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Article

Application of Symmetry Operation Measures in Structural Inorganic Chemistry

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This paper presents an application of the recently proposed symmetry operation measures to the determination of the effective symmetry point group of coordination polyhedra in inorganic solids. Several structure types based on octahedra are found to present distinct distortion patterns each, not strictly attached to the crystallographic site symmetry. These include the $(NH_4)_2[CuCl_4]$, CdI_2 (brucite), FeS_2 (pyrite), TiO_2 (rutile), $CaCl_2$, $GdFeO_3$, $PbTiO_3$, $LiNbO_3$, BiI_3, $CrCl_3$, Al_2O_3, and $NiWO_4$ structures. It is shown that a similar analysis can be applied to the Bailar and tetragonal Jahn−Teller distortions of molecular transition metal complexes, as well as to solids based on tetrahedra, such as the $ZnCl_2$, FeS, $BeCl_2$, SiS_2, and $KFeS_2$ structure types.

In recent years, the use of continuous shape measures and associated tools has allowed us to accurately describe the stereochemistry of metal coordination spheres, even in cases in which they significantly deviate from ideal polyhedral shapes.[1] The recent introduction by the group of Avnir and ourselves of continuous symmetry operation measures[2] is shown in this paper to complement the shape measures and provide consistent descriptions of the distortion modes of ideal polyhedra in a variety of structural types in solid state chemistry, as well as in related molecular systems. This study also shows that the effective symmetry of the coordination octahedron is in many instances higher than the crystallographic site symmetry, and that in most cases four symmetry operation measures are enough to determine the effective symmetry of a distorted octahedron.

In essence, the content of a symmetry operation $\mathbf{R}$ in a set of atoms AB_n is measured by the symmetry operation measure, $Z(\mathbf{R})$. A zero value of that measure indicates that AB_n is invariant to the symmetry operation, and increasing values of $Z(\mathbf{R})$ indicate increasing deviations from the ideal symmetry. More information on the definition and the calculation of $Z(\mathbf{R})$ is given in the Methodology section. Even if the main interest of such measures resides in their ability to calibrate symmetry loss in a continuous scale, it will still be useful for subsequent discussions to adopt a threshold value that we may consider as indicative of nonsignificant distortions. For the present study, we have found that it is reasonable to admit that a set of atoms has a given symmetry operation if the corresponding $Z(\mathbf{R})$ value is smaller than 0.1. On the other hand, the crystallographic symmetry operations give $Z(\mathbf{R}) = 0$ within numerical accuracy (0.0001).

In a recent analysis of the distortions of octahedrally coordinated d^0 transition metal oxides, we focused on the loss of inversion symmetry,[3] without paying attention to the specific distortion mode of the coordination octahedron. We now wish to explore a wider use of the symmetry operation measures for the analysis of distortions of coordination polyhedra in inorganic solids. Our goal is to set up a procedure capable of being incorporated into an automatic classification algorithm. Such a procedure should provide a clear description of the effective symmetry of the distorted polyhedron in a specific structure or in a family of compounds that crystallize with the same structural type.

It is well-known that molecules in the crystal state may have higher effective symmetry than that corresponding to their Wyckoff positions. Since in general that symmetry is only approximate, Motherwell and co-workers developed a molecular symmetry perception algorithm that determines whether a group of atoms belongs to a given symmetry

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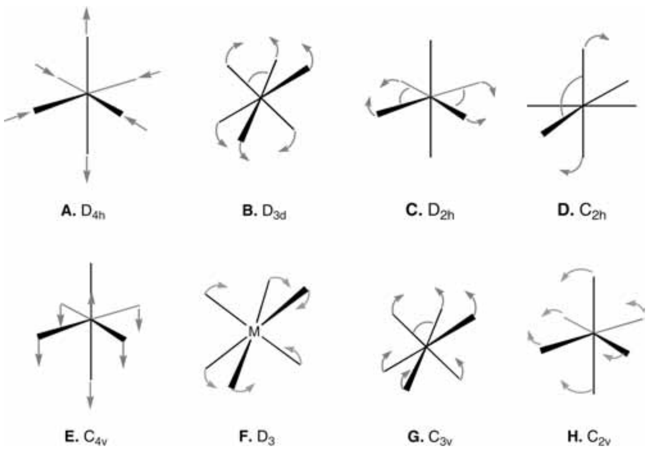
10.1021/ic801264n CCC: $40.75

Scheme 1



group, within a pre-established tolerance margin.[4] Interesting analyses of the relationships between molecular and crystal symmetry were subsequently carried out by that group.[5] At difference with the consideration of symmetry as a continuous property adopted in this work, the approach used by Motherwell et al. uses a binary logic, in which a molecule either belongs or does not belong to a given symmetry point group, even if the tolerance criterion allows slightly distorted molecules to be classified as having the desired symmetry. Another difference between that study and the work reported here is that the former focused only on molecular crystals, whereas we pay attention here mostly to ionic compounds with extended structures. Finally, while Motherwell et al. considered all types of compounds and took into account their molecular and crystal symmetries, we focus here on specific families of compounds with the same space group and analyze the loss of symmetry (octahedral or tetrahedral) of only the coordination spheres of specific atoms.

Distortions of the Octahedron in Solids

Let us start by considering several distortions of the octahedron. Since we have a tool that allows us to separately calibrate the loss of each symmetry operation in a real structure, it is useful first to have an overview of which operations are lost and which ones are retained upon symmetry descent through each of such distortions (Scheme 1). Our analysis, summarized in Table 1, tells us that in most cases four symmetry operation measures are enough to determine the symmetry point group of the distorted molecule. A special situation appears for the D_{2h} and C_{2h} subgroups, since both lose the 3- and 4-fold rotations but retain 2-fold rotations. However, the different number of C_2 rotations retained in each of these subgroups (3 and 1, respectively) allows us to make a correct assignment to one of them, since the algorithm applied provides us with the measures for the symmetry operations associated with any desired number of symmetry elements.

Table 1. Symmetry Operations Retained for Several Distortions of the Octahedron

	operation preserved				
distortion	C_4	C_3	C_2	i	symmetry subgroup
A	yes	no	yes	yes	D_{4h}
B	no	yes	yes	yes	D_{3d}
C	no	no	yes (3)	yes	D_{2h}
D	no	no	yes (1)	yes	C_{2h}
E	yes	no	yes	no	C_{4v} or C_4
F	no	yes	yes	no	D_3
G	no	yes	no	no	C_{3v} or C_3
H	no	no	yes	no	C_{2v} or C_2

Table 2. Shape and Symmetry Operation Measures for Compounds with the BiI_3 Structure[a]

compd	ICSD	S(oct)	$Z(C_4)$	$Z(C_2)$	$Z(i)$
BiI_3	78791	0.01	0.01	0.00	0.00
CmI_3	55878	0.05	0.03	0.01	0.03
YI_3	170773	0.06	0.04	0.00	0.06
SbI_3	56569	0.07	0.04	0.01	0.05
$TiBr_3$	39242	0.10	0.07	0.00	0.10
$ScCl_3$	74517	0.12	0.08	0.00	0.07
$CrCl_3$	22081	0.14	0.09	0.02	0.09
$FeBr_3$	410924	0.17	0.12	0.00	0.17
AsI_3	56568	0.20	0.13	0.00	0.11
$TiCl_3$	39426	0.24	0.16	0.00	0.23
$FeCl_3$	39764	0.29	0.19	0.00	0.29

[a] The $Z(C_3)$ measures are all zero within numerical precision.

It is worth stressing that in five of the eight symmetry subgroups (cases A−D and F in Table 1) reflections are perforce present as products of the symmetry operations preserved. Therefore, in those cases one can avoid checking the reflection measures. In contrast, for cases E, G, and H, two different subgroups may result depending on whether reflections are preserved or not, and the reflection operation measure is required for a full characterization of the effective symmetry subgroup found in each specific structure. We further note that the distortions discussed here can be separated into two groups, depending on whether the inversion is preserved (cases A−D) or not (cases E−H), a relevant distinction if we take into account the physical properties associated with acentricity.[6]

Compounds with the BiI_3 Structure. We consider first the compounds with an AB_3 stoichiometry and the BiI_3 structure, space group $R\bar{3}$ (No. 148). The BiI_3 structure can be described as a two-dimensional lattice formed by edge-sharing octahedra, resulting from occupying one-third of the octahedral holes in a hexagonal close packing. The octahedra, though, present varying degrees of distortion in the different compounds analyzed, evidenced by the corresponding shape measures, S(octahedron), given in Table 2. While the coordination sphere of the Bi atoms in BiI_3 is nearly perfectly octahedral, it is significantly distorted in $TiCl_3$ and $FeCl_3$ (Table 2). In this structure type, the A atoms occupy a 6c site with C_3 symmetry, a fact that is straightforwardly recognized by zero values of the corresponding $Z(C_3)$ measures. In addition, the negligible values of the $Z(C_2)$ measures tell us that the actual symmetry is higher than the

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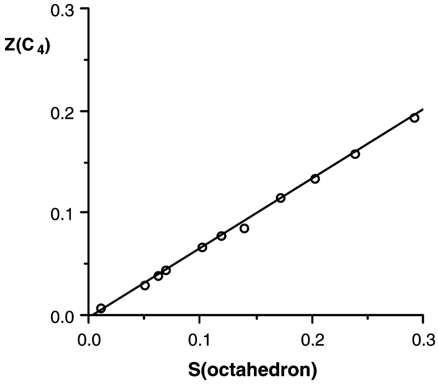

Figure 1. Correlation between the octahedral shape measure and the C_4 symmetry operation measure in the family of compounds with the BiI_3 structure.

Table 3. Shape and Symmetry Operation Measures for Compounds with the $CaCl_2$ Structure[a]

compd	ICSD	S(oct)	$Z(C_4)$	$Z(C_3)$	$Z(C_2)$	$Z(C_2')$	$Z(C_2'')$	symmetry
MgF_2	94280	0.21	0.11	0.11	0.00	0.00	0.00	D_{2h}
$YbBr_2$	26045	0.30	0.16	0.11	0.00	0.01	0.01	$\sim D_{2h}$
$CaBr_2$	56767	0.38	0.19	0.18	0.00	0.00	0.00	D_{2h}
GeO_2	281599	0.40	0.21	0.21	0.00	0.00	0.00	D_{2h}
$CaCl_2$	26158	0.41	0.13	0.21	0.00	0.00	0.00	D_{2h}
NiF_2	73728	0.50	0.25	0.25	0.00	0.00	0.00	D_{2h}
SnO_2	56676	0.66	0.34	0.19	0.00	0.06	0.06	C_{2h}
RuO_2	84619	0.89	0.45	0.44	0.00	0.00	0.00	D_{2h}
PtO_2	202407	0.93	0.48	0.28	0.00	0.07	0.07	C_{2h}

[a] All the structures have zero $Z(i)$ measures within numerical precision.

crystallographic site symmetry. The increasing values of $Z(C_4)$ and $Z(i)$ allow us to conclude, according to Table 1 (case F), that the common distortion present in this family of compounds is one that retains the D_3 point group, i.e., the Bailar twist that relates the octahedron with the trigonal prism through a rotation of two opposing triangular faces around a trigonal axis.[7] The presence of a Bailar distortion in those structures is verified by the small values of the path deviation functions[8] (of less than 5%). The extent of the distortions of the octahedra along the Bailar pathway are between 2 and 13%, according to the generalized polyhedral interconversion coordinates.[9] It is interesting to notice also that the loss of octahedricity is nicely correlated to the loss of the C_4 rotation, as seen in Figure 1, thus confirming that all the analyzed structures of this family undergo the same type of distortion to varying degrees.

$CaCl_2$ Structure. This family of structures illustrates how we can discriminate between D_{2h} and C_{2h} point groups only by the number of C_2 operations (cases C and D in Table 1). The symmetry operation measures of all the compounds of this family analyzed by us show clearly that 4- and 3-fold rotations are lost, whereas a 2-fold rotation and the inversion are retained. To decide whether these structures effectively belong to the D_{2h} or C_{2h} symmetry group, we calculated the C_2 symmetry operation measures relative to the three best axes. The results (Table 3) clearly identify two such compounds that retain only one 2-fold rotation, SnO_2 and PtO_2, thus indicating that their effective symmetry is coincident with the C_{2h} site symmetry. In contrast, the remaining structures retain three 2-fold rotations, corresponding to an effective D_{2h} symmetry. Nevertheless, given the small values of $Z(C_2')$ and $Z(C_2'')$ compared to $Z(C_4)$ and $Z(C_3)$, we can conclude that the effective symmetry in this family is D_{2h} to a good approximation.

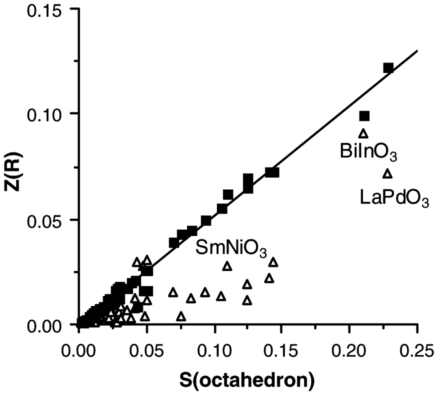

Figure 2. Correlation between the octahedral shape measure and the C_4 (black squares) or C_3 (white triangles) symmetry operation measures in the family of compounds with the $GdFeO_3$ perovskite structure.

$GdFeO_3$ Perovskite Structures. In this family of perovskites, both the inversion and 2-fold rotation operations at the octahedral site are preserved, even if that site has only inversion crystallographic symmetry (see Supporting Information for symmetry operation measures), while the distortion from the octahedron is mostly associated with the loss of 4-fold rotations, as can be seen by the nice correlation in Figure 2. With regard to the 3-fold rotation, the less distorted octahedra seem to retain most of that symmetry operation, with $Z(C_3)$ values smaller than 0.02, hence their predominant distortion mode corresponds to case B (D_{3d} symmetry, Table 1). Another group of structures also shows a significant loss of the 3-fold rotation, most notably $SmNiO_3$, $LaPdO_3$, $EuMnO_3$, and $YbMnO_3$, with $Z(C_3)$ values higher than 0.05 (the latter two fall outside the window shown in Figure 2). The loss of C_3 in the Mn^{III} and Pd^{III} compounds is clearly associated with a tetragonal Jahn–Teller distortion, which can also be detected to a lesser extent in, e.g., $SmNiO_3$ (Figure 2).

Other Structural Types. In addition to the cases discussed above, we have carried out an analysis of the symmetry operation measures of the octahedral sites in a variety of characteristic solid state structures in which a six-coordinated metal atom does not occupy a site with octahedral symmetry, and the results are summarized in Table 4 (more data is provided as Supporting Information). As discussed above for the BiI_3 structure, each structural family presents a specific distortion type, and the effective symmetry of the coordination spheres is in several families higher than the site symmetry. For each family of compounds we give also in Table 4 examples of the most and least distorted octahedra.

It is worth noting that within each family one can find structures in which the six-coordinate atom still retains a nearly perfect octahedral effective symmetry. Therefore, we can identify the distortion common to each family of compounds by looking at the whole set of structures, rather

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(9) Cirera, J.; Ruiz, E.; Alvarez, S. *Chem. Eur. J.* **2006**, *12*, 3162.

Table 4. Distortional Behavior of Several Structure Types Based on Octahedra

structure	space group	site	effective symmetry	distortion mode	examples: distorted	examples: undistorted
$(NH_4)_2[CuCl_4]$	$Cmca$ (No. 64)	4a [C_{2h}]	D_{4h}	A	$(NH_4)_2[CuF_4]$	Ca_2CuO_4
CdI_2 (brucite)	$P\bar{3}m1$ (No. 164)	1a [D_{3d}]	D_{3d}	B	$Ca(OH)_2$	PbI_2
FeS_2 (pyrite)	$Pa\bar{3}$ (No. 205)	4a [D_{3d}]	D_{3d}	B	$IrTe_2$	CdO_2
TiO_2 (rutile)	$Pa4_2/nmn$ (No. 136)	2a [D_{2h}]	D_{2h}	C	OsO_2	ReO_2
$CaCl_2$	$Pnnm$ (No. 58)	2a [C_{2h}]	$\sim D_{2h}$	D	PtO_2	
$GdFeO_3$ (perovskite)	$Pnma$ (No. 62)	4b [C_i]	D_{3d}	B	$LaLuO_3$	$CaVO_3$
			C_{2h}	D	$LaPdO_3$	
$PbTiO_3$	$P4mm$ (No. 99)	1b [C_{4v}]	C_{4v}	E	$PbTiO_3$	$NaNbO_3$
$LiNbO_3$	$R3c$ (No. 161)	6a [C_3]	C_{3v}	F	$CsPbF_3$	$HgTiO_3$
BiI_3	$R\bar{3}$ (No. 148)	6c [C_3]	D_3	F	$FeCl_3$	BiI_3
$CrCl_3$	$C2/m$ (No. 12)	4g [C_2]	D_3	F	YCl_3	$InBr_3$
Al_2O_3	$R\bar{3}c$ (No. 167)	12c [C_3]	$\sim C_{3v}$	G	Rh_2O_3	V_2O_3
$NiWO_4$	$P12/c1$ (No. 13)	2e [C_2]	C_2	H	$CdWO_4$	

than at each individual structure. On the other hand, in those cases in which the actual symmetry is coincident with the site symmetry, as in the case of the TiO_2 (rutile) or $CaCl_2$ structures, the symmetry operation measures tell us how close the coordination geometry of a particular cation is to the octahedron, giving interesting additional information that cannot be deduced from the site symmetry.

The effective symmetry of the coordination octahedron is not fully determined by the four symmetry operations analyzed in four structural families, that can be assigned to either C_{nv} or C_n groups: $PbTiO_3$, $LiNbO_3$, $NiWO_4$, and Al_2O_3. In the former, the fact that the site symmetry is C_{4v} leaves no doubt about the existence of symmetry planes and the coincidence between site and effective symmetries. For the compounds with the $LiNbO_3$ structures, we have found three planes for each structure with $Z(\sigma)$ values of at most 0.02, indicating that their effective symmetry is C_{3v}, at difference with the lower C_3 site symmetry. For the compounds with the $NiWO_4$ structure, reflection measures as large as 0.41 are found, indicating that the effective symmetry in this family is coincident with the C_2 site symmetry. Finally, the Al_2O_3 family presents reflection measures of up to 0.14 that suggest the absence of symmetry planes. However, if we compare those values with the corresponding measures for the other symmetry operations lost in those structures (C_4, C_2, and inversion), as large as 0.85, we could say that the effective symmetry is C_{3v} to a first approximation.

Distortions of the Octahedron in the Molecular World

Even if in this work we are concerned mostly with extended solids, we wish to make a short detour into the molecular world to show that the same approach can be applied to both molecules and solids. We thus focus on the homoleptic complexes of general formulas $[MR_6]$ and $[M(SR)_6]$, known to present structures that appear spread along the Bailar pathway[10] (case F in Table 1). Our symmetry analysis for such compounds (17 crystallographically independent data sets from 14 compounds) gives relatively small values for $Z(C_3)$ and $Z(C_2)$ (less than 0.36 and 0.52, respectively), but values as high as 4.21 and 14.39 for $Z(C_4)$ and $Z(i)$, respectively. These results show that the symmetry operation measures as applied here give the same qualitative conclusions as the application of continuous shape measures and minimal distortion paths reported earlier.[8]

The reader may have noticed how we can adopt different quantitative criteria when faced with quite different structural situations. Above we considered that the 4-fold rotations in the BiI_3 structure are lost upon distortion of the octahedron, taking into account $Z(C_4)$ and $Z(i)$ values of up to 0.2 and 0.3, respectively, whereas in these Bailar-distorted molecular complexes, we consider the 3- and 2-fold rotations to be preserved, even if the corresponding $Z(C_3)$ and $Z(C_2)$ values are as large as 0.4 and 0.5, respectively. The reason is that in the former case we are facing small distortions and compare the symmetry operation measures with those for the 2-fold rotation, which are less than 0.01, while in the molecular example we are comparing those values with the ones obtained for the 4-fold rotation and inversion, which are larger than 4.2 and 14.4, respectively. In other words, we may focus on the predominant distortion and neglect smaller ones in a first approximation.

Another well-known case of a distortion of the octahedron appears among six-coordinated Cu^{II} complexes, in which the Jahn−Teller effect results in elongated tetragonal bipyramids (case A).[11] For complexes with six N-donor monodentate ligands, we find that the C_3 rotation is lost to varying degrees, with values of $Z(C_3)$ as high as 1.69. The C_3, C_2 and inversion symmetry operations, in contrast, are essentially retained, with Z values smaller than 0.22, as expected for case A (Table 1). A more complex behavior is revealed by the analogous compounds with O-donor ligands. For them, the $Z(C_4)$ values are larger (up to 0.5), but still much smaller than the corresponding $Z(C_3)$ values. This means that the main distortion is again a tetragonal one, in which C_3 is lost (case A), but a weaker distortion that leads to a D_{2h} symmetry (case C, Table 1) is also present in many cases, even if bi-

Table 5. Symmetry of a Distorted Tetrahedron According to the Retained Symmetry Operations

case	operation preserved: S_4	operation preserved: C_3	operation preserved: C_2	symmetry subgroup
X	yes	no	yes	D_{2d}
Y	no	yes	no	C_{3v} or C_3
Z	no	no	yes	C_{2v} or C_2

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[10] Alvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M. *New J. Chem.* **2002**, *26*, 996.

[11] Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. *5*, pp 690−711.

Table 6. Distortional Behavior of Several Structure Types Based on Tetrahedra with Examples of the Least and Most Distorted Tetrahedra within Each Structural Type

					examples	
structure	space group	site	effective symmetry	distortion mode	distorted	undistorted
HgI_2 (coccinite)	$P4_2/nmc$ (No. 137)	$2a$ [D_{2d}]	D_{2d}	X	HgI_2	$ZnCl_2$
PbO/anti-PbO	$P4_2/nmm$ (No. 129)	$2a$ [D_{2d}]	D_{2d}	X	PbO	FeS
SiS_2	$Ibam$ (No. 72)	$4a$ [D_2]	D_{2d}	X		SiO_2
$KFeS_2$	$C2/c$	$4e$ [C_2]	D_{2d}	X	$RbFeSe_2$	$CsGaS_2$
$ZnBr_2$	$I4_1/acd$ (No. 142)	$32g$ [C_1]	C_{2v}	Z	GeS_2	$BeCl_2$

and polydentate ligands were explicitely omitted from the set of structures studied.

Distortions of the Tetrahedron

To study distortions of solid state structures based on tetrahedra we adopt criteria similar to those used above for analyzing octahedra. First we establish the symmetry subgroup according to the symmetry operations that are retained or lost (Table 5), considering now the two proper rotations C_3 and C_2, as well as the improper rotation S_4.

The results for five families of structures are summarized in Table 6. Similar to what was found for the octahedral structures discussed above, the loss of tetrahedricity in each family of compounds, indicated by their tetrahedral shape measures, shows an excellent correlation with the corresponding values of the symmetry operation measure for the highest order rotation lost upon distortion: S_4 for the $ZnBr_2$ structure (case Z) and C_3 for the other families analyzed (case X). While in the HgI_2 and PbO structures the distortion of the tetrahedron leads to the D_{2d} site symmetry, for the chains of tetrahedra in the SiS_2 and $KFeS_2$ structures the effective symmetry is also D_{2d}, even if the site symmetries are lower, D_2 and C_2, respectively. Also, in the $ZnBr_2$ structures the 2-fold rotation of the tetrahedron is retained (C_{2v}), despite the fact that the cation occupies a general position with no crystallographic symmetry.

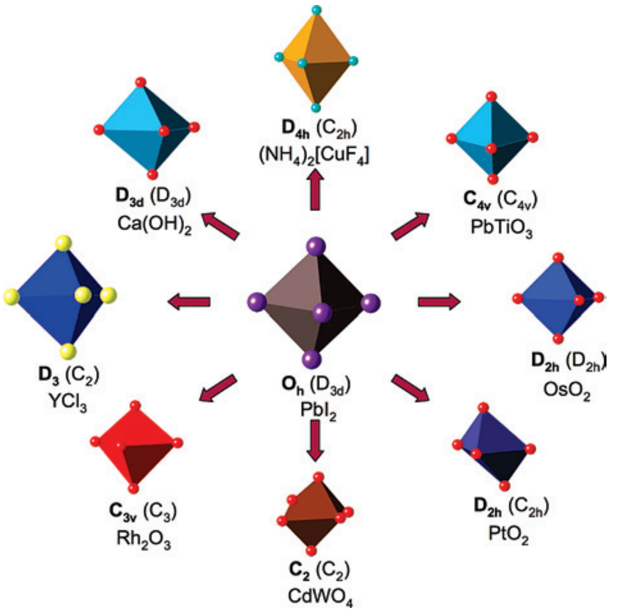

Figure 3. Examples of distortions of the octahedron in compounds of several structure types with nonoctahedral crystallographic symmetry, together with their effective symmetries as determined in this work, and their crystallographic site symmetries (in parentheses).

Concluding Remarks

A judicious choice of four symmetry operation measures provides enough information to decide on the type of distortion present in specific octahedra in solid state structures, as summarized for examples of several structure types in Figure 3. The effective symmetry detected in such a way is often higher than strict crystallographic symmetry. Moreover, when such an analysis is carried out for a whole family of related structures, the distortion seen in a specific structure is shown to correspond to a snapshot along a general distortion path covered by that family, as exemplified by the BiI_3 structural type. For those distortions leading to C_{nv} or C_n point groups, additional examination of the reflection measure is required for a distinction between the two alternatives. The local D_{2h} and C_{2h} symmetries can be easily discriminated by the presence of three or one 2-fold rotational operations, respectively.

Methodology

The symmetry operation measure of a symmetry operation $\hat{R}$ in a set of N atoms Q with coordinates $\mathbf{q}_k$, $k = 1,\ldots N$ $\hat{R}$, is defined in equation 1. $Z(Q,\hat{R})$ is the minimal distance between Q and its symmetry-transformed image T ($\mathbf{t}_k$, $k = 1,\ldots N$) obtained by operating $\hat{R}$ on Q, regardless of their position and orientation in space:

$$Z(Q,\hat{R}) = \min \frac{\sum_{k=1}^{N} |\mathbf{q}_k - \mathbf{t}_k|^2}{4\sum_{k=1}^{N} |\mathbf{q}_k - \mathbf{q}_0|^2} \cdot 100 \qquad (1)$$

The denominator in eq 1 is a size normalization factor in which $\mathbf{q}_0$ is the geometric center of the (q_k) set and the numerical factor in the denominator has been introduced to keep Z in the same scale (from 0 to 100) as used for the shape measures (relative to the octahedron or the tetrahedron in this case). $Z(Q,\hat{R})$ is minimized with respect to all mutual orientations of the original structure and its image or, equivalently, for all possible orientations of the symmetry element associated with the operation $\hat{R}$. The specific way in which such a minimization is performed for the different symmetry operations can be found in a previous publication.[2] In addition, eq 1 is minimized with respect to all possible vertex pairings between (q_k) and (t_k).

The set of structural data of six-coordinate transition metal complexes was obtained through systematic searches of the Cambridge Structural Database (version 5.29)[12]

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constraining the search to nonpolymeric structures with no disorder, *R* factors of at most 0.10, and excluding di- and polynuclear compounds. Solid state structures were retrieved from the Karlsruhe database (ICSD version 2003/7) through searches by structural type, restricted to stoichiometric binary or ternary compounds. When several structure determinations were available for the same compound, that with the lowest *R* value was used. Continuous shape and symmetry operation measures were calculated from the structural experimental data using the SHAPE[13] and SYMOP programs,[14] respectively, both developed in our research group.

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Supporting Information Available: Tables of octahedral shape measures and operation symmetry measures for compounds of the following structure types: $(NH_4)_2[CuCl_4]$, CdI_2 (brucite), FeS_2 (pyrite), TiO_2 (rutile), $GdFeO_3$ (perovskite), $PbTiO_3$ (macedonite), $LiNbO_3$, $CrCl_3$, Al_2O_3 (corundum), and $NiWO_4$, and of complexes of $[MR_6]$, $[M(SR)_6]$, $[Cu(N\text{-donor})_6]$, and $[Cu(O\text{-donor})_6]$. Table of octahedral and trigonal prismatic shape measures, deviation functions from the Bailar pathway, and generalized interconversion coordinates for the BiI_3-type structures. Table of tetrahedral shape measures and symmetry operation measures for compounds with the HgI_2 (coccinite), PbO or anti-PbO, $ZnBr_2$, SiS_2, and $KFeS_2$ structural types. This material is available free of charge via the Internet at http://pubs.acs.org.

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