance when M = Co(III).

If the resultant charge ze of an isolated complex be distributed equally among eight appropriate peripheral atoms, the destabilizing energy (kcal./mole) from coulombic repulsions is $U_c = 5.19\, z^2\Sigma R_{ij}^{-1}$ (diminished, in the case of multidentate ligands, by the often substantial coulomb energy present in the free complexing agent). Because this relation overestimates destabilization in aqueous solution and is only a part of the story for a crystalline arrangement, we use it primarily to estimate relative effects. It then appears (1) that the coulombic repulsive energies for idealized dodecahedral and antiprismatic charge configurations differ by only 0.083%, and (2) that neither energy can be reduced through varying the shape parameters (as outlined later) by more than 0.21%. There is more room for variation with multidentate ligands whenever the charges are associated with peripheral atoms which define configurations of distinctively non-ideal shape; coulombic repulsions then might be decisive in the selection of configurational type for the inner coördination group.

The practical difficulty is that we must determine structure in the crystal, and the shape of the complex always is affected to some degree by the packing relations. In the extreme case of the complex fluorides, not merely the shape, but the configurational type, and even the chemical constitution of the complex apparently may be chosen so as to minimize the crystal energy. From solutions which differ fundamentally only in the choice of cation, Na^+, K^+, Cs^+, the crystalline phases obtained are Na_3TaF_8, K_2TaF_7, $CsTaF_6$, containing the respective complex species, TaF_8^{-3}, TaF_7^{-2}, TaF_6^-; in each case the particular combination of cation and complex anion leads to an excellent salt-like arrangement in the crystal.[10] A further case in point is the orthorhombic structure[11] of K_2ZrF_6 and K_2HfF_6, in which dodecahedral MF_8 groups of required mm symmetry are present; half of the trapezoidal slant edges m (Fig. 1) are shared to give chains of composition $(ZrF_6)_n^{-2n}$. The adoption of this structural type in preference to highly satisfactory standard arrangements for $2K^+$ and octahedral MF_6^{-2} ions is especially noteworthy.

Despite these reservations, crystal structure data will be seen to furnish information on configurational shape which is interpretable in terms of ligand repulsions and other factors of developing significance.

Use of $n = 7$, while minimizing U_r of the antiprism with respect to l/s, yields, as compared with the hard sphere approximation, a decrease in this energy of 2.2%, $l/s = 1.057$, and $\theta = 57.3°$ (instead of 59.25°). Similar minimization of U_c ($n = 1$) yields a decrease in U_c of only 0.207%, $l/s = 1.111$. If $U_c \overline{<} 10U_r$, $1.057 \overline{<} l/s \overline{<} 1.075$; and if $U_c \overline{<} U_r$, as appears to be the case for the antiprismatic complexes discussed below, the influence of coulombic repulsions between ligands on the shape of the inner coördination group may be disregarded. We then note that maximization of the angle-dependent parts of the hybrid valence bond orbitals constructed from the set d^4sp^3 gives[12] $\theta = 57.6°$, $l/s = 1.049$, that maximization with admixture of d^5p^3 gives[12,13] $\theta = 60.9°$, $l/s = 0.955$, and, as compared with the first case, a "bond strength" larger by 0.3%; it gives also, however, an increase in the ligand repulsive energy, U_r, of 8.0%, about 4.5 kcal./mole for ZrO_8 groups.

In the zirconium(IV) acetylacetonate molecule[3] (with symmetry approximating closely to D_2-222) the averaged Zr–O bond distance is 2.198 ± 0.009 Å., and four of the eight edges s at 2.67–8 Å. seem to be fixed primarily by the internal constraints of ring formation. If these special values of s be omitted in computing the averaged l/s, we obtain 1.056, if included, 1.037. Antiprismatic ZrO_8 groups as structural elements in three-dimensional networks occur in the rather accurately determined structures of $Zr(IO_3)_4$[14] and $Zr(SO_4)_2 \cdot 2H_2O$[15]; the values obtained for l/s are, re-

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(8) *Cf.*, L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 509 *et seq.*

(9) *Cf.*, M. M. Jones, B. J. Yow, and W. R. May, *Inorg. Chem.*, **1**, 166 (1962).

(10) For Na_3TaF_8 see ref. 6; for K_2TaF_7, J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939); for $CsTaF_6$, J. D. Stroupe, "The Structure of Cesium Hexafluotantalate," Cornell University Thesis, 1941. The structural type of $CsTaF_6$ is that of $BaSiF_6$: J. L. Hoard and W. B. Vincent, *J. Am. Chem. Soc.*, **62**, 3126 (1940).

(11) H. Bode and G. Teufer, *Acta Cryst.*, **9**, 929 (1956).

(12) G. H. Duffey, *J. Chem. Phys.*, **18**, 746 (1950).

(13) G. Racah, *ibid.*, **11**, 214 (1943).

(14) A. C. Larson and D. T. Cromer, *Acta Cryst.*, **14**, 128 (1961).

(15) J. Singer and D. T. Cromer, *ibid.*, **12**, 719 (1959).

spectively, 1.03 and 1.075. Although subject to marked perturbations, the structural data support an averaged l/s of about 1.05 with $l - s \cong 0.13$ Å. for a ZrO_8 group.

It is a fair conclusion that σ-bonding in the antiprismatic configuration, whether formulated in terms of a molecular orbital or a valence bond approach, can make effective use only of the unique set of d^4sp^3 orbitals from the central atom; otherwise put, the stable d_{z^2} orbital, with lobes along the $\bar{8}$ axis and annular ring in the equatorial plane midway between the square faces, can contribute little or nothing to σ-bonding. Employment of this orbital for very weak (and quite unconventional) π-bonding is a possibility which may merit discussion in special circumstances. The obvious suitability of the d_{z^2} orbital for housing one or a pair of non-bonding electrons does suggest[12] that antiprismatic complexes of such atoms as Mo(IV) must be given serious consideration (*vide infra*).

The detailed shape of the dodecahedral configuration should be dependent upon whether the d_{xy} orbital in the valence shell of the central atom is occupied by non-bonding electrons; the four lobes of this orbital[16] are directed along the twofold axes—in Fig. 1, the radial lines bisecting opposite pairs of long edges b. The hybrid (d^4sp^3) valence bond orbitals[13,17] are in non-equivalent sets which maximize, singly or in combination, at values of θ_A and θ_B within the range of variation given pertinence by experimental data, and have "strengths" comparable with that of the antiprismatic orbitals. The somewhat greater "strength" (*ca.* 0.3–1.5%) and the larger fraction of d-character of the M–A orbitals suggest[17] that σ-bonding to atoms A actually should be stronger than to atoms B. Presently available structural data for Zr(IV) complexes, nevertheless, make M–B bonds shorter and presumably stronger than M–A bonds; it further appears that ligand repulsions and weak π-bonding involving the d_{xy} orbital contribute to this result.

The distortion from the hard sphere approximation which, with full maintenance of symmetry, tends to minimize the ligand repulsive energy from closed shell interactions can be visualized as a combination of (1) a moderate lengthening, for a uniform bond distance, of the more numerous edges g at the expense of both a and m, and (2) an increase, for a fixed averaged bond distance, of the bond length ratio M–A/M–B (toward a maximum which the direct bonding interactions never permit to be attained). The basis for the latter effect is that some 14–15% of the closed shell repulsive energy arises from A–A pairs, tenfold larger than from B–B pairs, while the contribution from A–B pairs is almost unchanged by small variations in the M–A/M–B ratio. A reinforcement of these effects which coulombic repulsions provide in case the atoms A and B carry net charges becomes important only when $U_c \gg U_r$.

The dodecahedral ZrO_8 grouping ($\bar{4}2m$ symmetry required) in zircon, $ZrSiO_4$, is not a discrete complex, but has some pertinence to the present analysis. A recent refinement of the structure yields the configuration data[18]: $Zr–O_A = 2.29$, $Zr–O_B = 2.15$, $a = 2.42$, $m = 2.54$, $g = 2.85$ Å. The distortions from the hard sphere approximation generally are of the expected type, but presumably are exaggerated by the exigencies of forming a three-dimensional network. The edge a, for example, is unduly short (by 0.10–0.15 Å.) because it is also an edge of a tetrahedral SiO_4 group. Strains incident to formation of the network weigh more heavily on the $M–O_A$ bonds.

In the $Zr(C_2O_4)_4^{-4}$ ion,[4] each oxalate spans an edge m, the averaged Zr–O bond distance is 2.199 ± 0.009 Å., but bonds M–A average 2.230 Å., M–B 2.168 Å. Also $a = 2.57$, $m = 2.56$, $g = 2.735$ Å. as compared with a uniform 2.63 Å. for the hard sphere approximation. The angles $\theta_A = 35.2°$, $\theta_B = 73.5°$ are each within a few minutes of the values corresponding to the maximum "strength" (2.999) for hybrid orbitals of M–A type[17] (the "strength" of M–B orbitals is 1.5% smaller).

The resultant charge (4*e*) of the complex is most plausibly to be divided among the eight uncomplexed oxygen atoms on the periphery. (Even so, the destabilizing energy from coulombic repulsions for a hypothetical *isolated* complex still would be >300 kcal./mole.) Some consequences of this type of charge distribution are: (1) a much smaller coulombic repulsive energy for the observed stereoisomer[4] than for any of its competitors, including those based upon the antiprismatic coördination group; (2) coulombic repulsions which minimize (with fixed average bond distance) for M–A/M–B < 1 and thus provide a moderate restraint on an increasing bond ratio; (3) a radial elongation, as observed,[4] of the five-membered rings with a concomitant small value of m.

Assuming that a short intra-ring O–O separation is demanded by the coulombic repulsions for any stereoisomer, it can be seen that the closed shell repulsive energy, U_r, of the inner coördination group is a good deal less (~8–10%) for the observed configuration than for any of its competitors, save one: adaptation to the oxalato complex of the antiprismatic arrangement described for zirconium acetylacetonate[3] yields a comparably satisfactory value of U_r (but not of the more important coulombic U_c). The calculated U_r using experimentally observed parameters is 2.2% less than for the hard sphere approximation.

Presumably the dodecahedral $Zr(C_2O_4)_4^{-4}$ can make some use of the uniquely stable d_{xy}-orbital of the central atom for π-bonding. Ligand atoms O_B are involved preferentially,[19] but in an awkward pattern which we have examined in graphical constructions. A lobe of a π2p oxygen orbital given a diameter of 1.40 Å. (the van der Waals radius) just touches a lobe of a $4d_{xy}$ zirconium orbital when the (varied) diameter of the latter reaches 2.0 Å., suggesting that real overlap is confined to regions of diffuse electron density. It

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(16) The commonly employed notation d_{xy} corresponds to x and y axes in the mirror planes and the systematic description $\bar{4}m2$ for D_{2d}. The internally consistent notations $\bar{4}2m$, $d_{x^2-y^2}$, for x and y along the twofold axes, correspond to the preferred crystallographic description.

(17) G. H. Duffey, *J. Chem. Phys.*, **18**, 1444 (1950).

(18) I. R. Krstanović, *Acta Cryst.*, **11**, 896 (1958).

(19) *Cf.*, L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

would seem further that accumulation of net negative charge on the central atom would be intolerable for this highly charged complex, and hence that any contribution from π-bonding would be accompanied by some loosening of σ-bonding associated with a compensating outward shift of bonding electron density. The net contribution of π-bonding to the stability of the complex probably is quite small.

The $TiCl_4\cdot$diarsine molecule[20] (diarsine $\equiv$ o-phenylenebisdimethylarsine) combines argon shell ligands ($n = 9$) with a central atom from the first transition period to yield a dodecahedral complex of full $\bar{4}2m$ symmetry.[20] Arsenic atoms are at positions A, chlorine at B, angular parameters correspond nearly to "maximum strength" of M–A type hybrid bond orbitals, and the detailed shape of the inner coördination group is essentially that for minimizing ligand repulsions. Formation of tight five-membered rings spanning the edges *a* in Fig. 1 requires the separation of contiguous arsenic atoms to be that of much smaller monodentate ligands and ensures easy contacts with chlorine atoms in the sterically very favorable B positions. No other stereoisomer, dodecahedral or antiprismatic, is so well adapted to take advantage of this special size effect. The difference between the reported[20] Ti–As (2.71 Å.) and Ti–Cl (2.46 Å.) bond lengths is 0.06 Å. larger than the difference between the appropriate bond radii[8] of As (1.18 Å.) and Cl (0.99 Å.), again providing evidence that M–A type bonds tend to be the weaker. The data from this neutral complex support the preceding stereochemical analysis of the highly charged $Zr(C_2O_4)_4^{-4}$ on all points of mutual pertinence.

Accurate stereochemical parameters for $Mo(CN)_8^{-4}$ itself, as derived from three-dimensional intensity data afforded by the orthorhombic $K_4Mo(CN)_8\cdot 2H_2O$[21] of the original analysis,[5] soon will be available. It is now clear (1) that the complex anion, of minimum required symmetry C_s-m in the crystal, approximates closely to the higher symmetry D_{2d}-$\bar{4}2m$, (2) that the bond length ratio $Mo–C_A/Mo–C_B$ is not significantly different from unity, and (3) that otherwise the shape of the inner coördination group is very like that of $Zr(C_2O_4)_4^{-4}$.

Orgel suggests[19] that back π-bonding involving the d_{xy}-orbital of Mo(IV) and the π*2p orbitals of carbon atoms B so stabilizes ligands B that substitution of OH^- for CN^- should occur in the A positions to give $[Mo(CN)_4(OH)_4]^{-4}$. (This implies substantially equal contributions from σ-bonding to the symmetry non-equivalent $Mo–C_A$ and $Mo–C_B$ bonds.) Were the matter this simple we should expect the $Mo–C_A/Mo–C_B$ bond length ratio to be greater than unity, more or less comparable with the 1.03 observed for $Zr–O_A/Zr–O_B$. It is probable that the electron pair in d_{xy} finds its most important role in repulsive interactions (generally coulombic) which produce an inhomogeneous swelling of the complex: that, in particular, the $Mo–C_B$ σ-bonding is loosened to a degree for which π-bonding cannot entirely compensate. That portion of the destabilizing repulsions which involves d_{xy} and the net charge of the complex presumably is mitigated in $Mo(CN)_8^{-4}$ through retreat of this charge to the nitrogen atoms, probably with some disproportionation[21] in favor of the N_A type.

Spectra recorded for the complex in solution have been interpreted by Stammreich and Sala,[22] and by König,[23] in terms of an antiprismatic configuration, whereas Perumareddi, Liehr, and Adamson[24] have pointed out difficulties in König's assignments, and have interpreted essentially identical data in terms of a dodecahedral configuration limited to the point group C_s-m. Golding and Carrington[25] have provided still another interpretation of the optical spectra in terms of a $\bar{4}2m$ dodecahedral configuration. (Differences in the interpretations of ref. 24 and 25 go beyond those implied by the differing point groups.)

One relatively unsatisfactory aspect of an antiprismatic version of $Mo(CN)_8^{-4}$ is to be noted. Four carbon and four nitrogen atoms at each end of the unique axis define a (rather shallow) frustum of a square pyramid within which the potential must be substantially negative. Both within and near this region there would appear to be a destabilizing accumulation of electron density from the π-bonding systems of the four cyanide groups and from a principal lobe of the d_{z^2} orbital of the central atom.

Complexes of the type $[Mo(CN)_8X_2]^{-4}$, X = NH_3, N_2H_4, H_2O (in part), the reality of which Jakób, *et al.*,[26] seem prepared to guarantee, provide a further spur to consideration of how an antiprismatic $Mo(CN)_8^{-4}$ might become stabilized without wholly losing its identity. An undersupply of stable orbitals on the central atom, an oversupply of electrons, and stringent geometric limitations on the stereochemical possibilities combine to make true ten-coördination (8C and 2N (or 2H) of NH_3 directly bonded to Mo) most implausible.[27] A capping of the square faces of the antiprismatic carbon framework, equivalent to a partial cupping into the frusta of the square pyramids described above, by not too large cations or appropriately oriented dipolar species might furnish the required stabilization through electrostatic interaction. Even the smallest cation (excepting H^+, which scarcely would stand by itself), and certainly the nitrogen of an ammonia molecule, would be centered well outside the square face defined by nitrogen atoms of four cyanide groups: these dimensional limitations are inherent in any capping of a square face of the carbon skeleton. An

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[20] R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature*, **192**, 222 (1961).

[21] T. A. Hamor, P. Brown, J. V. Silverton, and J. L. Hoard, IV in this series.

[22] H. S. Stammreich and O. Sala, *Z. Elektrochem.*, **65**, 149 (1961).

[23] E. König, *Theor. Chim. Acta*, in press.

[24] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, Columbus, Ohio, June, 1962, Paper C3.

[25] R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962).

[26] W. Jakób, A. Samotus, and Z. Stasicka, "Proc. Seventh Intern. Conf. Coördination Chem., Stockholm, 1962, pp. 238–240.

[27] We assume that Jakób, *et al.*, [26] not only recognized these limitations but had in mind something like the model to be described when they wrote ". . . that the antiprism, which has exactly two equivalent and privileged positions for two additional ligands, is stabilized by polar ligands."

ammonia molecule (or OH_3^+) to exemplify one stabilizing orientation, could have one hydrogen near the nitrogen square face, perhaps a little below the brim of the cup, with the other hydrogens well outside, but favorably near to cyanide-nitrogen atoms. A water molecule, with but two hydrogen atoms, would serve less well. There is also the prospect that cations might serve to bind antiprismatic $Mo(CN)_8^{-4}$ ions into infinite chains within a crystal.

This formulation, at best a moderately plausible attempt to solve a seemingly implausible problem, corresponds to a definite admixture of "outer complexing" while allowing Mo(IV) to retain in fact its proper maximum coördination number of eight. The result is describable as eight (*quasi*-ten)-coördination. What is presently certain is that in some circumstances, at least, $Mo(CN)_8^{-4}$ exists in the straightforward $\bar{4}2m$ dodecahedral configuration.

The tetrakisperoxychromate (V) ion in K_3CrO_8 is dodecahedral[28] with $\bar{4}2m$ symmetry required; like $Zr(C_2O_4)_4^{-4}$, it occurs as that one of nine stereoisomers provided by both coördination polyhedra which minimizes the coulombic repulsive energy of the charged ligands. Structural parameters are[29]: $Cr-O_A = 1.85$, $Cr-O_B = 1.94$, $O_A-O_B = 1.41$ Å., $\theta_A = 43.4°$, $\theta_B = 93.1°$. The edge length *m*, *i.e.*, the peroxy bond length O_A-O_B, is so short that θ_A and θ_B are larger by 8 and 20°, respectively, than the values expected for a monodentate CrO_8. Although a ligand field calculation by Swalen and Ibers[29] displays a modest contribution from π-bonding to $Cr-O_B$ bonds, we suggest that the principal role of the electron in d_{xy} is in loosening the $Cr-O_B$ σ-bonding. In contrast with $Mo(CN)_8^{-4}$, there are no atoms beyond the immediate coördination group to which the net charge can retreat, nor is there much prospect for disproportionation of net charge in favor of the more distant atoms of A type. In either case it would appear that π-bonding is no better than a palliative for the adverse effect on the over-all strength of M–B bonds produced by one or a pair of electrons in d_{xy}.

Stereochemical Synthesis and Applications

A partially ordered pattern having some predictive features can be synthesized from the preceding mixture of structural data and fragmented theory.

It is, we believe, a very good working hypothesis to take the energetics of direct bonding interaction as essentially equal for the two coördination polyhedra; the choice of coördination type then is to be ascribed to subsidiary, albeit highly cogent, interactions. On this basis our analysis suggests that the observed configuration is usually or always that of the energetically favored stereoisomer which, with discount of presumably small entropy differences, probably also is the thermodynamically stable species. Results of this nature become especially probable if the complex species in solution generally are highly labile. Such lability for the oxalato complexes of Zr(IV), Hf(IV), Th(IV), and U(IV) is indicated by the studies of Johnson and Larsen,[30] who could obtain no evidence for the existence of any of the numerous optically active stereoisomers. Nor can the evidence for lability of $Mo(CN)_8^{-4}$ in solution be ignored, although we do not regard it as conclusive.

It is convenient to discuss complexes in groups accordingly as the ligands are (I) monodentate, (II) bidentate, (III) multidentate (with arbitrary exclusion of II); of course there are also hybrid categories. We shall attempt the appraisal of relative stabilities for competing stereoisomeric types on a composite basis of (1) mutual closed-shell repulsions of atoms constituting the primary coördination group, (2) coulombic repulsions whenever the complex carries resultant charge, (3) geometrical constraints (in II and III) imposed primarily by the ligand character. The relative importance of the factors 1–3 when applied to the complex types I–III is appraised as follows.

Geometrical constraints attending the formation of interconnected rings or cages are expected to dominate (as discussed later) multidentate chelate stability. Given a charged complex in the unlikely circumstances that geometrical constraints allow about equally sound architecture for different stereoisomeric types, the stable isomer should be that one for which the charge configuration leads to the minimum coulombic repulsive energy. The shape of the inner coördination group thus selected, although usually required to depart somewhat from that which minimizes the closed-shell repulsive energy with monodentate ligands, will still correspond to attainment of a constrained minimum.

Given, in the case of bidentate complexes, rings of reasonably well established character, the choice of stable stereoisomer for a charged complex should be that which minimizes the coulombic repulsive energy. Thus, for example, a charged tetrakisbidentate complex having flat rings (and coulombic repulsions will aid in keeping the rings flat) should occur in the dodecahedral stereoisomeric type of maximum symmetry D_{2d}-$\bar{4}2m$ already exemplified by $Zr(C_2O_4)_4^{-4}$ and $Cr(O_2)_4^{-3}$. The *a priori* probability of this stereoisomer is especially large when the net charge is distributed over eight or more peripheral atoms, *i.e.*, over two or more atoms within each flat ring (*cf.* ref. 4 for details). For reasons already noted, this stereoisomer also is likely to be an excellent (but not unique) choice for minimizing closed-shell repulsions within the inner coördination group.

In neutral bidentate complexes, mutual repulsions of atoms constituting the inner coördination group assume real importance in narrowing the list from which the stable stereoisomer is to be chosen. This arises through a combination of two factors: Minimization of ring constraints, largely controlled by the stereochemical character of the ligand, leads to a rather

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[28] R. Stomberg and C. Brosset, *Acta Chem. Scand.*, **14**, 441 (1960).

[29] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

[30] F. A. Johnson and E. M. Larsen, *Inorg. Chem.*, **1**, 159 (1962).

well defined ring span—a term used conveniently for the intra-ring separation between the pair of atoms which are bonded to the central atom and thus define an edge of the coördination polyhedron. Minimization of the ligand repulsive energy, for either basic coördination figure, calls for shape parameters which differ significantly from those of the hard sphere model. A general minimization of constraints calls, therefore, for dimensional matching of ring span with appropriate polyhedron edges. Variations in the ligand repulsive energy as between different stereoisomers may mount readily to 5 kcal./mole. We subsequently discuss the neutral β-diketo complexes of M(IV) elements in the light of these considerations.

Passing now to what should be in principle the simplest case, that of monodentate complexes, we find that second-order effects are no longer sufficiently cogent to obscure our inability to handle the central problem of the direct bonding interactions on anything like a quantitative theoretical basis. So long as we use modestly compressible spheres, all alike, for the ligand atoms of the coördination polyhedron, we can choose most favorable shapes for both the antiprism and the dodecahedron which, as nearly as we can judge, do equally well in minimizing the closed-shell and (when necessary) the coulombic repulsive energies. It is gratifying, nonetheless, that the calculated shapes are in good agreement with experiment.

It is clear, however, that the A and B sites in the dodecahedral configuration display a practical degree of non-equivalence which is readily established by experiment. The bond length ratio $M{-}O_A/M{-}O_B > 1$ for Zr(IV) complexes is a case in point. If we choose ligands of different chemical types, say 4X and 4Y, and if X and Y differ in charge type, in size, or in any other significant structural feature, there can be sorting of ligands onto the appropriate A and B sites which will disturb the hitherto assumed energetic balance between antiprismatic and dodecahedral configurations to the definite benefit of the latter. If, for instance, it be a matter of differing sizes, the smaller ligands will go to the A sites, the larger to the B sites (*cf.* the earlier discussion of the $TiCl_4 \cdot$diarsine molecule).

Table I gives parameters for the "most favorable" shapes of the coördination polyhedra (neon-shell ligands), with those of the hard sphere models (HSM) included for comparison. The unit of length is the averaged bond distance, the same for both polyhedra.

TABLE I

PARAMETERS OF "MOST FAVORABLE" COÖRDINATION POLYHEDRA[a]

Antiprism (*cf.* Fig. 2)

D_{4d}-$\bar{8}$2m. $l = 1.258$, $s = 1.190$, $l/s = 1.057$, $\theta = 57.3°$
HSM: $l = s = 1.215$, $\theta = 59.25°$

Dodecahedron (*cf.* Fig. 1)

D_{2d}-$\bar{4}$2m. $a = m = 1.17$, $g = 1.24$, $b = 1.49$, $\theta_A = 35.2°$, $\theta_B = 73.5°$, M–A/M–B = 1.03
HSM: $a = m = g = 1.199$, $b = 1.499$, $\theta_A = 36.9°$, $\theta_B = 69.5°$, M–A/M–B = unity

[a] Valence shell of central atom free of non-bonding electrons.

The dodecahedral parameters correspond to a slightly idealized ZrO_8 group from $Zr(C_2O_4)_4^{-4}$, but a set based upon $Mo(CN)_8^{-4}$ would be equally satisfactory[21] for the objective we have in mind—the discussion of stereoisomerism in the β-diketo complexes of M(IV) elements.

The possible stereoisomers and associated maximum point group symmetries of a discrete eight-coördination complex, $M(X_2)_4$, having four chemically symmetric bidentate ligands XX are given in Table II.[31] Excepting the pair II_d and III_d, a stereoisomer is uniquely specified by listing the four edge types which must be spanned by 4XX.

TABLE II

STEREOISOMERS OF THE $M(X_2)_4$ CLASS

Antiprismatic sub-class			Dodecahedral sub-class		
I_a	*llll*	D_4-422	I_d[a]	*mmmm*	D_{2d}-$\bar{4}$2m
II_a	*ssss*	D_2-222	II_d[a]	*gggg*	S_4-$\bar{4}$
III_a	*llss*	C_2-2	III_d	*gggg*	D_2-222
			IV_d	*aabb*	D_2-222
			V_d	*mmgg*	C_2-2
			VI_d	*abmg*	C_1-1

[a] Optically inactive.

The stereoisomers IV_d and VI_d need not be considered further because they would require XX ligands to span polyhedron edges differing by fully 25% (Table I). III_a is a straightforward hybrid of I_a and II_a, as is V_d of I_d and II_d. Neither III_a nor V_d can minimize simultaneously the effects of both closed-shell repulsions and ring constraints (these latter cannot be indifferent to changes in ring-span of 0.10–0.20 Å.); in each case, then, one of the parent stereoisomers of higher symmetry must do the job better.[32] For neutral complexes, at least, these arguments suffice to exclude from further consideration those stereoisomers (IV_d, V_d, VI_d, III_a) which arbitrarily accord non-equivalent structural treatment to chemically identical chelating groups.

The only known crystalline modification of the tetrakisacetylacetonate of Zr(IV) (or of Hf(IV)) yields these data[3] for the molecule: symmetry, C_2-2 required, but D_2-222 very nearly achieved; stereoisomeric type, II_a-*ssss;* ring span, 2.675 Å., which, with Zr–O = 2.198 Å., is just the edge length of an equilateral antiprism. Ring spans computed with the aid of Table I for the most favorable polyhedron shapes are 2.57 and 2.62 Å., respectively, for I_d and II_a, 2.74 Å. for II_d and III_d, and 2.77 Å. for I_a. We do not get an obviously unique indication of the favored stereoisomer, nor would we even if the observed ring span lay unambiguously in either the low (*ca.* 2.60 Å.) or the high (*ca.* 2.75 Å.) range. It is easy to see, however, that the

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(31) Extensive isomer tables for coördination number 8 are given by L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).

(32) Strictly speaking III_a and V_d, which have the same connexity and the same point group, are variants of the same stereoisomeric type, and necessarily would be so considered in a fundamental quantum mechanical treatment. Similar remarks apply equally to III_d and II_a, which differ less in gross appearance than do III_a and V_d. III_d and V_d, moreover, are superficially quite similar, but have different connexities and symmetries. The customary practical distinctions seem well worth maintaining.

distortion demanded of II_a can be taken largely in the edges *s* with partial internal compensation; the four unspanned edges *s* come out at 2.59 Å., the averaged l/s is 1.04, and the departure from the most favorable shape is held to a minimum. More general and, for I_d and I_a at least, energetically more drastic modifications from the most favorable shapes are demanded of the competing stereoisomeric types. Although II_d and III_d appear to be less satisfactorily adaptable than II_a, rather elaborate computations would be required to resolve all doubt on this point.

A further complication remains, however. The acetylacetonate rings are folded[3] (through 22.6°) about the polyhedron edges with maintenance of D_2 symmetry in the observed II_a stereoisomer; the ring folding apparently is an aid to good packing relations, within and between molecules. Use of such rings in the I_d stereoisomer would limit the over-all symmetry to D_2 (alternatively to S_4, not the case of immediate interest). II_d, III_d, and the D_2-limited I_d (abbreviated as I_d-D_2) with the same connexity and maximum symmetry (D_2), become variants of a single theoretical stereoisomeric type which permits the inner coördination group to approach, at one extreme, the $\bar{8}$2m antiprism (a decahedron), at the other, the $\bar{4}$2m dodecahedron. Thus hybridization of II_a with III_d, or of II_a with I_d-D_2, becomes possible. The zirconium acetylacetonate molecule, although primarily II_a, bears the significant impress[3] of I_d-D_2. The possibility of a hybrid[33] which is primarily I_d-D_2 must be considered in the following cases.

In M(IV) tetrakisacetylacetonates for which M–O $\gtrsim$ 2.30 Å., *i.e.*, for M = Ce, Th, U, the expansion of the coördination group over that of the Zr(IV) complex will affect mainly the polyhedron edges not spanned by rings; constraints upon ring formation will permit so little increase in ring span that only configurations derived from II_a and I_d (limited to either S_4 or D_2 symmetry) can remain in contention. These are the more favored because a disproportionately large fraction of the formally computed ligand repulsive energy (itself substantially lower than for the Zr(IV) complex), namely, that associated with the relatively very short spanned edges, is a "fixed liability" for which ring constraints necessarily take primary responsibility.

Grdenić and Matković report[34] preparation of a crystalline β-thorium(IV) tetrakisacetylacetonate which is isomorphous with zirconium(IV) acetylacetonate, but which transforms spontaneously at room temperature to the more usually obtained and more complicated α-modification; the acetylacetonates of Ce(IV) and U(IV) were obtained only in the α-form.

It is highly probable that the thorium acetylacetonate molecule in the β-modification is, in first approximation, the "practical" stereoisomer II_a. But inasmuch as there can be no longer any difficulty of matching ring span to polyhedron edge for I_d-D_2, the degree of hybridization of the inner configuration might well be larger than in the Zr(IV) complex. Although there is no reason to suppose that the molecular packing in β-thorium acetylacetonate is less satisfactory than for the isomorphous Zr(IV) complex, it is possible that impetus for the spontaneous transformation β → α arises solely because still better packing relations exist within the α-crystalline arrangement. A more intriguing possibility, not necessarily independent of the first—perhaps, indeed, contributing to it—is that impetus for transformation comes from within the molecule: namely a tendency (or a docility) toward change in the coördination geometry from a predominantly II_a hybrid to a predominantly I_d-D_2 hybrid. The activation energy for the configurational alteration should be small.[35]

Outright rejection of any such change in configuration would seem to be provided in another report[36] by Grdenić and Matković that the molecule occurs as the II_a stereoisomer in α-thorium acetylacetonate were it not for the difficult and inconclusive circumstances of their preliminary X-ray study. No symmetry is required of the molecule by the space group, the projected electron densities based upon zonal photographic data dominated by thorium scattering necessarily show excessive overlap, and the few data reported, while insufficient to define fully the inner coördination group, are in one possibly critical respect more suggestive of I_d-D_2 than of II_a.

Indeed, we agree fully with Wolf and Bärnighausen[37] that the unambiguous determination of coördination type for α-thorium acetylacetonate, and for the isomorphous M(IV) tetrakisdibenzoylmethane series, M = Ce, Th, U, studied by them, demands the full power of three-dimensional X-ray data. Wolf and Bärnighausen, working from very badly overlapped electron density projections, propose a model for the M(IV) tetrakisdibenzoylmethane molecule which is readily seen to be a somewhat distorted example of the dodecahedral I_d stereoisomeric type. The apparent coincidence of the *quasi*-$\bar{4}$ axis of the molecule with the single twofold axis required in the crystal lends plausibility to their interpretation. The bulky ring systems, indeed, would seem to be well handled within the generally tetrahedral shape permitted by I_d.

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[33] One notes that *all* intermediate coördination figures are dodecahedra with triangular faces. It would be correct, but chemically and structurally misleading, to speak of the coördination figure in the zirconium acetylacetonate molecule as a "distorted dodecahedron"; it is in fact obtainable from the $\bar{4}$2m dodecahedron by requiring less than the full symmetry. It is both incorrect and misleading to speak of the $\bar{4}$2m dodecahedron as a "distorted antiprism"—the structurally valuable $\bar{4}$ operation is not an element of $\bar{8}$2m. When viewed in proper perspective (*cf.*, Fig. 1 and 2), the ideal polyhedra are seen to differ fundamentally. When viewed along a twofold axis, in projection or even in depth, the $\bar{4}$2m dodecahedron somewhat resembles the $\bar{8}$2m antiprism viewed along $\bar{8}$ (but not to the impossible degree which the diagram of a "new boron polyhedron," Fig. 2 of R. A. Jacobsen and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959), would have it).

[34] D. Grdenić and B. Matković, *Acta Cryst.*, **12**, 817 (1959).

[35] Comparatively small movements in just half of the coördinated atoms will transform one polyhedron into the other. Starting, say, from the hard sphere model of the dodecahedron, the stretching of one pair of opposite edges *b* (Fig. 1) from the length 1.250*a* to $\sqrt{2}a$ with simultaneous shrinking of the other pair to the length of *a* will give an equilateral antiprism; for a ZrO_8 group each oxygen atom O_B would be moved about 0.75 Å. The accompanying changes in symmetry axes are $2 \rightarrow \bar{8}$, $2 \rightarrow 2$, $\bar{4} \rightarrow 2$.

[36] D. Grdenić and B. Matković, *Nature*, **182**, 465 (1958).

[37] L. Wolf and H. Bärnighausen, *Acta Cryst.*, **13**, 778 (1960).