

# How High the Spin? Allowed and Forbidden Spin States in Transition-Metal Chemistry\*\*

Santiago Alvarez\* and Jordi Cirera

**Keywords:**

coordination compounds · ligand field theory · molecular orbital theory · spin states · transition metals

**“When I use a word,” Humpty Dumpty said in rather a scornful tone, “it means just what I choose it to mean—neither more nor less.”**  
**“The question is,” said Alice, “whether you can make words mean different things.”**

Lewis Carroll, *Through The Looking Glass* (1871)

## Introduction

The quest for new homoleptic complexes (those with identical ligands) is a common target of several research groups in the field of synthetic transition-metal chemistry. For instance, Menjón, Forniés, and co-workers have prepared a series of organometallic  $[MR_x]$  complexes ( $M$ =transition metal;  $R$ =polyhalophenyl group;  $x=4\text{--}6$ )<sup>[1]</sup> that cover almost all the  $d^n$  electron configurations and in most cases are paramagnetic. Even simpler in composition, a variety of homoleptic complexes with

methyl ligands were reported by Seppelt and co-workers.<sup>[2]</sup> Homoleptic cyano compounds have been known for a long time,<sup>[3]</sup> but some new elegant examples were recently reported<sup>[4\text{--}6]</sup> in view of their potential use as building blocks for polynuclear and extended structures with interesting magnetic properties.<sup>[7]</sup> Even such large families of complexes as the metal carbonyls<sup>[8]</sup> and alkoxides<sup>[9]</sup> are continuously expanding. To date, hundreds of thousands of transition-metal complexes have been structurally characterized, and the mainstream lines of research in that area are concerned with the self-assembly of large polynuclear systems that contain hundreds of atoms, tens or even hundreds of which can be transition-metal atoms.<sup>[10]</sup> The question is thus asked: Why then is there a renaissance of the chemistry of mononuclear complexes with only one type of relatively simple ligand?

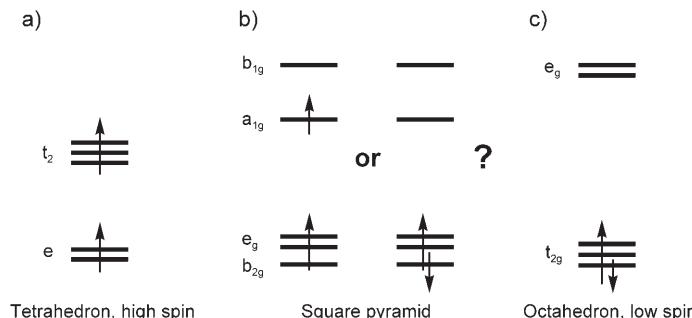
Clearly, there is a synthetic challenge as the preparation of compounds with only one type of ligand is not always an easy task. In our view, though, there is also the perception that the stereochemistry, electronic structure,

and chemical properties of such compounds are not so well understood, despite the tremendous advances in our capabilities to analyze them both crystallographically and computationally. Especially for those electron configurations that allow for more than one spin state, it is not always easy to predict which will be the ground state for a given combination of metal ion and ligands. The concepts of high-spin and low-spin states, and the related classification of low- and high-field ligands, derived from the crystal-field treatment of an octahedral compound, are usually extrapolated to other cases in a straightforward way, leading in some instances to ambiguities.

The case of the homoleptic cyano complexes illustrates the problems and lack of a unified use of the low-spin and high-spin labels. The  $[\text{Mn}(\text{CN})_6]^{4-}$  anion reported recently by Miller and co-workers is a textbook example of the general tendency of tetrahedral complexes to have their  $d$  electrons arranged with parallel spins, resulting in the highest possible spin state (Figure 1 a).<sup>[4]</sup> (We will see in the last section of the Essay

[\*] Prof. S. Alvarez, J. Cirera  
Departament de Química Inorgànica  
and  
Centre Especial de Recerca en Química  
Teòrica (CeRQT)  
Universitat de Barcelona  
Martí i Franquès 1–11  
08028 Barcelona (Spain)  
Fax: (+34) 93-490-7725  
E-mail: santiago@qi.ub.es

[\*\*] Financial support of this work was provided by the Ministerio de Ciencia y Tecnología (project no. CTQ2005-08123-C02-02/BQU) and through an MECD doctoral grant to J.C. The authors thank R. Poli and R. Hoffmann for illuminating discussions.



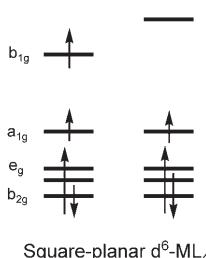
**Figure 1.** Splitting of  $d$  orbitals in a) a tetrahedral high-spin complex,  $[\text{Mn}(\text{CN})_6]^{4-}$ , b) a square-pyramidal complex,  $[\text{Cr}(\text{CN})_6]^{3-}$ , with high-spin (left) or low-spin configuration (right), and c) an octahedral low-spin complex,  $[\text{Cr}(\text{CN})_6]^{4-}$ .

that low-spin tetrahedral complexes do exist under certain circumstances.) Such a tendency is explained by the small splitting of the d orbitals in a tetrahedral environment, even in the presence of strong-field ligands such as cyanide. The octahedral  $[\text{Cr}(\text{CN})_6]^{4-}$  anion, on the other hand, presents a low-spin configuration with  $S=1$  (Figure 1c),<sup>[4]</sup> which can be explained by the large splitting of the d orbitals due to an octahedral environment of strong-field ligands. In both of these cases, two different factors determine the magnitude of the d-orbital splitting and, hence, the choice of the spin state: the molecular (coordination) geometry and the nature of the ligands. (Another factor, which we will comment on later, is the interelectronic repulsion.)

If we consider yet a third type of structure, such as the square-pyramidal or trigonal-bipyramidal geometries reported recently for the  $[\text{Cr}(\text{CN})_5]^{3-}$  anion,<sup>[5]</sup> should we expect all electrons to have parallel spins or not? Should the relevant energy gap between the  $a_{1g}$  and  $e_g$  orbitals in the presence of strong ligands such as cyanide be large (Figure 1c) or small (Figure 1a)? It has been shown experimentally that the high-spin electron configuration is preferred (Figure 1b).<sup>[5]</sup> However, could we have predicted the spin state beforehand by using qualitative molecular-orbital arguments? Moreover, if the  $[\text{Mn}(\text{CN})_5]^{3-}$  anion with an extra electron could be prepared, should we expect the fifth electron to lie parallel (occupying a  $b_{1g}$  orbital) or antiparallel (occupying a  $b_{2g}$  orbital)? Similarly, we could turn to lower coordination numbers and ask if the high-spin configurations found for three-coordinated  $\text{d}^7\text{-Fe}^{\text{I}}$  and  $\text{d}^6\text{-Fe}^{\text{II}}$  cations with the diketiminato bidentate ligand<sup>[11]</sup> is something we could have predicted without calculations or experiment.

Another possible source of ambiguity comes from labeling some compounds as having “intermediate” spin states. This label has been applied to Jahn-Teller-distorted six-coordinated metal ions, such as  $\text{Co}^{\text{III}}$  in  $\text{LaCoO}_3$ ,<sup>[12]</sup> to  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  porphyrin complexes in which the Fe ion is four-, five-, or six-coordinated,<sup>[13–15]</sup> and to a square-planar  $\text{Fe}^{\text{II}}$  dithiolato complex.<sup>[16]</sup> In the case of a square-planar  $\text{Fe}^{\text{II}}$  complex, taking

into account the typical d-orbital splitting pattern,<sup>[17]</sup> two alternative spin states can be expected in the presence of weak-field ( $S=2$ ) or strong-field ligands ( $S=1$ ; Figure 2). A ground spin



**Figure 2.** Splitting of d orbitals in a square-planar  $\text{d}^6\text{-ML}_4$  complex and its high-spin (left) or low-spin (right) configurations.

state with all electrons paired ( $S=0$ ) could be conceived, but, to the best of our knowledge, there is no experimental evidence for such a spin state in a square-planar  $\text{d}^6$ -metal complex. Should the configuration as shown on the right in Figure 2 be termed the low-spin state or the intermediate-spin state? Is the diamagnetic state possible?

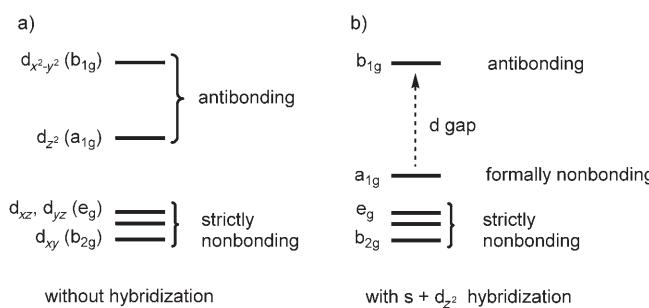
The correct characterization and description of the spin state of a transition-metal complex is very important given the different magnetic, structural, and chemical properties associated with different spin states.<sup>[18]</sup> However, in the most-recent revision of the IUPAC's *Nomenclature of Inorganic Chemistry*<sup>[19]</sup> the naming of spin configurations or states is completely overlooked. Therefore, we believe that it is timely to reflect on when and why are high-, intermediate-, or low-spin configurations possible. It would be convenient that the scientific community establishes some naming convention to avoid ambiguities and misunderstandings. For this reason, we present herein a qualitative revision of the orbital principles underlying the choice of spin states in transition-metal compounds. As the interplay of d-orbital splitting and electron repulsion determines the spin configuration, we start by looking at some general rules that govern the relative magnitude of these two effects. We present a general molecular-orbital scheme that provides a sound qualitative description of the relative energies of the metal d orbitals in complexes with any coordination

number and geometry and establish accordingly the possible spin states for different coordination geometries and  $\text{d}^n$  configurations. Last, we address the possibility of less-common orbital-splitting situations and provide some rationale for known exceptions to the rules proposed.

### Splitting of the d Orbitals

The use of high-spin and low-spin labels for electron configurations is associated with the well-known splitting pattern of the metal d orbitals into two degenerate sets in octahedral and tetrahedral complexes (Figure 1), when crystal-field or molecular-orbital theories are applied. In both cases, there are only two distinct choices of electron configuration, characterized by the highest and lowest possible spin for  $n$  electrons in the five d orbitals. However, the situation is less clear for other coordination geometries, for which more than two sets of symmetry-equivalent orbitals can be found, as in square-planar (Figure 2) and square-pyramidal complexes (Figure 1b). Therefore, let us try to establish some rules that allow us to treat these less symmetric cases in a simple but reliable way. We do so by considering the molecular orbitals of an idealized complex with predominant metal d character.

When d orbitals interact with the symmetry-adapted linear combinations (SALC)<sup>[20]</sup> of ligand orbitals, they form bonding and antibonding molecular orbitals for each symmetry representation. Atomic d orbitals that do not match the symmetry of the SALCs are strictly nonbonding, as is the case for the  $t_{2g}$  metal set in an octahedral environment (assuming only  $\sigma$ -donor ligands) or for the  $b_{2g}$  and  $e_g$  orbitals in a square-planar four-coordinate complex (Figure 3a). For the purpose of the present discussion, we focus on the antibonding combinations, whose largest contribution comes in most cases from the metal d orbitals, such as the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals in a square-planar complex. For simplicity, we refer to these molecular orbitals as d-MOs to differentiate them from the unperturbed atomic d orbitals. Thus, now we can classify the d-MOs into two sets: those



**Figure 3.** d Molecular orbitals in square-planar  $\text{ML}_4$  complexes: a) without hybridization; b) with  $s + d_{z^2}$  hybridization.

with antibonding character and those with strictly nonbonding character (Figure 3a).

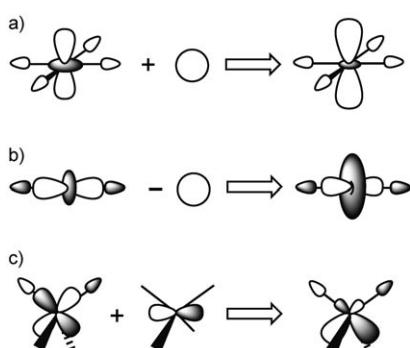
However, there are two different situations regarding the antibonding d-MOs, depending on whether or not there are valence s or p metal orbitals of the same symmetry. In the presence of symmetry-matched valence s or p orbitals, energy minimization of the system imposes extensive mixing of orbitals of the same symmetry, in such a way as to make the lower one as little metal-ligand antibonding as possible, while the upper, unoccupied one (formerly s or p), accumulates most of the antibonding character. Such a hybridization converts the corresponding d-MOs into *formally* nonbonding orbitals, as happens with  $d_{z^2}$  in the case of a square-planar complex; it is hybridized with the s orbital (both being  $A_{1g}$ -symmetric; Figure 4a). Conversely, in a linear complex hybridization occurs with the opposite sign (Figure 4b). A similar situation appears, for example, for the  $t_2$  set of d-MOs in a tetrahedral complex which hybridize

with metal p orbitals that have the same symmetry (Figure 4c).

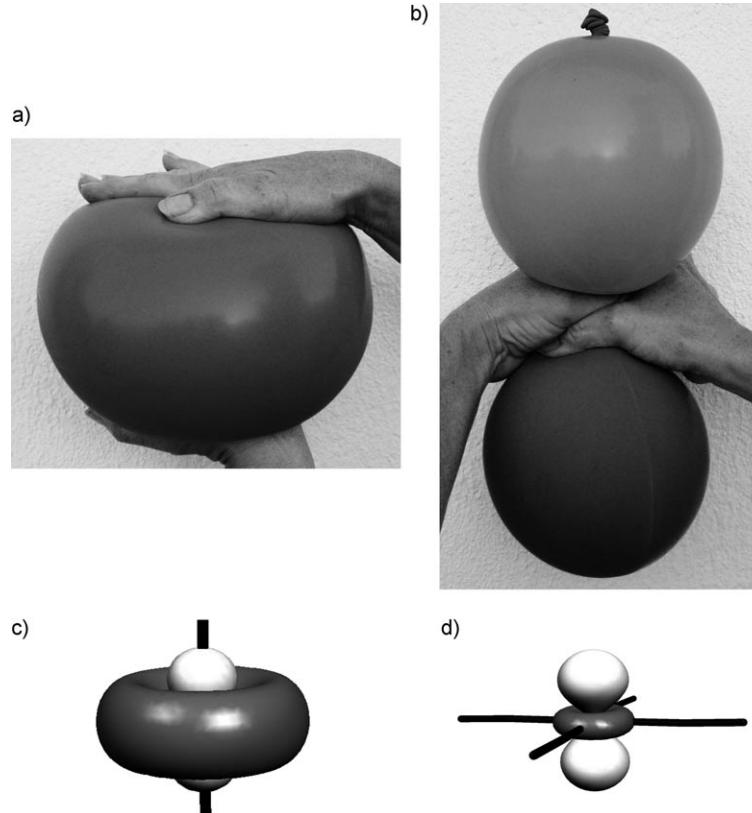
In those cases the d-MOs are hybridized such that their electron density is concentrated away from the ligands, appearing similar to a balloon when subject to pressure. The effect of pressing a balloon in axial and equatorial directions (Figure 5a,b) can be compared with the hybridization found for the  $d_{z^2}$  orbital in  $\text{ML}_2$  and  $\text{ML}_4$  complexes (Figure 5c,d). In summary, we should expect the d-MO manifold to be

split into two distinct sets, with the lower energy set containing the nonbonding (both strictly and formally) orbitals and the higher energy set comprising the metal-ligand antibonding orbitals. The sets of orbitals are separated by a significant d-orbital energy gap.

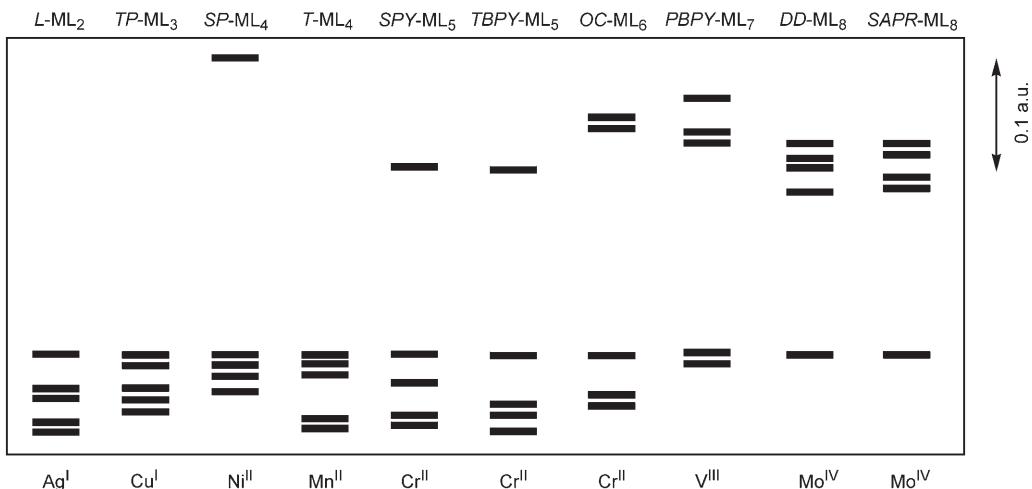
Let's pretend that the splitting between nonbonding and antibonding d-MOs is much larger than the energy differences within each of these two orbital sets; it is therefore this energy gap that should be taken into account when considering alternative spin configurations.<sup>[21]</sup> There are good reasons for this assumption, as illustrated by the splitting of the d orbitals in different homoleptic cyano complexes (Figure 6) according to density functional theory (DFT) calculations.<sup>[22]</sup> In each case, the symmetry of the coordination sphere determines which orbitals belong to each of these two sets (see Table 1). It can be seen that the number of antibonding d-MOs corresponds to the number of d orbitals that participate in the valence-bond hybridization



**Figure 4.** Minimization of antibonding character through hybridization of d-MOs:  $s + d_{z^2}$  hybridization in a) square-planar  $\text{ML}_4$  and b) linear  $\text{ML}_2$  complexes, and c) p+ $d$  hybridization in tetrahedral complexes.



**Figure 5.** Effect of applying pressure to a balloon along the z axis (a) and circularly in the xy plane (b), compared to the shape of the  $d_{z^2}$  orbital (see Figure 4 a, b) in linear  $[\text{Ag}(\text{CN})]^-$  (c) and in square-planar  $[\text{Ni}(\text{CN})]^{2-}$  (d), as obtained from DFT calculations.



**Figure 6.** Relative energies of the d molecular orbitals in several homoleptic cyano complexes, from left to right: linear  $[\text{Ag}(\text{CN})_2]^-$ , trigonal-planar  $[\text{Cu}(\text{CN})_3]^{2-}$ , square-planar  $[\text{Ni}(\text{CN})_4]^{2-}$ , tetrahedral  $[\text{Mn}(\text{CN})_4]^{2-}$ , square-pyramidal  $[\text{Cr}(\text{CN})_3]^{2-}$ , nearly trigonal-bipyramidal  $[\text{Cr}(\text{CN})_5]^{4-}$ , octahedral  $[\text{Cr}(\text{CN})_6]^{4-}$ , pentagonal-bipyramidal  $[\text{V}(\text{CN})_7]^{4-}$ , and dodecahedral and square-antiprismatic  $[\text{Mo}(\text{CN})_8]^{4-}$ . To facilitate comparison of the energy gaps, the orbital energies of each compound are referred to that of the highest formally nonbonding d-MOs ( $0.1 \text{ a.u.} = 2.19 \times 10^4 \text{ cm}^{-1}$ ).

**Table 1:** Expected hybridization of the metal atom in  $\text{ML}_n$  complexes and formal bonding nature of the metal d orbitals when considering metal–ligand  $\sigma$  interactions only.

Symbol <sup>[a]</sup>	Geometry	Hybridization	Nonbonding <sup>[b]</sup>	Antibonding
<i>L</i> -ML <sub>2</sub>	linear	sp	all	none
<i>TP</i> -ML <sub>3</sub>	trigonal plane	sp <sup>2</sup>	all	none
<i>T</i> -ML <sub>4</sub>	tetrahedron	sp <sup>3</sup>	all	none
<i>SP</i> -ML <sub>4</sub>	square plane	dsp <sup>2</sup>	d <sub>z<sup>2</sup></sub> , d <sub>xp</sub> , d <sub>xz</sub> , d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>
<i>TBPY</i> -ML <sub>5</sub>	trigonal bipyramidal	dsp <sup>3</sup>	d <sub>xz</sub> , d <sub>yz</sub> , d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>xy</sub>	d <sub>z<sup>2</sup></sub>
<i>SPY</i> -ML <sub>5</sub>	square pyramid	dsp <sup>3</sup>	d <sub>xz</sub> , d <sub>yz</sub> , d <sub>xy</sub> , d <sub>z<sup>2</sup></sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>
<i>OC</i> -ML <sub>6</sub>	octahedron	d <sup>2</sup> sp <sup>3</sup>	d <sub>xp</sub> , d <sub>xz</sub> , d <sub>yz</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>z<sup>2</sup></sub>
<i>TPR</i> -ML <sub>6</sub>	trigonal prism	d <sup>2</sup> sp <sup>3</sup>	d <sub>xp</sub> , d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>z<sup>2</sup></sub>	d <sub>xz</sub> , d <sub>yz</sub>
<i>PBPY</i> -ML <sub>7</sub>	pentagonal bipyramidal	d <sup>3</sup> sp <sup>3</sup>	d <sub>xz</sub> , d <sub>yz</sub>	d <sub>z<sup>2</sup></sub> , d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>xy</sub>
<i>OCF</i> -ML <sub>7</sub>	capped octahedron	d <sup>3</sup> sp <sup>3</sup>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>xy</sub>	d <sub>z<sup>2</sup></sub> , d <sub>xz</sub> , d <sub>yz</sub>
<i>TPRS</i> -ML <sub>7</sub>	capped trigonal prism	d <sup>3</sup> sp <sup>3</sup>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>xy</sub>	d <sub>z<sup>2</sup></sub> , d <sub>xz</sub> , d <sub>yz</sub>
<i>CU</i> -ML <sub>8</sub>	cube	d <sup>3</sup> sp <sup>3</sup>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , d <sub>xy</sub>	d <sub>z<sup>2</sup></sub> , d <sub>xz</sub> , d <sub>yz</sub>
<i>DD</i> -ML <sub>8</sub>	dodecahedron	d <sup>4</sup> sp <sup>3</sup>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	d <sub>z<sup>2</sup></sub> , d <sub>xp</sub> , d <sub>xz</sub> , d <sub>yz</sub>
<i>SAPR</i> -ML <sub>8</sub>	square antiprism	d <sup>4</sup> sp <sup>3</sup>	d <sub>z<sup>2</sup></sub>	d <sub>xp</sub> , d <sub>xz</sub> , d <sub>yz</sub> , d <sub>x<sup>2</sup>-y<sup>2</sup></sub>

[a] IUPAC polyhedral symbol. [b] The metal atomic orbitals identified as “nonbonding” may be strictly so, as imposed by symmetry (e.g., the t<sub>2g</sub> set in octahedral complexes), or only formally nonbonding as discussed in the text.

scheme.<sup>[23]</sup> As an example, the dsp<sup>2</sup> hybridization expected for a square-planar complex is translated into a molecular-orbital scheme with only one antibonding d orbital, whereas the d<sup>4</sup>sp<sup>3</sup> hybridization expected for a dodecahedral, eight-coordinated metal corresponds to a splitting into one nonbonding and four antibonding d-MOs.

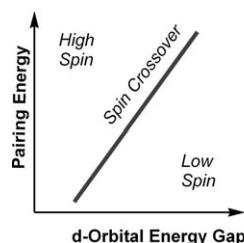
### High-Spin and Low-Spin Configurations

The size of the d-energy gap is determined by the strength of the orbital

interaction between the metal center and the donor atoms, and is controlled by the overlap and difference in electronegativity of both  $\sigma$ - and  $\pi$ -type metal-ligand interactions. Its magnitude obtained from visible spectra, for example, is empirically expressed through the spectrochemical series of the ligands and of the metal ions.<sup>[24]</sup> On the basis of such information, cyanide, phosphines, or CO are considered strong ligands, while O-donor ligands (including water) and halides are referred to as weak ligands. (The nature of the metal also has an effect on the magnitude of the gap; it increases with the oxidation

state of the metal and also upon descending a periodic group.)

The choice of the spin state in a particular case, however, depends on both the d-orbital energy gap and the electron repulsion associated with the occupation of the same orbital by two electrons with opposed spins (“pairing energy”). Thus, a large gap and a small pairing energy favor a low-spin state, whereas a small gap combined with large pairing energy favors a high-spin state. Intermediate situations are harder to predict and are best exemplified with spin-crossover complexes, which can change their spin state through changes in temperature or pressure or by irradiation.<sup>[25]</sup> To get a feel for how much the pairing energy can change from one metal to another and with oxidation state, one can take a look at the values of the Racah electron-repulsion parameters for free ions.<sup>[26]</sup> The following trends are observed: 1) for metal ions with the same oxidation state, the pairing energy increases with atomic number along a transition series; 2) for metal ions belonging to the same group, the pairing energy decreases down the group; and 3) for the same metal atom, the pairing energy increases with increasing oxidation state. In Figure 7, the factors that influence the magnitudes of these two parameters are summarized according to the magnitudes of the pairing energy and the d-orbital energy gap. A qualitative map is also shown that indicates the



Pairing Energy:		d-Orbital Energy Gap	
Metal	- oxidation state	Metal	Geometry → pattern
	- transition series		Spectrochemical series → magnitude
	- periodic group	Ligands	
Ligands	- covalency (electronegativity) (nephelauxetic effect)		- oxidation state
			- transition series
		Ligands	
			- $\sigma$ donor
			- $\pi$ donor / $\pi$ acceptor

Figure 7. Factors that influence the magnitudes of the pairing energy and the d-orbital energy gap.

regions of high- and low-spin states, separated by a region in which spin crossover can occur. With so many factors in action, it is not easy to predict the most-stable spin configuration for a given complex. However, we can try to predict at least which spin states can be reasonably expected in the limiting cases of strong and weak fields.

Taking into account the classification of d orbitals in nonbonding and antibonding sets, we can establish the possible spin configurations for a given coordination number and geometry (Table 2). As an example, let us consider the case of a  $d^5$  ion in tetrahedral and octahedral geometries, for which three spin states can be envisaged:  $S=5/2, 3/2$ , or  $1/2$ . For the octahedron ( $OC\text{-}ML_6$ ),

the highest spin ( $S=5/2$ ) is attained if the d-orbital splitting (energy gap) is small compared to the pairing energy, and the lowest spin ( $S=1/2$ ) is obtained in the opposite case. In contrast, the  $S=3/2$  state is forbidden because the pairing of the fourth and fifth electrons in  $t_{2g}$  orbitals is either favorable for both ( $S=1/2$  preferred) or unfavorable for both ( $S=5/2$  preferred), but cannot be preferred for one electron and unfavorable for the other one (as required for  $S=3/2$  to be the ground state). For the tetrahedron ( $T\text{-}ML_4$ ), both the  $S=3/2$  and  $S=1/2$  spin states are forbidden because the energy difference between the e and  $t_2$  orbital sets is small regardless of the nature of the metal and ligands. The experimental realization of

these cases is exemplified by  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $[\text{Mn}(\text{CN})_4]^{2-}$ . For the two octahedral complexes, the  $S=5/2$  ( $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ) and  $S=1/2$  ( $[\text{Fe}(\text{CN})_6]^{3-}$ ) states observed correspond to the two allowed situations at the extremes of weak-field ( $\text{H}_2\text{O}$ ) and strong-field ( $\text{CN}^-$ ) ligands. The  $S=5/2$  spin state observed for  $[\text{Mn}(\text{CN})_4]^{2-}$ , even with a strong ligand, corroborates the negligible effect of the splitting within nonbonding orbitals on the electron configuration. Thus, for the case of a  $d^5$  metal ion, it is sensible to refer to the  $S=5/2$  and  $S=1/2$  states of octahedral complexes as the high-spin and low-spin configurations, respectively, while for isoelectronic tetrahedral compounds there is no need to refer to a “high-spin” situation as there is only one observed spin state. The intermediate spin for that configuration is not expected to exist as a ground state, at least not for homoleptic complexes.

With a “map” in hand of the possible spin states for a variety of coordination geometries and different d-electron configurations, and considering only the splitting of the d orbitals in two broad sets of nonbonding and antibonding orbitals (Table 2), we can establish some generalities as well as some specificities.

- Three spin states are possible only for the  $d^4$ ,  $d^5$ , and  $d^6$  electron configurations. Nevertheless, for a given coordination geometry only two or even just one of those spin states are allowed, if we disregard spin-pairing within the nonbonding set, before it is half-filled.
- For  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$  configurations, only two spin states are possible, but in many instances the spin state with the highest multiplicity only is allowed.
- From Table 2, a general rule for tetrahedral complexes ( $T\text{-}ML_4$ ) is that only the highest spin state should be expected in all cases (see the discussion in the next section).
- The highest spin state should be expected also for linear two-coordinate ( $L\text{-}ML_2$ ) and trigonal-planar three-coordinate ( $TP\text{-}ML_3$ ) complexes. In these cases, all the d molecular orbitals are formally nonbonding (Figure 6) and a negligible d-orbital energy gap should be expected. Recently reported examples

Table 2: Allowed spin configurations (✓) for different coordination geometries and numbers of d electrons, considering only an energy gap between formally nonbonding and  $\sigma$ -antibonding orbitals.<sup>[a]</sup>

Configuration	Spin	$T\text{-}ML_4$	$SP\text{-}ML_4$	$SPY\text{-}ML_5$	$OC\text{-}ML_6$	$PBPY\text{-}ML_7$	$DD\text{-}ML_8$
$d^2$	1	✓	✓	✓	✓	✓	✓
	0	–	–	–	–	–	✓
$d^3$	3/2	✓	✓	✓	✓	✓	✓
	1/2	–	–	–	–	✓	✓
$d^4$	2	✓	✓	✓	✓	✓	✓
	1	–	–	–	✓	–	✓
	0	–	–	–	–	✓	–
$d^5$	5/2	✓	✓	✓	✓	✓	✓
	3/2	–	✓	✓	–	–	✓
	1/2	–	–	–	✓	✓	–
$d^6$	2	✓	✓	✓	✓	✓	✓
	1	–	✓	✓	–	✓	–
	0	–	–	–	✓	–	–
$d^7$	3/2	✓	✓	✓	✓	✓	✓
	1/2	–	✓	✓	✓	–	–
$d^8$	1	✓	✓	✓	✓	✓	✓
	0	–	✓	✓	–	–	–

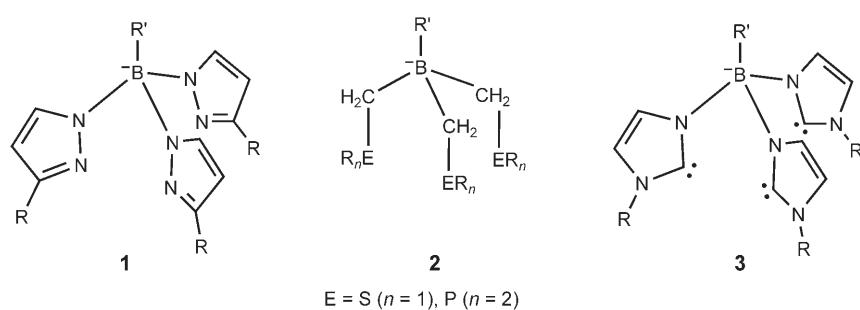
[a] The forbidden cases correspond to spin configurations that imply electron pairing within the set of (formally and strictly) nonbonding d orbitals. Polyhedral symbols as reported in Table 1.

of two-coordinate complexes with  $d^4$  to  $d^8$  electron configurations all presented high-spin states.<sup>[27]</sup> Similarly, three-coordinate complexes seem in most cases to appear in their high-spin configurations.<sup>[28,29]</sup> (Exceptions are discussed in the next section.)

- e) For eight-coordinate complexes with four or more d electrons ( $DD\text{-ML}_8$  or  $SAPR\text{-ML}_8$ ), the state with the lowest spin multiplicity is always forbidden because it would imply unnecessary electron-pairing within the antibonding orbitals (Figure 6).
- f) Given the different d-orbital splitting patterns, the allowed spin states change with the coordination number. Thus, for the  $d^6$  configuration the state with all spins paired is forbidden in square-planar ( $SP\text{-ML}_4$ ), square-pyramidal ( $SPY\text{-ML}_5$ ), and pentagonal-bipyramidal ( $PBPY\text{-ML}_7$ ) complexes, while it is allowed for octahedral geometries. On the contrary, the  $S=1$  state is allowed in the former cases but forbidden in the latter. A similar situation arises for the  $d^5$  configuration.
- g) A spin-paired configuration is forbidden for octahedral complexes of  $d^2$  or  $d^3$  metals. However, the high-low spin state dichotomy exists for seven- and eight-coordinated metal ions with these electron configurations, and  $d^2$ -configured octacyanometallates are indeed low-spin complexes.

### Electron-Pairing within the Nonbonding Orbital Set

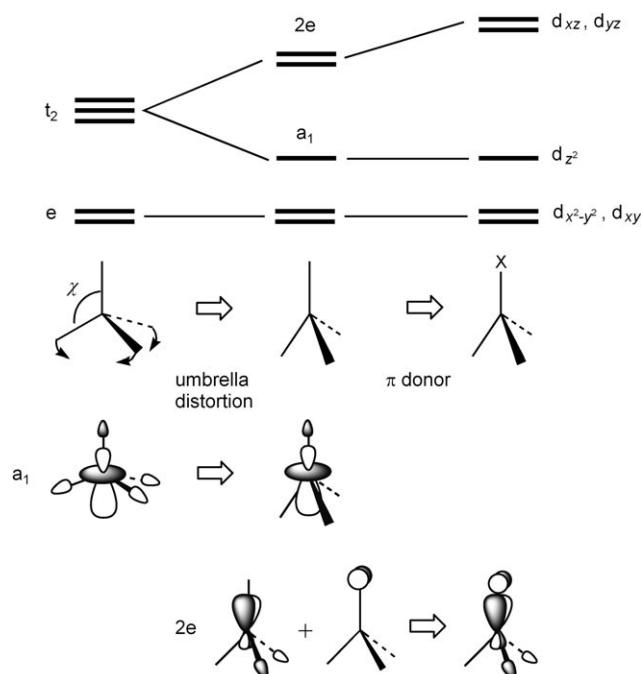
So far, we have relied on the assumption that differences in energy within the set of nonbonding d orbitals are not large enough as to induce spin pairing. However, we have neglected metal-ligand  $\pi$  interactions in our arguments. Let us now consider some examples in which  $\pi$  bonding may invalidate such a hypothesis. The exceptions correspond mostly to pseudotetrahedral  $\text{Fe}^{II}$  and  $\text{Co}^{II}$  complexes of the type  $[\text{M}(\text{BE}_3)\text{X}]$ , where  $\text{BE}_3$  represents tridentate ligands such as trispyrazolylborates ( $\text{E=N}$ ),<sup>[30]</sup> triphosphineborates ( $\text{E=P}$ ),<sup>[31,32]</sup> trithioborates ( $\text{E=S}$ ),<sup>[33]</sup> or tris(carbene)borates<sup>[34]</sup> (see 1–3, Figure 8).



**Figure 8.** Tridentate ligands that appear, supplemented with a monodentate  $\pi$ -donor ligand, in pseudotetrahedral  $\text{Fe}^{II}$  and  $\text{Co}^{II}$  complexes with low-spin configurations.

ure 8). These compounds adopt a low-spin configuration when the fourth ligand, X, is a  $\pi$  donor. A somewhat different case is that of diamagnetic tetrahedral  $\text{Ni}^{IV}$  compound,  $[\text{NiBr}(\text{norbornyl})_3]$ ,<sup>[35]</sup> in which all ligands are monodentate. In all these compounds there are varying degrees of umbrella-type distortions of the tetrahedron. This distortion is in contrast to the more commonly found spread distortion path<sup>[36]</sup> that ultimately leads to a square-planar complex. Such distortions can be calibrated by the sum of the E-M-E bond angles ( $\Sigma$ ), which is expected to be  $328.4^\circ$  for the ideal tetrahedron but is found to be  $300.2^\circ$  for the  $\text{Ni}^{IV}$  complex and between  $264^\circ$  and  $298^\circ$  in the compounds with tridentate ligands.

An explanation for the stability of the low-spin state in these systems was proposed on the basis of DFT calculations by Peters and co-workers.<sup>[32]</sup> The distortion of the coordination tetrahedron results in the splitting of the  $t_2$  set of d orbitals (Figure 9), and the  $a_1$  ( $d_{z^2}$ ) orbital thereby loses its antibonding character as the E donor atoms approach its nodal cone (at  $\Sigma = 270^\circ$ ). In addition, the  $\pi$ -donor nature of X adds  $\pi$ -antibonding character to the  $2e$  ( $d_{xz}, d_{yz}$ ) degenerate pair. Such a  $\pi$  interaction is enhanced as a result of the balloon effect discussed before (Figure 4c). Note also that such a hybridization increases with the umbrella distortion, as the overlap between the ligand lone pairs and metal  $d_{xz}$



**Figure 9.** Effect of an umbrella distortion and of a  $\pi$ -donor apical ligand X on the d-orbital splitting. The loss of  $\sigma$  overlap in the  $a_1$  orbital and the enhanced  $\pi$  overlap in the  $2e$  orbital explain the deviation of the orbital splitting from the  $e + t_2$  pattern of the tetrahedron.

$d_{yz}$  orbitals increases. In summary, the umbrella distortion stabilizes the  $a_1$  ( $d_{z^2}$ ) orbital, while the presence of a  $\pi$ -donor ligand X combined with the umbrella distortion strongly destabilizes the  $2e$  set. The resultant wide energy gap stabilizes the low-spin configuration.

Consistent with the orbital picture just discussed, all the  $d^6$  and  $d^7$  complexes of ligands **1–3** with a  $\sigma$ -donor or  $\pi$ -acceptor ligand X appear in their high-spin configurations, as the  $2e$  orbitals lack the  $\pi$ -antibonding character that leads to a significant d-orbital energy gap. On the other hand, those complexes in which X is a  $\pi$ -donor ligand present a good correlation between the degree of umbrella distortion and the spin of the ground state: Compounds with strong distortions have a low-spin ground state, whereas those with weaker distortions appear in their high-spin configuration. The borderline appears at  $\Sigma \approx 277^\circ$ .

If we turn now to the pseudotetrahedral complex  $[\text{NiBr}(\text{norbornyl})_3]$ ,<sup>[35]</sup> we note that it has two of the requisites to present a low-spin state: an umbrella distortion and a  $\pi$ -donor ligand. However, as the umbrella distortion is not strong ( $\Sigma = 300^\circ$ ) it does not comply with the third requisite. Current studies in our research group indicate that even with four  $\sigma$ -donor ligands (e.g., alkyl groups), a tetrahedrally coordinated metal in its +IV oxidation state presents a large enough gap between the  $t_2$  and  $e$  orbitals as to favor the low-spin state. This behavior has been experimentally found for the  $[\text{Co}(\text{norbornyl})_4]^y$  complexes ( $y = -1, 0, +1$ ), which appear in their low-spin states.<sup>[37]</sup>

We have already noted above that the d-orbital splitting depends not only on the donor ability of the ligands but also increases with the metal oxidation state. Hence, the different behavior of the tetrahedral  $[\text{Mn}(\text{CN})_4]^{2-}$  and  $[\text{NiBr}(\text{norbornyl})_3]$  complexes, which present high- and low-spin configurations, respectively, are well accounted for by the general rules of d-orbital splitting if we assume that for metal oxidation states of +IV or higher the metal–ligand interaction is so strong that the p+d hybridization is insufficient to make the  $t_2$  orbitals formally nonbonding. In other words, they become

effectively antibonding. Another interesting recent case is that of a four-coordinate  $d^4\text{-Ru}^{\text{IV}}$  nitrido complex with a tridentate ligand that adopts an approximately square-planar geometry ( $SP\text{-ML}_4$ ) but a low-spin state ( $S = 0$ ).<sup>[38]</sup> Three factors that favor the unusual low-spin state can be identified in that compound: a second-series transition metal, a high oxidation state, and asymmetric  $\pi$  bonding.

Three-coordinate complexes also present exceptions that require closer inspection. According to the discussion above, all the d orbitals should be nonbonding in such a case ( $TP\text{-ML}_3$  in Table 1 and Figure 6). In fact, most three-coordinate complexes for which magnetic moments have been reported present their maximum spin multiplicity.<sup>[28]</sup> However, there are a few with a spin-paired configuration, such as  $[\text{Rh}(\text{PPh}_3)_3]^+$ ,<sup>[39]</sup>  $[\text{Ni}(\text{mesityl})_3]^-$ ,<sup>[40]</sup>  $[\text{M}(\text{mesityl})_3]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ),<sup>[41]</sup> or  $d^2$  imido complexes.<sup>[42]</sup> The coordination geometry in the  $[\text{Rh}(\text{PPh}_3)_3]^+$  and  $[\text{Ni}(\text{mesityl})_3]^-$  complexes should be described as T-shaped rather than trigonal planar, and therefore the orbital scheme that applies<sup>[28]</sup> is similar to that found for square-planar complexes ( $SP\text{-ML}_4$  in Figure 6). A singlet state should be expected for  $d^8$  ions. In the case of the Rh and Ir mesityl complexes the coordination sphere is far from planar, and agostic interactions with methyl groups of the ligands have been identified. These account for an effective octahedral ligand field for which an  $S = 0$  situation is conceivable ( $OC\text{-ML}_6$  in Table 2). Such a situation has been shown through computational studies for a  $\text{Cr}^{\text{II}}$  alkoxy complex, in which the  $d_{x^2-y^2}$  orbital is strongly destabilized by  $\pi$  interactions, even if in this case the  $d^4$  configuration precludes a low-spin state.<sup>[43]</sup> As for the  $d^2$  imido complexes, again the strong  $\pi$ -donor character of the ligands in an anisotropic arrangement, combined with high oxidation states in those  $\text{W}^{\text{IV}}$ ,  $\text{Re}^{\text{V}}$ , and  $\text{Os}^{\text{VI}}$  complexes, should result in a strong destabilization of both the  $e'$  and  $e''$  sets of orbitals (Figure 10). As discussed above for the case of pseudotetrahedral complexes with one  $\pi$ -donor ligand, the hybridization required to alleviate the  $\sigma$ -antibonding nature of some d orbitals enhances the  $\pi$ -antibonding effect.

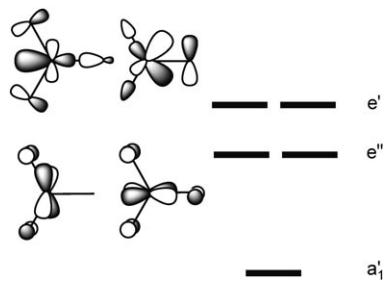


Figure 10. Destabilization of the  $e'$  and  $e''$  sets by strong  $\pi$ -donor ligands in  $d^2$  tricoordinate imido complexes.

### Some Final Considerations

The general tendency to label spin states as either high or low spin reflects the duality of the choice of spin state that is rooted in the general rules that govern the energy patterns for the d-MOs in transition-metal complexes. These orbitals can, in general, be divided into two subsets with nonbonding and antibonding character relative to the metal–ligand bonds. These two subsets are separated by a significant energy gap, the magnitude of which, together with the electron-pairing energy, ultimately determines the relative energies of the allowed spin states. Although some of the formally nonbonding MOs have antibonding contributions, these are minimized by hybridization with metal s and p orbitals of the same symmetry, resulting in only a small increase in energy relative to the strictly nonbonding orbitals. As a consequence, electron pairing within the nonbonding subset is forbidden before all its orbitals are half-occupied. This simplified orbital scheme, which is strongly dependent on the coordination number and geometry and disregards  $\pi$  interactions in a first approximation, allows us to qualitatively predict two or three allowed spin states for a variety of electron configurations and coordination geometries (Table 2). Exceptions to these rules arise from the promotion of one or more of the formally nonbonding orbitals to the antibonding set and are caused by one or more of three possible causes: 1) Severe distortions from the ideal geometries, 2) strongly anisotropic interaction with  $\pi$ -donor ligands, and 3) a high oxidation state of the metal atom in combination with strong  $\sigma$ -donor ligands.

Eventual references to intermediate-spin states are not in contradiction with the dual nature of the spin state but lies with the fact that three spin states are conceivable for some d<sup>n</sup> configurations. Then, it is the specific geometrical and bonding situation of each compound that determines which of these are the two allowed spin states. References to intermediate-spin states are found mostly in metal porphyrin complexes. If two additional ligands are coordinated to the metal atom besides the porphyrin ligand, only the highest and lowest spin states should be expected for a strictly octahedral coordination sphere (OC-ML<sub>6</sub> in Table 2). However, when the two axial ligands are much weaker donors compared to the porphyrin ring (e.g., tetrahydrofuran, ethanol, or water),<sup>[14]</sup> the d-orbital splitting pattern is closer to that of the square-planar complexes, for which the allowed spin states are different for d<sup>5</sup> and d<sup>6</sup> electron configurations (SP-ML<sub>4</sub> in Table 2). A similar situation is found in LaCoO<sub>3</sub>, for which the intermediate-spin state is stabilized by a tetragonal, Jahn-Teller-driven distortion of the coordination octahedron.<sup>[12]</sup>

It is clear that the traditional way of naming spin states for octahedral and tetragonal complexes, referring to the two allowed spin states as high and low, leads to inconsistencies when dealing with these systems, because one does not know beforehand whether a particular compound should be considered as octahedral or tetragonal from the orbital point of view. Other inconsistencies result from the traditional labeling of spin states. Consider, for example, the lowest allowed spin states of d<sup>5</sup>-ML<sub>5</sub> and d<sup>5</sup>-MXL<sub>5</sub> complexes, which are related by ligand association/dissociation. Even if we refer to a low-spin configuration in both cases, we are actually talking about different spin states, S = 3/2 and S = 1/2, respectively (see SPY-ML<sub>5</sub> and OC-ML<sub>6</sub> in Table 2).

To avoid the above inconsistencies in the naming of spin states, maybe some convention could be established that considers all the situations discussed here as well as potential new developments. Because in all cases there are, at most, three possible spin states, one could refer to high- and low-spin states for those electron configurations with

only two possibilities (d<sup>2</sup>, d<sup>3</sup>, d<sup>7</sup>, and d<sup>8</sup>), and to high-, intermediate-, and low-spin states for the d<sup>4</sup>, d<sup>5</sup>, and d<sup>6</sup> cases, regardless of whether such states in different geometries are allowed. There are some precedents for referring to square-pyramidal<sup>[15]</sup> or square-planar<sup>[16]</sup> complexes as having intermediate spin, but it would certainly change the way we usually name spin states in, for example, octahedral complexes. For instance, all known octahedral “low-spin” d<sup>4</sup>-metal complexes should be renamed as “intermediate spin”. In return, such nomenclature should allow for a clearer correlation between complexes that are related by association or dissociation of a ligand, and the name of the spin state would be unequivocally associated to the S value.

Experience shows that changes in nomenclature are rarely smoothly and universally adopted, and it may well be that the introduction of a new naming convention for the spin states finally brings about more confusion than it avoids. In any case, we hope that the reflections presented in this essay may help clarify the concepts that describe spin states and that more data and new ideas can be proposed in the near future by other researchers along these lines. Whatever convention is adopted in each particular case, to avoid ambiguities and misinterpretations the most important point is to be aware of the strong interdependence of spin states and coordination geometry and to be sure to have at hand a clear picture of the splitting pattern of the d molecular orbitals and of the factors that affect the choice of spin state. No matter how high or low one considers the spin of a given compound, probably the wisest choice is to specify in all cases the total spin or the spin multiplicity.

Published online: April 10, 2006

García-Monforte, A. Martín, B. Menjón, G. Rodríguez, *Chem. Commun.* **1997**, 1721; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Chem. Commun.* **2001**, 2138; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, C. Rillo, *Chem. Eur. J.* **2002**, 8, 4056; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Chem. Commun.* **2002**, 728; P. J. Alonso, L. R. Falvello, J. Forniés, M. A. García-Monforte, B. Menjón, *Angew. Chem.* **2004**, 116, 5337; *Angew. Chem. Int. Ed.* **2004**, 43, 5225; I. Ara, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Chem. Commun.* **2004**, 10, 4186; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Organometallics* **2005**, 24, 1269; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Chem. Eur. J.* **2005**, 11, 4713; J. Forniés, A. Martín, L. F. Martín, B. Menjón, *Organometallics* **2005**, 24, 3266.

- [2] S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J.* **1998**, 4, 1687; S. Kleinhenz, K. Seppelt, *Chem. Eur. J.* **1999**, 5, 3573; B. Toessler, S. Kleinhenz, K. Seppelt, *Chem. Commun.* **2000**, 1039.
- [3] K. Dunbar, R. A. Henitz, *Prog. Inorg. Chem.* **1997**, 45, 283.
- [4] W. E. Buschmann, A. M. Arif, J. S. Miller, *Angew. Chem.* **1998**, 110, 813; *Angew. Chem. Int. Ed.* **1998**, 37, 781.
- [5] K. J. Nelson, I. D. Giles, W. W. Shum, A. M. Arif, J. S. Miller, *Angew. Chem.* **2005**, 117, 3189; *Angew. Chem. Int. Ed.* **2005**, 44, 3129.
- [6] W. R. Entley, C. R. Treadway, S. R. Wilson, G. S. Girolami, *J. Am. Chem. Soc.* **1997**, 119, 6251.
- [7] M. Verdaguer, G. S. Girolami in *Magnetism: Molecules to Materials*, Vol. V (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2005**, p. 283; L. M. C. Beltran, J. R. Long, *Acc. Chem. Res.* **2005**, 38, 325.
- [8] E. Bernhardt, C. Bach, B. Bley, R. Wartchow, U. Westphal, I. H. T. Sham, B. von Ahsen, C. Wang, H. Willner, R. C. Thompson, F. Aubke, *Inorg. Chem.* **2005**, 44, 4189; M. Finke, E. Bernhardt, H. Willner, C. W. Lehmann, F. Aubke, *Inorg. Chem.* **2005**, 44, 4206; H. Willner, F. Aubke, *Organometallics* **2003**, 22, 3612; J. E. Ellis, *Organometallics* **2003**, 22, 3322.
- [9] M. V. Metz, Y. Sun, C. L. Stern, T. L. Marks, *Organometallics* **2002**, 21, 3691; T. C. Rosen, K. Kirschbaum, D. M. Giolando, *Dalton Trans.* **2003**, 120; M. C. Buzzeo, A. H. Iqbal, C. M. Long, D. Millar, A. Patel, M. A. Pellow, S. A. Saddoughi, A. L. Smerton, J. F. C. Turner, J. D. Wadhawan, R. G. Compton, J. A. Golen, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.* **2004**, 43, 7709.

- [10] N. T. Tran, D. R. Powell, L. F. Dahl, *Angew. Chem. Int. Ed.* **2000**, *39*, 4121; A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.* **1999**, 1347; S. Dehnen, A. Eichhofer, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, 279.
- [11] S. A. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar, E. Münck, *Inorg. Chem.* **2005**, *44*, 4915.
- [12] K. Knížek, P. Novák, Z. Jirák, *Phys. Rev. B* **2005**, *71*, 054420; J. Wang, Z. D. Wang, W. Zhang, D. Y. Xing, *Phys. Rev. B* **2002**, *66*, 064406.
- [13] S. Obara, H. Kashiwagi, *J. Chem. Phys.* **1982**, *77*, 3155; T. Ikeue, T. Saitoh, T. Yamaguchi, Y. Ohgo, M. Nakamura, M. Takahashi, M. Takeda, *Chem. Commun.* **2000**, 1989; H. Goff, G. N. La Mar, C. A. Reed, *J. Am. Chem. Soc.* **1977**, *99*, 3641.
- [14] J.-P. Simonato, J. Pécaut, L. Le Pape, J.-L. Oddou, C. Jeandey, M. Shang, W. R. Scheidt, J. Wojaczynski, S. Wolowiec, L. Latos-Grazynski, J.-C. Marchon, *Inorg. Chem.* **2000**, *39*, 3978; T. Sakai, Y. Ohgo, T. Ikeue, M. Takahashi, M. Takeda, M. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13028.
- [15] K. M. Barkigia, M. W. Renner, J. Fajer, *J. Porphyrins Phthalocyanines* **2001**, *5*, 415.
- [16] K. Ray, A. Begum, T. Weyhermüller, S. Piligkos, J. van Slageren, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* **2005**, *127*, 4403.
- [17] T. A. Albright, J. K. Burdett, W.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**.
- [18] R. Poli, *Chem. Rev.* **1996**, *96*, 2135; R. Poli, J. N. Harvey, *Chem. Soc. Rev.* **2003**, *32*, 1; J. N. Harvey, R. Poli, K. M. Smith, *Coord. Chem. Rev.* **2003**, 238–239, 347; R. Poli, *J. Organomet. Chem.* **2004**, *689*, 4291.
- [19] *Nomenclature of Inorganic Chemistry. IUPAC Recommendations 2005* (Eds.: N. G. Connelly, T. DAmhus, R. M. Hartshorn, A. T. Hutton), Royal Society of Chemistry, **2005**.
- [20] F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., Wiley-Interscience, New York, **1990**.
- [21] “And here I wish I could tell you half the things Alice used to say, beginning with her favourite phrase ‘Let’s pretend.’” Lewis Carroll, *Through The Looking Glass* (1871).
- [22] The orbital patterns shown in Figure 6 were obtained from DFT-B3LYP calculations on the low-spin states of the compounds indicated at their experimental structures by using the Gaussian package (Gaussian03 (Revision B.4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**). A test calculation for the high-spin state of  $[\text{Cr}(\text{CN})_6]^{4-}$  indicates that the d-orbital energy gap is only slightly reduced and the semiquantitative picture of Figure 6 is still valid.
- [23] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins, New York, **1993**.
- [24] M. Gerloch, E. C. Constable, *Transition Metal Chemistry*, VCH, Weinheim, **1994**.
- [25] J. A. Real, A. B. Gaspar, M. C. Muñoz, *Dalton Trans.* **2005**, 2062.
- [26] J. S. Griffith, *Theory of Transition Metal Ions*, Cambridge University Press, Cambridge, **1961**.
- [27] T. Nguyen, A. Panda, M. M. Olmstead, A. F. Richards, M. Stender, M. Brynda, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 8545; W. M. Reiff, A. LaPointe, E. H. Witten, *J. Am. Chem. Soc.* **2004**, *126*, 10206.
- [28] S. Alvarez, *Coord. Chem. Rev.* **1999**, 193–195, 13.
- [29] J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857.
- [30] J. L. Detrich, R. Konecný, W. M. Vetter, D. Doren, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.* **1996**, *118*, 1703; J. D. Jewson, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, K. H. Theopold, *Organometallics* **1999**, *18*, 300; O. M. Reinaud, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.* **1994**, *116*, 1703; N. Shirasawa, M. Akita, S. Hikichi, Y. Moro-oka, *Chem. Commun.* **1999**, 417; N. Shirasawa, T. T. Nguyet, S. Hikichi, Y. Moro-oka, M. Akita, *Organometallics* **2001**, *20*, 3582.
- [31] T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 10782; T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 6252; S. D. Brown, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 322; S. D. Brown, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 4538.
- [32] S. D. Brown, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 1913; D. M. Jenkins, J. C. Peters, *J. Am. Chem. Soc.* **2005**, *127*, 7148.
- [33] P. J. Schebler, B. S. Mandimutsira, C. G. Riordan, L. M. Liable-Sands, C. D. Incarvito, A. L. Rheingold, *J. Am. Chem. Soc.* **2001**, *123*, 331; P. J. Schebler, C. G. Riordan, I. A. Guzei, A. L. Rheingold, *Inorg. Chem.* **1998**, *37*, 4754.
- [34] I. Nieto, F. Cervantes-Lee, J. M. Smith, *Chem. Commun.* **2005**, 3811.
- [35] V. Dimitrov, A. Linden, *Angew. Chem.* **2003**, *115*, 2735; *Angew. Chem. Int. Ed.* **2003**, *42*, 2631.
- [36] J. Cirera, P. Alemany, S. Alvarez, *Chem. Eur. J.* **2004**, *10*, 190.
- [37] E. K. Byrne, K. H. Theopold, *J. Am. Chem. Soc.* **1989**, *111*, 3887.
- [38] A. Walstrom, M. Pink, X. Yang, J. Tomaszewski, M.-H. Baik, K. G. Caulton, *J. Am. Chem. Soc.* **2005**, *127*, 5330.
- [39] Y. W. Yared, S. L. Miles, R. Bau, C. A. Reed, *J. Am. Chem. Soc.* **1977**, *99*, 7076; C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Beehnken, M. F. Hawthorne, *J. Am. Chem. Soc.* **1984**, *106*, 2990.
- [40] R. Hay-Motherwell, G. Wilkinson, T. K. Sweet, M. B. Hursthouse, *Polyhedron* **1996**, *15*, 3163.
- [41] D. M. Roddick, T. D. Tilley, A. L. Rheingold, S. J. Geib, M. B. Hursthouse, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* **1990**, 1242; R. S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1992**, 3477.
- [42] D. F. Eppley, P. T. Wolczanski, G. D. Van Duyne, *Angew. Chem.* **1991**, *103*, 616; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 584; J. T. Anhaus, T. P. Kee, M. H. Schofield, R. R. Schrock, *J. Am. Chem. Soc.* **1990**, *112*, 1642; D. S. Williams, R. R. Schrock, *Organometallics* **1993**, *12*, 1148; D. S. Williams, J. T. Anhaus, M. H. Schofield, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1991**, *113*, 5480.
- [43] O. L. Sydora, P. T. Wolczanski, E. B. Lobkovsky, C. Buda, T. R. Cundari, *Inorg. Chem.* **2005**, *44*, 2606.