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The Trigonal Prism in Coordination Chemistry

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Abstract: Herein we analyze the accessibility of the trigonal-prismatic geometry to metal complexes with different electron configurations, as well as the ability of several hexadentate ligands to favor that coordination polyhedron. Our study combines i) a structural database analysis of the occurrence of the prismatic geometry throughout the transition-metal series, ii) a qualitative molecular orbital analysis of the distortions expected for a trigonal-prismatic geometry, and iii) a computational study of complexes of several transition-metal ions with different hexadentate ligands. Also the tendency of specific electron configurations to present a *cis* bond-stretch Jahn–Teller distortion is analyzed.

Keywords: Jahn–Teller distortion · manganese · Ray–Dutt mechanism · stereochemistry · transition metals · trigonal prisms

Introduction

Nel mezzo del cammin di nostra vita,
mi ritrovai per una selva oscura
ché la diritta via era smarrita.
Dante Alighieri, *Divina Commedia* (Inferno, I, 1-3)

Although the stereochemistry of six-coordinate metal complexes is dominated by the octahedron, the trigonal prism has attracted increasing interest[1] since the first independent molecules with such a coordination geometry were reported in tris(dithiolene) complexes of Re, Mo, and W in 1965.[2] The first metal atom with a trigonal-prismatic coordination, though, was found much earlier in molybdenite (MoS_2), and reported in the first publication of a graduate student at Caltech named Linus Pauling,[3] in collaboration with his advisor Roscoe Dickinson.[4] Shortly after, van Arkel reported the structure of the isomorphous tungstenite (WS_2).[5] Almost four decades later, in the third edition of his book *The Nature of the Chemical Bond*,[6] Pauling still discussed the structure of those two sulfides as a rarity, stating that the trigonal-prismatic configuration had not been recognized in any other compounds of molybdenum and tungsten.

The situation has dramatically changed in the last few decades. Nowadays many more molecular, covalent, and ionic solids are known with trigonal-prismatic coordination. We also know, for instance, that molybdenum and tungsten active sites in a variety of enzymes present trigonal-prismatic (sometimes twisted) coordination spheres.[7] The trigonal-prismatic geometry is also important because it may appear as an intermediate or a transition state in the intramolecular racemization reactions of octahedral tris(chelate) complexes[8] through either the Bailar[9] or Ray–Dutt[10] mechanisms.

A crucial discovery was the trigonal-prismatic coordination geometry for the $[ZrMe_6]^{2-}$ ion by Morse and Girolami in 1989,[11] together with the theoretical prediction that $[WMe_6]$[12,13] and other d^0 homoleptic complexes with monodentate σ-donor ligands[14] should present the same geometry, followed by the experimental confirmation of its structure in the gas phase[15] and in the solid state.[16,17] Although hexamethyltungsten, explosive under atmospheric oxygen,[18] had been synthesized in 1973 by Shortland and Wilkinson,[19] it was assumed to be octahedral, as had been established for the related hexamethyl Cr^{III} and Mn^{IV} anions.[20] In successive years, other hexamethyl complexes of the early transition metals were synthesized and structurally characterized,[17,21] including those of Re^{VI}, Ta^{V}, Nb^{V}, and Mo^{VI},[16] as well as related aryl complexes.[22] The more recent report of trigonal-prismatic arylthiolatozirconium complexes,[23] is also worth being remarked upon.

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Interesting reports concerning the interplay between trigonal-prismatic and octahedral coordination focus on the pH-driven switching between the two geometries,[24] the change in nuclearity associated with the adoption of one or the other coordination geometry,[25] or the correlation between the degree of trigonal twist and the magnetic properties in spin crossover complexes.[26]

Nowadays it seems clear that for the more covalent metal–ligand combinations (soft donor atoms and central metal in a high oxidation state) with d^0, d^1, or d^2 configurations, the trigonal prism is the preferred geometry. Ligand field theory predicts equal energies for the octahedron and the trigonal prism for the d^0, d^1, low-spin d^2, high-spin d^5 and d^6, and d^{10} electron configurations, and a more stable octahedral conformation for the rest.[1] A molecular orbital study based on extended Hückel calculations on a simple model complex found the trigonal prism to be favored over the octahedron for d^0–d^4 and d^{10} configurations.[27] However, little theoretical work has been done with more accurate molecular orbital or density functional theory approaches regarding the electronic structure and bonding in trigonal-prismatic complexes of transition metal ions with d^3 to d^{10} configurations. We have recently shown that the d^9 copper(II) complexes, when forced by ligand design to be in a trigonal-prismatic environment, present Jahn–Teller distortions with two longer metal–ligand distances in *cis* relative position, in contrast with the ubiquitous *trans* tetragonal distortion present in pseudo-octahedral copper(II) complexes. It was further shown that for copper(II) coordination spheres intermediate between the octahedron and the trigonal prism both *cis* and *trans* distortions can be observed.[28] In that work, a qualitative molecular orbital analysis suggested that such a Jahn–Teller distortion should also be present in d^4 metal ions surrounded by a trigonal-prismatic set of donor atoms.

Herein we analyze the feasibility of the trigonal-prismatic geometry in d^3–d^{10} metal complexes, and the ability of several hexadentate ligands to favor it. Our study combines i) a structural database analysis of the occurrence of the prismatic geometry throughout the transition-metal series, ii) a qualitative molecular orbital analysis of the distortions expected for a trigonal-prismatic geometry, and iii) a computational study of complexes of several transition-metal ions with different hexadentate ligands. This work also expands our preliminary study on Jahn–Teller distortions of trigonal-prismatic copper(II) complexes to manganese(III) and chromium(II) analogues.

The stereochemistry of the coordination sphere will be characterized in this work by continuous shape measures and derived parameters.[29] In essence, a continuous shape measure calibrates the deviation of a given structure from an ideal shape,[30,31] such as the octahedron or the trigonal prism in the present case. The octahedral shape measure of a coordination polyhedron, S(OC-6), will be zero if it is perfectly octahedral, and adopt progressively higher positive values as the structure deviates from ideality. Similarly, a zero trigonal-prismatic shape measure, S(TP-6), indicates a perfect trigonal prism with all edges of the same length. Since we will only deal with six-vertex polyhedra in this work, we will omit from here on the numerical suffix of the polyhedral labels for the octahedron (OC) and trigonal prism (TP).

Since many of the structures to be studied present geometries intermediate between the octahedron and the trigonal prism (referred to as metaprisms), it will be useful also to describe each molecule by its position relative to the minimal distortion interconversion path between those two ideal polyhedra, known as the Bailar twist, by means of two parameters. On one hand, the path deviation function, $\Delta_{OC,TP}(Q)$, measures the distance of a structure Q to the minimal distortion pathway between OC and TP (in percentage of the path length).[32] On the other hand, for structures Q on the minimal distortion path we can measure the percentage of conversion from one ideal polyhedron to the other one, by means of the generalized interconversion coordinate, $\varphi_{OC\rightarrow TP}(Q)$.[33] As defined, a generalized coordinate only applies to polyhedra Q that are on the minimal distortion (Bailar) path or, in an approximate way, to those that deviate slightly from it. It can adopt values from 0 for the perfect octahedron to 100% for the ideal trigonal prism. It can be shown that the usually employed twist angle θ and the generalized coordinate $\varphi_{OC\rightarrow TP}$ are equivalent and linearly related [Eq. (1)]. We prefer to use the latter, because its calculation is straightforward with the program SHAPE, while the twist angle requires some more effort to identify the atoms that form the two trigonal faces of the metaprism that define a torsion angle. Nevertheless we will in several instances provide also twist angles θ for reference to those readers more familiar with this parameter.

$$\theta = 60 - \tfrac{3}{5}\varphi_{OC\rightarrow TP} \quad (1)$$

Abstract in Spanish: *En este artículo se analiza la accesibilidad de la geometría prismático-trigonal para los complejos metálicos con diferentes configuraciones electrónicas, así como la capacidad de diversos ligandos hexadentados de favorecer dicho poliedro de coordinación. Nuestro estudio combina i) un análisis de bases de datos estructurales para establecer la existencia de la geometría prismático-trigonal a lo largo de las series de transición, ii) un análisis cualitativo de orbitales moleculares de las distorsiones que cabe esperar para una geometría prismático-trigonal, y iii) un estudio computacional de complejos de varios metales de transición con diferentes ligandos hexadentados. Finalmente se analiza la tendencia de algunas configuraciones electrónicas a presentar una distorsión Jahn–Teller de elongación de enlaces en cis.*

Occurrence and Relevance of the Trigonal Prism as a Coordination Motif

Because the octahedron is rightly perceived as the most ubiquitous coordination polyhedron in transition-metal chemistry, and the trigonal prism is often considered as a rarity, it might be appropriate to have first an overview of the frequency with which trigonal-prismatic coordination appears throughout the transition-metal series. We will also look at the occurrence of the trigonal prism among different families of transition-metal compounds, including those with mono-, di-, or tetradentate ligands, organometallic complexes, bioinorganic compounds, or extended solids. Hexadentate ligands that might enforce a trigonal-prismatic geometry will be dealt with in a subsequent section.

Let us start by showing the relative abundance of trigonal-prismatic complexes for the different transition metals (see Computational Section for details) in the Cambridge Structural Database (CSD) (see Figure 1). Although the number of trigonal prisms throughout the transition-metal series is barely 1.0% of the six-coordinate metal centers, the distribution is highly inhomogeneous. Thus, the frequency of trigonal-prismatic structures is highest for the leftmost transition metals (Groups 3 and 4), Ag, and Group 12 elements. The existence of a non negligible proportion of trigonal-prismatic structures for metals of Groups 5 to 7 and Fe is also noteworthy. The only metals for which no trigonal-prismatic structures have been found in the CSD are Cr, Rh, Ir, Pd, Pt, and Au, although some of them do form trigonal prisms in some extended solids (see below). However, it must be mentioned that in the case of gold only five structurally characterized six-coordinate complexes have been found.

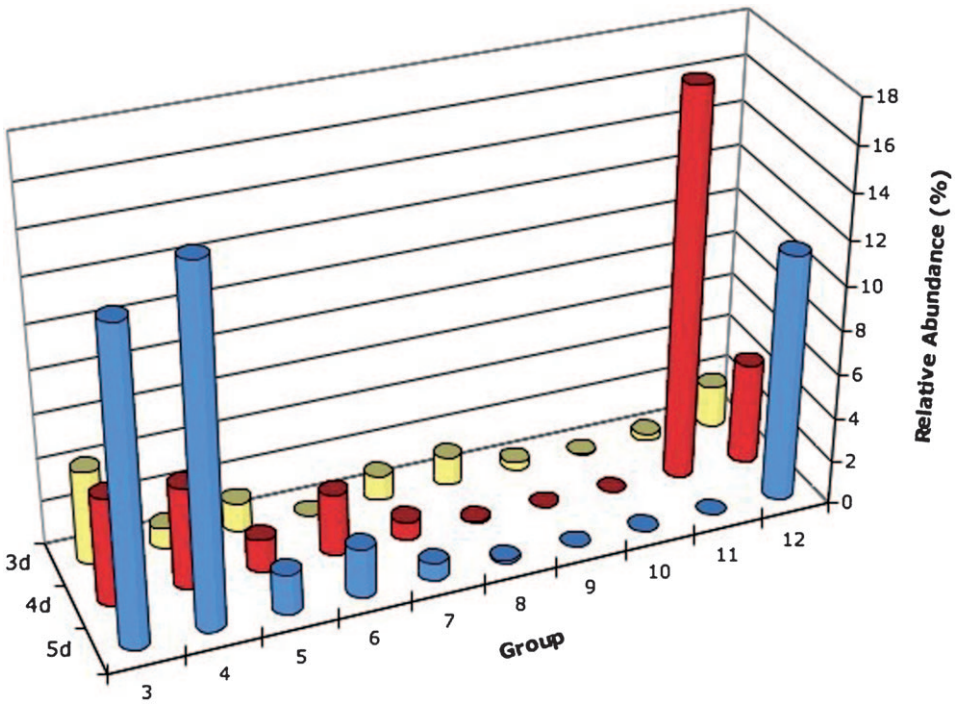


Figure 1. Frequency of trigonal prismatic structures found in the CSD throughout the transition-metal series, given as the percentage of six-coordinate metal centers for each metal. A metal center has been classified as trigonal prismatic if its corresponding shape measure is smaller than 4.0.

Monodentate ligands: After looking at the stereochemical preferences by metal, we adopt now the opposite point of view, focusing on specific families of complexes, starting by those bearing monodentate ligands only. Among homoleptic hexacoordinate complexes with the d^6 configuration, the octahedron is always the preferred structure. That is the case for the complexes with the simplest σ-donor ligand, the hydride. The structures of $[MH_6]^{n-}$ ions, determined by X-ray and neutron diffraction for M = Mn^{I}, Re^{I}, Fe^{II}, Ru^{II}, Os^{II}, Rh^{III}, Ir^{III}, and Pt^{IV}, are all octahedral. In contrast, d^0 $[WH_6]$, isolated in a neon matrix and characterized by IR spectroscopy, has C_{3v} symmetry resulting from a non-Bailar distortion of the trigonal prism.[34]

An analysis of the stereochemistries of some families of homoleptic hexacoordinate complexes with monodentate ligands,[30] shows that the $[MR_6]$ alkyl and aryl complexes of d^0 and d^1 metal ions (Zr^{IV}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}, and Re^{VI})[11,16,17,21,22,35] are trigonal prismatic with only moderate distortions therefrom ($68 \leq \varphi_{OC\rightarrow TP} \leq 100\%$). In contrast, analogous homoleptic alkyl compounds with other electron configurations (Cr^{III}, V^{II}, Mn^{IV}, Rh^{III}, and Ir^{III}),[20,36] present octahedral coordination ($2 \leq \varphi_{OC\rightarrow TP} \leq 35\%$).

Thiolato complexes $[M(SR)_6]$ of d^0 to d^2 configurations can be found with a variety of stereochemistries, from trigonal prismatic[23,37,38] to octahedral,[37,39] including intermediate metaprismatic structures[23,40] ($15 \leq \varphi_{OC\rightarrow TP} \leq 99\%$). A particular remarkable case is that of a trinuclear Ti^{IV} compound, in which the central titanium atom is trigonal prismatic and the terminal ones are octahedral, while in the related dinuclear complex the two Ti atoms are practically halfway between the octahedron and the trigonal prism.[40] A theoretical study has concluded that in the thiolato complexes the degree of Bailar rotation for a given compound is determined by the subtle interplay of the electronic structural preference and the repulsion between the sulfur lone pairs of π character with respect to the M–S bonds.[41]

A rather surprising fact is that good σ donors and π acceptors, such as the cyano and isonitrile ligands, give only octahedral complexes. Thus, cyano complexes of the early transition metals such as $[Ti(CN)_6]^{3-}$, $[V(CN)_6]^{3-}$, and $[Mo(CN)_6]^{2-}$ are as perfectly

octahedral as their late transition metal analogues. The only exception among homoleptic complexes we are aware of is the tantalum acetylide complex $[Ta(C{\equiv}CSi\{t\mathrm{Bu}\}_3)_6]^-$, which is very close to the trigonal prism,[42] while its isoelectronic Zr^{IV} and Hf^{IV} analogues are octahedral.[42] Another interesting finding is that the Mo^{II} and W^{II} complexes with between two and four π-acid ligands may present trigonal-prismatic[43,44] or octahedral[44,45] geometries (Figure 2). Although such structures present significant twisting degrees from the ideal polyhedra, the absence of structures at the middle of the Bailar pathway suggests the existence of two potential energy minima and therefore the possibility of isolating octahedral and trigonal prismatic estereoisomers of compounds belonging to this family.

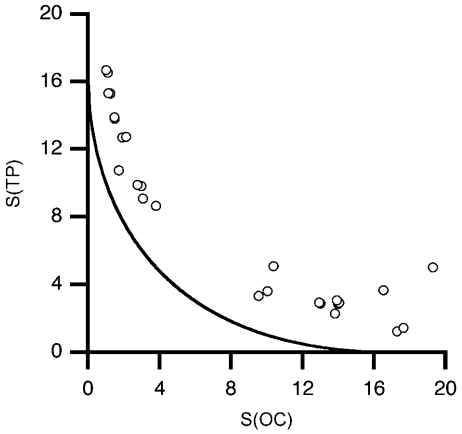


Figure 2. Distribution along the Bailar pathway (continuous line) of Mo^{II} and W^{II} complexes with between two and four π-acid ligands (circles).

Tris(chelate) complexes: Tris(chelate) complexes constitute a highly interesting family with regard to the choice between trigonal prismatic and octahedral stereochemistries for two reasons. First, because tris(dithiolato) complexes of Re, Mo, and W were the first molecular complexes to be reported with a trigonal-prismatic geometry.[2] Second, because of the interplay of the electron configuration and the ligand's bite angle in determining octahedral, trigonal-prismatic, or intermediate geometries with varying twist angles between two opposing trigonal faces. Almost five decades after their discovery, there is still a great deal of interest associated to their stereochemistry and to the non-innocent character of the ligands.[46] A variety of dithiolato complexes are now known to display trigonal prismatic coordination,[46] and diselenolato ligands also give trigonal prismatic W^{IV} and W^{VI} complexes.[47]

In tris(chelate) complexes, a nice correlation has been found between the normalized bite of the ligand and the Bailar twist angle:[30,48] the smaller the normalized bite, the closer the coordination geometry is to the trigonal prism. However, in general the twist angles forced just by chelation are still far from those corresponding to the trigonal prism. A quite different behavior is exhibited by dithiolene and diselenolene complexes, for which there seems to be a clear correlation between electron configuration and geometry. Hence, most of those compounds with d^0 to d^2 electron configurations are closer to the trigonal prism than to the octahedron, with $\varphi_{OC\rightarrow TP} \geq 55\,\%$ (i.e., $\theta \leq 28°$). There is only a handful of exceptions that show $\varphi_{OC\rightarrow TP}$ values between 28 and 45 % ($34 < \theta < 45°$), still indicating significant twists of the octahedron. In contrast, complexes with three or more d electrons are all much closer to the octahedron than to the trigonal prism ($\varphi_{OC\rightarrow TP}$ values of at most 38 %).

A particularly interesting case is that of the π-bonded tris(diene) complexes, $[Mo(2,3\text{-}Me_2butadiene)_3]$, $[W(2,3\text{-}Me_2butadiene)_3]$,[49] and $[Zr(\eta^4\text{-naphthalene})_3]^{2-}$.[50] Considering the centroids of the C=C double bonds as the coordination positions, one finds that the coordination geometry around the metal atoms is neatly trigonal prismatic, the ligands being best described as 2-butene-1,4-diyl groups with the terminal carbon atoms coordinated in an η^2 mode with formal oxidation states for the metals of Mo^{VI}, W^{VI}, and Zr^{IV}, whose d^0 electron configurations are consistent with the trigonal-prismatic geometry observed. A more detailed discussion, accompanied with quantum-chemical calculations, has been given by Kaupp.[14] A related situation seems to explain the trigonal prismatic coordination of Ti, Zr, Hf, and W complexes with biphosphinine (the phosphorous analogue of bipyridine),[51,52] which, according to structural and theoretical studies, are best described as composed of dianionic ligands and d^0 metal ions.[52,53]

Finally, two remarkable complexes of d^{10} ions with trigonal-prismatic coordination spheres must be noted. One is the $[Zn(BH_4)_3]^-$ ion[55] in which the tetrahydroborate ligands act as bidentate, forming a compressed trigonal prism. The other example is provided by the $[Hg(en)_3]^{2+}$ ion,[54] in which the chelate rings are not arranged parallel to the trigonal axis as usual, but with two ligands spanning parallel edges of the two triangular faces, and the third one parallel to the pseudo trigonal axis (Figure 3), as in the intermediate proposed in the Ray–Dutt mechanism for racemization of tris(chelate) complexes.[10] We have been unable to identify another similar structure in a systematic search for tris(chelate) complexes with ethylenediamine, dithiolate, dithiocarbamate, diphosphine, or bipyridine ligands.

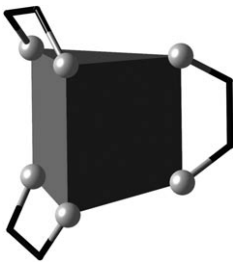


Figure 3. Ray–Dutt trigonal-prismatic structure of the $[Hg(en)_3]^{2+}$ ion.[54]

Tetradentate macrocyclic ligands: Trigonal-prismatic coordination spheres are frequently found with tetradentate mac-

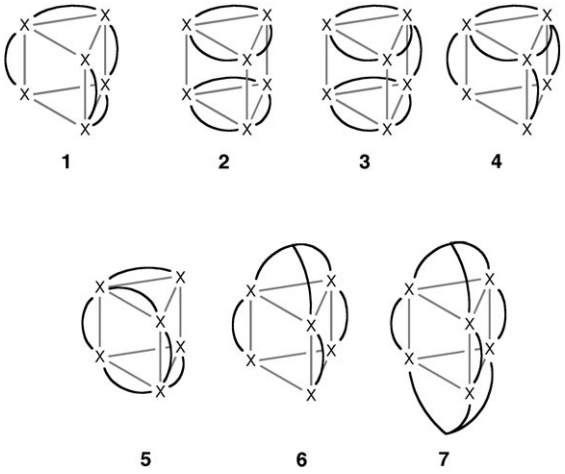
rocyclic ligands such as phthalocyaninato and porphyrinato with the general formula $[M(L)X_2]$, where X stands for a monodentate ligand. In this family, the early transition metals with d^0 to d^2 configurations (e.g., Sc^{III}, Ti^{IV}, Hf^{IV}, Zr^{IV}, and Nb^{IV}) appear in a *cis* conformation with the macrocyclic ligand occupying a square face of a trigonal prism,[56] in contrast to other metal ions that form *trans* octahedral complexes (see **8a** below). Exceptions to this trend correspond to Fe^{III} porphyrinato complexes with an additional bidentate ligand that are per force *cis*, and a Mo^{II} compound with two π-acid ligands,[57] similarly to what was found with only monodentate ligands above. A similar behavior can be found with other tetradentate macrocycles.[58]

Metalloenzymes: Molybdenum and tungsten active sites in a variety of enzymes present trigonal-prismatic (sometimes twisted) coordination spheres, which most often include two dithiolene ligands.[7,59] That is the case of molybdenum and tungsten in the oxidized state of formate dehydrogenases,[60] dmso-reductases,[61] and in nitrate reductases.[62] Enzymes of the xanthine oxidase family catalyze hydroxylation reactions of several substrates, and the mechanism proposed implies a trigonal-prismatic intermediate in which the substrate is coordinated to a molybdenum atom,[63] whose geometry is supported by computational studies.[64] Several copper sites present coordination environments that are described as intermediate between the trigonal prism and the octahedron, including a copper amine oxidase,[65] copper-substituted human lactoferrin,[66] and superoxide dismutases,[67] although their deviations from the Bailar pathway are quite large. Also the environment of the Fe atom in enterobactin has a twisted geometry that, however, is closer to the octahedron than to the trigonal prism (see the Supporting Information), while the vanadium(IV) enterobactin complex[68] is practically midway between the octahedron and the trigonal prism ($\varphi_{OC\rightarrow TP}=54\,\%$).

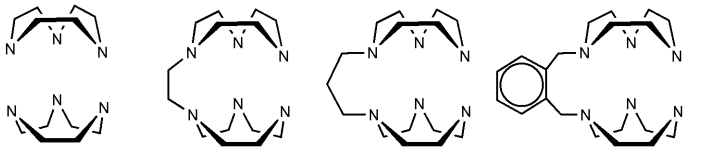
Inorganic solids: Besides the compounds with the molybdenite structure mentioned in the introduction,[69] trigonal prismatic coordination is found among extended solids in the families of compounds with the WC, PtB (anti NiAs), NbS_2, NbAs, and $NaNbO_3$ structures. Similarly, in compounds with an A_3BMO_6 stoichiometry and K_4CdCl_6 or Sr_4PtO_6 structural types,[70] the M and B atoms form stacks of alternating octahedra (M) and trigonal prisms (B) through face-sharing, for example, in Sr_3BMO_6 (B = Ni, Cu, Zn; M = Rh, Ir) and Ca_3NiMnO_6. In the $MM'N_2$ nitrides[71] (M = Li, Cr, Mn, Fe; M′ = Mo, W) and in the related $CrTiS_2$, layers of fused MN_6 (or CrS_6) octahedra and $M'N_6$ (or TiS_6) trigonal prisms alternate.[72] Copper(II) sites with trigonal-prismatic geometry can be found in minerals such as lyonsite, buttbengachite, connellite, and claringbullite.[73] A review of trigonal-prismatic oxo-rhodates can be found in the literature,[74] while other examples of metals in trigonal-prismatic coordination are found in Ba_2NiSi_3, $NaNbO_2$, and $LiNbO_2$.[75]

Stereochemistry of Complexes with Hexadentate Ligands

Several multidentate ligand topologies are supposed to provide a relatively stiff skeleton that might favor a trigonal prismatic arrangement of the donor atoms. We have explored a variety of ligand families with different degrees of rigidity and analyzed their ability to favor a trigonal prismatic coordination sphere by means of a structural database study. The families considered, sketched in **1**-**7**, include open chain hexadentate ligands **1**; two tridentate macrocyclic ligands, independent as in **2**, or strapped as in **3**; one tridentate macrocycle with three pendant coordinating units **4**; the tetradentate macrocyclic ligands tetraazacyclododecane (cyclen) or tetraazacyclotetradecane (cyclam), supplemented with two coordinating (e.g., pyridyl or carboxylate) arms (**5**); extended tripodal ligands **6**, or encapsulating sepulchrate ligands such as sarcophagine (**7**).[76,77]

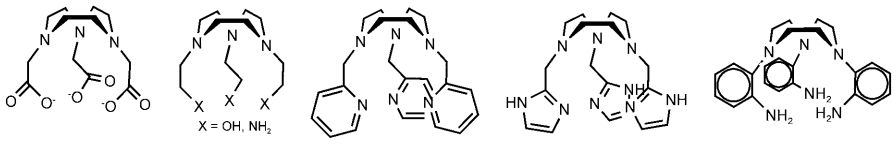


Macrocyclic tridentate skeletons: Within this family, we look first at ligands formed by two tridentate macrocycles joined by one linker (**3**). Two independent tridentate macrocycles (**2a**) give coordination geometries much closer to the octahedron than to the trigonal prism, as indicated by the small values of $\varphi_{OC\rightarrow TP}$. However, joining the two macrocycles by a strap, as in **3**, induces rotation towards the prism of at least a 33 %, even if none of the reported structures goes beyond 60 % of the Bailar pathway. Comparison of complexes with ethyl (**3a**) and propyl (**3b**) linkers with the same metal ion (Ni^{II}, Cu^{II}, or Zn^{II}) shows that the former favors a larger twist toward the trigonal prism. The complexes with *o*-xylyl linkers (**3c**) exhibit a larger flexibility, and several Ni^{II} complexes are found to be between 16 and 36 % along the Bailar pathway to the prism. Although one may imagine that analogous doubly or triply strapped systems should be closer to the trigonal prism, no such compounds have been structurally characterized and we will computationally analyze such an option below.



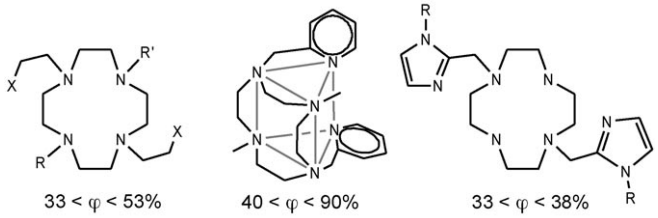
2a **3a** **3b** **3c**

A variety of ligands with topology **4** are known, the most common of which are shown in **4a** - **4e**. These have a triazacyclononane skeleton appended with three coordinating arms. The position of those complexes along the Bailar pathway can be anywhere between a slightly rotated octahedron and the ideal trigonal prism, as shown by their generalized coordinates $\varphi_{OC\rightarrow TP}$ or their rotation angles θ. Thus, the rigidity of these ligands suffices only to slightly twist the coordination sphere away from the octahedron, while other factors are likely to be responsible for large degrees of rotation towards the trigonal prism. The presence of double-bond character within the ligands' arms (in ligands **4c**–**e**) seems to limit a little more the approach to the octahedron compared to those with only single bonds (**4a** and **b**).



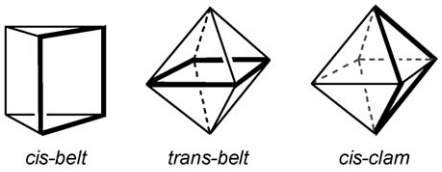
4a **4b** **4c** **4d** **4e**

Macrocyclic tetradentate skeletons: Tetradentate macrocycles appended with two coordinating arms include cyclen derivatives such as **5a**–**c** (X = O, N, S) with a *cis* arrangement of the two side arms. The six-coordinate complexes formed by these ligands significantly deviate from the octahedron. Moreover, the more rigid ligand **5b** allows geometries closer to the trigonal prism than the saturated analogues **5a**, as indicated by the generalized coordinates for the Bailar twist. The narrow range of twist found for **5c** is not significant, since only Ni^{II} complexes have been structurally characterized with these ligands so far.



5a **5b** **5c**

For complexes with the tetradentate macrocyclic ligands cyclam or cyclen, we have seen that the size and conformation of the macrocycle are of importance in determining a trigonal-prismatic geometry. The conformations of coordinated cyclam, usually termed *trans*-I to *trans*-IV, and *cis*-V,[78] can be grouped according to the *trans*- or *cis*-topology of the N_4 donor set in their octahedral complexes (**8b** and **8c**, respectively). The planar conformation of the donor set present in the octahedral *trans* isomer is also suitable for coordinating to a trigonal prism with *cis* geometry (**8a**). We therefore prefer to adopt a labeling of those conformations that is independent of the coordination polyhedron in a specific compound, referring to the nearly planar arrangement (**8a** and **8b**) as a *belt* conformation, and to the bent disposition of the donor set (**8c**) as a *clam* conformation. Such a conformational definition applies equally well to the cyclen macrocycle. We remark that cyclam appears in the experimental structures of metal complexes with any of the three geometries **8a**–**8c**, whereas cyclen has not been found so far in the octahedral *trans* geometry **8b**. This means that whenever the coordinated cyclen macrocycle is in a belt conformation, a trigonal prismatic coordination sphere might be expected.



8a **8b** **8c**

To distinguish the three possible situations **8a**–**c**, we have used two parameters. The X-M-X bond angle involving the non macrocyclic donor atoms, α, discriminates between *cis* and *trans* isomers, while the angle between two N_3 planes of the macrocycle, γ, can distinguish the *belt* and *clam* conformations of the macrocycle. An analysis of all six-coordinate complexes with cyclam and cyclen clearly shows that the three geometries sketched in **8** can be mapped as a function of those two parameters (Figure 4). According to the parameter map, we have identified cyclam complexes with the *belt-cis*-trigonal prism geometry of Zr^{II}, Hf^{II}, and Cd^{II},[79] and more abundant cyclen analogues of Co^{II}, Cu^{II}, Ag^{I}, Zn^{II}, Cd^{II}, and Hg^{II}.[80]

It must be noted that a *cis-belt* conformation of a tetradentate macrocyclic ligand is a necessary but not sufficient condition for having a trigonal prism. In most complexes, the two additional ligands are twisted from the ideal trigonal prism (Scheme 1), and can be envisaged as describing a pathway for a possible fluxional behavior.

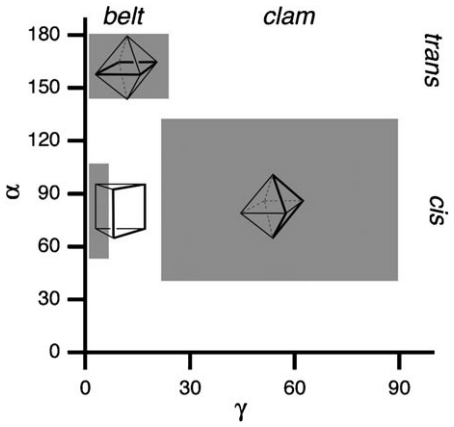
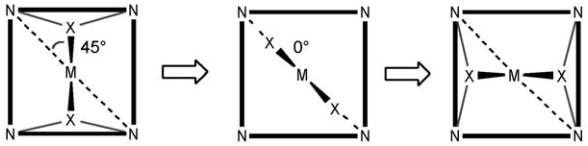


Figure 4. Regions of existence of geometries **8a–c** in six-coordinate transition-metal complexes with cyclam and cyclen macrocyclic ligands, indicated by the gray areas. The two geometrical parameters correspond to the angle between two N_3 planes (γ) and the X-M-X bond angle involving the non macrocyclic donor atoms (α).



Scheme 1.

An analysis of the structural data for several families of macrocyclic complexes with topology **5**, shows that their deviations from the trigonal prism are correlated to the twist sketched in Scheme 1 (Figure 5).

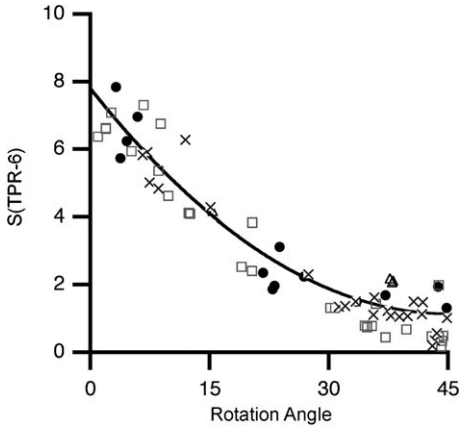
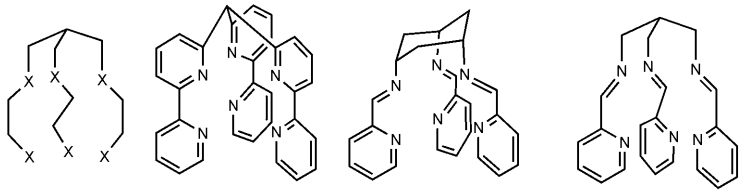


Figure 5. Dependence of the trigonal-prismatic measure on the rotation angle defined in Scheme 1 for the families of cyclen (triangles), cyclam (circles), unsaturated macrocycles (crosses) and porphyrin or phthalocyanine (squares) complexes with the *cis-belt* conformation.

Hexadentate macrocyclic ligands: Complexes with hexadentate eighteen-member macrocyclic ligands do not adapt very well to the trigonal prismatic geometry. So far, the closest one can get to the trigonal prism with this type of ligand appears in a Hg^{II} complex, whose coordination sphere is a trigonal prism distorted as sketched in **9** due to the strain of the hexaazacyclooctadecane macrocycle, with a trigonal prismatic measure of 2.60.[81]

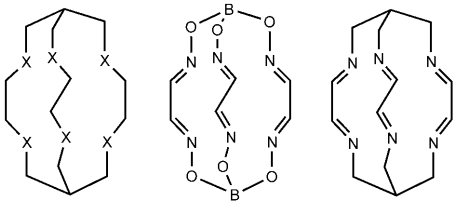
9

Extended tripodal ligands: The extended tripodal ligands with topologies **6** behave similarly to those based on tridentate macrocycles discussed above. Those with a saturated skeleton (**6a**) are quite flexible, and the two sets of donor atoms related through the trigonal axis can adapt to the octahedral coordination, as shown by the small values of the generalized coordinates ($\varphi_{OC\rightarrow TP}$ in the range 9–21%). It must be noted, however, that the structural data found with these ligands feature only Cr^{III}, Co^{II}, Co^{III}, or Ni^{II} as central ions. The presence of double bond character in ligands **6b–d** forces coordination geometries more twisted from the octahedron, giving trigonal prismatic complexes with Mn^{II}, Co^{II}, Zn^{II}, or Cd^{II} as central metals. The best trigonal prisms are $[Co^{II}(\mathbf{6c})]$ and $[Zn^{II}(\mathbf{6c})]$,[82] whereas the most octahedral ones are Fe^{II} and Ni^{II} complexes.



6a **6b** **6c** **6d**

Encapsulating ligands: The encapsulating ligands **7** are conceivably the most rigid frameworks for a trigonal prismatic set of six donor atoms. However, the saturated ligands **7a** such as sepulchrate (X = NH) can still host metal ions in an octahedral coordination (Figure 6). Among the most octahedral complexes with ligands **7a**, the predominance of Co^{III} is overwhelming, complemented with some examples of Cr^{III}, Fe^{II}, Ni^{II}, Ru^{II}, Ru^{III}, Rh^{III}, and Pt^{IV} derivatives. On the other hand, the geometries closest to the trigonal prism obtained



7a **7b** **7c**

with those ligands ($\varphi_{OC\rightarrow TP}$ in the range 55–100%) are found for V^{IV}, Mn^{II}, Cu^{II}, and Zn^{II}. The related ligand with propyl groups linking the donor atoms instead of ethyl groups also shows a wide range of twist angles, from practically octahedral to perfectly trigonal prismatic ($8 < \varphi_{OC\rightarrow TP} < 100\%$), the latter corresponding to Cd^{II} and Hg^{II} complexes.

The more rigid tris(glyoximato)bis(boronate) ligands **7b** clearly give a large number of trigonal prismatic structures, as can be appreciated in Figure 6, precluding rotation angles closer to the octahedron ($\varphi_{OC\rightarrow TP} > 48\%$ in all cases). The most trigonal prismatic compounds have Fe^{II}, Fe^{III}, Co^{II} and Ru^{III} as central ions. Although structures with sepulchrene ligands **7c** are not known, we will use that skeleton in our computational study below to facilitate comparison with the saturated analogue **7a**.

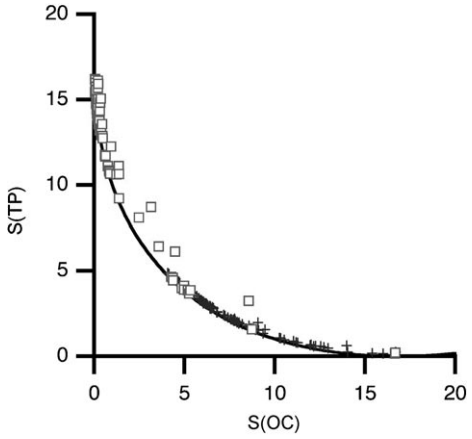


Figure 6. Coordination spheres of transition metal complexes with sepulchrate ligands of types **7a** (squares) and **7b** (crosses), plotted in a shape map relative to the octahedron and the trigonal prism. A zero value of S(OC) corresponds to a regular octahedron, and a zero value for S(TP) to an ideal trigonal prism; the continuous line represents the minimal distortion interconversion pathway.

Discussion and overview: The degree of twisting of the coordination sphere presented by complexes with different hexadentate ligands is graphically summarized in Figure 7. There it can be seen that those ligands exert only a moderate control on the metal coordination sphere. The most we can expect from some of those ligands is to restrict the Bailar angle within certain limits. For instance, the most favorable ligand for trigonal prismatic coordination is **7b**, which guarantees geometries that are at least nearly halfway along the path to the trigonal prism.

Not unexpectedly, within a family of topologically related ligands, those containing an unsaturated skeleton favor rotation angles closer to the trigonal prism, probably a manifestation of an enhanced rigidity. Compare, for example, the degree of trigonal twist of the saturated ligands **5a** with that of the unsaturated analogues **5b**, or the range of trigonal twists obtained with **6a** with that for **6b–d**.

The wide range of twist angles found for a given ligand clearly tells us that the nature of the central metal and, pos-

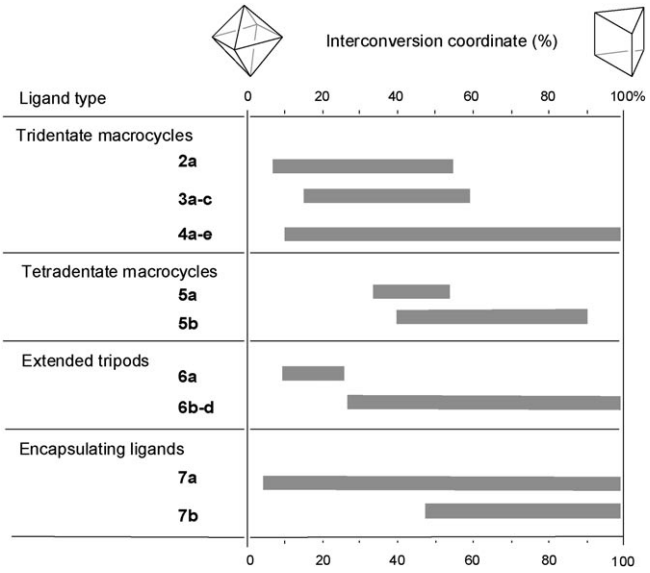


Figure 7. Ranges of coordination geometries found for transition metals with different multidentate ligands, represented by the interconversion coordinate from the octahedron to the trigonal prism.

sibly, other steric or electronic effects are important for achieving the trigonal prismatic geometry. A preliminary analysis of the metal centers found in the two extremes of the accessible degrees of twisting for each family of ligands indicates that the most trigonal-prismatic complexes are formed by V^{IV}, Zr^{II}, Hf^{II}, Mn^{II}, Fe^{III}, Co^{II}, Cu^{II}, Ag^{I}, Zn^{II}, Cd^{II}, and Hg^{II}. On the other hand, the most octahedral compounds are found for Cr^{III}, Ru^{II}, Co^{III}, Rh^{III}, Ni^{II}, and Pt^{IV}. Finally, for Fe^{II} and Ru^{III} we have found examples in the two extremes of the accessible portion of the Bailar pathway.

Qualitative Orbital Analysis

Trigonal prism—octahedron dichotomy: a Jahn–Teller approach: To try to establish the preferences between octahedral and trigonal-prismatic coordination of metal complexes with different electron configurations we resort to the d-block orbital Walsh diagram along the Bailar interconversion pathway. Here we consider as a starting point the trigonal prism, the preferred geometry for covalent complexes without d electrons.[12] The Walsh diagram shown in Figure 8, obtained from our DFT calculations, is essentially coincident to that reported earlier by Hoffmann and coworkers, based on extended Hückel calculations.[27] In the trigonal-prismatic geometry the d orbitals are split into three sets (Figure 8). While the a'_1 orbital is strictly nonbonding (disregarding π interactions), the 2e′ and e″ sets have different degrees of σ-antibonding character. The antibonding character of the 2e′ set, though, is curtailed by mixing with the high-lying orbitals of the same symmetry involving the empty metal 3e′ (p_x, p_y) ones (Figure 9). At the same time, mixing of 1e′ and 2e′ enhances the bonding character of the former.

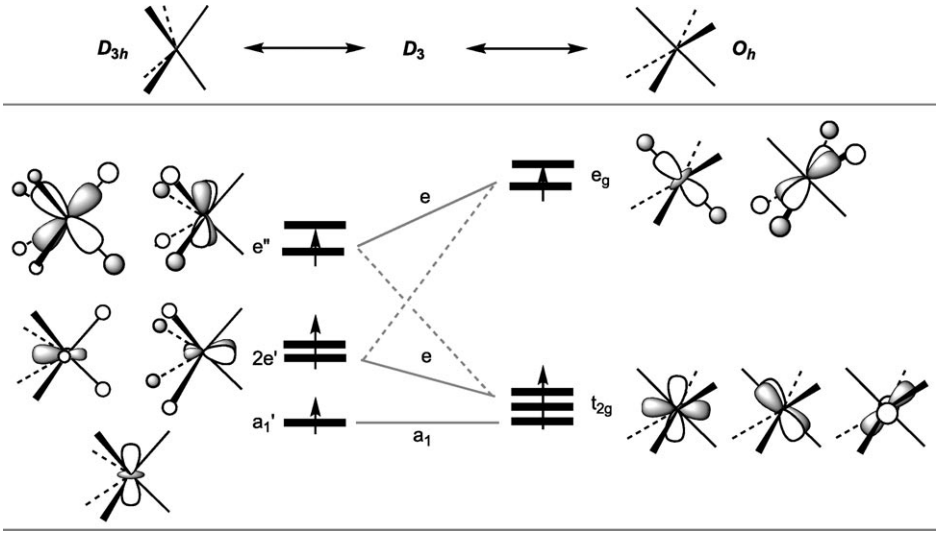


Figure 8. Correlation diagram for the d-block orbitals between the trigonal prism (left) and the octahedron (right). The orbital occupation shown corresponds to a high spin d^4 configuration, characteristic of Cr^{II} and Mn^{III}.

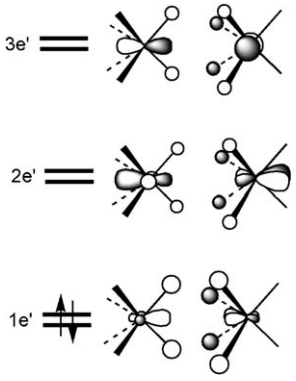


Figure 9. Schematic depiction of the three sets of molecular orbitals of E' symmetry in the trigonal prism with hybridization. The 1e′ set is essentially composed of ligand lone pair orbitals.

We note that mixing of 1e′ and 2e′ is forbidden in the octahedral geometry because they have different symmetries (T_{1u} and T_{2g}, respectively). As a consequence, 1e′ has less metal–ligand bonding character in the octahedron than in the trigonal prism. The outcome is a preference for the trigonal-prismatic geometry for complexes with d^0, d^1, or low-spin d^2 electron configurations, in which 2e′ is empty. This preference is more pronounced for highly covalent metal–ligand bonds (i.e., a metal in a high oxidation state and ligands with donor atoms of low electronegativity).[12] For other electron configurations, the preference for the trigonal prism is fine-tuned by the opposing effect that occupation of the 2e′ and e″ orbitals have on the relative energy of the trigonal prism and the octahedron (Figure 8).

For electron configurations other than d^0, d^1, or low-spin d^2, the twist of the trigonal prism towards the octahedron can be explained as a second-order Jahn–Teller (SOJT) effect. A SOJT effect produces a stabilization of the molecule through mixing of nearby occupied and empty orbitals that become of the same symmetry species upon distortion. Symmetry rules require a SOJT distortion mode[83] to belong to a symmetry representation that is contained in the direct product of the symmetry representations of the orbitals being mixed. Furthermore, for a symmetry-allowed distortion mode, a substantial stabilization results only if those orbitals are close in energy and have the right topology,[84] which means that they must have large coefficients in neighboring atoms whose relative positions change upon distortion.

According to the symmetry rules that govern first- and second-order Jahn–Teller effects, the allowed distortion modes for configurations involving the $a'_1/2e'$ and $2e'/e''$ sets are those given in Table 1. The $A"_1$ mode, corresponding to the Bailar twist toward the octahedron, is expected for configurations involving a higher number of electrons in the 2e′ than in the e″ orbitals. The orbital mixing leading to a stabilization by twisting the trigonal prism is schematically shown in Figure 10.

Table 1. Jahn–Teller distortion modes associated with different orbitals of the d-block in trigonal-prismatic complexes.

	Orbital(s)	Mode	Description[a]	Symmetry descent
second order	2e′/e″	A''_1	Bailar twist	D_3
		A''_2	pyramidal truncation	C_{3v}
		E″	*trans* stretching	C_2
		E″	Ray–Dutt twist	C_2
first order	e′	E′	*cis* stretching	C_{2v}
	e″	$A'_1 + A'_2 + E'$	*cis* stretching	C_{2v}

[a] See ref. [85].

The stabilization resulting from the SOJT distortion that converts the trigonal prism into an octahedron is expected to depend on the difference in population between the 2e′ and e″ orbitals, which we will represent by δ from here on. All d^n configurations in trigonal-prismatic coordination can therefore be classified according to the difference in occupation of those two orbital sets (Table 2). Accordingly, we expect the trigonal prismatic geometry to be most easily attainable for complexes of metal ions with $\delta = 0$, that is, with electron configurations d^0, d^1, low-spin d^2, high-spin d^5 or d^6, and d^{10}. In contraposition, a strong drive toward the octahedron should be expected for complexes with, among others, high-spin d^3, low-spin d^6 or d^8 configurations ($\delta \geq 2$).

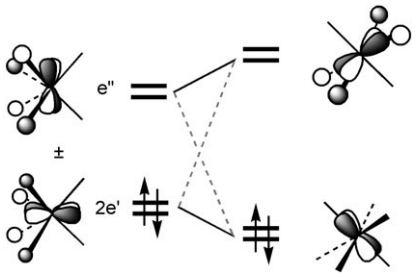


Figure 10. Mixing of the 2e′ and e″ d-block orbitals associated with the A''_1 distortion (Bailar twist) of a trigonal prism due to the second-order Jahn–Teller effect expected when e″ is less populated than 2e′.

Table 2. Preference for octahedral or trigonal-prismatic geometry for different d^n configurations, classified according to the difference in occupation between the 2e′ and e″ orbital sets in the trigonal-prismatic geometry (δ).[a]

Trigonal prism ← → Octahedron

δ:	0	1	2	3	4
	d^0, d^1				
	l.s. d^2	h.s. d^2			
		l.s. d^3	h.s. d^3		
		h.s. d^4	l.s. d^4		
	h.s. d^5			l.s. d^5	
	h.s. d^6				l.s. d^6
		h.s. d^7		l.s. d^7	
			d^8		
		d^9			
	d^{10}				

[a] h.s. = high spin; l.s. = low spin.

To check the predictive character of these rules, we analyzed the structures of sepulchrate complexes **7a**, in which the ligand is supposed to geometrically favor the trigonal prism. In fact the uncoordinated ligands are already preorganized with a practically trigonal-prismatic arrangement of the donor atoms.[86] On the other hand, a N_6 donor set is expected to favor a high-spin configuration for most divalent 3d transition metals. The structural data found in a CSD search were grouped according to the difference in occupation of the 2e′ and e″ orbitals δ, and the average generalized coordinate $\varphi_{OC\rightarrow TP}$ for each group of structures is represented in Figure 11 as a function of δ. It is clearly seen that for those configurations for which δ is larger than one, the SOJT effect favors rotation of the trigonal prism toward the octahedron. If, on the contrary, δ is zero or one, the complex is close to the trigonal prism. It must be stressed that the average generalized coordinates of the nearly 40 compounds with δ values of two and four have rather small standard deviations, indicating how strong the constraint for a nearly octahedral coordination is for those electron configurations.

It is now clear that the distribution of trigonal-prismatic geometries throughout the transition-metal series (Figure 1) hides a more elaborate distribution based on the electron configuration of the metal atom, hence on its oxidation state. We have therefore carried out a systematic analysis of all transition-metal six-coordinate compounds in the CSD according to metal and oxidation state. A full listing of all

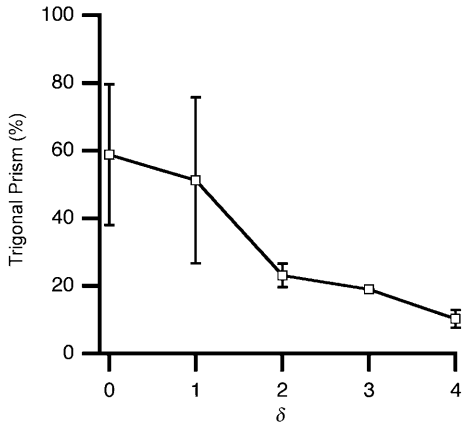


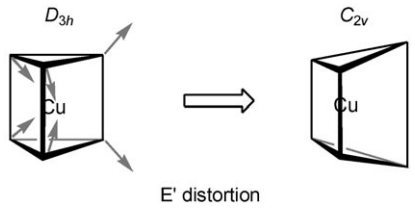
Figure 11. Average generalized coordinate along the Bailar path from the octahedron to the trigonal prism for sepulchrate complexes **7a**, as a function of the difference in occupation of the 2e′ and e″ orbital sets (δ). The bars indicate the standard deviation.

molecules found to be nearly trigonal prismatic (see Computational Details for the criteria adopted for assigning a "nearly trigonal-prismatic" geometry), classified by metal and oxidation state, is available as Supporting Information. The most relevant trends found are:

a) The largest part (88.6%) of the metal atoms identified as trigonal prismatic correspond to electron configurations for which the 2e′ and e″ orbitals are equally occupied (i.e., $\delta = 0$) and, together with the $\delta = 1$ configurations make up 96.4% of the trigonal prisms.
b) All the trigonal prisms with δ higher than one have ligands belonging to one of three families: i) non-innocent ligands such as catecholate or dithiolates, ii) between two and four π-acid ligands, or iii) tris(glyoximate)bis(boronate) ligands **7b**.
c) The trigonal prism is quite common among the molybdenum and tungsten complexes in oxidation states +4, +5, and +6 (i.e., electron configurations d^2, d^1, and d^0). In contrast, practically no trigonal prisms are found for lower oxidation states, with the only exceptions of compounds with two to four π-acid ligands in a molybdenum(III)[87] and several molybdenum(II) and tungsten(II) complexes.[43,44] These unusual d^4 diamagnetic trigonal prisms have been the object of an early theoretical study.[88] In the case of the $[M(dithiolene)_2(CO)_2]^{2-}$ complexes (M = Mo, W), DFT calculations reported by Fomitchev et al. have shown that reduction of the M^{IV} parent complexes introduces the extra electrons in the π system of the non-innocent ligands rather than reducing the metal.[87]
d) Among the early transition metals (Groups 3–5), the trigonal prism is relatively common, but only in the high oxidation states corresponding to d^0, d^1, and d^2 electron configurations. Metals of these periodic groups with other electron configurations are not found in trigonal-prismatic environments, fulfilling the expectations set out in Table 2.

e) An interesting example of the influence of the electron configuration on the stereochemical choice is found in a compound that bears one Mn^{II} and one Mn^{IV} center with ligand **4c**. While the former is trigonal prismatic, the latter presents a nearly octahedral coordination.[89]

Bond-stretch distortions: In a recent communication,[28] we have shown that the $(a'_1)^2(2e')^4(e'')^3$ electron configuration of a trigonal-prismatic copper(II) complex is susceptible to a first-order Jahn–Teller distortion associated to the inhomogeneous occupation of e″. Such a distortion corresponds to an E′ mode (see Scheme 2 and Table 1), which induces the



Scheme 2.

simultaneous elongation of two *cis* and shortening of the other four bonds or vice versa,[85] with a possible additional SOJT distortion of the resulting C_{2v} complex that implies the asymmetrization of the two long metal–ligand bonds.[28] In our preliminary communication we provided evidence for the presence of the *cis* Jahn–Teller distortion in a variety of Cu^{II} compounds, including minerals and metalloenzymes. As an example, we show in Figure 12 the coordination polyhedron of copper in Sr_3CuRhO_6.[90]

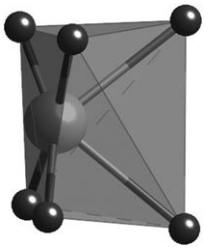


Figure 12. *cis*-stretched trigonal prism of oxygen atoms around a Cu^{II} ion in the crystal structure of Sr_3CuRhO_6.[90]

For intermediate geometries along the Bailar interconversion path (D_3 point group), both the *cis* and *trans* distortions are Jahn–Teller active, as theoretically predicted and confirmed by structural data for Cu^{II} compounds.[28] One should expect the same distortions to be present in high-spin complexes of d^4 ions such as Mn^{III} or Cr^{II}. Since all Cr^{II} centers in the CSD have been found to be nearly octahedral (octahedral shape measures smaller than 2.0), we search for the bond-stretch distortion among the Mn^{III} compounds. In our survey of the CSD we found this ion to appear essentially with octahedral geometry. The only mononuclear Mn^{III} compounds whose coordination spheres are midway between the octahedron and the trigonal prism are two sarcophagine (**7c**) complexes,[76,77] with a twisted metaprismatic geometry ($\varphi_{OC\rightarrow TP}=55$ and 50%, respectively). Even if those structures are still far from the trigonal prism, the one that is closest exhibits the expected E′ distortion, with two *cis*-coordinated nitrogen atoms presenting distances to the metal 0.10 Å longer than the other four, despite the topological equivalence of the six donor atoms. As found for Cu^{II} complexes, both *cis* and *trans* distortions can be found in Mn^{III} structures along the Bailar path, with the former appearing even in a practically octahedral complex,[91] at $\varphi_{OC\rightarrow TP}=17\%$. It must be said, however, that the *trans* distortion is more common among compounds with trigonal-prism measures higher than 11.0. Conversely, a *trans* distorted compound can be found with an octahedron significantly twisted along the Bailar path,[92] with $\varphi_{OC\rightarrow TP}=42\%$.

Computational Study

The third section of the work reported here consists on density functional calculations for selected metal complexes with several hexadentate ligands that are supposed to enforce trigonal prismatic coordination. The aim of such a computational study is to validate the qualitative trends found in the previous section and to set forth a general framework for the understanding of the stereochemical choice between the octahedron and the trigonal prism. First we consider a family of $[M(tacn)_2]$ complexes, in which the ligands impose a trigonal symmetry, and calculate the energy profile along the Bailar path for several metal ions to calibrate the effect of the electron configuration on the stereochemical preference. We then analyze several ligands with varying topologies and degrees of rigidity to test their ability to enforce different degrees of twisting along the octahedral to trigonal prism pathway in their Mn^{III} complexes. Finally, we study the extent of the twisting toward the trigonal prism that different metal ions may undergo with selected hexadentate ligands.

The potential energy profiles calculated for $[M(tacn)_2]$ complexes are shown in Figure 13, where M is one of several metal ions with different electron configurations: Ti^{IV} (d^0), V^{IV} (d^1), Mn^{IV} (d^3), Mn^{III} (high- and low-spin d^4), Mn^{II} (high- and low-spin d^5), Co^{III} (low-spin d^6), Co^{II} (low-spin d^7), Ni^{II} (d^8), Cu^{II} (d^9), and Zn^{II} (d^{10}). Our first observation is that the d^0 and d^1 ions have a clear preference for the trigonal prism, even if the potential energy curve is rather shallow. Other configurations for which δ is zero (d^{10} and high-spin d^5) have a minimum at a nearly octahedral geometry, with quite shallow potential energy curves. Therefore, it should be relatively easy to force metal ions with those configurations into a trigonal-prismatic coordination by using suitable ligands. For the rest of the electron configurations we can see that the octahedron is also the preferred geome-

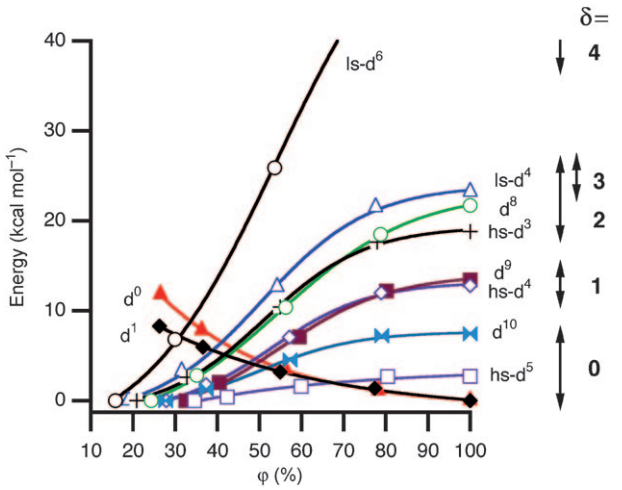
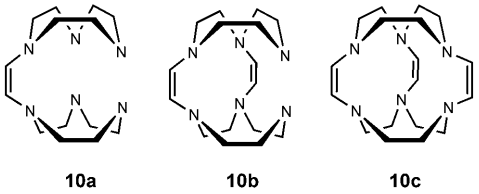


Figure 13. Calculated energies along the Bailar pathway from the pseudo-octahedral to the trigonal-prismatic geometry of $[M(tacn)_2]$ complexes with different electron configurations. The numbers given at the right are the differences in orbital occupation δ. The curves for low-spin Mn^{II} and Co^{II} ($\delta=3$), practically coincident with that for the low-spin d^4 case, are not shown for clarity.

try, and that the relative energy of the trigonal prism increases with δ. When this parameter is two or higher, the relative energy of the prism is so high that we would not expect ligand design to overcome this electronic energy barrier.

The calculated potential energy curves thus support our qualitative reasoning based on molecular orbital arguments (Table 2). It is also remarkable that the potential energy profiles calculated for such simple model molecules summarize so well the frequency of trigonal-prismatic structures experimentally found in a variety of complexes, as can be seen by comparing Figure 11 and 13.

For the second part of our computational study we have chosen Mn^{III} in its high-spin state[93] for two reasons. On one hand, because the analysis of structural data and qualitative MO arguments in the previous sections indicate that a high-spin d^4 configuration has an intermediate resistance to adopt a trigonal-prismatic geometry (Figure 13). On the other hand, because such an electron configuration is amenable to a bond-stretch Jahn–Teller distortion that could lead to either *cis*- or *trans*-distorted isomers, as found earlier for the d^9 Cu^{II} ion.[28] As ligands we have chosen a series of strapped bis-macrocyclic derivatives, with either saturated (**3a**) or unsaturated (**10a–c**) straps, as well as sepulchrate ligands with saturated (**7a**) or unsaturated (**7c**) skeletons. We



10a **10b** **10c**

have also optimized the structure of a complex with two independent macrocycles, $[Mn(tacn)_2]^{3+}$, in which the ligand-imposed trigonal coordination allows in principle different degrees of rotation along the Bailar path, to compare with the results of the strapped ligands.

The results of our calculations for Mn^{III} complexes are summarized in Table 3. Comparison of the optimized structures of the sepulchrate complex (**7a**) with the experimental structures of analogous compounds[76,77] shows an excellent agreement in the short Mn–N distances (data provided as Supporting Information) and in the degree of Bailar twist, while the Jahn–Teller distorted Mn–N distances are somewhat overestimated in our calculations. The analysis of all optimized structures (Table 3) with different ligands allows us to draw several conclusions:

a) The donor atoms of the two independent tridentate macrocyclic ligands in $[Mn(tacn)_2]^{3+}$ form a nearly octahedral structure. A slight rotation toward the trigonal prism (28%) can probably be attributed to an avoided steric repulsion between the H atoms at the two ligands.
b) As expected, these high-spin d^4 complexes give minima with either *cis* or *trans* bond lengthening distortions. In several cases we have been able to locate two minima at similar energies corresponding to the two types of distortions, in what could be appropriately considered as bond-stretch isomers.[94]
c) Linking the two macrocyclic tacn ligands by an ethyl bridge (**3a**) introduces some degree of rigidity that forces a coordination sphere intermediate between the octahedron and the trigonal prism.

Table 3. Generalized coordinate along the octahedron-trigonal prism path ($\varphi_{OC\rightarrow TP}$, in %), type of Jahn–Teller distortion, and metal–ligand bond lengths in optimized high-spin d^4-Mn^{III} complexes ($\delta=1$).

Compound	Ligand	$\varphi_{OC\rightarrow TP}$	Distortion	Energy[a]	Short M–N [Å]	Long M–N [Å]	
$[Mn(tacn)_2]^{3+}$	**2a**	28.1	*trans*		2.10–2.12	2.313	2.314
$[Mn\{(tacn)_2C_2H_4\}]^{3+}$	**3a**	47.9	*trans*[c]	0	2.09–2.13	2.330	2.343
		54.8	*cis*[b]	+2.3	2.09–2.19	2.276	2.296
$[Mn\{(tacn)_2C_2H_2\}]^{3+}$	**10a**	61.6	*trans*[c]	0	2.03–2.07	2.339	2.345
		72.6	*cis*[b]	+0.2	2.11–2.16	2.324	2.321
$[Mn\{(tacn)_2(C_2H_2)_2\}]^{3+}$	**10b**	78.2	*trans*	+0.6	2.11–2.15	2.306	2.308
		78.4	*cis*[c]	0	2.10–2.15	2.301	2.328
$[Mn\{(tacn)_2(C_2H_2)_3\}]^{3+}$	**10c**	79.4	*cis*[b]		2.09–2.12	2.284	2.284
$[Mn(sepulchrate)]^{3+}$	**7a**	43.0	*trans*		2.07–2.13	2.305	2.325
$[Mn(sepulchrene)]^{3+}$	**7c**	83.4	*cis*		2.03–2.07	2.245	2.245
$[Mn(cyclenMe_2py_2)]^{3+}$	**5c**	83.1	*cis*		2.06–2.22	2.403	2.409

[a] Relative energy of the *cis* and *trans* bond-stretch isomers (kcal mol^{-1}). [b] The two long M–N bonds correspond to the two N atoms connected through an ethyl bridge. [c] The two long M–N bonds correspond to unstrapped N atoms.

d) The use of an unsaturated ethenyl link between the two macrocycles (**10a**) favors higher degrees of rotation towards the trigonal prism in comparison with a saturated bridge.
e) Going from one (**10a**) to two straps (**10b**) between the macrocycles favors structures closer to the trigonal prism. However, the change from the double-strapped to the triple-strapped (**10c**) ligand has little effect on the degree of trigonal rotation.
f) The sepulchrate ligand **7a** is not as efficient as one would think on forcing trigonal-prismatic environments, which do not go much farther than a 50% of the Bailar path from the octahedron to the prism. We must recall, however, that the free sepulchrate ligands[86] are already preorganized with metaprismatic N_6 donor sets ($\varphi_{OC\rightarrow TP}$ of up to 60% in diaminosarcophagine), indicating that the deviation from the trigonal prism in the Mn^{III} complex should be essentially attributed to the electronic preference of the metal atom.
g) Unsaturation of the sepulchrate ligand leading to sepulchrene **7c** seems to be the most effective strategy to force a trigonal prismatic coordination of metal ions whose electron configuration favor an octahedral geometry. This result is consistent with the disribution of experimental structures throughout the Bailar path with the related ligand **7b** (Figure 7).
h) The tetradentate macrocycle cyclen supplemented with two unsaturated coordinating arms (**5c**) is another very good choice for forcing trigonal-prismatic coordination.

If we compare now the optimized structures of manganese complexes with sepulchrate ligands **7a** and **7c** in different oxidation states (Table 4), we see that the degree of twisting toward the trigonal prism increases in the order $Mn^{II} > Mn^{III} > Mn^{IV}$, in keeping with their corresponding δ values (0, 1, and 2, respectively). We can also see that Mn^{III} complexes may present either *trans* or *cis* Jahn–Teller distortions, whereas the Mn^{II} and Mn^{IV} analogues have all metal–ligand distances similar. Such a behavior is consistent with the high spin configurations expected from the MO diagram (Figure 1), for which only Mn^{III} has different occupations in the two e" orbitals that give raise to the *cis* Jahn–Teller distortion: $(a'_1)^1(2e')^2$ for Mn^{IV}, $(a'_1)^1(2e')^2(e")^1$ for Mn^{III} and $(a'_1)^1(2e')^2(e")^2$ for Mn^{II}.

It is remarkable that the calculated manganese complexes with the sepulchrene ligand **7c** in different oxidation states span practically the same range of twisting ($55 \leq \varphi_{OC\rightarrow TP} \leq 100$%, Table 4) as the experimental structures with the related unsaturated ligand **7b** ($48 \leq \varphi_{OC\rightarrow TP} \leq 98$%; Figure 6, crosses). It can also be seen (see the Supporting Information) that the optimized structure of the [Mn(sepulchrate)]$^{2+}$ ion is in excellent agreement with its experimental counterpart.[77]

An optimized isoelectronic Cr^{II} compound, for which there is no experimental counterpart, presents essentially the same structural features: a very similar degree of twisting and a bond-stretch Jahn–Teller distortion. Still more interesting, a model low-spin Co^{II} compound (Table 4) also has a similar structural behavior in spite of its different electron configuration. Such distortions have been already reported in the experimental structure of d^7-cobalt(II) compounds.[95] In short, metals with high-spin d^4 and low-spin d^7 electron configurations show a similar Jahn–Teller behavior to that of the previously studied d^9-copper(II) compounds.[28]

The last model complexes optimized were [Fe(sepulchrate)]$^{3+}$ and [Fe(sepulchrate)]$^{2+}$ in both their high- and low-spin states, since several Fe^{II} complexes with sepulchrate ligands have been found to be either diamagnetic or high spin in the solid state, but to present spin equilibria in solution.[93,96] A look at Table 2 leads to the qualitative prediction that a change in spin state for those complexes should go hand in hand with a significant change in the twist angle. Since no crystal structure has been reported for those compounds, geometry optimization for the two spin states should provide a reasonable estimate of the amount of twisting that should accompany the spin crossover. Our calculations (Table 5) estimate a twist of about 25° for both Fe^{III} and Fe^{II} complexes toward the trigonal prism in the high spin state. Furthermore, the calculated enthalpy difference between high- and low-spin states is of the same order of magnitude as that deduced from experimental data for Fe^{II} ($1000\ cm^{-1}$).[93] Similarly, the higher energy difference between the high- and low-spin states found for Fe^{III} is consistent with the experimental finding that its sepulchrates are of low spin, whereas the Fe^{II} analogues show spin equilibria.

Table 4. Shape parameters, type of Jahn–Teller distortion, and metal–ligand bond lengths in optimized metal complexes with encapsulating ligands. All compounds were calculated in their high spin states, except for Co^{II} ($S = 1/2$).

Ligand	Complex	δ	$\varphi_{OC\rightarrow TP}$ [%]	Distortion	Short distances [Å]	Long distances [Å]
10c	$[Mn\{(tacn)_2(C_2H_2)_3\}]^{3+}$	1	79.4	*cis* [a]	2.09–2.12	2.284
	$[Cr\{(tacn)_2(C_2H_2)_3\}]^{2+}$	1	81.9	*cis* [a]	2.13–2.16	2.381
	$[Co\{(tacn)_2(C_2H_2)_3\}]^{2+}$	3	70.7	*cis* [a]	2.04–2.10	2.311
7a	$[Mn(sepulchrate)]^{2+}$	0	55.3	no	2.28–2.29	
	$[Mn(sepulchrate)]^{3+}$	1	43.0	*trans*	2.07–2.13	2.305, 2.325
	$[Mn(sepulchrate)]^{4+}$	2	24.0	no	2.11	
	$[Cu(sepulchrate)]^{2+}$	0	52.6	*cis*	2.06–2.21	2.435
7c	$[Mn(sepulchrene)]^{2+}$	0	99.3	no	2.181	
	$[Mn(sepulchrene)]^{3+}$	1	83.4	*cis*	2.03–2.07	2.245
	$[Mn(sepulchrene)]^{4+}$	2	55.2	no	2.04	

[a] The two long M–N bonds correspond to the two N atoms connected through an ethyl bridge.

Conclusions

We have given structural, theoretical, and computational evidence that hexadentate ligand design may be instrumental in creating a trigonal-prismatic coordination sphere around a

Table 5. Generalized coordinate along the Bailar path, twist angle, relative energies, and metal–ligand bond lengths in optimized iron sepulchrate complexes in their high- and low-spin states.

Complex	$\varphi_{OC\rightarrow TP}$ [%]	θ [°]	Energy [cm^{-1}]	Fe < C-N [Å]
h.s.-[Fe(sepulchrate)]$^{3+}$	57.2	26	1680	2.20
l.s.-[Fe(sepulchrate)]$^{3+}$	14.2	52	0	2.06–2.07
h.s.-[Fe(sepulchrate)]$^{2+}$	54.7	28	346	2.25
l.s.-[Fe(sepulchrate)]$^{2+}$	13.5	53	0	2.08

transition-metal ion, except for some specific electron configurations for which it represents a high-energy stereochemistry.

The simple rule deduced to predict the preference for an octahedral or a trigonal-prismatic structure focuses on the occupation of the metal d-block orbitals, which appear in the energy order $a'_1 < 2e' < e''$. In essence, all metal complexes can be classified in one of three groups according with the electron configuration they would have in a trigonal-prismatic environment, depending on δ, the difference in occupation between 2e′ and e": a) when δ is zero, there is a preference for the trigonal prismatic geometry or a rather flat potential energy surface for the Bailar twist; b) when δ is one or two, the octahedral geometry is preferred, but the higher energy of the trigonal-prismatic coordination can be overcome by relatively rigid hexadentate ligands, and c) when δ is three or four, the trigonal-prismatic geometry is highly unfavorable and even rigid sepulchrate ligands are unable to force that stereochemistry.

In nearly-trigonal prismatic coordination, metal ions with high-spin d^4, low-spin d^7 or d^9 electron configurations present bond-stretch Jahn–Teller distortions that may affect either two *cis* or two *trans* metal–ligand bonds. Our computational results predict the possibility of bond-stretch isomerism in those complexes.

The commonplace that trigonal-prismatic coordination is rare has to be refined taking into account the findings of this work. Thus, trigonal prisms are indeed non-existing in the molecular realm (as far as their structural characterization is concerned, at least) for Cr, Rh, Ir, Pd, Pt, and Au. In contrast, the proportion of trigonal prisms among the experimental structures of Mo, W, Tc, and Re is quite large in their highest oxidation states, while none is found for oxidation states +3 or lower. Our computational results for manganese complexes also indicate a strong oxidation state dependence of the degree of trigonal twist, which increases in the order $Mn^{II} > Mn^{III} > Mn^{IV}$.

There are some interesting prospective developments regarding trigonal prismatic complexes. First, the metals and oxidation states for which no trigonal-prismatic coordination have been found constitute challenging synthetic targets. Second, given the large differences in Bailar twist expected for the same metal in different oxidation states, trigonal-prismatic units are appealing building blocks for potential molecular devices with electrochemically or redox-controlled rotational motion. Similarly, the differences in Bailar twist angle shown by some metal ions in their high- and low-spin states, makes them appealing for temperature- or light-driven magneto-mechanical processes associated to spin crossover behavior, of potential application in molecular machinery.

Although we have not paid any attention in this paper to chirality, we must not forget that the twisted trigonal prisms have at most D_3 symmetry, their degree of chirality varies along the Bailar pathway, with a maximum at an intermediate degree of twisting,[97] and chirality control could be achieved by a rational choice of the ligand and the electron configuration of the metal.

With the exception of the complexes of Fe^{II} and Ru^{II} with unsaturated sepulchrates that deserve a closer theoretical examination, a strongly coercive rule that stems from our combined theoretical–structural analysis suggests that metal ions with at least two more electrons in the 2e′ orbitals than in the e″ set should abandon all hope of reaching a trigonal-prismatic coordination by entering into a sepulchrate ligand.

Lasciate ogni speranza, voi ch'entrate.
Dante Alighieri, *Divina Commedia* (Inferno, III, 9).

Computational Details

DFT calculations were carried out with Gaussian03,[98] using the B3LYP hybrid functional[99] and a triple-ζ all-electron Gaussian basis set[100] supplemented with polarization functions for the metal atoms. All calculated structures reported in Tables 3 and 4 were characterized as true minima through vibrational analysis. Structural searches were carried out in the CSD,[29,101] version 5.29 with four updates covering a total of 494228 structures. Continuous shape measures[29,101] of experimental and calculated structures were obtained with the SHAPE code.[102] The Walsh diagram and qualitative orbital schemes in Figure 8 and 9 are simplified versions of the Kohn–Sham orbitals resulting from our DFT calculations.

For the analysis of the distribution of trigonal-prismatic complexes in the CSD,[103] we carried out a search for all six-coordinate transition-metal atoms with σ-bonded ligands only. A total of 77023 crystallographically independent six-coordinate metal centers were found, of which 795 with trigonal-prismatic shape measures of less than 4.0 have been selected as nearly trigonal prismatic (see the Supporting Information), equivalent to twist angles θ smaller than 28° for structures along the Bailar path. Those metal centers have been then classified according to their oxidation states in order to analyze the trigonal prismacity as a function of the electron configuration. The same criterion has been used to identify some trigonal-prismatic Mo and W sites in metalloenzymes from the Protein Data Bank (PDB). Exploratory searches for trigonal-prismatic centers in extended solids were carried out in the ICSD from Karlsruhe.[104]

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