Determination of the Centroid or 'the Best Centre' of a Coordination Polyhedron

Tonči Balić Žunić[a] and Emil Makovicky[b]

*[a]Haldor Topsøe A/S, Nymøllevej 55, DK-2800, Lyngby, Denmark, and [b]Geological Institute,
University of Copenhagen, Østervoldgade 10, DK-1350 Copenhagen K, Denmark*

Abstract

The geometric parameters related to the point in the coordination polyhedron having the minimum variation of distances to the vertices ('the centroid of the coordination polyhedron') are proposed as a measure of polyhedral irregularity or deformation. The numerical method for the determination of the centroid coordinates is described. Knowing these coordinates, the radius of the sphere circumscribed to the coordination polyhedron, the degree of sphericity of coordination, the principal axes of the ellipsoid fitted to the polyhedron and the displacement of the central atom from the centroid are calculated. These quantities are measures for various aspects of irregularity in the coordination polyhedron. The centroid calculation has been applied to the family of ABS_2-type sulfides with cations in slightly to highly deformed octahedral coordinations.

1. Introduction

The coordination of an atom in a crystal structure is usually examined in one of the following two ways. (1) A Dirichlet domain (Voronoi polyhedron) is constructed around the atom and its geometric parameters are used for the analysis of the coordination. Several approaches have been proposed and used to obtain the crystal chemical parameters from such polyhedra (Carter, 1978; Fischer & Koch, 1979; Koch & Fischer, 1980). (2) The coordination of an atom is represented by a polyhedron termed a coordination polyhedron, the vertices of which are placed in the centres of surrounding atoms (ligands). The geometrical characteristics of the coordination polyhedra are used especially for the analysis of the coordination number, bond lengths and bond angles around the central atom (*e.g.* Robinson, Gibbs & Ribbe, 1971). In several cases, the dihedral angles between the normals of adjacent faces of a coordination polyhedron are examined to estimate its regularity (Porai-Koshits & Aslanov, 1972; Muetterties & Guggenberger, 1974). An interesting method is also the fitting of the position of atoms in a coordination polyhedron to the set of points with specific geometrical characteristics (Dollase, 1974; Drew, 1977).

To our knowledge, the geometric parameters connected with the point which comes closest to the condition of being equidistant to all the coordinated ligands have never been used for crystal chemical analyses. For this point we propose the name 'centroid of the coordination polyhedron'. It is obvious that in a regular polyhedron the centroid coincides with the central atom, but this is usually not the case in an irregular polyhedron where knowledge of the centroid position should be of significant crystal chemical interest.

We show that for every coordination polyhedron it is possible to find a point for which the variation of the distances to the ligand atoms is at a minimum. We also describe a method for the calculation of its coordinates and suggest several geometric parameters which can be calculated for a coordination polyhedron, knowing the coordinates of its centroid.

2. The calculation of the centroid of coordination

Let a polyhedron be represented by a set of n points (vertices) with orthogonal coordinates (x_1,y_1,z_1) to (x_n,y_n,z_n). A distance of an arbitrary point (x_0,y_0,z_0) to the ith vertex of the polyhedron is given by

$$d_i = \left[(x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2\right]^{1/2}.$$

We wish to find the point for which the variance of distances $\Sigma(d_i - \Sigma d_j/n)^2$ is minimum, but to avoid irrational expression we find the minimum for the variance of the squares of distances (d^2) instead. The expression to be minimized is

$$\Sigma\left(d_i^2 - \Sigma d_i^2/n\right)^2.$$

We express d_i and d_j in terms of the orthogonal coordinates

$$
\begin{aligned}
d_i^2 - \Sigma d_j^2/n = {}& 2(\Sigma x_j/n - x_i)x_0 + 2(\Sigma y_j/n - y_i)y_0 \\
& + 2(\Sigma z_j/n - z_i)z_0 + x_i^2 + y_i^2 + z_i^2 \\
& - \Sigma x_j^2/n - \Sigma y_j^2/n - \Sigma z_j^2/n
\end{aligned}
\tag{1}
$$

The square of (1) is then

$$
\begin{aligned}
\left(d_i^2 - \Sigma d_j^2/n\right)^2 = {}& 4x_0^2(\Sigma x_j - nx_i)^2/n^2 \\
& + 4y_0^2(\Sigma y_j - ny_i)^2/n^2
\end{aligned}
$$

$$+ 4z_0^2(\Sigma z_j - nz_i)^2/n^2$$
$$- 4x_0 C(\Sigma x_j - nx_i)/n^2$$
$$- 4y_0 C(\Sigma y_j - ny_i))/n^2$$
$$- 4z_0 C(\Sigma z_j - nz_i)/n^2$$
$$+ 8x_0 y_0(\Sigma x_j - nx_i)(\Sigma y_j - ny_i)/n^2$$
$$+ 8y_0 z_0(\Sigma y_j - ny_i)(\Sigma z_j - nz_i)/n^2$$
$$+ 8z_0 x_0(\Sigma z_j - nz_i)(\Sigma x_j - nx_i)/n^2$$
$$+ \dots \tag{2}$$

where

$$C = \Sigma x_j^2 + \Sigma y_j^2 + \Sigma z_j^2 - n\left(x_i^2 + y_i^2 + z_i^2\right).$$

The terms which do not contain x_0, y_0 or z_0 are not explicitly written because they disappear on subsequent derivation.

Summing expressions (2) over all i values

$$\Sigma\left(d_i^2 - \Sigma d_j^2/n\right)^2 = 4\left[\Sigma x_i^2 - (\Sigma x_i)^2/n\right]x_0^2$$
$$+ 4\left[\Sigma y_i^2 - (\Sigma y_i)^2/n\right]y_0^2$$
$$+ 4\left[\Sigma z_i^2 - (\Sigma z_i)^2/n\right]z_0^2$$
$$+ 4(\Sigma x_i^2 \Sigma x_i/n + \Sigma y_i^2 \Sigma x_i/n$$
$$+ \Sigma z_i^2 \Sigma x_i/n$$
$$- \Sigma x_i^3 - \Sigma y_i^2 x_i - \Sigma z_i^2 x_i)x_0$$
$$+ 4(\Sigma x_i^2 \Sigma y_i/n + \Sigma y_i^2 \Sigma y_i/n$$
$$+ \Sigma z_i^2 \Sigma y_i/n$$
$$- \Sigma x_i^2 y_i - \Sigma y_i^3 - \Sigma z_i^2 y_i)y_0$$
$$+ 4(\Sigma x_i^2 \Sigma z_i/n + \Sigma y_i^2 \Sigma z_i/n$$
$$+ \Sigma z_i^2 \Sigma z_i/n$$
$$- \Sigma x_i^2 z_i - \Sigma y_i^2 z_i - \Sigma z_i^3)z_0$$
$$+ 8(\Sigma x_i y_i - \Sigma x_i \Sigma y_i/n)x_0 y_0$$
$$+ 8(\Sigma y_i z_i - \Sigma y_i \Sigma z_i/n)y_0 z_0$$
$$+ 8(\Sigma z_i x_i - \Sigma z_i \Sigma x_i/n)z_0 x_0$$
$$+ \dots \tag{3}$$

To find the minimum, the partial derivatives of (3) on x_0, y_0 and z_0 are set equal to zero. The resulting equations (4) are linear in terms of x_0, y_0 and z_0

$$2[\Sigma x_i^2 - (\Sigma x_i)^2/n]x_0 + 2(\Sigma x_i y_i - \Sigma x_i \Sigma y_i/n)y_0$$
$$+ 2(\Sigma z_i x_i - \Sigma z_i \Sigma x_i/n)z_0 = \Sigma x_i^3 + \Sigma y_i^2 x_i + \Sigma z_i^2 x_i$$
$$- \Sigma x_i^2 \Sigma x_i/n$$
$$- \Sigma y_i^2 \Sigma x_i/n$$
$$- \Sigma z_i^2 \Sigma x_i/n \tag{4a}$$

$$2(\Sigma x_i y_i - \Sigma x_i \Sigma y_i/n)x_0 + 2[\Sigma y_i^2 - (\Sigma y_i)^2/n]y_0$$
$$+ 2(\Sigma y_i z_i - \Sigma y_i \Sigma z_i/n)z_0 = \Sigma x_i^2 y_i + \Sigma y_i^3 + \Sigma z_i^2 y_i$$
$$- \Sigma x_i^2 \Sigma y_i/n$$
$$- \Sigma y_i^2 \Sigma y_i/n$$
$$- \Sigma z_i^2 \Sigma y_i/n \tag{4b}$$

$$2(\Sigma z_i x_i - \Sigma z_i \Sigma x_i/n)x_0 + 2(\Sigma y_i z_i - \Sigma y_i \Sigma z_i/n)y_0$$
$$+ 2\left[\Sigma z_i^2 - (\Sigma z_i)^2/n\right]z_0 = \Sigma x_i^2 z_i + \Sigma y_i^2 z_i + \Sigma z_i^3$$
$$- \Sigma x_i^2 \Sigma z_i/n$$
$$- \Sigma y_i^2 \Sigma z_i/n$$
$$- \Sigma z_i^2 \Sigma z_i/n. \tag{4c}$$

The simultaneous solution of (4) gives the centroid coordinates (x_0, y_0, z_0). This calculation has been incorporated in the computer program *IVTON* (Balić Žunić & Vicković, 1994).

The calculated values are orthogonal coordinates and a conversion to the crystal system follows as the last step. For a non-degenerated polyhedron with four vertices, the centroid is always equidistant to all of them. For irregular polyhedra with more vertices, the variance of the distances is in general larger than zero; it is an inverse measure of the 'sphericity' of the coordination polyhedron, describing its deviation from the circumscribed sphere. For coordination number (CN) 3, the solution is not unique. For such a case the solution is found in the program *IVTON* by calculating the equations for three planes, two perpendicular to, and bisecting, the two edges of the coordination triangle and the third containing all its vertices.

3. Crystal-chemical parameters related to the centroid of coordination

The crystal chemical parameters described below have been calculated using the program *IVTON*, after the coordinates of the centroid have been determined. The crystal structure data for the examined structures were obtained from and are referenced in the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983).

3.1. *Average distance r from the centroid to the ligands*

This value can be used in evaluating the 'crystal radius' of the volume occupied by a coordination polyhedron. In Table 1 the results of an analysis on a family of geometrically related structures are presented. The sulfides of the type ABS_2 with both cations in distorted octahedral coordinations were compared. The average centroid–ligand distance (or the radius of the circumscribed sphere) is compared with the sum of the effective ionic radii of the cation and S^{2-} (Shannon,

Table 1. *The sums of effective ionic radii (Å) of cations and S^{2-} (Shannon, 1976), the average distances to the six closest S atoms, and the average centroid radii for sulfides of the ABS_2 type with distorted octahedral coordinations*

Cation	Li^+	Na^+	K^+	Rb^+	Cu^+	Ag^+	Tl^+	As^{3+}	Sb^{3+}	Bi^{3+}
Sum of ionic radii	2.60	2.86	3.22	3.36	2.61	2.99	3.34	2.42	2.60	2.87
Average distance	2.71	2.92	3.18	3.35	2.93	2.90	3.23	2.95	3.01	2.98
Centroid radius	2.71	2.92	3.18	3.37	2.81	2.86	3.28	3.25	3.16	3.02

Table 2. *Selected centroid parameters for the atoms in sulfides of ABS_2-type with distorted octahedral coordinations*

Centroid radius refers to the circumscribed sphere (the average centroid–ligand distance), sphericity is calculated from the standard deviation of centroid–ligand distances, the displacement is relative to the position of the centroid. The number of coordination polyhedra used for calculations is given at the element symbol. With several coordination polyhedra for an element, the values represent the minimum, the maximum and the average.

Atom	Li(1)	Na(2)	K(1)	Rb(2)	Cu(2)	Ag(3)	Tl(4)	As(4)	Sb(12)	Bi(2)
Centroid radius (r)	2.714	2.905–2.928 2.917	3.183	3.266–3.445 3.369	2.787–2.831 2.809	2.784–2.987 2.864	3.251–3.304 3.275	3.023–3.598 3.245	2.916–3.492 3.156	2.970–3.069 3.019
Sphericity ($1 - \sigma_r/r$)	0.977	0.999–0.971 0.985	0.994	1.000–0.980 0.991	0.753–0.745 0.749	0.921–0.832 0.880	0.984–0.969 0.977	0.992–0.894 0.942	0.993–0.880 0.958	1.000–0.955 0.978
Displacement (Δ)	0.115	0.026–0.053 0.041	0.003	0.000–0.155 0.097	1.242–1.289 1.265	0.146–0.651 0.369	0.246–0.403 0.292	1.201–1.845 1.483	0.679–1.650 1.085	0.000–0.806 0.403

1976) and to the average distance of the central atom to the six S atoms. For the alkali cations there is practically no difference between the average bond distance and the centroid radius, although the significant differences between the centroid radius and the sums of the ionic radii should be noted. For cations with the s^2 lone pair (Tl^+, As^{3+}, Sb^{3+} and Bi^{3+}), the centroid radii are consistently larger than the average distances to ligands. Moreover, there is no substantial difference between As, Sb and Bi in the latter distances, showing the inferiority of the average bond length to the centroid concept for a quantitative description of a lone-pair cation. Note that for small cations with a high degree of covalent bonding (Cu^+ and Ag^+), the centroid radius, in contrast, is smaller than their average distance to the ligands. In Fig. 1 the correlations of centroid radii for the two different cations in the structure are represented for the investigated ABS_2 sulfides.
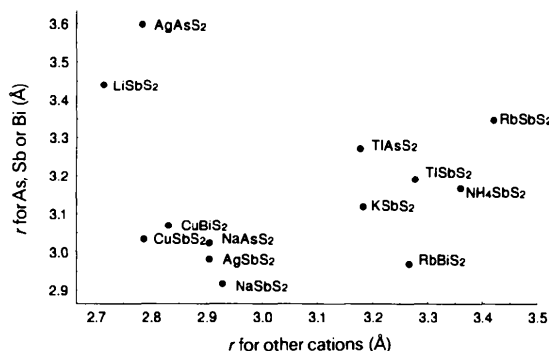
3.2. Standard deviation σ_r of distances from the centroid to the ligands

We suggest its modification ($1 - \sigma_r/r$) as a measure of 'sphericity' for the coordination polyhedron. Its dependence on the type of central atom and ligands may be of considerable interest. In Table 2 the values for atoms in ABS_2 compounds are presented. Significant differences are recorded for different cations. The best sphericities are obtained for alkali cations. For cations with highly active lone-electron pairs (As^{3+} and Sb^{3+}) sphericities can be significantly lower, while for Ag^+ and especially Cu^+ the deviation from sphericity becomes remarkable.

3.3. Centroid–central atom distance

This distance describes the displacement Δ of the central atom from the 'best' centre of the ligand arrangement. Δ can be used as a measure of stereochemical activity (Andersson & Åström, 1972) for the s^2 lone pair of the central atom. The direction of displacement is assumed to be opposite to the orientation of the lone pair on this atom. In Fig. 2 this displacement is related to the radius of the sphere, *i.e.* the average centroid–ligand distance. For atoms with a highly active lone pair, a very striking correlation can be observed offering a new insight into this stereochemical activity.

3.4. A triaxial ellipsoid

A triaxial ellipsoid with the centre in the centroid and the surface fitted to the ligand positions describes the anisotropy of the ligand arrangement, especially for high coordination numbers. Calculation of this surface can be attempted for CN $\geq$ 6.

If the set of points lies on the surface of an ellipsoid, their orthogonal coordinates (related to the ellipsoid

Fig. 1. Correlation between the radii of the circumscribed spheres for the *A* and *B* cations in ABS_2 compounds. For sulfides with *B* = Sb, the two branches with large and small *A* cations, respectively, can be discerned, intersecting at NaSbS$_2$.

centre) satisfy the quadric

$$x_i^2 e_{11} + y_i^2 e_{22} + z_i^2 e_{33} + 2x_i y_i e_{12} + 2x_i z_i e_{13} + 2y_i z_i e_{23}$$
$$= 1,$$

where e_{11}, e_{22}, e_{33}, e_{12}, e_{13} and e_{23} are matrix components. With six or more points lying close to the surface of an ellipsoid, it is in principle possible to obtain the best values for the components of the ellipsoid matrix by the linear least-squares method. If the least-squares calculation produces matrix components of a positive definite ellipsoid, it is possible to obtain the orientations and the lengths of the principal axes of
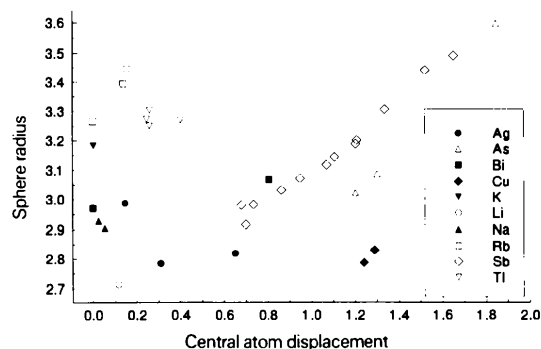
this ellipsoid from the eigenvectors and the positive eigenvalues of the matrix. Also, the volume of the ellipsoid can be calculated as $V = 4\pi r_1 r_2 r_3/3$, where r_1, r_2 and r_3 are the values of the principal half-axes. In Fig. 3 the ellipsoid volumes are related to the volumes of circumscribed spheres for the ABS_2 structures. It can be seen that a very large number of calculated coordinations produced satisfactory fits. The graph gives a useful check of the reliability of fitting an ellipsoid to the coordination polyhedron. The volumes of ellipsoids and corresponding spheres lie very close in almost all the calculated cases and the fit can be accepted as reliable and the ellipsoid axes used in determining the 'sense of deformation'. Only in the case of K in the $KSbS_2$ structure does the difference between volumes appear to be unreasonably large and this fit should be considered unsuccessful, together with others that produced ellipsoids with negative eigenvalues.

Fig. 2. Correlation of the centroid sphere radius and the central atom displacement for selected ABS_2 compounds with octahedrally coordinated (except for Cu) cations.
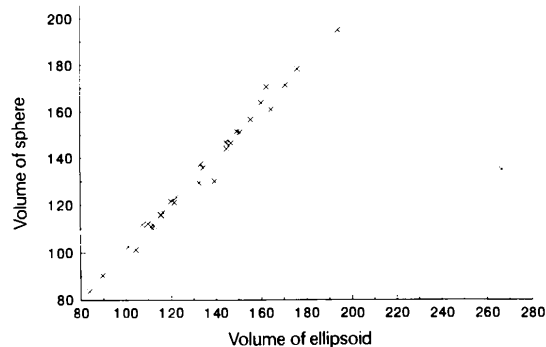

Fig. 3. Correlation of the volumes of the sphere and ellipsoid fitted to the same coordination polyhedron for cations in selected ABS_2 compounds. The point with the large deviation from the 1:1 line belongs to K in $KSbS_2$.

References

Andersson, S. & Åström, A. (1972). Solid State Chemistry, Proceedings of the 5th Material Research Symposium, pp. 3–14.

Balić Žunić, T. & Vicković, I. (1994). *IVTON. A Program for the Calculation of Geometrical Aspects of Crystal Structures and Some Crystal Chemical Applications.* Geological Institute, Univ. of Copenhagen.

Bergerhoff, G., Hundt, R., Sievers, R. & Brown, I. D. (1983). *J. Chem. Inf.* **23**, 66–69.

Carter, F. L. (1978). *Acta Cryst.* B**34**, 2962–2966.

Dollase, W. A. (1974). *Acta Cryst.* A**30**, 513–517.

Drew, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.

Fischer, W. & Koch, E. (1979). *Z. Kristallogr.* **150**, 245–260.

Koch, E. & Fischer, W. (1980). *Z. Kristallogr.* **153**, 255–263.

Muetterties, E. L. & Guggenberger, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748–1756.

Porai-Koshits, M. A. & Aslanov, L. A. (1972). *J. Struct. Chem.* **13**, 244.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.