Acta Crystallographica Section B
**Structural
Science**
ISSN 0108-7681

On measuring the size of distortions in coordination polyhedra

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Received 22 February 2006
Accepted 11 April 2006

There is no unique index that measures the size of the distortion found in a coordination polyhedron because different indices can result in a different ordering depending on the mode of the distortion (*i.e.* the third and higher moments of the bond-length distribution). This paper proposes the increase in the average bond length as a suitable index as this is directly related to the increase in volume of the coordination polyhedron and hence of the unit cell. Some examples are discussed.

1. Introduction

Using Shannon's information theory, Lalik (2005) recently proposed that ΔH defined in (1) could be used as a measure of the size of the distortion of a coordination polyhedron.[1]

$$\Delta H = (A/V)\sum_i [s_i \ln(s_i/s')] = A\langle (s_i/s')\ln(s_i/s')\rangle, \qquad (1)$$

where the summation is over the N bonds in the coordination polyhedron, $\langle\rangle$ indicates an average over the N bonds, A is a constant equal to 1/ln2 if ΔH is measured in bits of information, V is the formal oxidation state of the central cation (atomic valence), s_i is the valence (order) of the ith bond and s' is the average valence of the bonds in the coordination sphere, *i.e.* it is the valence a bond would have in a regular coordination polyhedron.

The bond lengths, R_i, enter this equation through the bond length–bond valence correlation (Brown, 2002, pp. 26ff):

$$s_i = \exp[(Ro - R_i)/B], \qquad (2)$$

where Ro and B are constants determined empirically for each type of bond, Ro being the notional length of a bond of unit valence and B a measure of the softness of the bond, often taken to be 0.37 Å. These parameters have been tabulated for most bond types by Brown (2006).

Other measures of distortion have been proposed but most are unsatisfactory in one or more ways. Indices based on how closely a regular coordination polyhedron can be fitted to the observed distorted polyhedron are sensitive to the method of fitting (Dollase, 1974; Lueken *et al.*, 1987; Makovicki & Balić-Zunić, 1998). Hoppe's (1979) effective coordination number (ECoN) and mean fictive ionic radii (MEFIR) involve complex calculations. Hardcastle & Wachs' (1990) use of the valence of the strongest bond does not sample the whole bond-length distribution and is particularly susceptible to experimental uncertainties. The second moment of the bond-length distribution used by Urusov (2003) requires that all the ligands be the same and ignores the significant influence of the higher moments. It is these higher moments that ensure that there is no unique way of ranking distortions according to size alone; different measures lead to different orderings depending on the mode of distortion. However, Lalik (2005) found a reasonable correlation between ΔH and many of the earlier distortion measures, albeit with some scatter.

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[1] This measure, like most other measures of the distortion in coordination environments, includes only the deviation of the bond lengths from their average value. It does not measure the deviations of the bond angles from their ideal values and such angular deviations are ignored in the present study.

An alternative index of bond distortion is suggested by the distortion theorem of the bond-valence model (Brown, 2002, p. 33). This theorem, which can be derived from (2), states that the average bond length in a coordination polyhedron increases with increasing distortion, providing the sum of the bond valences at the central atom remains constant. Using the increase in the average bond length, ΔR, as an index has the advantage that ΔR is directly related to the increase in the volume of the coordination polyhedron. Furthermore, ΔR is (at least in principle) a directly measurable quantity and, as shown below, can be used even when the coordination polyhedron contains a mixture of ligands.

2. Calculation of ΔR

ΔR is determined by subtracting the average bond length, R', found in a regular coordination polyhedron from the average bond length in the observed distorted polyhedron, $\langle R \rangle$:

$$\Delta R = \langle R \rangle - R'. \tag{3}$$

While $\langle R \rangle$ is easy to calculate from the observed bond lengths, there are problems with determining R' since in some cases, *e.g.* $V^{5+}O_6$ octahedra, undistorted coordination environments are unknown, and even where such environments are known, the observed values of R' cover a range that is similar in size to ΔR. The internal strains responsible for these variations unfortunately tend to be more common in the high-symmetry structures where regular coordination is most likely to be observed, making such structures unsuitable sources for R'.

The influence of these strains can, however, readily be removed by converting the bond lengths to bond valences using (2).

Setting $\delta R_i = R_i - R'$, (3) can be written as

$$\Delta R = \langle R \rangle - R' = (1/N) \sum \delta R_i, \tag{4}$$

where N is the coordination number, *i.e.* the number of bonds formed by the central atom.

Rewriting (2) in the form

$$\ln(s_i) = (Ro - R_i)/B, \tag{5}$$

it is readily shown that

$$\ln(s_i/s') = -\delta R_i/B. \tag{6}$$

Combining (4) and (6) yields

$$\Delta R = -(B/N)\Sigma \ln(s_i/s') = -B\langle \ln(s_i/s') \rangle. \tag{7}$$

B is a constant which can be taken as 0.37 Å, and s_i is calculated from R_i using (2) and the tabulated constants for Ro and B.[2] Ideally s' should be set equal to V/N, but to allow for experimental uncertainties and the internal strains found in the real crystal, V should be replaced by the sum of the observed bond valences, $\sum s_i$, as this ensures that $\sum s_i = \sum s'$, the condition required by the distortion theorem. The average bond valence s' is then equal to $\sum s_i/N$, which is the bond valence expected for a bond in the undistorted environment. This procedure ensures that the measure of the distortion, ΔR, is independent of the measure of the strain, $\sum s_i - V$, allowing the two effects to be analyzed separately.

A comparison of (7) with (1) shows that, apart from the constant terms, the difference between ΔR and ΔH lies in the weighting used when calculating the average of the logarithm term. This is sufficient to result in a different ordering of distortions, as can be seen in the selection of distortion indices shown in Table 1. The largest value of ΔH is found for the Tl atom in Tl_2TeO_3, but there are five other coordination polyhedra that have larger values of ΔR. The exceptionally large value of ΔH for this compound is attributable to the presence of one very short bond, which gives excessive weight to the largest logarithm term. To help in the comparisons, Table 1 includes a couple of indicators of the mode of distortion, namely the coordination number split out as a triplet indicating the number of bonds significantly stronger than average, the number close to average and the number significantly weaker than average. In addition, the range of observed bond valences is shown.

Table 1
Distortion indices around various cations.

The three coordination numbers indicate the number of bonds shorter than average, the number close to average and the number longer than average. Number references are to the Inorganic Crystal Structure Database (Belsky *et al.*, 2002).

Compound	Cation	ΔR	ΔH	$\Delta R/\Delta H$	Coordination numbers	Range (s/s')	Reference
α-VPO_5	V	0.136	1.876	0.072	1, 0, 5	0.07–2.21	629
β-VPO_5	V	0.095	1.615	0.059	1, 1, 4	0.14–2.17	9413
ZnV_2O6	V	0.094	1.521	0.062	2, 2, 2	0.14–1.70	30880
$MgTiO_3$	Ti	0.016	0.373	0.043	3, 0, 3	0.71–1.29	65794
$NaNbO_3$	Nb	0.009	0.200	0.045	2, 2, 2	0.70–1.08	23239
$CoTa_2O6$	Ta	0.000	0.005	0.048	2, 0, 4	0.96–1.05	15854
$CuCrO_4$	Cu	0.048	0.910	0.053	4, 0, 2	0.40–1.30	60825
Cu_2P2O7	Cu	0.117	1.568	0.075	4, 0, 2	0.09–1.50	67316
CuO	Cu	0.146	2.084	0.070	4, 0, 2	0.15–1.44	16025
[CuO_2N2Cl2]	Cu	0.145	1.918	0.076	4, 0, 2	0.07–1.36	Table 2
[CuO_3NCl2]	Cu	0.136	1.996	0.068	4, 0, 2	0.17–1.45	Table 2
TlV_3O8	Tl	0.034	0.768	0.044	3, 3, 2	0.53–1.79	65773
Tl_2TeO3	Tl	0.105	2.427	0.043	2, 1, 3	0.31–2.66	200965
$TlBO_3$	Tl	0.001	0.013	0.042	0, 3, 0	0.32–0.38	101096

The first six entries in Table 1 illustrate distortions found around d^0 transition metals. They indicate that the octahedron around V^{5+} is much more distorted than those around Nb^{5+}, Ta^{5+} and Ti^{4+}. The next five entries illustrate the Jahn–Teller distortion around Cu^{2+}. Typical values of ΔR and ΔH for this effect are 0.14 and 2.0, respectively. $CuCrO_4$ is included because it shows an unusually small distortion and $Cu_2P_2O_7$ is an example of a structure in which one of the two long bonds is atypically short (2.33 Å). The last three entries show the effects of a lone pair. Where the lone pair is only weakly stereoactive, as around the eight-coordinated Tl atom in TlV_3O_8, the indices are small. In Tl_2TeO_3, where the stereoactivity is more pronounced, the distortion indices are larger, but surprisingly the distortion indices for the fully stereoactive lone pair found in $TlBO_3$ are once again small because the weak bonds are no longer part of the coordination polyhedron and the three remaining bonds are all about the same length. The values of the distortion indices are therefore sensitive to how the bond length cut-off is chosen.

Both ΔH and ΔR can be used in cases where the central atom is bonded to different ligands. In this case it is less clear what is meant by an undistorted coordination polyhedron. For example, if both oxygen and chlorine ligands are present, the different sizes of the atoms would make it unlikely that the M—O and M—Cl bonds will have the same length, but if they do the Cl atoms will be more strongly bonded than the O atoms. Converting the bond lengths to bond valences removes the influence of ligand size, allowing regular coordination to be defined as that in which all the bonds have the same valence, thus allowing (1) and (7) to be used. Table 2 shows two examples of typical Jahn–Teller distortions around Cu atoms with

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[2] While (7) is independent of the value used for Ro, ΔR varies directly as B. As it is difficult to determine an accurate value for B for each type of bond, a universal value of 0.37 Å is often assumed. The true value of B may be different, but if the standard value of 0.37 Å is used the values of ΔR can be directly compared.

Table 2
Bond lengths and valences in the two Cu heteroleptic polyhedra in $[CuCl(C_6H_6N_4)\text{-}H_2O][CuCl(C_4H_5NO_4)]H_2O$ (Gao *et al.*, 2005).

Bond	Length	Valence	Bond	Length	Valence
Cu1—O5	1.974	0.451	Cu2—O4	1.935	0.501
Cu1—N3	1.996	0.454	Cu2—O2	1.965	0.462
Cu1—N1	2.003	0.446	Cu2—N5	1.991	0.460
Cu1—Cl1	2.250	0.509	Cu2—Cl2	2.235	0.530
Cu1—Cl2	2.831	0.106	Cu2—O5	2.721	0.060
Cu1—O2	3.030	0.026	Cu2—Cl1	3.071	0.055

three different kinds of ligand. Although the bond lengths vary over a considerable range, the bond valences show the typical Jahn–Teller pattern, reflected in the values of the distortion indices given in Table 1.

Like ΔH, ΔR satisfies most of the criteria that are desirable in a distortion index. Both indices can be used in any situation where bond valences can be calculated, *i.e.* in any coordination polyhedron in which the bonds are polar, including most coordination compounds. Both sample the complete distribution of bond lengths, both are easily and robustly calculated, they do not require that all the ligands be the same, and they are zero for an undistorted polyhedron and are otherwise positive. However, ΔR additionally has the property of being directly related to the increase in the size of the coordination polyhedron and hence of the unit cell. For example, Brown *et al.* (1997) used ΔR for the dynamic distortion accompanying thermal agitation to calculate thermal expansion.

The author thanks Professor Urusov for many interesting discussions on the problem of measuring distortions in coordination polyhedra.

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