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Review

Shape maps and polyhedral interconversion paths in transition metal chemistry

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Abstract

A systematic study of the stereochemistry of the coordination sphere of transition metal compounds has been carried out recently from the point of view of the continuous shape measures (CShM). In this review, the concept of the continuous shape measures is summarized and the derived tools, the shape maps and the path deviation functions are described. The main stereochemical trends that have been deduced from the application of such tools to more than 23,000 crystallographically independent fragments of coordination numbers between four and eight are also summarized.

Keywords: Continuous shape measures; Stereochemistry; Coordination polyhedra

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1. Introduction

Coordination chemistry was born as a scientific discipline when Alfred Werner divided metal ammino complexes in two

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classes, those with coordination number 6 and those with coordination number 4, proposed octahedral and square planar configurations for these two families, respectively and showed how such a stereochemical proposal could explain the isomerism of a variety of cobalt and platinum compounds [1,2]. This finding supplemented the theory of the tetrahedral carbon atom established earlier by Van't Hoff and Le Bel and together constitute the cornerstone of molecular stereochemistry. The Platonic figures that comprise the tetrahedron and the octahedron are loaded with high symmetry and symbolism. Suffice it to remember that Plato related such polyhedra with the four *elements*: cube = earth, octahedron = air, tetrahedron = fire, icosahedron = water and that Kepler built a cosmology in which the orbits of the then known planets were represented by a Russian-doll arrangement of such polyhedra. Platonic polyhedra also play a central role in the description of a variety of molecular structures. However, given the wealth of coordination numbers (i.e., polyhedral vertices) and the plasticity of the coordination sphere in transition metal compounds, the Platonic solids can only account for a limited number of the molecular structures that we deal with. Other less regular polyhedra are therefore incorporated to our stereochemical toolbox, including Archimedean or Catalan solids and also less symmetric figures are needed, such as the prisms, antiprisms, pyramids, bipyramids and some of the 92 Johnson polyhedra [3]. With all these reference polyhedra at hand, though, we face two problems to describe the position of the donor atoms around the central metal in a given compund: Which is the polyhedron that best describes the coordination sphere? How close is the molecular structure to the ideal polyhedron?

Avnir and coworkers have proposed that symmetry [4] and shape [5] should be defined as continuous properties and have defined *continuous symmetry measures* (CSM) and *continuous shape measures* (CShM) that provide quantitative parameters to calibrate the deviation of structures from a given symmetry or shape at the same scale, independent of their size or number of vertices. Later on, we showed that one can define a minimal distortion interconversion path between two polyhedra in terms of continuous shape measures and therefore numerically evaluate not only the deviation of a given structure from a particular polyhedron, but also its deviation from a polyhedral interconversion path [6]. In this review we present the general stereochemical pictures that arise from the application of such measures to a large number of experimental structures of transition metal compounds with coordination numbers from 4 to 8. Similar criteria can be applied to measure the degree of chirality of coordination compounds, but a summary of the application of continuous chirality measures to transition metal chemistry can be found elsewhere [7]. In the first section we make a preliminary discussion on the difference between shape and symmetry, then present a short introduction to the concepts and methodology of continuous shape and symmetry measures and subsequent sections are devoted to the description of the main results for the different coordination numbers, as well as for organometallic compounds.

2. Shape and symmetry

Although molecular shape and symmetry are intimately associated, it is important to stress here the main differences between these two properties. Let us consider two examples. Think first on the three Archimedean polyhedra with 24 vertices shown in Fig. 1: they all have octahedral symmetry (i.e., they belong to the O_h symmetry point group), but they differ in the number and type of faces and the reader would probably agree that they have different shapes.

Consider as a second example the trigonal prisms shown in **1**. All of them have the same number of vertices and the same symmetry (D_{3h}). However, the ratio between the sides of the triangles and the edges connecting them are different: it is larger than one in **1a**, exactly one in **1b** and **1c** (i.e., the lateral faces are squares) and less than one in **1d**. Even if **1b** and **1c** look different at first sight, they differ only in size and in orientation but are otherwise identical. In contrast, **1a** is distinctly different from all other prisms shown. How can we tell? Because it cannot be superimposed to the others by the combination of an isotropic scale factor, translations and

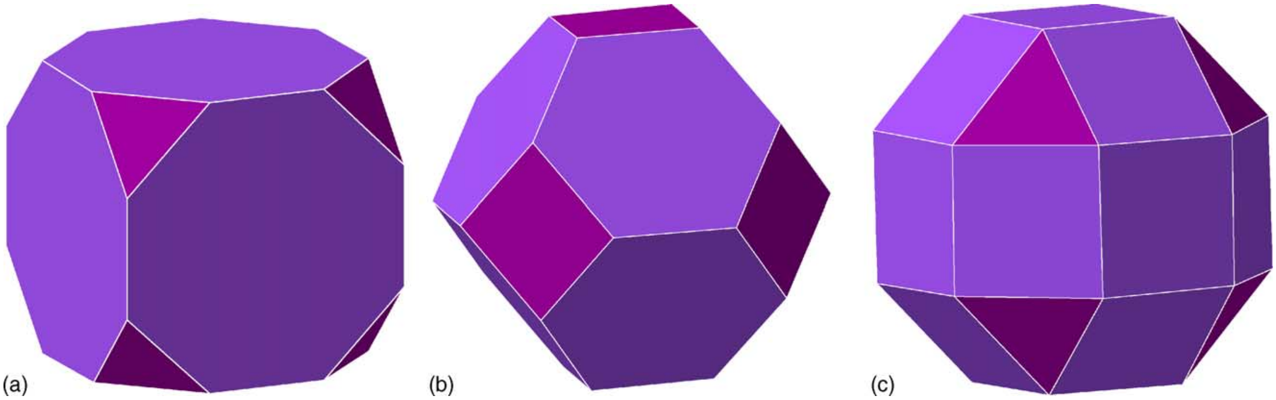
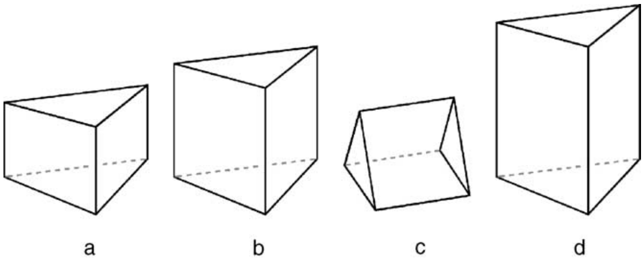


Fig. 1. Three archimedean polyhedra with 24 vertices that have the same (O_h) symmetry but different shapes (from left to right): truncated cube, truncated octahedron and rhombicuboctahedron.

rotations. Hence, among the prisms shown in **1** we have three different shapes, even if all of them have the same symmetry and their edges have the same topology. We can make an infinite number of trigonal prisms by just varying the ratio of the two types of edges of rectangular faces, all of them having the same symmetry but different shapes.



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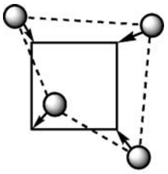
In summary, we say that two objects (molecules) have the same shape if they differ only in size, position or orientation in space. Alternatively, we can say that two objects (molecules) have the same shape if they can be superimposed by combinations of translations, rotations and isotropic scaling. From these examples we can also conclude that shape is a more stringent criterion than symmetry. There are, however some cases in which shape and symmetry are equivalent and this corresponds precisely to the Platonic polyhedra, since, e.g., all four vertex polyhedra with tetrahedral symmetry have the same shape and the same happens for the octahedron, the cube, the dodecahedron and the icosahedron. Among the Archimedean polyhedra, only for the cuboctahedron and the icosidodecahedron are shape and symmetry equivalent.

3. Continuous shape and symmetry measures

According to the proposal of Avnir and coworkers [4,8], in order to obtain a shape or symmetry measure for a structure P (represented in **2** by the circles joined by dashed lines) we need first to search for the reference shape R (represented in **2** by a square) that is closest to our problem structure. This search requires optimization with respect to size, orientation in space and pairing of vertices of the two structures. Once the reference shape is found, we calculate the distances between the equivalent atomic positions in the two structures, q_k, from which we calculate the shape measure according to the following formula, where N is a normalization factor that makes the CShM values size independent:



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$$S_P(R) = \frac{\sum_{k=1}^{N} q_k^2}{N} \times 100 \qquad (1)$$

From the definition of Eq. (1) it can be shown that the $S_P(R)$ values must lie between 0 and 100. The resulting value is zero if the problem structure P has exactly the desired shape R and will increase with the degree of distortion. As will be seen in the subsequent sections, the maximum values found for transition metal compounds, even if they may vary with the type of molecules under study and with the number of vertices, are about 40. As a rule of thumb we can say that chemically significant distortions should give CShM values of about 0.1 or higher, while values larger than about 3 indicate important distortions [9]. Since all CShM values are in the same scale, independently of the reference shape adopted and the number of vertices, we can compare, for instance, the deviation of a given structure from different reference shapes or of different structures with respect to the same ideal shape.

4. Reference polyhedra

If we wish to compare coordination polyhedra with ideal shapes, the obvious choice is the set of Platonic solids: tetrahedron, octahedron, cube, icosahedron and dodecahedron. These are the most regular polyhedra, each having all its edges, faces and vertices equivalent. Second to the Platonic solids in regularity come the Archimedean polyhedra, in which all vertices (but not faces or edges) are equivalent. These two families provide shapes that are univocally defined. Their shortcoming is the limited number of shapes available within these two families with between 4 and 12 vertices, those required to describe the stereochemistry of most coordination spheres.

The third family at hand is that formed by the prisms and antiprisms. We can make them a set of univocally defined shapes if we impose the restriction that all edges must be of the same length and, therefore, all the faces be regular polygons. All reference shapes discussed so far (Platonic, Archimedean, prisms and antiprisms) have in common that they are spherical, since all the vertices are at the same distance from their geometric center or, in other words, all vertices are on the surface of a sphere. If more reference shapes are needed we can make recourse to the 92 Johnson polyhedra [10,11], defined as those that have as faces only regular polygons with edges of the same length, excluding the Platonic, Archimedean, prismatic and antiprismatic polyhedra. In general, the Johnson polyhedra are not spherical. However, in many instances we can define Johnson-like polyhedra imposing sphericity, whereupon the faces may no longer be all regular polygons with edges of the same length. In that case, the choice of ideality may not be unique and we further impose the condition to such a spherical reference shape to correspond to a hard spheres model (i.e., it must maximize the distances between all pairs of vertices). From here on, we will use the prefix **J-** to refer to a Johnson polyhedron, but the prefix **s-** to indicate the Johnson-like spherical analogue. From the very definition of Johnson and spherical Johnson-like polyhedra it follows that the former are more adequate for the description of edge-bonded polyhedral molecules such as boranes or metal clusters, whereas the spherical versions are more appropriate for describing coordination polyhedra. We will introduce in subsequent sections the Johnson polyhedra needed for coordination numbers 4–8, but a more systematic study of such polyhedra and of their presence in other fields of Chemistry can be found elsewhere [3].

5. Shape maps and distortion paths

For the stereochemical analysis of families of compounds we have found it useful to represent scatterplots of their shape measures relative to two alternative ideal polyhedra with the same number of vertices (e.g., P and T), that we have called *shape maps*. In these maps, the lower left limit always corresponds to the interconversion path between the two reference polyhedra, as illustrated by the Bailar path that transforms the octahedron into a trigonal prism and vice versa (Fig. 2). The shape measures of all structures X along the minimal distortion interconversion path between polyhedra P and T must obey the following relationship:

$$\arcsin\frac{\sqrt{S_{\mathrm{X}}(P)}}{10}+\arcsin\frac{\sqrt{S_{\mathrm{X}}(T)}}{10}=\theta_{\mathrm{PT}} \tag{2}$$

$$\Delta_i(P,T)=\frac{1}{\theta_{\mathrm{PT}}}\left[\arcsin\frac{\sqrt{S_i(P)}}{10}+\arcsin\frac{\sqrt{S_i(T)}}{10}\right]-1 \tag{3}$$

where θ_{PT} is a constant for each pair of polyhedra, the *symmetry angle* [6]. Structures that are not exactly along the minimal distortion path do not obey Eq. (2) and their distance to that path can be callibrated by means of the *path deviation function* defined in Eq. (3), where i refers to an arbitrary structure.

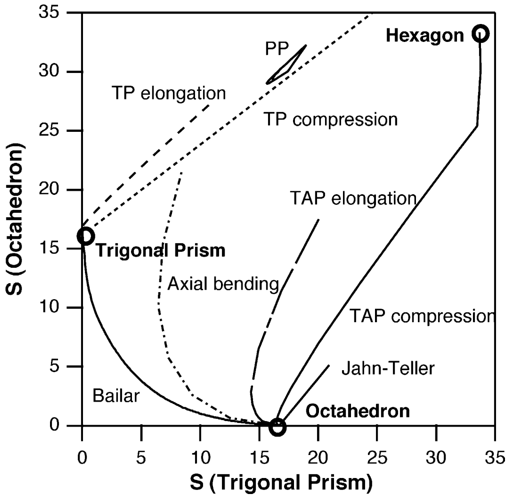


Fig. 2. Shape map for geometrical distortions of the octahedron and the trigonal prism. The circles indicate the position of three ideal shapes labeled in boldface. Several distortion paths depicted in Scheme 3 and in **6** are also plotted in the map. Adapted from Ref. [5] with permission from the Royal Society of Chemistry and CNRS.

Table 1
Constants (θ_{PT}, in degrees) that define the minimal distortion polyhedral interconversion pathways (Eq. (1)) for the paths discussed in this review

Vertices	Polyhedra		θ_{PT}
4	Tetrahedron	Square	35.264
6	Octahedro1n	Trigonal prism	24.149
7	Capped octahedron	Capped trigonal prism	7.099
	Capped octahedron	Pentagonal bipyramid	16.852
	Capped trigonal prism	Pentagonal bipyramid	14.934
8	Dodecahedron	Square antiprism	9.716
	Square antiprism	Hexagonal bipyramid	25.444
	Dodecahedron	Hexagonal bipyramid	23.326
	Dodecahedron	Cube	16.379
	Square antiprism	Cube	19.360

The interconversion constants θ_{PT} of Eq. (2) for the paths discussed in this review are collected in Table 1. With such tools we can (i) detect very easily those structures that are intermediate between two polyhedra, (ii) obtain a quantitative description of how close (or how far) a given structure is from a path and (iii) obtain molecular models of the shapes that correspond to steps along the interconversion path. According to the proposal that crystal structure data offer clues to reaction pathways [12–14], the analysis of crystal structures from the point of view of minimal distortion paths should be helpful in gaining insight into chemical reactivity aspects. In a shape map we can also represent the characteristic distortion paths of the two reference polyhedra. This is illustrated in Fig. 2 for the case of hexacoordinate compounds, where we can see that each distortion occupies a specific region of the shape map. The reader must be warned that, except for the interconversion path, the position of a given structure in the shape map does not allow us to unequivocally decide which is the distortion present in that structure. However, our experience from the analysis of a large number of structures tells us that in most cases we can obtain reliable hints on the nature of the distortion.

6. Tetracoordinate compounds

A general shape map for tetrahedrally coordinated atoms is defined as a scatterplot of the square planar and tetrahedral shape measures, in which some common distortion paths from the tetrahedron and the square (as calculated for molecular models) are represented (Fig. 3). In that map, the positions of three specific shapes (the tetrahedron, a sawhorse made by emptying two *cis* positions of an octahedron, and the square) correspond to the points marked by circles. The types of distortion represented in the shape map are schematically depicted in Scheme 1. From these, the spread, scissoring and umbrella distortions seem to delimit the inhabitable region of this shape map. The *spread* mode that traces the interconversion between the tetrahedron and the square has been studied in several papers [6,15,16] and has been shown to correspond to a minimum distortion path [6]. The plier and

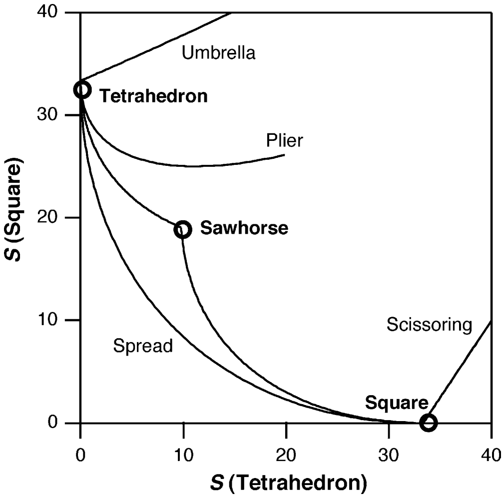
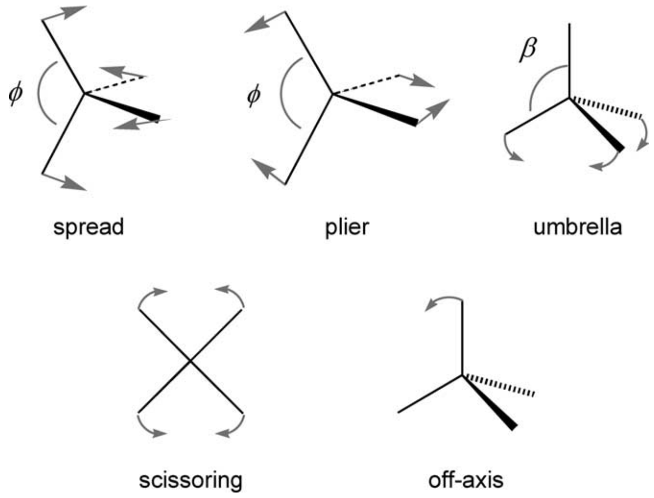


Fig. 3. Shape map for geometrical distortions of the tetrahedron and the square (see Scheme 1) within the chemically significant region. The circles indicate the position of three ideal shapes labeled in boldface. Adapted with permission from Ref. [16].

scissoring distortions are to be expected in the presence of bidentate ligands that can enforce bond angles around the central atom quite different from those corresponding to the ideal shapes, whereas the umbrella distortion can be anticipated for tridentate ligands with cyclic or tripodal topologies.

The analysis of the CShMs of more than 13,000 structures of tetracoordinate transition metal compounds [16] has shown that most of them (72%) can be described as square planar, a significant portion (23%) as tetrahedral and a small group (3%) as geometries intermediate between the tetrahedron and the square, whereas the remaining 2% are quite far from those two ideal geometries as well as from their interconversion path. The stereochemical preferences are clearly influenced by the electron configuration of the central metal. Thus, d^0, d^1, d^2, d^5 and d^{10} configurations prefer the tetrahedral geometry, d^8 and d^9 configurations show a strong preference for the square planar geometry, those of d^3, d^4, d^6 and d^7 metals can be found both as tetrahedra and as squares and an important fraction of the d^9 compounds appear with structures intermediate between the tetrahedron and the square. For the d^3, d^6 and d^{10} configurations, an important number of structures cannot be adequately described as tetrahedral, square planar or intermediate.



Scheme 1.

Besides the tetrahedron and the square, we have found it useful to define as a reference shape a sawhorse structure, built from an octahedron with two vacant vertices. This has allowed us to detect a small but significant number (0.7%) of compounds whose structures are much better described as sawhorses than as distorted tetrahedra or squares. A large fraction of the sawhorse structures correspond to Hg^{II} compounds, a surprising result, given the preference of d^{10} ions for a tetrahedral coordination. A more detailed analysis indicates that the Hg atom in these compounds should be described as linearly coordinated with two additional *contacts* to two of the supposed ligands at distances significantly larger than the sum of the atomic radii. The opposite situation is found in a tetracoordinate compound of a d^8 metal ion, the anionic $[RuH_4]^{4-}$ complex characterized as its Mg salt [17]. That anion presents a sawhorse structure rather than the expected square planar geometry. Closer inspection of that structure (Fig. 4) tells us that the two vacant octahedral positions are occupied by Ru atoms from neighboring anions, with Ru–Ru distances of 3.24 Å, similar to those found in Ru clusters, thus indicating that there are no discrete anions in that compound but rather anionic chains (Fig. 4), in excellent agreement with the 18 electron rule.

We have also analyzed the effect of bi-, tri- and tetradentate ligands on the stereochemical preferences of tetracoordinated transition metals. The bidentate ligands with a small normalized bite (dithiocarbamates and diphosphinomethanes such as dppm) only form square planar complexes, whereas those ligands with larger bites (ethylenediamine, bipyridine or dithiolates) can adapt to both tetrahedral and square planar coordination spheres. As for tridentate ligands, those with a *mer* topology (such as terpyridine) have not been found in tetrahedral complexes, whereas those of *fac* type (e.g., trispyrazolylborate or triazacyclononane) appear only in tetrahedral complexes. Tripod tetradentate ligands give only tetrahedral complexes, even if with marked

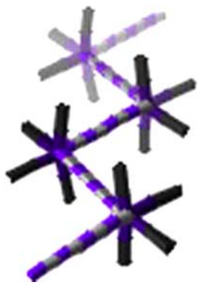


Fig. 4. Chain structure of the supposedly tetracoordinate anionic complex $[RuH_4]^{4-}$ with a sawhorse structure, showing the short Ru–Ru contacts that form zig-zag chains (dashed sticks).

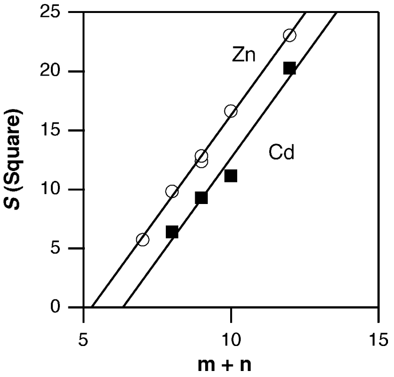
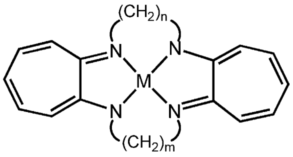


Fig. 5. Variation of the square planar shape measure as a function of the combined length of the alkyl tethers in the tropocoronand (**3**) complexes of Zn (circles) and Cd (squares). Reproduced with permission from Ref. [16].

umbrella-type distortions. Finally, rigid tetradentate macrocyclic ligands (e.g., porphyrins of phthalocyanins) seem to impose a square planar coordination even for d^{10} ions such as Zn^{II}, whereas more flexible ligands such as *cyclam* (1,4,8,11-tetraazacyclotetradecane) allow for geometries distorted toward the tetrahedron. One of the best examples of how one can manipulate the flexibility of macrocyclic ligands to control the geometry of the coordination sphere has been provided by Lippard and coworkers [18], who obtained structures with varying degrees of distortion from the square to the tetrahedron by progressively increasing the length of the aliphatic chain in the family of tropocoronand ligands **3**. The excellent correlation between the square planar CShM of the Zn^{II} and Cd^{II} complexes in these families and the combined length of the side aliphatic chains can be seen in Fig. 5. It is worth noting that the intercepts of the two lines reflect the different ionic radii of these two metals, while the slope is the same.



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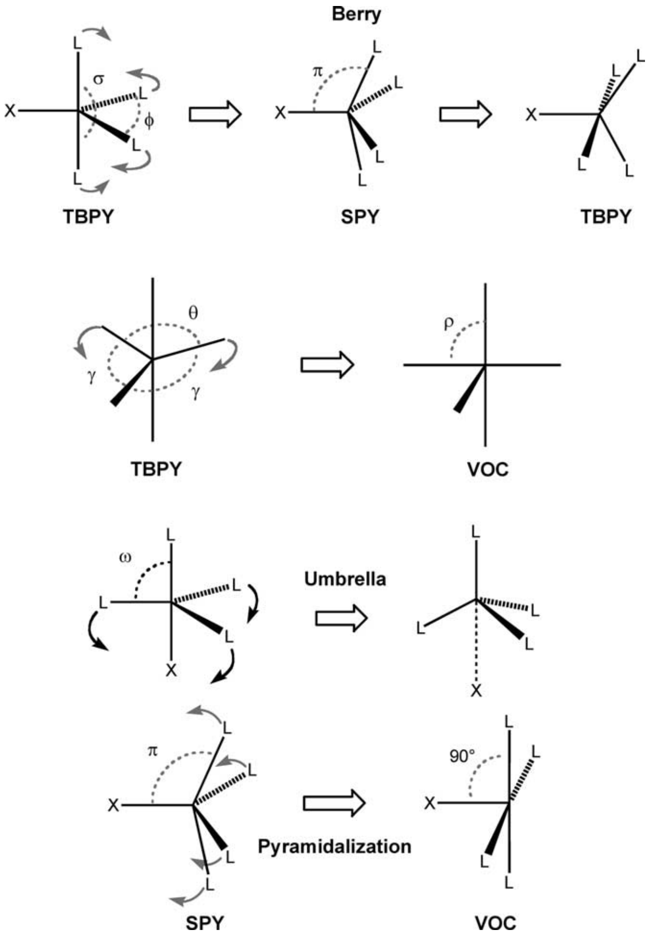
7. Pentacoordinate compounds

A thorough analysis of the shape measures of pentacoordinate complexes relative to the trigonal bipyramid was reported by us, analyzing the Berry pseudorotation and other non-Berry distortion paths (see Scheme 2) [19]. Later on, we have shown that the Berry pseudorotation is a minimum distortion path between the trigonal bipyramid and a square pyramid with apical-basal L–M–L bond angles of 104.48° [6] and more recently we have developed the shape map relative to the trigonal bipyramid and the square pyramid and have analyzed the stereochemical preferences by electron configuration of the central metal atom [20]. For pentacoordinate complexes, the angular parameter τ defined by Reedijk and coworkers [21], $\tau = (\sigma - \phi)/60$ (where σ and ϕ are the largest and second largest bond angles around the central metal), is frequently used to identify the position of pentacoordinate structure along the Berry pathway, since such a parameter adopts the values 1 and 0 for a trigonal bipyramid and a square pyramid (regardless of the bond angle between apical and basal ligands, π), respectively. The trigonal bipyramid shape measure adopts values between 0 and 5.37 along the Berry pathway, the latter corresponding to the square pyramid and it has some advantages compared to the angular parameter τ. In particular, there are three cases in which the value of τ is not appropriate: (i) it does not allow for discrimination between square pyramids that differ in the deviation of the central atom from the basal plane (measured by the bond angle π in Scheme 2), (ii) it does not discriminate between structures that fall along the Berry path and those along the non-Berry path that takes from the trigonal bipyramid to a vacant octahedron and (iii) gives values larger than 1 for the umbrella opening or closing favored by tripod ligands.



Scheme 2.

In the shape map for pentacoordination we plot the shape measures relative to the trigonal bipyramid and to the square pyramid with $\pi = 104.48°$, which corresponds to the middle point of the Berry pathway and will be referred from

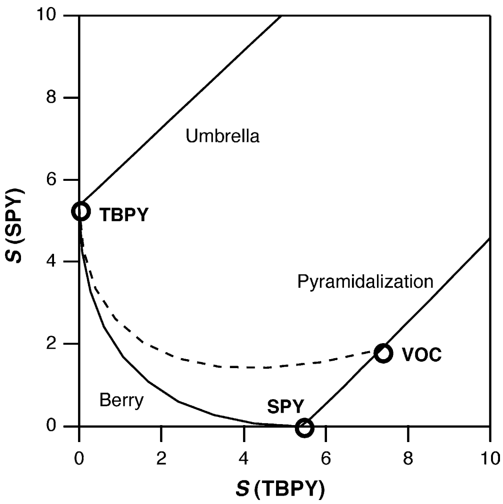
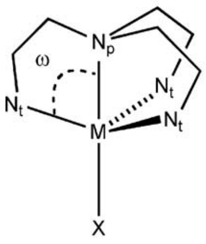
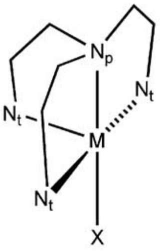


Fig. 6. Shape map for geometrical distortions of the trigonal bipyramid (TBPY) and the Berry square pyramid (SPY, see Scheme 2 within the chemically significant region. The circles indicate the position of three ideal shapes labeled in boldface. The dashed line indicates the path that takes from the trigonal bipyramid (TBPY) to the vacant octahedron (VOC).

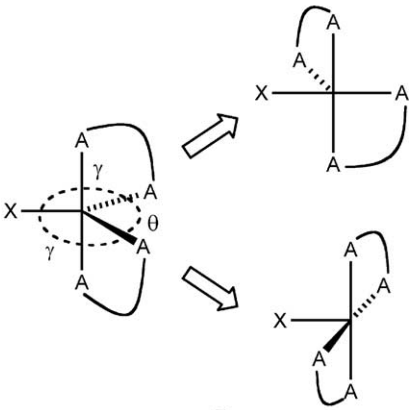
here on as the Berry square pyramid. The main distortions of the trigonal bipyramid and the Berry square pyramid are represented as lines in the shape map (Fig. 6), as obtained for molecular models. There we can easily recognize the Berry pathway as the lower left curve typical of the minimal interconversion path between the two reference polyhedra. Other interesting distortions that are easily recognizable are the umbrella deformation of the trigonal bipyramid (Scheme 2), the path corresponding to changes in the degree of pyramidalization of the square pyramid, in which we have marked (Fig. 6) the position corresponding to the vacant octahedron (i.e., $\pi = 90°$) and a pseudo-Berry path that leads directly from the trigonal bipyramid to the vacant octahedron.



4a



4b



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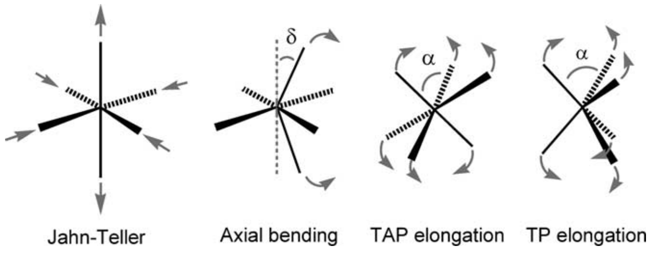
The analysis of the experimental structures of pentacoordinated transition metals classified by their electron configuration shows no exclusive preference for the trigonal bipyramid or the square pyramid. However, for some configurations the square pyramid is far more common than the trigonal bipyramid, these are d^1, d^2, d^5, d^6 and d^9. Also deviations from the Berry pathway are seen to be quite common. A special behavior found for π-bonded olefin complexes will be discussed below, in the section devoted to organometallic complexes.

The complexes with tripod tetradentate ligands, of general formula [M(tripod)X] show two distinct types of distortion from the trigonal bipyramid that can be easily identified from their shape measures. One of them is an umbrella distortion, characterized by an increase in the value of S(TBP) of the MN_4X group and by a decrease of the value of $S(T_d)$ of the MN_3X group in which the pivotal N atom of the tripod ligand is omitted, that corresponds to the angular distortion shown in **4a**. The second type of distortion, found in some Cu^{II} compounds, presents a T arrangement of the equatorial donors and corresponds to a non-Berry pathway that converts the trigonal bipyramid into a square pyramid (**4b**). The analysis of several families of pentacoordinate complexes with bidentate ligands $[Cu(bipy)_2X]+$, $[Cu(phen)_2X]+$ and $[M(dppe)_2X]n+$, tells us that they present distortions of the trigonal bipyramidal coordination sphere that cannot be described through the Berry pathway. In those cases, the transformation of the trigonal bipyramid into a square pyramid proceeds through two alternative paths. Hence, compounds of the bidentate bipyridine and phenanthroline ligands are displayed along a pathway of C_s symmetry in which the monodentate ligand X shifts to a basal coordination position of the square pyramid (**5**, above), whereas the diphosphine complexes appear mostly along a pathway of C_{2v} symmetry in which the monodentate ligand occupies the apical position of the square pyramid (**5**, below). Complexes with the terpyridine ligand, of general formula $[M(terpy)X_2]$, are ambivalent and can be found along either of these two pathways.

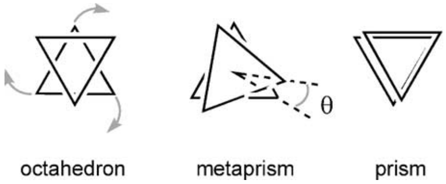
8. Hexacoordinate compounds

The most ubiquitous polyhedron in transition metal chemistry is without doubt the octahedron, whose vertices are



Scheme 3.

occupied by the donor atoms in most hexacoordinate complexes. An alternative six vertex polyhedron is the trigonal prism. Aside from the fundamental interest of the stereochemical choice between octahedron and trigonal prism, the interconversion of these two polyhedra through the Bailar trigonal twist (**6**) [22] has been proposed as the most likely reaction pathway for the racemization of tris(chelate) complexes. Other distortions of the octahedron and the trigonal prism that appear in the shape map are schematically depicted in Scheme 3. The CShM analysis of the experimental structures of hexacoordinate transition metal compounds [5] has been carried out with the help of shape maps of the type shown in Fig. 2. Such an analysis has shown that some families of compounds appear along the Bailar path, thus presenting geometries of trigonal metaprisms. This happens even for homoleptic complexes with monodentate ligands such as thiolates or alkyls, but also for tris(chelate) complexes with dithiolene ligands (Fig. 7). Since the intermediate trigonal metaprisms belong to the D_3 symmetry point group, those structures are chiral, in contrast with the two extreme geometries of the Bailar twist, the octahedron and the trigonal prism (O_h and D_{3h} point groups, respectively), that are achiral.



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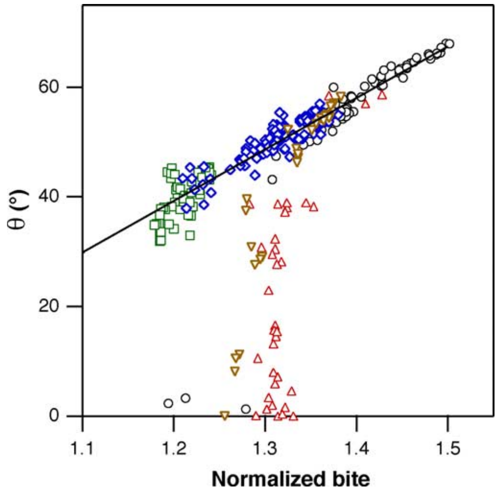


Fig. 8. Bailar twist angle θ as a function of the normalized bite of the bidentate ligand for several families of tris(chelate) complexes: dithiocarbamates (green squares, average $b = 1.21$), ethylenediamine (blue diamonds, av. $b = 1.34$), β-diketonates (circles, av. $b = 1.41$), encapsulating ligands (inverted brown triangles), dithiolenes and diselenolenes (red triangles, av. $b = 1.43$). Adapted from Ref. [5] with authorization of the CNRS and The Royal Society of Chemistry.

The fact that homoleptic complexes of the type, e.g., $[M(SR)_6]$ are chiral [23,24], has gone unnoticed until recently, the generally accepted idea being that to have a chiral hexacoordinate complex one needs either to have at least three different monodentate ligands in one of the isomers of $[MA_2B_2C_2]$ or at least two bidentate ligands. Not only can those complexes with monodentate ligands be chiral, but we have also shown [25] that chirality in tris(chelate) complexes is mostly associated with the chirality of the first coordination shell (i.e., the metal and the six donor atoms). Why then do we associate chirality only to the presence of bidentate ligands? If we characterize a rigid bidentate ligand by its normalized bite, we can see that there is a relationship between the bite and the Bailar rotation angle θ (Fig. 8, where θ can in principle adopt values between −60 and 60°: a value of ±60° corresponds to an octahedron, a value of 0° to a trigonal prism and any

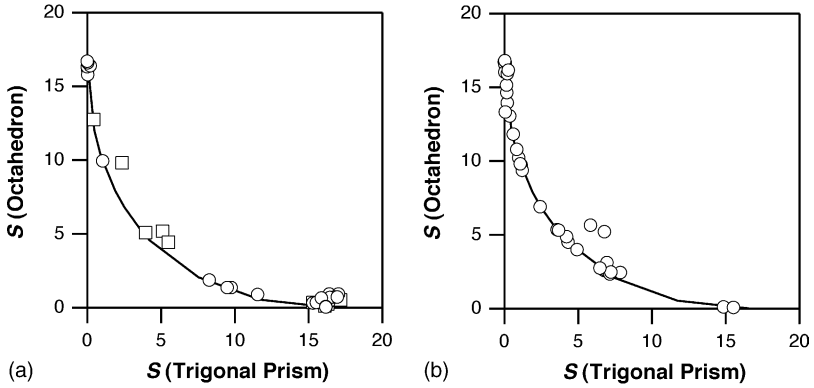


Fig. 7. Experimental structures of hexacoordinate complexes, represented in the octahedron/trigonal prism shape map. Left: Homoleptic complexes with thiolato (squares) and with alkyl or aryl (circles) ligands (Data from Refs. 5 and 42). Right: Homoleptic complexes with bidentate dithiolato ligands, reproduced from Ref. [5] with authorization of the CNRS and The Royal Society of Chemistry.

intermediate value to a metaprism, see **6**). Since the ideal L–M–L bond angle is 90° in an octahedron, but 81.8° in the trigonal prism, ligands with a small bite (e.g., dithiocarbamates) favor the trigonal prismatic geometry, whereas ligands with larger bites (e.g., the β-diketonates) favor the octahedral geometry. It is interesting to observe that a group of structures deviate from the general behavior, since their twist angles span a wide interval with practically the same normalized bite (about 1.3). Most of them are dithiolene complexes of metals with electron configurations between d^0 and d^2. In summary, what Fig. 8 is telling us is that complexes with d^0 to d^2 electron configurations have a clear preference for the trigonal prismatic structure, while other configurations prefer the octahedral structure that may be distorted due to the constraints imposed by bidentate ligands (notice that in those cases one never reaches values of θ close to 0°), thus resulting in chiral metaprismatic coordination spheres. A corollary of the stereochemical effect of the bite of bidentate ligands is the correlation between molecular symmetry and other properties (e.g., magnetic moment, applied pressure, temperature or density) that has been found for spin crossover complexes [26].

Other compounds that captured our attention are those with encapsulating ligands (cage-like hexadentate polycyclic ligands) that supposedly favor a trigonal prismatic coordination of the central metal. However, the situation of their structures in the shape map clearly indicates that they behave in the same way as the complexes with three independent bidentate ligands. In other words, encapsulating ligands are much more flexible than we figure out and they can adapt their conformation without difficulty to any geometry along the Bailar path.

Although the octahedron is the most common shape found for the hexacoordinated atoms in solid state compounds, trigonal prismatic geometry is not rare at all. It can be found for the metal atom in the compounds with WC or MoS_2 structures and for the main group element in the NiAs and AlB_2 structures. Other examples of metal atoms with trigonal prismatic coordination are found in PtB, ZrS_3, $ZrSe_3$, Ba_2NiSi_3, $LiMoN_2$ and $NaNbO_2$. A plot of the shape measures for those atoms in a shape map clearly shows the presence of mostly elongation and compression distortions that preserve the trigonal prism (Fig. 9). Furthermore, we can see that all main group atoms in the NiAs structures present compressed trigonal prismatic geometries. From that map it is easy to recognize the world records of elongated (Ni in Ba_2NiSi_3) and compressed (Pt in PtB) trigonal prisms, shown at the same scale in Fig. 9.

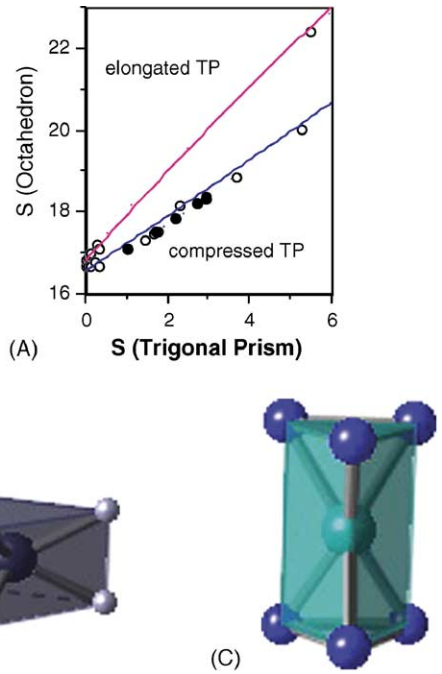
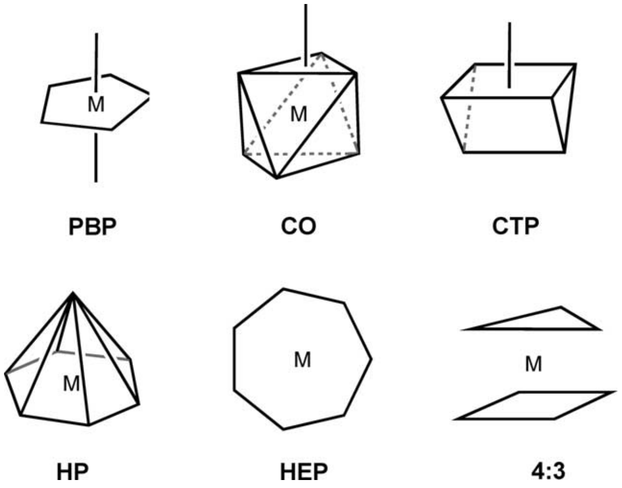


Fig. 9. Detail of the shape map for hexacoordinate atoms in extended solids with approximately trigonal prismatic geometry. The continuous lines indicate the ideal compression and elongation distortions of the trigonal prism that retain the full D_{3h} symmetry. The empty circles correspond to experimental structural data of compounds with the NiAs structure, crosses to compounds with the AlB_2, WC, MoS_2 or other structures.

9. Heptacoordinate compounds

Since there are no Platonic or Archimedean polyhedra with seven vertices, to describe the coordination sphere of heptacoordinate complexes we must use less regular polyhedra (Scheme 4), such as the pentagonal bipyramid, PBP (a Johnson polyhedron, J13, of which we use the spherical version, s-PBP), the capped octahedron, CO, the capped trigonal prism, CTP (J49, again we use a spherical s-CTP version here) or the hexagonal pyramid, HP, to which we can add the corresponding regular polygon, the heptagon and a purported 4:3 geometry that has been proposed for some compounds. The choice of the adequate polyhedron to describe the coordination sphere of a heptacoordinate complex is not straightforward by visual inspection of the molecular structure, a fact that is associated with the similar energies of the



Scheme 4.

most common geometries (CO, CTP and PBP) and with the fact that the symmetry of the metal site is in general lower than that required by these symmetric polyhedra (C_{3v}, C_{2v} and D_{5h}, respectively). Although the choice of an ideal polyhedron for CO and CTP is not unique, we have adopted a hard spheres model and found that the uncertainty introduced in the shape measures through this arbitrary choice is less than 0.2 units and does not significantly affect the ability of the CShM approach to discriminate between alternative seven vertex polyedra. The shape map relative to the capped octahedron and the capped trigonal prism presented in Fig. 10 shows the interconversion paths between the three most common shapes. It is to be noted that the distance between the CO and the CTP is rather small compared to those between the tetrahedron and the square, or between the octahedron and the trigonal prism (see Table 1 for numerical values).

The analysis of the shape measures of about a thousand heptacoordinate transition metal compounds relative to the ideal shapes [27] has allowed us to extract some conclusions about their stereochemical preferences. Thus, heptacoordination among transition metals is mostly found for those having electron configurations between d^0 and d^4, with the exception of the first transition series elements, Zn or Cd with N- or O-donor ligands. The most common coordination polyhedron is the pentagonal bipyramid, although only about one third of the analyzed structures can be described by one of the ideal polyhedra to a good approximation. However, a polyhedral shape can be assigned to most compounds if we adopt the criterion of assigning the polyhedron that gives the smallest CShM value. In some cases, though, it has been found that the best description of the coordination polyhedron is at intermediate geometries along the interconversion path between two ideal polyhedra. No heptacoordinate complexes with heptagonal coordination sphere have been found and only one Ag compound with hexagonal pyramidal structure has been detected [28]. Even if the hexagonal pyramid is rare among transition metals, we have found that it is a common shape for 18-crown-6 complexes of the alkaline metals.

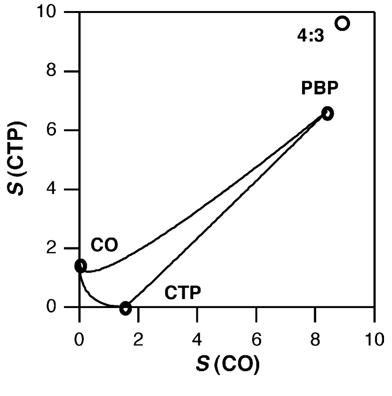


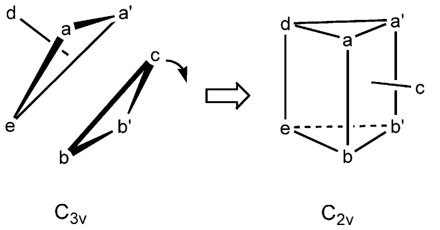
Fig. 10. Shape maps for seven vertex polyhedra showing the position of some ideal shapes: capped octahedron (CO), capped trigonal prism (CTP), pentagonal bipyramid (PBP) and 4:3 geometry (Scheme 4). The lines represent minimum distortion interconversion paths.

Illustrative of the stereochemical variability of heptacoordinate complexes is the case of $[WF_7]^-$, that may appear as CTP or PBP, depending on the counterion.

An attempt has been made also to see if different ligands may favor specific stereochemistries. For homoleptic complexes with monodentate ligands, which presumably impose no geometrical restrictions, a clear pattern of stereochemical preference is found depending on neither the type of ligand nor the metal electron configuration. As for mixed ligand complexes, we have seen that those in the $[M(PR_3)_3X_4]$ family, where X is a halide, may appear as a capped octahedron or as a capped trigonal prism or as intermediate structures, but not as pentagonal bipyramids. On the contrary, the tetrahydrofuran complexes $[M(thf)_5L_2]$ (M = Y, La) and the oxo complexes $[MOL_6]$ prefer the pentagonal bipyramid, in the latter case with the oxo ligand occupying an axial coordination position. It is worth stressing also that among the heptacoordinate metallo-sites in biomolecules (Mn, Cd or Mo), the known structures are aligned along the interconversion paths between the pentagonal bipyramid and the capped octahedron or the capped trigonal prism, but none of them is close to either of the latter two polyhedra.

The presence of one or two small bite bidentate ligands (dithiocarbamates, carboxylates, nitrate) favors the pentagonal bipyramid, in which the bidentate ligands occupy equatorial edges. Among the tridentate ligands analyzed, neither triazacyclononane nor tris(pyrazolyl)borate present a clear stereochemical preference, giving raise to a variety of coordination polyhedra. The pentadentate crown ethers 15-crown-5 clearly favor the pentagonal bipyramidal structure in which the crown ether occupies the five coordination positions of the equatorial plane. In contrast, the analogous hexadentate ethers, 18-crown-6, favor the hexagonal pyramid for alkaline metals, as well as in the only transition metal compound found with this type of ligand.

As for the purported 4:3 geometry that had been proposed for the monoclinic form of ZrO_2 and for the cationic complex [29] $[WI(CO)_3([9]aneS_3]^+$, in both cases it is found that the geometries are not far from the capped octahedron, but are very distant from true 4:3 geometries that appear in the cyclobutadiene complexes of formula $[M(\eta^4\text{-}C_4R_4)L_3]$, as seen from the position of such an ideal shape in Fig. 10.



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A nice description of polyhedral interconversion paths has been obtained from experimental structural data [27]. We selected a set of heptacoordinate complexes that were seen to be close to the pathway that leads from the capped octahedron to the capped trigonal prism. The only symmetry operation that persists along the minimal distortion path is a symmetry

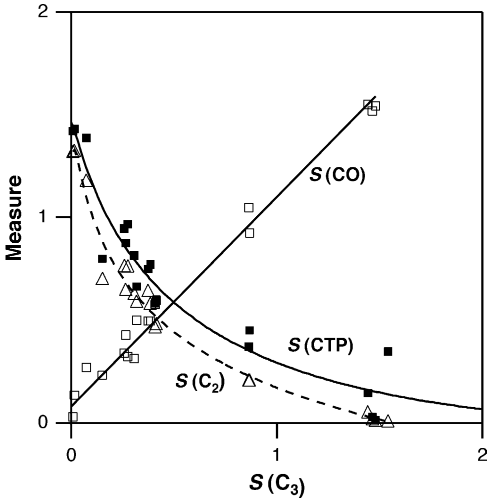
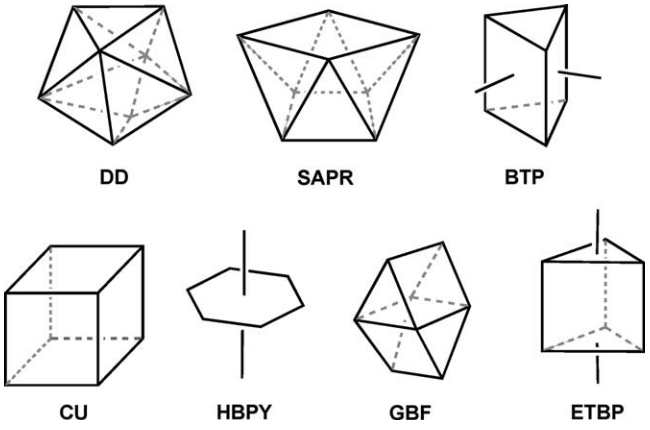


Fig. 11. Evolution of shape and symmetry measures as a function of the loss of C_3 symmetry along the CO to CTP pathway for a group of experimental structures: white squares for S(CO), black squares for S(CTP) and triangles for $S(C_2)$.

plane, which is the only one that the C_{3v} and C_{2v} symmetry groups of CO and CTP have in common (i.e., the *cde* plane in **7**). If we choose to follow this transformation by the amount of C_3 symmetry present, as measured by the corresponding symmetry measure $S(C_3)$ (it is 0 when there is strict trigonal symmetry and increases as C_3 symmetry is progressively lost), we can see in Fig. 11 how the CShM relative to the CO increases, that relative to CTP decreases, eventually reaching zero, while the C_2 symmetry also appears as C_3 is lost. Thus, in this case, we can follow changes in both shape and symmetry along the interconversion path.

10. Octacoordinate compounds

Octacoordination is characterized by having a wide variety of associated polyhedra as well as by not showing clear stereochemical preferences. The most relevant eight vertex polyhedra are represented in Scheme 5. Those in the upper row, the triangular dodecahedron (DD), the square antiprism (SAPR) and the bicapped trigonal prism (BTP) seem to be the most common ones among octacoordinate complexes and were termed by Muetterties and Wright “low energy polyhedra” [30]. From the analysis of their mutual shape measures (Table 1), it can be seen that those three polyhedra are quite close in shape, in spite of their differences in symmetry. The cube (CU) and the hexagonal bipyramid (HBPY) are a little farther, while other polyhedra are at larger distances, as reflected in the two shape maps shown in Fig. 12.



Scheme 5.

A shape analysis of structurally characterized octacoordinate transition metal compounds [31] has shown that the most common shapes appear in the region around the SAPR, the DD and the BTP, at the lower left corner of the maps shown in Fig. 12B. However, a non negligible number of structures are found in other regions of the shape map, such as the paths that take from the dodecahedron toward the cube or to the hexagonal bipyramid. No structures were found to correspond to heptagonal pyramids or to octagons. It is to be noted that structures are found not only around the positions of the low energy polyhedra, but are spread throughout the whole range of intermediate structures.

It has been found [31] that the most common electron configuration among octacoordinate transition metal compounds is the d^0 one. Significant numbers of compounds are also found for d^1, d^2 and d^{10} configurations, while only a few cases of other electron configurations have been structurally characterized. The analysis of the shape measures of these compounds, grouped by electron configuration, indicates that the stereochemical preferences for d^0 to d^2 metals are quite similar, with most of the structures appearing in the region corresponding to SAPR, DD, BTP and their interconversion paths, as illustrated in Fig. 13 for the case of the d^0 compounds. However, a few nearly cubic structures can be easily recognized (along the upper left line of the shape map), which correspond to $[Y^{III}L_2]$ and $[La^{III}L_2]$ complexes, where L is either a tripod [32–34] or a tetradentate macrocyclic ligand [35]. For d^1 compounds, a set of structures falls neatly along the SAPR–DD interconversion pathway, composed mostly of complexes with at least two bidentate ligands that form five-member chelate rings, whereas those that deviate from such a path are mostly complexes with four dithiocarbamate ligands. Stereochemical preferences are clearly different for complexes of the d^{10} ions: (a) nearly half of the structures correspond to geometries along the cube to square antiprism interconversion pathway, (b) some 26% of the structures can be classified as hexagonal bipyramids and (c) no dodecahedral structures appear in this family.

If the octacoordinate complexes are classified according to their ligands, a clearer stereochemical picture emerges for some families. The stereochemical preferences found are summarized in Fig. 14. There, those families whose members are close to a given polyhedron are indicated with a circle under the label of the corresponding polyhedron, whereas families that present a variety of structures between two reference polyhedra are represented by rectangles. Hence,

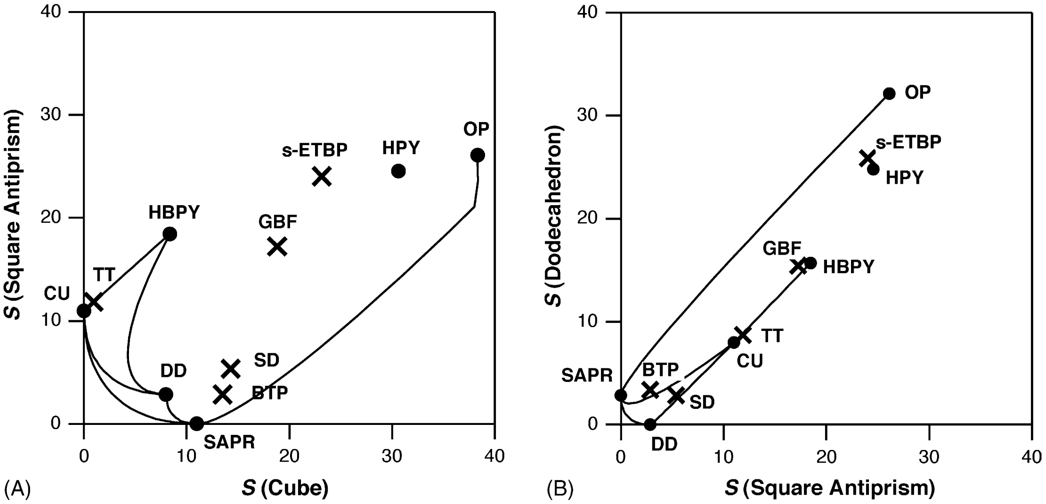


Fig. 12. Two shape maps for eight-vertex polyhedra (see Scheme 5 for acronyms) within the chemically significant region. The circles indicates the position of three ideal shapes labeled in boldface. Several distortion paths depicted in Scheme 5 are also plotted in the map. Adapted with permission from Ref. [31].

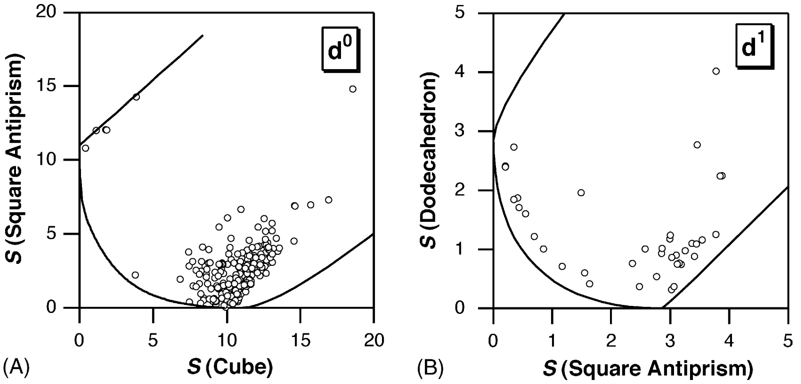
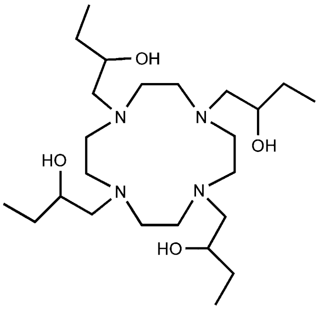


Fig. 13. Shape maps for transition metal octacoordinate complexes with different electronic configurations. The lines shown in the Square Antiprism–Cube map correspond (from left to right) to the CU–HBPY, CU–SAPR and SAPR–OP interconversion paths, whereas those in the Dodecahedron–Square Antiprism maps correspond to the SAPR–OP, SAPR–DD and DD–CU-HBPY paths (see Scheme 5) Reproduced with permission from Ref. [31].

whereas no general trend can be found for compounds with only monodentate ligands, the octacyano complexes appear scattered along the path for the interconversion of the dodecahedron and the square antiprism. Among the complexes with four bidentate ligands, it is seen that those with larger normalized bites, such as oxalate and β-diketonates, favor structures along the same DD–SAP path, whereas those with smaller bites, such as dithiocarbamates or nitrate, present mostly dodecahedral structures distorted toward the cube.

Some multidentate ligands seem to be efficient in promoting less common geometries. Thus, complexes with two tripod ligands present cubic coordination spheres and so do compounds with cryptate ligands, whereas the hexadentate crown ethers favor the hexagonal bipyramidal geometry. Complexes with two tetradentate macrocyclic ligands clearly impose their fourfold symmetry while allowing for a wide degree of rotation angles between the two ligands, therefore covering the whole interconversion path between the cube and the square antiprism. A similar behavior is presented by tentacular ligands formed by a tetradentate macrocycle with four pendant arms bearing one additional donor atom each, of which one example is illustrated in **8**.



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Finally, our CShM analysis allowed us to identify at a glance some unusual structures. These comprise the gyrobifastigium (GBF) that approximately describes the metal coordination sphere in $[Ce(NO_3)_2Cl_4]^{2-}$ and $[Cd(NO_3)_4]^{2-}$. The ideal gyrobifastigium is a Johnson octahedron (Scheme 5) that could be described as the result of fusing together two trigonal prisms through square faces rotated 90° relative to

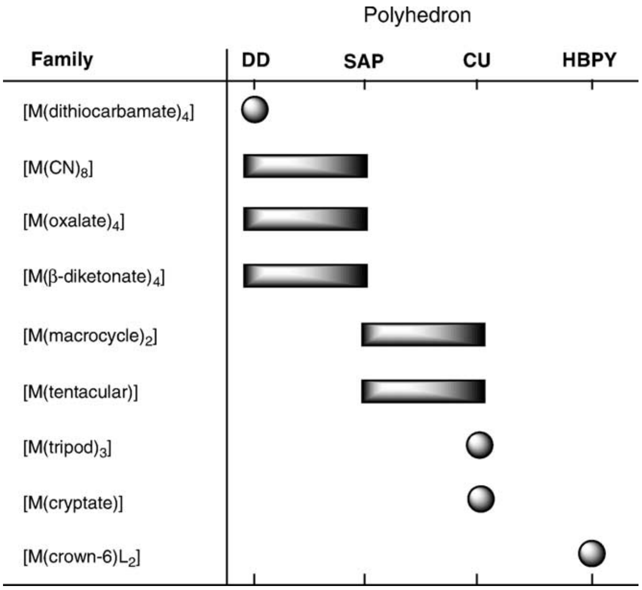


Fig. 14. Preferred polyhedra for octacoordinate transition metal complexes, grouped by ligands. A circle indicates the preferred polyhedron, a bar indicates that structures are found for the two polyhedra at the extremes as well as for intermediate geometries along the interconversion path. Reproduced with permission from Ref. [31].

each other. Although we have found no octagonal coordination complexes, two structures have been detected that have gone a long way from the square antiprism toward the octagon, those of the $[MAs_8]^{n-}$ complexes ($M = Nb^V$ or Mo^{VI}) [36,37], in which the metal atom sits at the center of a non planar As_8 ring. Their path deviation functions show that these structures fall right along the path that connects those two polyhedra (deviation functions smaller than 0.001 in both cases).

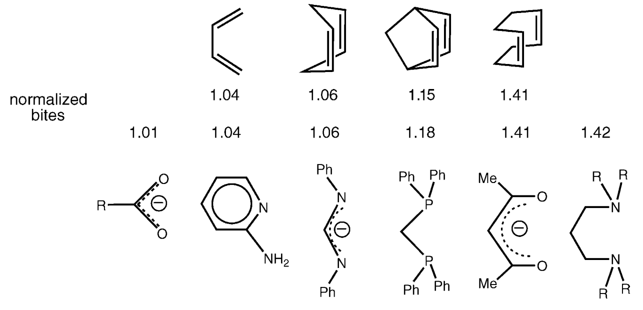
The coordination spheres of octacoordinated transition metals in the extended structures present in solid state materials behave in much a similar way as those of the molecular complexes, although some specific findings are worth mentioning [31]. Thus, the bicapped trigonal prism is as common in solids as it is in molecules, but the former deviate significantly from the ideal polyhedron because of the existence of element–element bonds between some of the vertices. For example, this is the case of $CrAs_2$, in which the As atoms form part of $(As^0)_\infty$ layers of fused hexagons and $(As^-)_\infty$ chains. An uncommon structure that can be found among the extended solids is that of the trigonal prism capped at the two trigonal faces (appropriately called *extended trigonal bipyramid* or, in short, ETBP, schematically illustrated in Scheme 5), to be found in the Re coordination sphere of ReB_2.

Also the minimal distortion polyhedral interconversion paths are useful to describe the structures of a variety of solids. For instance, the Y atom in $Y_2Ti_2O_7$ has relatively large shape measures relative to both the cube (2.10) and the hexagonal bipyramid (2.93), but its small deviation function (0.08) undoubtedly tells that its geometry is along the path that links these two polyhedra. Another interesting example is found in the garnet structure corresponding to compounds with the general formula $A^{II}_3M^{III}_2(SiO_4)_3$, where A^{II} can be Ca, Sc, Mg, Fe or Mn and M^{III} can be Al, Cr or Fe. O'Keefe and Hyde [38] pointed out that the coordination geometry of the A^{II} ions in these compounds is described by different authors as a "skew cube", a "distorted square antiprism" or a "distorted dodecahedron". A continuous shape analysis of the alkaline earth coordination sphere in a sample of garnet structures indicates that for none of the AO_8 cores can the geometry be unequivocally assigned to an ideal polyhedral shape because CShM values in excess of 2.0 are found for all the polyhedra. However, in all cases the deviation functions from the CU–SAPR path have rather small values (largest deviation from the path is 0.12), clearly indicating that the coordination polyhedra are very well described as intermediate between the cube and the square antiprism, also called *square metaprisms*. Furthermore, for those cases (andradite and grossular) for which X-ray diffraction structures have been reported at different temperatures [39–41], the AO_8 metaprisms are seen to rotate toward the cube as the temperature is lowered.

11. Organometallic compounds

A shape analysis of homoleptic $[MR_n]$ organometallic complexes (R = Me, Ph) [42] shows that the stereochemistry of these compounds does not significantly differ from the classical Werner coordination compounds, presenting mostly nearly perfect shapes in compounds with coordination numbers between three and eight in nine different geometries. A few particular cases, though, have been straighforwardly detected, such as the presence of the $[TiMe_5]^-$ anion in two crystallographic sites which are close to the square pyramid and the trigonal bipyramid, respectively. Whenever the shape measures indicate significant deviations from the ideal polyhedron, the distortion falls along the well established polyhedral interconversion paths, according to the small values of the path deviation functions. As examples we can mention the spread distortion of the square toward the tetrahedron in $[MnMe_4]^-$, or the Bailar twist of some nearly octahedral (Cr^{III}, Rh^{III} and Ir^{III}) and trigonal prismatic (Zr^{IV} and Ta^V) compounds. Tetracoordinate homoleptic complexes (including derivatives of aryl groups such as C_6Cl_5, C_6F_5 or MePh), obey the following stereochemical preferences, in agreement with the general behavior of tetracoordinate complexes [16] (see above): metals with d^1, d^2, d^3 and d^{10} electron configurations appear in the tetrahedral geometry, those with d^7 or d^8 configurations are square planar and d^4 ions can be either tetrahedral or square planar.

The stereochemistry of complexes having π-bonded ligands can also be analyzed with the CShM approach by defining the centroid of the π-bonded atoms as occupying a coordination site in the metal coordination sphere.



Scheme 6.

Thus, the formally hexacoordinate complexes [M(olefin)L_5], [M(alkyne)L_5], [M(η^3-allyl)L_5] and [M(olefin)$_2L_4$] can be described as being practically octahedral, although significant deviations from the octahedron are observed in some Zr, Hf and Mo complexes, in which two ligands *cis* to the π-bonded group are bent away, forming L—M—L bond angles of about 150°. A different behavior is found for the analogous families of formally tetracoordinate complexes, which appear clustered around the tetrahedron and the square and significant distortions from these two shapes fall along their interconversion path. A couple of examples of Ir complexes that are approximately midway between the tetrahedron and the square have been identified, since they present very small values of the corresponding path deviation function. As for formally pentacoordinate complexes with d^8 electron configuration, two very different geometry choices have been found for the mono- and bis-olefin complexes, since they show a clear preference for the trigonal bipyramidal and for the square pyramidal geometries, respectively. This behavior is to be compared to the general finding for d^8 pentacoordinate complexes, which show no clear preference between these two shapes, as discussed in a previous section.

If we can consider a C=C double bond as a single vertex of the coordination polyhedron, there is no reason why we should not consider a coordinated diolefin as a bidentate ligand. From this viewpoint, we could therefore define for diolefins the most characteristic geometrical parameter of bidentate ligands: their normalized bite (defined as the ratio of the donor–donor and the average metal-donor distances). On so doing, we can put on the same footing, e.g., cyclooctadiene and a β-diketonate (Scheme 6), since both ligands have normalized bites of 1.41 for first row transition metals. Thus, butadiene, cyclohexadiene, norbornadiene and cyclooctadiene can be compared (Scheme 6) to paradigmatic bidentate ligands such as carboxylates, aminopyridine, formamidinate, acetylacetonate or propanediamine. Deviations of the coordination geometries of diolefin complexes from the ideal polyhedra can therefore be ascribed to bite angle effects, including a large bond angle between the ligands in *trans* (101°) associated to the quite small angle between the centroids of the two C=C bonds (60°) in the butadiene complex [Cr(CO)$_2$(PMe$_3$)$_2$(η^4-2,4-hexadiene)] [43] (Fig. 15) and similarly in other two Cr and Ti butadiene complexes.

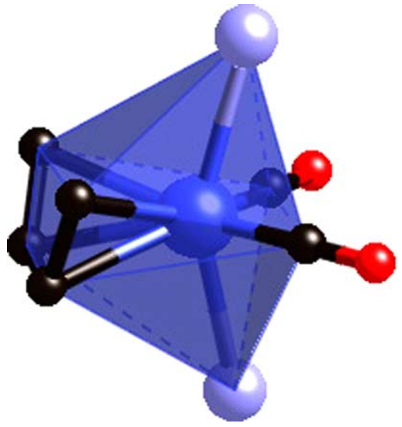


Fig. 15. Coordination polyhedron of the Cr atom in a complex with substituted butadiene as a bidentate ligand [Cr(CO)$_2$(PMe$_3$)$_2$(η^4-2,4-hexadiene)].

A particularly interesting case is that of tris(diene) complexes of Mo, W and Zr [44–46], for which the shape measures of the centroids of the C=C double bonds clearly show that the coordination sphere is trigonal prismatic, not octahedral. However, such a geometry is inconsistent with the consideration of the diolefins as neutral ligands, since this assumption would lead to oxidation states Mo(0), W(0) and Zr(-II), respectively, with d^6 electron configurations and it is known that d^6 complexes prefer the octahedral geometry. If one considers the butadienoid fragments to be 1,4-diyl ligands with the terminal carbon atoms coordinated in an η^1 mode, then the metal atoms become formally Mo^{VI}, W^{VI} and Zr^{IV}, whose d^0 electron configurations are consistent with the trigonal prismatic coordination geometry observed. This description is also consistent with the distribution of the C—C bond distances within the diolefin skeleton and with significant differences in the M—C distances of the two carbon atoms of each double bond. Moreover, the metal coordination sphere considering the terminal carbon atoms as attachment points is much closer to the ideal trigonal prism than that the polyhedron that results from taking the centroid of the diene double bonds as the vertices.

A similar treatment of π-bonded cyclopentadienides has also been carried out. In particular, for the family of piano stool complexes of general formula [M(η^5-Cp)L_3], one could describe the metal coordination sphere in two alternative ways: either as a tetrahedron in which one vertex is occupied by the centroid of the organic ring (**9**) or as an octahedron in which one face is occupied by the ring (**10**). The latter results from considering that the cyclopentadienide is a six electron donor and hence replaces three monodentate ligands in the coordination sphere. To see which of the two models offers a more accurate description of the experimental structures, we have calculated their shape measures relative to the tetrahedron and to a trigonal pyramid (the one that results from replacing a face of an octahedron by its geometrical center). The results indicate that the structures are grouped around the two ideal shapes, **9** and **10**, but with significant

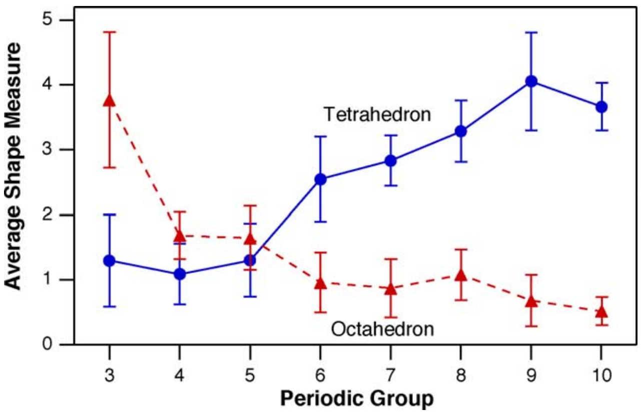
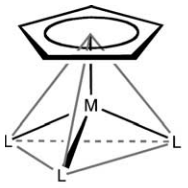
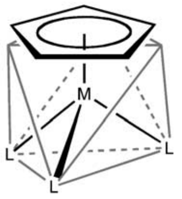


Fig. 16. Evolution of the tetrahedral (circles) and *fac*-trivacant octahedral (triangles) shape measures of the [M(η^5-Cp)L_3] complexes along the transition metal series. Reproduced from Ref. [42] with permission of the American Chemical Society.

deviations from ideality in many cases. These deviations correspond mostly to (a) variations in the M–Cp distance and (b) changes in the angles between the legs. Focusing on the changes in bond angles and analyzing the evolution of the shape measures along the transition series, we have found that the early transition metals (groups 3–5) prefer the pseudotetrahedral geometry **9** and there is an increasing tendency to a pseudooctahedral situation when moving to the right, as illustrated in Fig. 16.



9



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12. Concluding remarks

The application of the CShM approach to transition metal compounds with coordination numbers between four and eight has shown to be an efficient way to describe the stereochemistry of their coordination spheres. Thus, we can say (i) which polyhedron gives the best description of its coordination geometry, (ii) how close is it from such an ideal polyhedron and (iii) in which position it is along a given polyhedral interconversion path. In this way, it is straightforward also to detect, e.g., both the most perfect and the most distorted examples of a given polyhedron, or to pinpoint uncommon structures, such as the eight-vertex gyrobifastigium or nearly hexagonal hexacoordinate complexes.

The analysis of the CShM values of a large number of transition metal compounds, comprising more than 23,000 crystalographically independent fragments, has allowed us to establish stereochemical trends for each coordination number according to the electron configuration of the metal atom or to the type of ligands present in the coordination sphere.

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