9.4. Typical interatomic distances: inorganic compounds

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9.4.1. Introduction

In inorganic compounds, the intrinsic interatomic distances vary over a wide range, depending on atomic size, oxidation state, coordination number, bonding type, conditions of state, *etc*. The experimental values depend also on the conditions of measurement and possibly the defect structure of the sample in question.

To a first approximation, interatomic distances can be calculated from the sum of ionic radii taken from various tables. Mean values from experimental values from a limited number of structures determined up to 1960 are listed in *International Tables for X-ray Crystallography* (*IT* III, 1962). Today, databases allow all experimental results determined up to the present to be summarized and subjected to statistical analyses. For the Inorganic Crystal Structure Database (ICSD) (Bergerhoff & Brown, 1987), this analysis has been performed starting with 24 496 structure determinations in the 1990 version for all combinations of ions and atoms. For 8329 combinations, at least one distance inside the range 0 to 500 pm could be calculated. The statistical procedure is described in the following Section, and the results are given in Tables 9.4.1.1 to 9.4.1.12 for many pairs for which more than two distances had been determined. For more detailed discussions, and other ion pairs, the CD-ROM version of the ICSD is recommended. With the command 'check distances' in the *CVIS* program for the ICSD, the general distance distribution of a combination of elements can be compared with the distance distribution in a specific phase. Extreme values can be traced to their origin.

9.4.2. The retrieval system

By means of the retrieval system *CRYSTIN* (Sievers & Hundt, 1987), sets of structures were selected and combined; these contained:

(i) one ion in a specific oxidation state (if appropriate);
(ii) the other ion of the pair in a specific oxidation state (if appropriate);
(iii) structures determined at room temperature;
(iv) structures determined at normal pressure;
(v) no disordered structures;
(vi) no solid solutions;
(vii) no defect structures;
(viii) structures for which atomic coordinates were given;
(ix) only structures with $R < 6\%$ when there were many determinations.

For the M structures so defined, n interatomic distances were calculated for the atoms and ions in question. In so doing, all symmetrically equivalent and non-equivalent distances were taken into account. From these, a frequency distribution was calculated automatically. All distances d were collected into ranges of 2 pm. In (9.4.2.1)–(9.4.2.2), $n(d)$ is the number of distances in the range with midpoint d, d_1 is the midpoint of the lowest range, and d_2 is the midpoint of the highest range selected for the calculation of the mean. The choice of d_1 and d_2 is discussed in Section 9.4.3. The mean and the standard uncertainty (s.u.) of one set of distances were calculated by means of the equations

$$N = \sum_{d_1}^{d_2} n(d), \tag{9.4.2.1}$$

$$\text{mean} = \mu = N^{-1} \sum_{d_1}^{d_2} dn(d), \tag{9.4.2.2}$$

$$\text{s.u.} = \left(N^{-1} \sum_{d_1}^{d_2} (d - \mu)^2 n(d) \right)^{1/2}. \tag{9.4.2.3}$$

9.4.3. Interpretation of frequency distributions

It is obvious that the results have to be interpreted carefully when they are applied to crystal-structure discussions. In performing the analysis, the frequency distribution was inspected for each pair of ions. If all values were distributed around a single maximum, then d_1 and d_2 were set equal to zero and 500 pm, respectively. If there were two or more maxima, one was carefully selected and d_1 and d_2 were set to the left and right in such a way that the frequency was zero at both limits. In combinations with oxygen, so many distances were available for the most probable maximum that the program could select d_1 and d_2 automatically.

Maxima outside the selected range may come from errors in data or distances to ions in the second coordination sphere [*e.g.* Mg^{2+}—Cl^- in $Mg(H_2O)_6Cl_2$]. Generally, different oxidation states give rise to different maxima, which therefore have been tabulated separately (*e.g.* Cr^{2+}, Cr^{3+}, Cr^{4+}, Cr^{5+}, Cr^{6+} in combination with O^{2-}). In some typical cases, oxidation states cannot be clearly defined. Then the oxidation states have been omitted (*e.g.* Os—F, Rh—Br, N—S). Nevertheless, sometimes one oxidation state can be separated (*e.g.* W—Cl and W^{6+}—Cl^{1-}). Atomic distances between equally charged ions will be contact distances and vary over a wide range (*e.g.* O^{2-}—O^{2-} distances within SO_4^{2-} ions and between such ions).

references