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Shape and Spin State in Four-Coordinate Transition-Metal Complexes: The Case of the d^6 Configuration

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Abstract: Generalized polyhedral interconversion coordinates are defined within the framework of Avnir's continuous shape measures. The application of such interconversion coordinates to the study of the potential energy surfaces that define the stereochemical choice in four-coordinate transition metal complexes with different spin states is presented, and the correlation between potential energy curves and distribution of experimental structures along the tetrahedron to square interconversion path is shown for the case of the d^6 transition-metal complexes.

Keywords: shape measures • solid-state structures • spin states • symmetry measures • transition metals

Introduction

Four-coordinate complexes are widespread throughout the transition-metal series and a knowledge of their stereochemical preferences is a must for controlling their architecture and properties. The two most symmetric structures for a four-coordinate complex are the tetrahedron (T_d symmetry), and the square (D_{4h} symmetry). In a recent paper[1] we have analyzed the structures of more than 13000 four-coordinate transition-metal centers from the point of view of their tetrahedral and square shape measures. For the specific case of d^6 four-coordinate complexes, it has been stated that they adopt preferentially a *cis*-divacant octahedral (or sawhorse) structure,[2] and theoretical geometry optimization on several compounds seems to support this assertion.[2,3] However, the distribution of four-coordinate d^6 structures found indicates that tetrahedra and square-planar structures are more common than the sawhorse, even if a non-negligible number of structures are significantly distorted from these two ideal shapes. In fact, different geometrical preferences are expected for different spin states. According to Poli,[4] the high-spin configuration ($S=2$) adopts the tetrahedral geometry, whereas the intermediate spin one ($S=1$) appears with square-planar structures. However, no systematic theoretical study of the potential energy curves for the tetrahedron-square interconversion of transition-metal complexes in their different spin states has been reported so far. A better knowledge of the general form of those potential energy curves should allow us to explore the expected correspondence between potential energy surface and statistical distribution of experimental structures in four-coordinate complexes.

Within the framework of the continuous symmetry and shape measures (abbreviated CSM and CShM, respectively) proposed by Avnir et al.,[5] one can calibrate how distorted is a given coordination sphere from the tetrahedron and from the square by means of the corresponding shape measures, $S(T_d)$ and $S(D_{4h})$.[6] A zero value of $S(T_d)$, for instance, indicates a perfectly tetrahedral geometry. For structures that are close neither to the tetrahedron, nor to the square, one can also measure how far (or how close) it is from the minimum distortion interconversion path between these two shapes, that happens to be the well known spread distortion.[7] This is done with a path deviation function proposed previously by us and briefly described below.

Herein, we describe a generalized polyhedral interconversion coordinate that makes use of minimal distortion paths between two shapes with the same number of atoms. Such a coordinate can be applied in a common scale to any pair of shapes, independent of their number of atoms. It is then used to analyze the potential energy surfaces of the three al-

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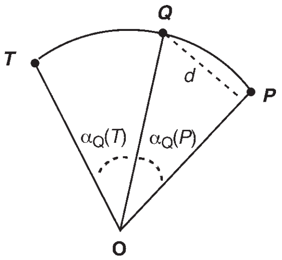
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Optimized geometries and energies of alternative spin states of $[FeMe_4]^{2-}$, $[FeCl_4]^{2-}$, $[NiBr(norbornyl)_3]$, $[NiBrMe_3]$ and $[Fe(Xyl)_2(PH_3)_2]$. List of the structurally characterized d^6 complexes along the interconversion path, including generalized fractional coordinates, magnetic moment when available, CSD refcodes and references.

ternative spin states of two homoleptic d^6 model complexes with σ- and π-donor ligands, $[FeMe_4]^{2-}$ and $[FeCl_4]^{2-}$, along the interconversion path between the tetrahedron and the square. The calculated relationship between spin state and stereochemistry will be shown to match the experimental distribution of structures of d^6 four-coordinate complexes. Application of the generalized interconversion coordinates presented here to the study of theoretical and crystal structure data for a proton transfer reaction between an ammonium cation and a cobalt carbonylate will be described elsewhere.[8]

Results and Discussion

Generalized minimal distortion shape interconversion pathways: In the CShM space, every *N*-atomic structure can be identified by its position in a 3*N* dimensional shape hypersphere of radius *N*.[7] If we focus on two specific shapes *T* and *P*, we can represent an arc of the hypersphere that contains both structures as in Scheme 1, where O is the origin of coordinates. Hence, the minimal distortion path between *T* and *P* is the arc shown, and any structure *Q* that falls strictly along that path is univocally described in terms of its CShMs relative to the two reference shapes, $S_Q(T)$ and $S_Q(P)$. The deviation of *Q* from the two extremes of the path can be either measured by the angles $\alpha_Q(T)$ and $\alpha_Q(P)$, or by the corresponding distances (the shape measure $S_Q(P)$, e.g., is proportional to the square of the distance *d* in Scheme 1), and the two parameters are related through Equation (1). Since the sum of the two angles for any point along the path is a constant for a given pair of polyhedral shapes [Eq. (2)], we can describe the relative position along the path from *T* to *P* by the angular path fraction defined in Equation (3). With such a definition, $\varphi_Q(T\rightarrow P)$ is zero when the structure is coincident with *T*, 100 when it is at the end of the path, having the shape *P*, and all structures along the minimal distortion interconversion path have intermediate $\varphi_Q(T \rightarrow P)$ values that correspond to the portion of the path covered (in percentage). Notice that the relative position along the reverse path (*P* to *T*) can be obtained from Equation (3) by replacing $S_Q(T)$ by $S_Q(P)$.



Scheme 1.

$$S_Q(T) = 100 \sin^2\alpha_Q(T) \tag{1}$$

$$\alpha_Q(T) + \alpha_Q(P) = \theta_{TP} \tag{2}$$

$$\varphi_Q(T \rightarrow P) = 100\frac{\alpha_Q(T)}{\theta_{TP}} = \frac{100}{\theta_{TP}}\arcsin\left(\frac{\sqrt{S_Q(T)}}{10}\right) \tag{3}$$

The fractional reaction coordinate defined in Equation (3) has several interesting properties: a) It fits fully into the conceptual and formal framework of Avnir's continuous shape measures; b) it is defined only for structures that fall along the minimal distortion interconversion path, even if it can be applied to structures that deviate little from that pathway; c) at difference with the shape measures, the distances to the two reference shapes in terms of fractional coordinates are additive, that is, $\varphi_Q(T\rightarrow P) + \varphi_Q(P\rightarrow T) = 100$; d) it gives a percentual measure of the progress of an interconversion reaction; e) the direct and reverse paths are related by inversion, and f) it gives a common measure for the progress of any shape interconversion path, independent of the number of atoms that define the shape and of the distance between the two reference shapes, and it could be appropriately termed *generalized polyhedral interconversion coordinate.*

Although the generalized coordinates defined in Equation (3) apply only to structures that fall along the minimal distortion path between two polyhedra, one could use them also for structures that are close to that pathway. We have found it useful to measure the deviation of a given structure from a minimal distortion path through the *path deviation function*.[7] That function adopts a zero value for structures that are exactly along the path, and increasing values as the structures are farther away from it. The values of the path deviation function are given as percentages of the total length of the path. Thus, a deviation of a 100% indicates that the structure is at the same distance from the interconversion path than the two ideal polyhedra are from each other. Preliminary examination of a large number of structures and several polyhedral interconversion paths makes us think that one can reasonably use the fractional coordinates $\varphi_Q(T\rightarrow P)$ for structures that deviate at most a 15% from the corresponding pathway.

Abstract in Spanish: *En este artículo se definen las coordenadas generalizadas de interconversión de poliedros dentro del marco de las medidas continuas de forma de Avnir. Se presenta la aplicación de dichas coordenadas al estudio de las superficies de energía potencial que definen las preferencias estereoquímicas de complejos tetra-coordinados en diferentes estados de spin. También se muestra la correlación existente entre las curvas de energía potencial y la distribución de estructuras experimentales a lo largo del camino de interconversión entre el tetraedro y el cuadrado para el caso de complejos de metales de transición con configuración d^6.*

Preferred geometries for the quintet and triplet states of d^6 ions: To study the relationship between spin state and stereochemistry in four-coordinate complexes, we have calculated the energies of model compounds with all d^n electron configurations ($0 \leq n \leq 10$). Herein, we present the results for one of the most significative cases, that of the d^6 configuration. In this case we have chosen the $[FeMe_4]^{2-}$ ion as a model with σ-donor only ligands, in three different spin states,[9] fixing the dihedral angle between the ligands and optimizing the rest of the structure, in such a way as to have 11 steps along a minimal distortion interconversion path. The resulting energies are represented in Figure 1 as a function of the fractional reaction coordinate. There we can see that the most stable stereochemistry for the quintet state is a slightly distorted tetrahedron, with an energy minimum at $\varphi_Q(T_d \rightarrow D_{4h}) \approx 10\,\%$, whereas the triplet state is most stable with a square-planar geometry. Conversely, the ground spin state for a tetrahedral geometry is the quintet, and that for a square-planar structure is the triplet. It can also be seen that the two energy surfaces are rather shallow around their minima, and somewhat distorted structures are not unexpected. We note that the crossing of the two spin states at $\varphi_Q(T_d \rightarrow D_{4h}) \approx 75\,\%$ points to the possibility of obtaining spin crossover systems. Finally, the singlet state is found to be significantly higher in energy all along the interconversion path, as could be expected from qualitative molecular orbital arguments.[10]

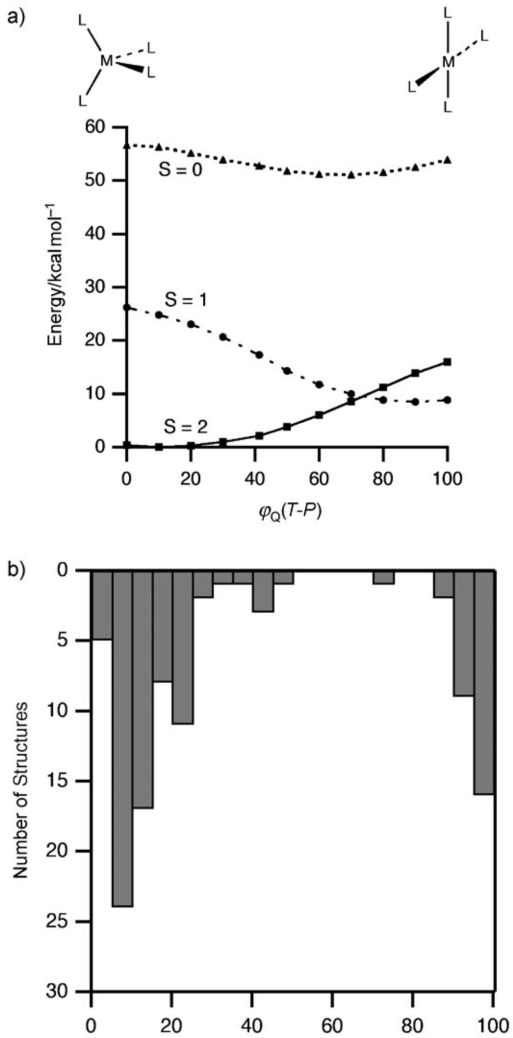


Figure 1. a) Potential energy curves as a function of the fractional reaction coordinate for the conversion of an $[FeMe_4]^{2-}$ tetrahedron into a square in three different spin states. b) Distribution of the experimental structures of four-coordinate transition-metal complexes along the tetrahedron to square interconversion path (only structures that deviate at most by 15 % from that path are shown).

Full optimization of the quintet and triplet states of $[FeMe_4]^{2-}$ yield geometries that correspond to nearly perfect tetrahedral and square planar geometries, as indicated by its shape measures, $S(T_d) = 0.07$ and $S(D_{4h}) = 0.01$, respectively. The tetrahedral measure of the quintet, even if small, is significant enough to indicate the presence of some distortion, and the deviation function from the tetrahedron to square minimal distortion path (1.6 %) points to an incipient distortion toward the square, that can be measured through the fractional reaction coordinate of Equation (3) as an evolution of 5 % in that direction. The tetrahedral quintet state is predicted to be more stable than the square-planar triplet by 8.8 kcal mol^{-1}. The diamagnetic (S = 0) state has also been optimized and found to be 51.1 kcal mol^{-1} above the high-spin state, with a geometry closer to the sawhorse (S(sawhorse) = 2.88) that deviates significantly from the tetrahedron to square interconversion path. We note that the three spin states show some degree of distortion from the most symmetric structures, as expected from the Jahn–Teller theorem.

The distribution of the experimental structures of d^6 complexes along the interconversion path[11] has been analyzed discarding those (65 out of 180) that deviate by more than 15 % from the minimal distortion path. The results are shown in Figure 1, alongside the calculated energy curves. It can be seen that the energy minima of the two spin states are mirrored by maxima in the distribution of the experimental structures. If we focus only on those compounds whose spin state has been reported, we find that the structures close to the tetrahedron correspond to quintets, whereas those closer to the square have a triplet ground state (magnetic data and references provided as Supporting Information).

A most interesting outcome of the crossing of the spin states along the polyhedral interconversion path is that one might be able to prepare four-coordinate d^6 complexes that exhibit spin crossover behavior. In fact, some such examples may have been already prepared, but the temperature dependence of their magnetic behavior has not been the object of a close scrutiny. Indeed, the structure of a tetrathiolatocobalt(III) compound[12] appears to be roughly at the expected spin crossover point for our model system. For that compound, the magnetic moment at room temperature has been found to be 3.5 μ_B, but its temperature dependence has not been reported. Another interesting set of examples is provided by two tropocoronand cobalt(III) complexes reported by Lippard and co-workers.[13] One of these is practically square-planar, another one is significantly distorted toward the tetrahedron, with $\varphi_Q(T_d \rightarrow D_{4h}) = 73\%$, and their room-temperature magnetic moments of 3.1 and 3.6 μ_B would be consistent with an increased thermal population of the $S = 2$ state when distorting from square to tetrahedral geometry around the metal atom (Figure 1).

Even if the potential energy curves for the model compound used seem to provide a sound qualitative rationale for all the experimental information available, both structural and magnetic, one might expect that compounds with weak σ-donor and strong π-bonding character should affect the potential energy map in a significant way. Therefore, we have also made calculations for the $[FeCl_4]^{2-}$ ion (Figure 2).

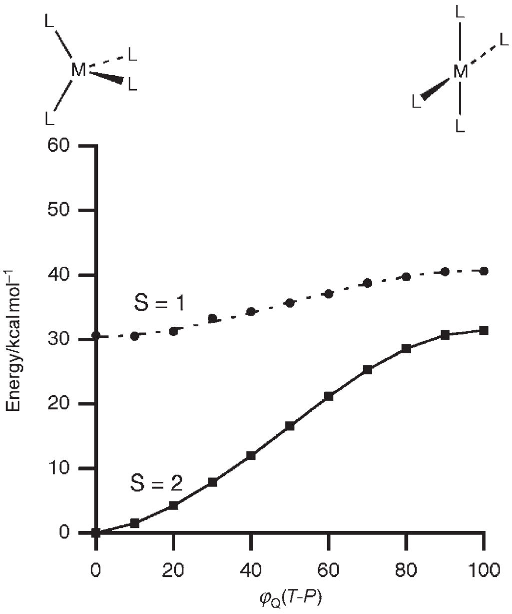


Figure 2. Potential energy curves as a function of the fractional reaction coordinate for the conversion of an $[FeCl_4]^{2-}$ tetrahedron into a square in two different spin states. The curve corresponding to $S = 0$ appears at higher energies, out of the energy window shown.

The $S = 2$ state is again the most stable one for the tetrahedron, with the optimized structure slightly deviating from the perfect tetrahedron ($S(T_d) = 0.09$, bond angles of 106 and 111°) due to a Jahn–Teller effect, as discussed recently by Vrajmasu et al.[14] The relative energy of the square geometry for this spin state is now much higher compared to that of the methyl derivative (Figure 1). At the same time, the $S = 1$ and $S = 0$ states are strongly destabilized relative to the high spin situation, and only a triplet tetrahedral structure is expected for those compounds. These theoretical results are nicely reflected by the structural distribution of the d^6 $[FeX_4]^{2-}$ ions, that are all nearly tetrahedral with fractional coordinates of at most $\varphi_Q(T_d \rightarrow D_{4h}) = 17\%$, to be compared with the wider distribution found for the whole family of d^6 compounds (Figure 1, below).

If a wider applicability is to be attributed to the stereochemical and spin state preferences of d^6 complexes set forward by the energy curves shown in Figures 1 and 2, we must identify all possible exceptions and try to understand why they do not follow the general rule. One such an exception is represented by [NiBr(norbornyl)$_3$], a tetrahedral diamagnetic Ni^{IV} complex reported by Dimitrov and Linden.[15] According to the general view for compounds with all σ-donor ligands (Figure 1) as well as for those with σ- and π-donor ligands (Figure 2), we would expect it to be either a tetrahedral quintet or a square-planar triplet. Calculations on this specific compound in its experimental tetrahedral geometry correctly predict it to be diamagnetic (with the $S = 1$ and $S = 2$ states 36 and 80 kcal mol^{-1} higher in energy, respectively). This behavior cannot be explained by differences in σ-donor abilities of the bromide and norbornyl ligands, since replacement of one alkyl group by a weaker σ-donor cannot increase the energy gap within the d manifold and still a high-spin state would be preferred.

At difference with the other exceptions discussed below, the metal atom in this compound presents a + 4 oxidation state. For tetrahedral complexes with other d^n configurations (Fe^{IV} and Co^{IV}) we have found through calculations that the energy gap between the e and t_2 orbital sets is large enough as to favor a low-spin ground state, as experimentally found also for [Co(norbornyl)$_4$][16] and for a pseudotetrahedral Fe^{IV} compound.[17] Another factor that may favor diamagnetism for this Ni^{IV} compound is an umbrella distortion (i.e., average Br-Ni-C bond angles of 117.7°, much larger than in a tetrahedron), that destabilize the *xz* and *yz* degenerate orbitals due to enhanced σ overlap with the norbornyl donor orbitals. Steric bulk of the norbornyl ligands cannot be blamed responsible for this distortion, since the norbornyl-Ni-norbornyl bond angles are smaller than the Br-Ni-norbornyl ones. A related, much less sterically congested model compound, [NiBrMe$_3$], behaves in the same way, both in its geometry and in the relative stabilities of its spin states (see Supporting Information). Finally, a strong π-donor interaction of the bromide with the metal atom further destabilize those two d orbitals, contributing to the large gap and a low spin state. In summary, the unusual diamagnetic behavior of [NiBr(norbornyl)$_3$] results from the combination of three factors: a) a high oxidation state of the Ni atom, b) a significant umbrella distortion of the coordination sphere, and c) an anisotropic π interaction of the d orbitals with only one π-donor ligand present.

Another apparent exception to the stereochemical trends discussed here is found in the case of an Ir^{III} complex, $[Ir(H)_2R_2]^+$ (R = *N,N'*-di(tertbutyl)imidazol-2-ylidene).[18] The coordination sphere of the Ir atom is in this case a sawhorse and the NMR spectra indicate that it is diamagnetic. Since we have found that the singlet spin state for a four-coordinate d^6 metal ion is in all cases much higher in energy than both the triplet and the quintet, both the geometry and spin state of this compound are quite surprising. A closer look at its structure, though, reveals that there are two agostic interactions that complement the tetradentate ligand to form an effective octahedral coordination sphere (octahedral shape measure = 3.03), for which the singlet ground state is a reasonable choice in the presence of strong field ligands.

Chirik and co-workers[19] have prepared several *cis*- and *trans*-square-planar Fe^{II} complexes with two mesityl ligands. In general, those compounds present structures and spin states consistent with the predictions of Figure 1. However, in one compound in which the coordination sphere is completed with phosphine ligands (PMe_3 and PEt_2Ph) the *trans*-square-planar stereochemistry with S = 1 is found, while one would expect the tetrahedral S = 2 choice to be more stable, according to the potential energy curves of Figure 1. Geometry optimization of the analogous $[Fe(Xyl)_2(PH_3)_2]$ complex (Xyl = 2,6-xylyl) in its S = 2 state shows that, even if the tetrahedral geometry is the most stable one, the *trans*-square-planar isomer is also a minimum 4.9 $kcal\,mol^{-1}$ higher in energy, with a 27 % distortion toward the tetrahedron, and practically isoenergetic with the S = 1 state for the square planar geometry (1.1 $kcal\,mol^{-1}$ above), in excellent agreement with the qualitative picture of Figure 1 (notice that the optimized structure at $\varphi_Q(T_d \rightarrow D_{4h}) = 73\,\%$ is practically at the crossover point). Thus we can conclude that Chirik's compound is nearly perfectly square-planar due to the enhanced steric congestion associated to the presence of the bulkier phosphine ligands compared to the PH_3 ones in our model compound that prevents the conversion of the *trans*-square-planar structure to the tetrahedral one. Yet an open question is whether such an enhanced steric congestion makes the tetrahedral shape unattainable or the two isomers could be obtained. The fact that a compound with mesityl and depe ligands appears in the expected tetrahedral geometry makes us think that the tetrahedral isomer of $[Fe(Mes)_2(PR_3)_2]$ should be obtainable.

Conclusion

In conclusion, a generalized polyhedral interconversion coordinate described here has allowed us to represent the energy of the different spin states of all d^n four-coordinate transition-metal complexes as their coordination spheres rearrange from tetrahedral to square planar. The distribution of experimental structures along such a pathway mirrors the calculated energy curves for the available spin states of each electron configuration. Herein, we have illustrated our findings with the case of model d^6 complexes with σ-only and π-donor ligands, $[FeMe_4]^{2-}$ and $[FeCl_4]^{2-}$. For the σ-donor ligand, the S = 1 spin state adopts a square-planar geometry, while the S = 2 state is more stable as a tetrahedron. For the π-donor ligand, the S = 2 spin state with tetrahedral geometry is always preferred. The S = 0 spin state is too high in energy to be the ground state in the cases studied, although some hints are given for the factors that may stabilize this unusual spin state.

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