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Spin Density Distribution in Transition Metal Complexes: Some Thoughts and Hints

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The spin density distribution in transition metal complexes is discussed in qualitative terms, taking into account the coexistence of spin delocalization and spin polarization mechanisms, with the help of numerical results for several complexes obtained from density functional calculations. The covalent character of the metal–ligand bonds as well as the σ- or π-characteristics of the partially filled d orbitals must be taken into account to qualitatively predict the sign of the spin density at a particular atom within a ligand. The same patterns can be applied to binuclear complexes and can be helpful in determining the ferro- or antiferromagnetic character of the exchange coupling between two paramagnetic ions when the energy gap between the partially occupied molecular orbitals is small. An attempt is made to establish a link between the qualitative Hay–Thibeault–Hoffmann model of exchange coupling and the of spin polarization model.

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Key Words: *spin density, spin polarization, spin delocalization, exchange coupling*

The distribution of the unpaired spin density has long been recognized to be important in determining the NMR isotropic shift of the different nuclei in paramagnetic molecules.[1–5] Notice, however, that NMR spectra are only sensitive to the electron spin density at the nucleus and provide information only on that part of the spin density associated with s orbitals. The hyperfine coupling of the electron spin density with nuclear spin has traditionally been detected in the EPR spectra. In that case, comparison of the isotropic and anisotropic hyperfine couplings is needed in order to obtain the sign of the spin density.[6] Another technique that provides information on the spin density distribution is the polarized neutron diffraction (abbreviated in what follows as pnd).[44] Such data can be fitted to a set of atomic orbitals at various levels of sophistication. The validity of the method has been critically discussed, and other methods are available that do not introduce an *a priori* theoretical model to fit the experimental data, such as the so-called *magnetic wave function modeling*[7] or the *maximum entropy* method.[8] In the framework of the qualitative approach of this paper, the fitting of the experimental pnd data to a set of atomic orbitals has the advantage of allowing direct comparison with theoretical estimates, provided that the set of orbitals used for such fitting is consistent with the basis sets used for theoretical studies, which is not always the case. A renewed interest in the study of spin density distribution has bloomed in recent years because its understanding is foreseen as a useful tool for the design of ferro- or antiferromagnetic interactions between paramagnetic centers in polynuclear systems.

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Before going on it is worth commenting on the expression *spin density*. This term, even though widely used, can be misleading. The electron density, defined as the number of electrons per unit volume, $\rho(\mathbf{r}) = |\Psi(\mathbf{r})|^2$, is always positive. This is not the case for the spin density, for which positive or negative values can be found. By convention, the electron density associated with a spin aligned parallel to the applied field (up-magnetization in pnd) is taken as a positive spin density, whereas that corresponding to antiparallel spin (down-magnetization in pnd) is denoted as negative. The expression spin population would probably be more appropriate than spin density.[6] However, to the best of our knowledge this point is not fixed by an international agreement, and we shall use the usual expression *spin density* for the sake of understandability.

By appropriately taking into account the molecular orbital description of the electronic structure of a complex, one should be able to qualitatively explain most features of the electron spin density distribution. In this paper

we attempt to provide a few general rules and hints for such qualitative description of the spin distribution in a coordination compound, illustrating the discussion with the experimental and calculated data for selected compounds. Our qualitative discussion will avoid, whenever possible, those cases in which the spin is not a good quantum number and mixes strongly with orbital moment, e.g., those octahedral complexes having a T ground term. Therefore, we exclude those systems with a fully delocalized electron between the two magnetic centers in a double exchange process,[9] and disregard also those cases in which a charge transfer excited electronic configuration is close in energy to—and can mix with—the ground configuration.[10] Finally, we deal only with systems than can be considered as isotropic, with negligible dipolar, anisotropic and antisymmetric interactions.

SPIN DELOCALIZATION AND SPIN POLARIZATION

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There are two mechanisms through which an unpaired electron of a transition metal ion can place some spin density at the other atoms of the molecule. First, an unpaired electron can be described by a molecular orbital φ_i, expressed as a linear combination of atomic orbitals χ_μ [Eq. (1)]. Hence, the probability of finding the unpaired electron at a particular atomic orbital χ_μ is related to the square of the coefficient $c_{i\mu}$ with which that AO participates in the singly occupied molecular orbital (SOMO), as reflected by the Mulliken population analysis [Eq. (2)], where $S_{\mu\nu}$ are the overlap integrals between atomic orbitals). Since we adopt the convention that the unpaired electron has a positive spin, its delocalization results in a distribution of positive spin density throughout the molecule determined by the composition of the SOMO. The resulting distribution of spin density is said to arise from a *spin delocalization mechanism*. Summing up the spin densities of the different atomic orbitals of one atom, one obtains the corresponding atomic spin density.

$$\varphi_i = \sum_\mu c_{i\mu}\chi_\mu, \tag{1}$$

$$\rho_\mu = c_{i\mu}^2 \sum_\nu c_{i\mu}c_{i\nu}S_{\mu\nu}. \tag{2}$$

There is a second mechanism through which the positive spin at the paramagnetic center may induce some spin density of the opposite sign at the atoms bonded to it. This effect propagates through the molecule

away from the paramagnetic center, thus generating spin densities of alternating sign and is known as *spin polarization*. The net spin density at a particular AO or atom therefore results from the combination of the two mechanisms that can add up to give a positive value (when both mechanisms contribute a positive spin density) or compensate in part to give either a small positive (delocalization mechanism predominant) or negative (spin polarization predominant) total spin density.

To understand the spin polarization mechanism one must consider the interaction of the unpaired electron with an electron pair in a bonding or non-bonding molecular orbital. It is just a combined result of the Coulomb and exchange terms that appears in the Hartree–Fock expression for the energy of the molecule:

$$E_{HF} = 2\sum_i h_{ii} + \sum_i \sum_j \left(2J_{ij} - K_{ij}\right) + V_{NN} \tag{3}$$

where h_{ii} are one-electron integrals, V_{NN} is the internuclear repulsion term, and J_{ij} and K_{ij} are the Coulomb and exchange integrals between molecular orbitals i and j, respectively:

$$J_{ij} = \left\langle \varphi_i(1)\varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_i(1)\varphi_j(2) \right\rangle, \tag{4}$$

$$K_{ij} = \left\langle \varphi_i(1)\varphi_j(2) \left| \frac{1}{r_{12}} \right| \varphi_j(1)\varphi_i(2) \right\rangle. \tag{5}$$

It is important to note that the integrals in Eqs. (4) and (5) are always positive. Therefore, to minimize the energy [Eq. (3)], the molecular orbitals must have a composition that makes the J_{ij} integrals as small as possible, but the K_{ij} integrals as large as possible. In contrast to what occurs with the overlap integrals, for each differential of volume the product $\varphi_i\varphi_j$ appears squared in Eqs. (4) and (5). Hence, Coulomb and exchange integrals between orthogonal orbitals can be non-zero provided the two orbitals have large coefficients at the same atoms of the molecule. The exchange integrals are non-zero only for electrons with the same spin.[11] Therefore, spin-orbitals with the same spin tend to be centered on the same atoms to produce large K_{ij} values. In contrast, the spin-orbitals with opposite spin tend to segregate in different zones of the molecule as to make those J_{ij} values as small as possible. This result is closely related to the empirical Hund's rule for atoms, which states that for a given electron configuration the term with the highest spin multiplicity has the lowest energy.

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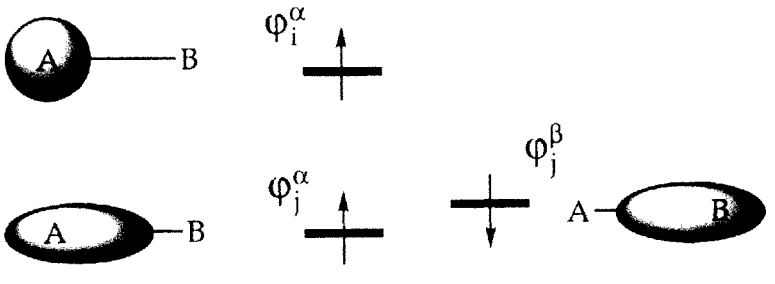
We illustrate this with a hypothetical system AB with three electrons and net spin $S = 1/2$, represented by the three spin-orbitals **1** in an unrestricted Hartree–Fock (UHF) approach, in which the molecular orbitals for α and β spins are allowed to have different composition and energies. Let us assume that the molecular orbital carrying the unpaired electron (with positive spin), φ_i^{α}, is mostly localized at atom A. Then the function φ_j^{α} must also be localized at atom A to make K_{ij} as large as possible. Consequently, the φ_j^{β} function will be largely localized at atom B, to give small values of the Coulomb integrals between α and β spin-orbitals. The net result is that a negative spin density appears at atom B, i.e., the electron pair described by φ_i^{α} and φ_j^{β} is *polarized*, with the electron having positive spin localized closer to atom A and that with the negative spin closer to atom B.

Extending these ideas to a transition metal complex is straightforward considering that the unpaired electrons in this case are mostly localized at the metal atom. For a bonding electron pair, the exchange term makes more stable a spatial distribution with the α electron closer to the unpaired electron (**2a**) than one with the same distribution for the α and β electrons (**2b**). Notice that for spin polarization to appear in computa-



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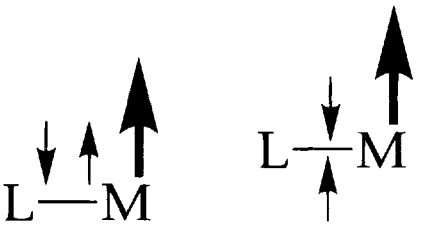

2a 2b

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tional studies one then needs to use an unrestricted approach (e.g., UHF) or include electron correlation in some way (configuration interaction or multiconfiguration calculations), since a restricted approach, with identical orbitals for the α and β electrons, is unable to provide for the spatial separation represented in **2**.

A COMPUTATIONAL APPROACH

Several approaches can be used to calculate the spin density distribution in a coordination compound. To evaluate the different approaches, we have carried out test calculations for several complexes for which pnd experimental data is available. In this section we briefly comment on the main results of such studies, to give the reader a feeling for the degree of agreement between the calculated and experimental values. After showing the good agreement between calculations and experiment, we will consistently use calculations on several compounds to illustrate the main hints for the interpretation and prediction of experimental spin density distribution.

Density functional (DFT) calculations were performed for several mononuclear transition metal complexes for which pnd experimental data is available. After several test calculations, we have chosen to use a double-ζ basis set (eventually employing effective core pseudopotentials, as for the hexacyano complexes discussed below) and the B3LYP method,[12-14] together with a Mulliken population analysis, which yield a fair description of the general pattern for the spin distribution throughout the molecule as compared to the experimental pnd data. In Fig. 1 we show the good correlation between the calculated and the experimental spin densities, when the former are obtained using the B3LYP method and a Mulliken population analysis. The largest discrepancies between the calculated and experimental data correspond to the sum of the 4s and 4p orbitals of the metal atoms in three different complexes. In one case, there is also a strong disagreement for the values of the 3d orbitals of t_{2g} type that practically compensates for the error in the 4s/4p density. Apparently, these discrepancies could be attributed to differences between the orbital basis used for the fitting of the experimental data and the valence basis set used in the MO calculations.

An interesting result is that the spin density of a particular atom comes from its valence orbitals only, with negligible spin densities for the core

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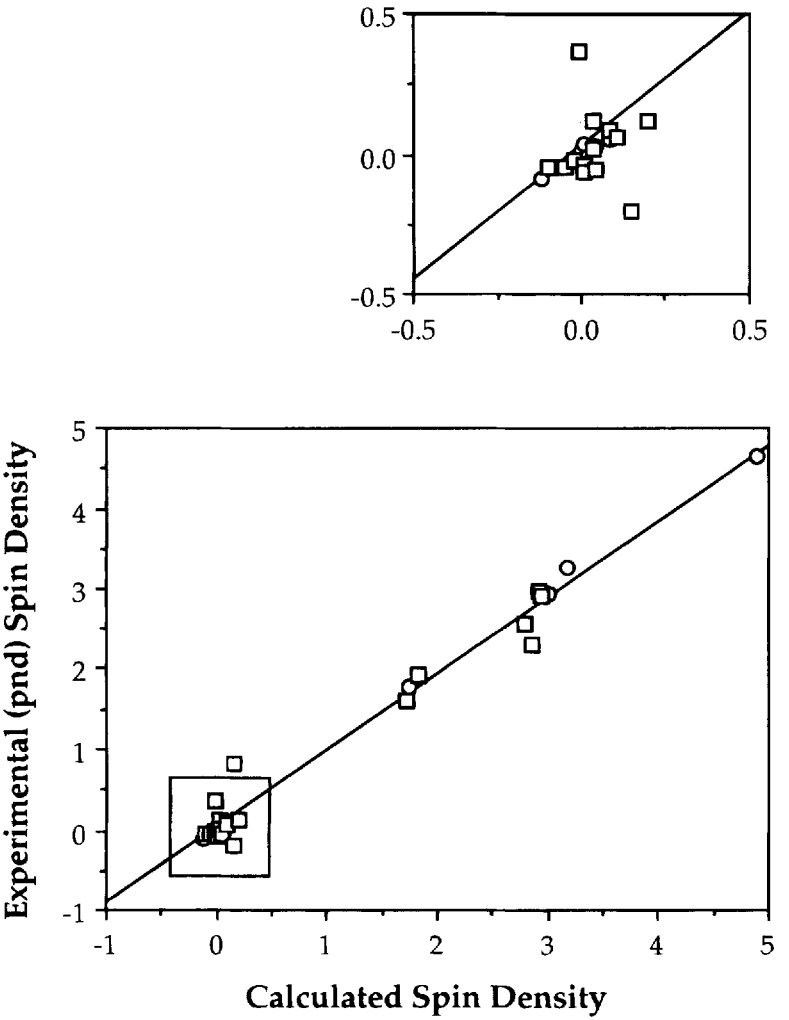

FIGURE 1 Comparison of calculated spin densities and experimental data from polarised neutron diffraction experiments for the complexes, $[Mn(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{2+}$, $[Cr(CN)_6]^{3-}$ and $[Ni(H_2O)_6]^{2+}$ (Table II). Circles correspond to atomic, squares to orbital spin densities. Experimental data from Refs. 15–19.

orbitals, as checked exhaustively with different methods and population analysis schemes for $[Cr(CN)_6]^{3-}$. This makes the discussion of the spin density distribution simpler. Furthermore, the use of an effective core potential can be envisaged for the computational study of the spin distribution in coordination compounds without loss of precision.

It is worthwhile to stress that the spin densities at different AO's of the same atom may have different signs. This is an important point since there is an extended tendency to think of spin density distribution in terms of atomic populations, which for some purposes may be an oversimplification. We will show below that in some instances one cannot understand the spin density distribution at the atomic level unless it is first understood at the orbital level.

SPIN DISTRIBUTION OF t_{2g} ELECTRONS: π-BASIC AND π-ACID LIGANDS

Much insight can be gained into the mechanisms of spin density distribution by looking at the results obtained for complexes with π-donor or π-acceptor ligands. Let us discuss first some halo complexes of d^3 ions. Later on we will focus on the related Cr^{3+} cyano compound to discuss the effects associated with π acid ligands. All the data needed for the subsequent discussion are displayed in Table I.

To illustrate the two mechanisms, we consider the case of $[CrCl_6]^{3-}$, for which the unpaired electrons are expected to occupy a set of $2t_{2g}$ orbitals centered mainly at the Cr atom and Cr–Cl π-antibonding in character (see **3**). When the molecular orbitals for the α and β electrons are obtained as independent linear combinations of the atomic orbitals (unrestricted approach), the α-$2t_{2g}$ orbitals are more stable than the β-$2t_{2g}$ ones, as a result of the Coulomb and exchange contributions to the orbital energies ϵ_i (eq. 6). Therefore the α-$2t_{2g}$ orbitals are occupied and β-$2t_{2g}$ are empty (**4**). As a consequence, a total spin density of +3.00 (i.e., 3 electrons) should result for the t_{2g} molecular orbitals. Since the major contributions to such MO's come from the Cr d_{xy}, d_{xz} and d_{yz} atomic orbitals, a large part of the three spins can be ascribed to such t_{2g} atomic orbitals (2.79 in our calculations, Table I). The remaining spin density is delocalized to the p_π orbitals of the chlorides (0.035 per ligand) due to their contribution to the $2t_{2g}$ MO's (**4**). In summary, the number of unpaired electrons (3.00 in this case) gives, to a first approximation, the

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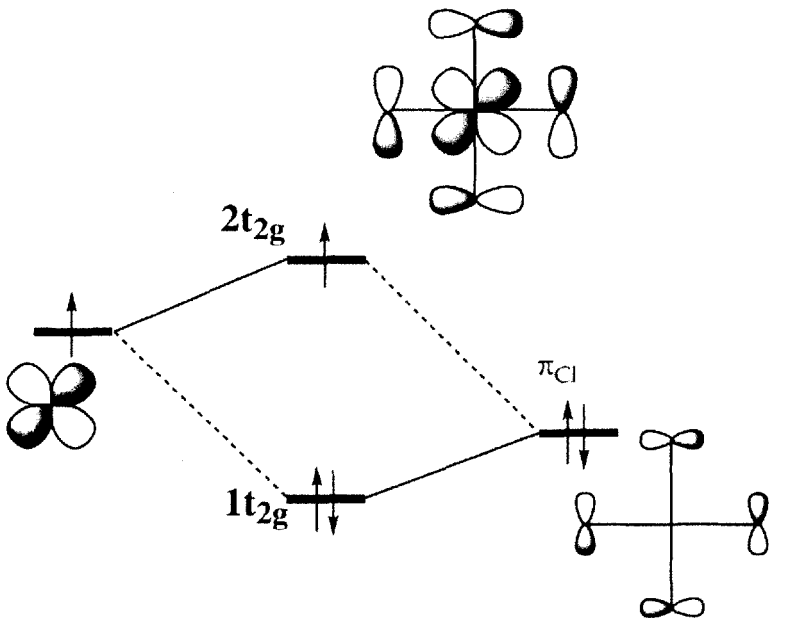
TABLE I

Calculated orbital and atomic spin densities for several octahedral complexes with t_{2g}^3 electron configuration.

Atomic Orbitals	$[CrF_6]^{3-}$	$[CrCl_6]^{3-}$	$[Cr(CN)_6]^{3-}$	$[MoCl_6]^{3-}$	$[WCl_6]^{3-}$
M: e_g	0.103	0.261	0.196	0.112	0.091
t_{2g}	2.794	2.791	2.822	2.625	2.632
s	0.012	0.028	0.042	0.023	0.045
$p_{x,y,z}$	0.0003	0.0234	0.042	0.021	0.036
total M	2.919	3.101	2.889	2.476	2.470
X: $s + p_\sigma$	–0.022	–0.052	–0.061	–0.027	–0.029
p_π	0.035	0.035	–0.056	0.063	0.062
total X	0.013	–0.017	–0.117	0.037	0.033
N: $s + p_\sigma$			0.009		
p_π			0.079		
total N			0.088		
Total π (M + L)	3.004	3.001	2.960	3.003	3.004



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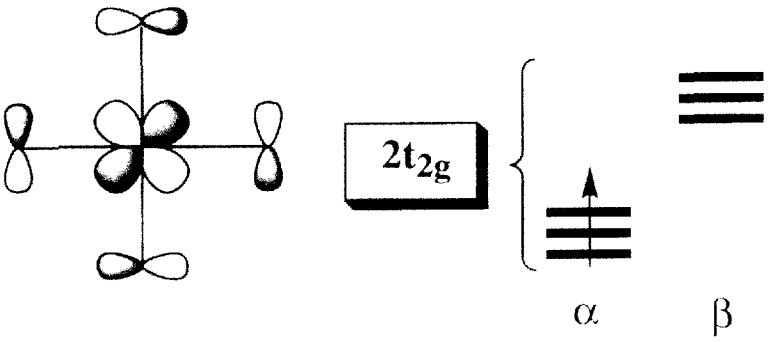

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total spin density that is spread through the atomic orbitals with effective participation in the SOMO's (the $2t_{2g}$ molecular orbitals in this case). This is what is called the *spin delocalization* mechanism.

$$\epsilon_i = h_{ii} + \sum_j (J_{ij} - K_{ij}). \tag{6}$$

Let us now see how the spin polarization appears in molecular orbital calculations. Other electrons of this molecule that can be affected by the presence of unpaired electrons in the metal t_{2g} orbitals are those in bonding MO's (a_{1g}, t_{1u} and $1e_g$), with large contributions from the atomic orbitals of the chlorides. We consider one of the two degenerate $1e_g$ bonding MO's as an example. Due to the effect of the Coulomb and exchange terms discussed above, a topology of these two orbitals results such that the α MO is polarized toward the metal atom, while the β MO is polarized toward the ligand (the actual calculated wavefunctions are schematically shown in **5**). As a result, the bonding orbitals place some additional positive spin density at the atomic e_g-type orbitals ($d_{x^2-y^2}$ and d_{z^2}), and the same amount of negative spin density at the σ-type AO's of the six chloride ligands (the numerical data in Table I illustrate this). The generation of a finite spin density by polarization of a couple of paired electrons is known as the *polarization mechanism*. Notice that in this case, in which the delocalization is small due to the ionic nature and π character of the singly occupied molecular orbitals (SOMO's), the spin density arising from the polarization mechanism (s and p_σ orbitals of Cl) is of similar magnitude to that found for the delocalization pathway (p_π of Cl).

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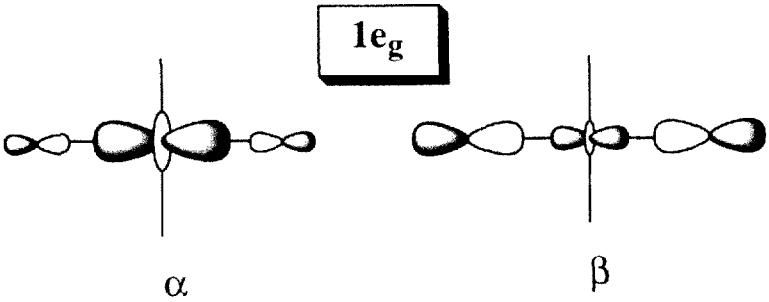

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In much the same way described above for the e_g electron pair, the a_g and t_{1u} σ-bonding electron pairs, involving the metal s and p orbitals, respectively, are polarized by the $2t_{2g}$ spin density localized at the Cr atom. Hence, a small amount of positive spin density appears at the Cr-4s and 4p orbitals, and the total spin density at this atom becomes higher than that coming from the t_{2g} unpaired electrons (3.101 versus 2.791). Apparently, the spin polarization is much more important for the metal 3d ($1e_g$ electron pair) than for the metal 4s and 4p orbitals. The concentration of the positive spin of the bonding electron pairs close to the metal atom (0.26) implies a buildup of a similar amount of negative spin density (–0.31) at the s and p_σ orbitals of the six chlorides.

It is important to realize that in the same Cl atom coexist a positive spin density (in the p_π orbitals), resulting from the delocalization mechanism, and a negative spin density (in the s and p_σ orbitals), resulting from spin polarization. The net spin density for the Cl atom is thus the sum of the σ and π components. In the present case, in which electron delocalization is due to a π-type interaction, spin delocalization and spin polarization have similar magnitudes and the net spin at the donor atom is small, either positive (fluoro complex) or negative (chloro complex). Substitution of the central Cr atom by Mo or W, with more diffuse atomic orbitals, results in a larger delocalization. Finally, it is interesting that the combined spin density of the π-type orbitals of the metal and the six ligands adds up to the number of unpaired electrons. Hence, it appears that the spin density in the π orbitals can be explained by making use of the spin delocalization mechanism only.

The analysis of the spin density distribution for a related compound with π-acid ligands, $[Cr(CN)_6]^{3-}$ reveals new interesting features. In prin-

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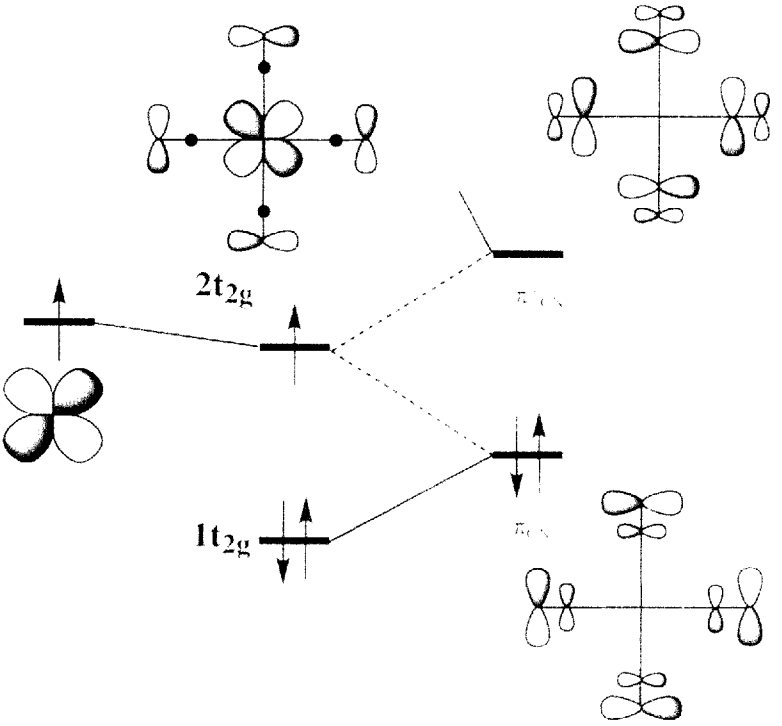
ciple, π-delocalization should also affect the spin density at the donor atoms, but the topology of the molecular orbitals in this case gives a different result than in the one just discussed. Since the metal d orbitals of the t_{2g} block interact both with the π and π* orbitals of the cyano groups, the SOMO's have practically no contribution at the carbon atoms but a sizable contribution at the nitrogen atoms (see **6**; for a more detailed discussion of the topology of these orbitals, see Ref. 20). The outcome is that a relatively large positive spin density is delocalized to the p_π orbitals of the nitrogen atoms, resulting in a net positive density at those atoms. Since the carbon atoms experience no spin delocalization, all their atomic orbitals are spin-polarized. Hence, the atomic spin density is positive at the nitrogen and negative at the carbon atoms, due to the peculiar orbital topology of the cyano complex. Let us remark that the combined spin density of the π orbitals of the metal and ligand atoms adds up to 3.00,



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which is probably a result of the symmetry separation of the σ and π orbitals in the octahedral molecules. Not unexpectedly, the degree of spin polarization is roughly proportional to the number of unpaired electrons. In Fig. 2 we show how the spin polarization effect on the empty orbitals of the metal atom and on the donor atom increases with the number of unpaired electrons, regardless of the nature of the SOMO's.

SPIN DISTRIBUTION OF t_{2g} AND e_g ELECTRONS; σ-DONOR LIGANDS

It is interesting to discuss now the spin distribution in a complex with mostly σ metal–ligand bonding and polyatomic ligands. For this purpose we use the calculated data for aqua-complexes of divalent transi-

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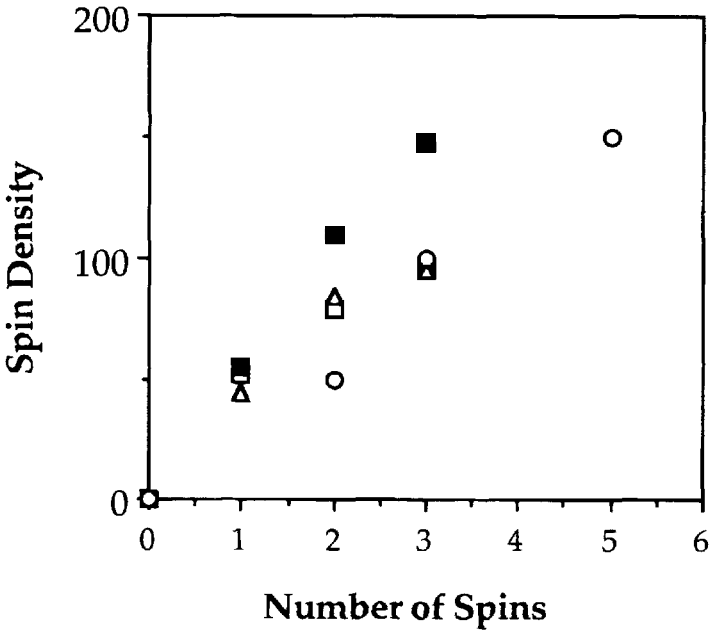

FIGURE 2 Spin density (× 10^3) as a function of the number of unpaired electrons for the s and p metal orbitals in $[M(H_2O)_6]^{2+}$ (circles), the e_g metal orbitals in $[M(CN)_6]^{3-}$ (open squares and triangles), and for the C atoms of the cyano ligands in $[M(CN)_6]^{3-}$ (absolute values, closed squares).

tion metal ions with the maximum number of unpaired electrons in the t_{2g} or in the e_g orbitals, or in both (Table II). The pnd data for these compounds is known[15-17] and is in general consistent with the theoretical data presented here. The only exception is that pnd gives a negative spin for the e_g orbitals of V^{2+} and for the s and p orbitals of Mn^{2+}, whereas the calculated values are positive as expected from a spin polarization mechanism. We believe that such disagreement is due to the use of a restricted set of functions for the fitting of the pnd data.

The large spin density at the formally occupied d-block orbitals is consistent with the electron configurations, if somewhat decreased because of partial delocalization onto the ligands. The spin polarization mechanism induces a smaller positive spin density at the metal atomic orbitals that are doubly occupied (i.e., t_{2g} in Ni^{2+}) or empty (i.e., e_g in Cr^{3+} and 4s, 4p in the three cases). When unpaired electrons are present in e_g orbitals (Ni^{2+} and Mn^{2+}), their metal–ligand σ^* character delocalizes them onto the oxygen donor atoms, and a positive spin density is found there. The larger density found at the oxygen atoms for Ni^{2+} than for Mn^{2+} should be attributed to the more covalent character of the Ni–O bond, as reflected by the nephelauxetic series.[21] For the V^{2+}, Cr^{3+} and Mn^{2+} complexes, the π-type unpaired t_{2g} electrons are less delocalized to the ligands, as evidenced by a spin density close to unity at each t_{2g} orbital (Table II). In that case, only the spin polarization mechanism is effective for the donor atoms, and they present a small negative spin density. Thus, it can be said that a positive spin appears at the donor atoms as a result of delocalization, except when the donor atoms are the most

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TABLE II

Calculated orbital and atomic spin densities for hexaaqua complexes of divalent transition metal ions with different occupations of the t_{2g} and e_g orbitals. Experimental values given in parentheses.

Atomic Orbital	Cr^{3+} t_{2g}^3	V^{2+} t_{2g}^3	Ni^{2+} $t_{2g}^6 e_g^2$	Mn^{2+} $t_{2g}^3 e_g^2$
t_{2g}	2.838	2.940 (2.910)	0.006 (–0.060)	2.960 (2.960)
e_g	0.134	0.041 (–0.050)	1.732 (1.600)	1.852 (1.930)
4s + 4p	0.024	0.031 (0.120)	–0.004 (0.370)	0.039 (–0.200)
total M	2.995	3.013 (2.940)	1.733 (1.770)	4.849 (4.640)
total O	–0.006	–0.006 (–0.013)	0.044 (0.032)	0.022 (0.036)
H-1s	0.003	0.003 (0.012)	0.000 (0.003)	0.002 (0.012)

electronegative F and O and the unpaired electrons are in a π-type (t_{2g}) MO. In this group of complexes, with rather ionic metal–ligand bonds, very little spin density can be found at the H atoms, and we defer a discussion of the spin density in hydrogen atoms to a later section.

AN EXAMPLE OF SPIN DELOCALIZATION AND POLARIZATION THROUGH A POLYATOMIC LIGAND

The simplest cases to qualitatively analyze the spin distribution in transition metal complexes correspond to the complexes with e_g^n configurations, with n = 1–3, because the e_g SOMO's are metal–ligand σ* and present a sizable delocalization of the unpaired electron(s) to the donor atom of the ligand. Detailed experimental information on spin distribution at the atomic level is known from NMR experiments for the complex [Ni(acac)$_2$py]. This compound, with a square pyramidal structure (**7**) has two unpaired electrons in the e_g-like molecular orbitals with largely Ni-3d character. Understanding the spin delocalization and polarization throughout the ligands can provide helpful hints for the interpretation of the spin density distribution in complex ligands coordinated to paramagnetic metal ions. Although the symmetry is much lower than octahedral in this compound, we will continue to use the labels e_g and t_{2g} for the 3d metal orbitals of σ and π character, respectively.

The calculated spin densities for the different atoms in these molecules (Table III) are in good agreement, both in their signs and their relative values, with the ^{1}H- and ^{13}C-NMR paramagnetic shifts reported in the literature.[1] However, since the NMR experiments provide information only on the spin density at the ns orbitals, we will use our theoretical data in

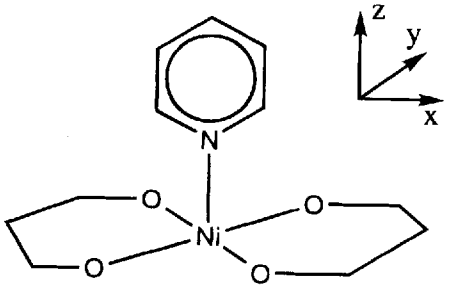

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TABLE III

Calculated spin densities for the atomic orbitals and atoms in [Ni(acac)$_2$py].

Ni		acac		Pyridine	
e_g: xy	0.739	s(O)	0.004	s(N)	0.025
z^2	0.766	p_z(O)	0.008	p_z(N)	0.068
t_{2g}	0.018	p_x(O)	0.048	p_x(N)	0.004
	0.008	p_y(O)	0.013	p_y(N)	0.009
	0.007	total O	0.073	total (N)	0.108
4s	0.016				
$4p_x$	0.003	s(C_1)	–0.0018	s(C_α)	–0.0016
$4p_y$	-0.003	p_x(C_1)	–0.0030	p_x(C_α)	–0.0018
$4p_z$	0.033	p_y(C_1)	–0.0022	p_y(C_α)	–0.0078
total Ni	1.588	p_z(C_1)	–0.0086	p_z(C_α)	–0.0011
		total (C_1)	–0.012	total (C_α)	–0.012
		s(C_2)	0.0013	s(C_β)	0.0014
		p_x(C_2)	0.0018	p_x(C_β)	0.0028
		p_y(C_2)	0.0014	p_z(C_β)	0.0042
		p_z(C_2)	0.0024	total (C_β)	0.009
		total (C_2)	0.0069		
				s(C_γ)	–0.0016
		total (H_1)	0.013	p_x(C_γ) π	–0.0068
		total (H_2)	–0.0007	total (C_γ)	–0.009
		total *acac*	0.154	H_α	0.0045
				H_β	0.0010
				H_γ	0.0006
				total *py*	0.103

discussing the general features of the spin distribution to be expected for such e_g^2 complexes. First, one must note that the largest spin density is positive and appears at the metal d_{xy} and d_{z^2} orbitals where the unpaired electrons are expected to be. However, the spin density is less than one because the e_g molecular orbitals have contributions from the ligands; hence, part of the corresponding electron density is delocalized through the ligands. The missing spin density at the d_{xy} orbital (0.23 e^-) corresponds practically with that located at the equatorial σ-type orbitals of the four oxygen atoms of the acetylacetonato ligands (s, p_x and p_y: 0.26 e^-). For the d_{z^2} orbital, however, only part of the missing spin density (0.26 e^-) can be found in the axial σ-type orbitals of the N atom of pyridine (0.09 e^-), clearly indicating a stronger delocalization consistent with the more covalent character of the Ni–N bond compared to the Ni–O ones. In summary, a large positive spin density (less than one) is expected

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for the orbitals of the metal atom in which an unpaired electron is formally located, and a small positive density is to be found for the σ-type orbitals of the donor atoms, its numerical value being dependent on the degree of covalence of the M–L bond.

The other doubly occupied t_{2g}-type orbitals are spin-polarized by the e_g unpaired electrons localized mostly at the metal atom (small positive values, Table III). On the other hand, the 4s and 4p atomic orbitals of the paramagnetic center, formally empty, participate in bonding molecular orbitals, which are also polarized by the unpaired electrons at the metal center. Hence, one should expect small positive spin densities for the Ni 4s and 4p orbitals. The fact that in the present case the Ni 4s orbital presents a spin density comparable to those of the t_{2g} orbitals is due to its mixing with d_{z^2} in one of the SOMO's. The small negative values found for the nickel p_x and p_y orbitals can be simply explained neither by a delocalization nor by a polarization mechanism.

The positive spin delocalized to the donor atoms polarizes the electron pairs in other atomic orbitals of the same atom, as seen for p_x and p_y of the pyridine N atom. Since delocalization to other atoms of the ligands is much smaller, at two-atoms distance from the paramagnetic center and farther away, spin polarization is in general the predominant mechanism, and the characteristic sign alternation of the spin density appears at the carbon atoms of the pyridine and acetylacetonato ligands. It is worth remarking that negative spin is mostly located at the π-type atomic orbitals of the ligands (e.g., p_y of C_α and C_γ in pyridine, p_z of C_1 in $acac^-$). To explain this one needs to consider that for the σ-type atomic orbitals the negative spin resulting from polarization is partly compensated by the small positive spin resulting from delocalization. In contrast, since in this case the unpaired electrons are not delocalized through the π system, the π-type orbitals are only affected by spin polarization. For those atoms bonded to the donor, the polarization mechanism predominates and spin alternation can be expected from there on as getting away from the paramagnetic metal atom. With this in mind the reader can go back to Table II and interpret the spin density values found for the hydrogen atoms in the aqua complexes.

In contrast to the results for the carbon atoms of the axial ligands, the spin at their hydrogen atoms is positive in all cases, as seen from both the experimental and calculated data. This indicates that the delocalization mechanism is predominant for the hydrogen atoms (the same result is obtained with piperidine as axial ligand). In contrast to other atoms, in

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the hydrogen atom there are no orbitals other than that involved in the σ bonding. Hence, there are fewer pathways available for the spin polarization mechanism (in particular, the π pathway is quenched), and even a small degree of delocalization can produce a positive spin density at the H atoms. Nevertheless, the spin density decreases much more from H_α to H_β than from H_β to H_γ, indicating that the delocalization to H_β is in part decreased by negative spin polarization.

SPIN DENSITIES AND EXCHANGE COUPLING IN BINUCLEAR COMPLEXES

Now that the general trends for the spin density distribution in mononuclear complexes have been discussed, we address the problem of the spin distribution in complexes with two paramagnetic centers that may be ferro- or antiferromagnetically coupled. In essence, there is an extended belief that, if one is able to predict the spin distribution in such molecules, their ferro- or antiferromagnetic character can be qualitatively predicted. This is generally done by using a pure spin polarization model, in which the sign alternation resulting from spin polarization is used to predict the ferro- or antiferromagnetic nature of the exchange interaction between two paramagnetic centers.[22,23] As an example, let us recall here that in the family of organic bis(carbenes), those compounds with an even number of intervening carbon atoms are antiferromagnetic, whereas those with an odd number of spacers are ferromagnetic.[24–26] Since here we are dealing only with intramolecular interactions, the reader is referred to recent papers that deal with the McConnell model of spin polarization[22] for intermolecular interactions[25–27] or with the charge transfer model for mixed organic–organometallic donor–acceptor systems.[28–30]

In the realm of coordination chemistry, an increasing tendency to use the polarization model in a qualitative way for binuclear complexes has evolved recently. As an example, the weak ferro- or antiferromagnetic nature of the exchange coupling in a series of Mo(V) binuclear complexes bridged by different bipyridine ligands could be explained by invoking the spin polarization mechanism.[21] However, the spin density distribution qualitatively proposed by Thompson *et al.* (**8**) has been determined neither experimentally nor theoretically. Only in one case was the spin density of a symmetric binuclear complex determined from pnd experiments,[31] in a ferromagnetic hydroxo-bridged Cu(II) compound. Besides,

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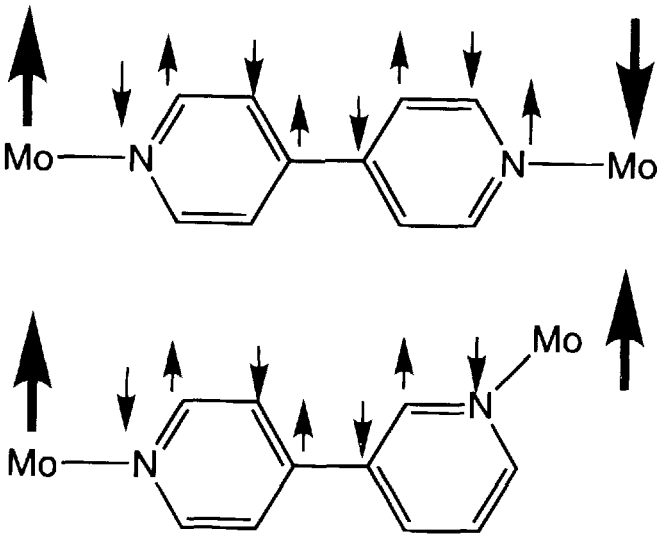

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the spin density distributions of heterobinuclear (or polynuclear) complexes have been reported only for the antiferromagnetic phenoxo-bridged Cu(II)–Ni(II)[32] and oxamido-bridged Cu(II)–Mn(II)[33] compounds, and for the ferrimagnetic heteronuclear Cu(II)–Mn(II) chain compound.[34]

Also for compounds with intramolecular spin interaction between a transition metal ion and an organic radical has the polarization model been applied successfully. Iwamura *et al.* prepared two Cr^{3+} complexes in which the unpaired electron of a nitroxide group interacts with the 3d electrons of the Cr ion. When the nitroxide ligand is 3-(N-oxy-amino)pyridine, the interaction is ferromagnetic, whereas for 4-(N-oxy-amino)pyridine, antiferromagnetic coupling is observed.[35]

There are indications, though, that the pure polarization model cannot be generally applied for intramolecular coupling. As an example, consider the family of bis(hydroxo-bridged) Cu^{2+} complexes. The polarization model would predict a ferromagnetic interaction for these compounds, as sketched in **9a**. However, we must recall the well-known magneto-structural correlation for his family of compounds, for which one can find from relatively strong antiferromagnetism ($2J \approx -600\ cm^{-1}$) to moderate ferromagnetism ($2J \approx +200\ cm^{-1}$) depending on the

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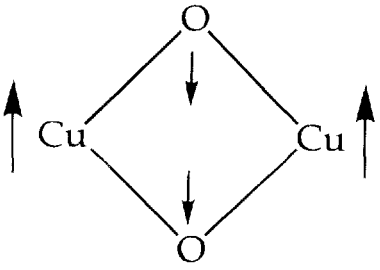
Cu–O–Cu bond angle and on the deviation of the OH groups from the Cu_2O_2 plane.[36] The antiferromagnetic complexes should be expected to exhibit a spin distribution of type **9b**. It is thus clear that the polarization mechanism is not able to correctly predict the sign of the exchange coupling in all cases, and a more detailed analysis is needed.

Let us briefly recall the formalism deduced by Hay, Thibeault and Hoffmann for the coupling of two paramagnetic centers.[37] These authors proposed an approximate expression for the single–triplet splitting in a binuclear system with two unpaired electrons:

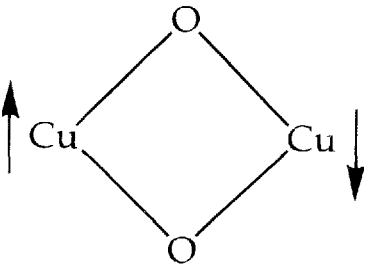
$$E_S - E_T = 2J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{bb}} \qquad (7)$$

where J is a coupling constant, ϵ_1 and ϵ_2 are the energies of ϕ_1 and ϕ_2, the two singly occupied molecular orbitals (SOMO's) of the complex. K_{ab}, J_{aa}, and J_{bb} are two-electron integrals involving the two localized versions of these orbitals. $\phi_a = N(\phi_1 + \phi_2)$ and $\phi_b = N(\phi_1 - \phi_2)$. Of the two terms in Eq. (7), the first one is a ferromagnetic contribution to the magnetic exchange constant that accounts for the stability of the triplet state, while the second one represents an antiferromagnetic term favoring a singlet ground state.

Since the spin polarization mechanism is associated with the Coulomb and exchange terms, as discussed above, the prediction of a ferromagnetic state by a polarization-only model is equivalent to assuming the existence of an important ferromagnetic contribution K_{ab} in Eq. (7). In such case, *if* the antiferromagnetic contribution [second term in Eq. (7)] happens to be negligible, the ground state should be expected to be ferromagnetic. On the other hand, when the polarization model indicates an antiferromagnetic state, it actually means that $K_{ab} \approx 0$ and, *if* there is a



9a



9b

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sizable antiferromagnetic contribution, an antiferromagnetic ground state should be expected. Let us stress that the spin polarization model would correctly predict ferromagnetic states whenever the splitting between the two SOMO's, $\epsilon_1 - \epsilon_2$ is very small. This is the case for the weak intermolecular interactions or for those intramolecular ones for which there is a symmetry- or topology-imposed quasi-degeneracy of the SOMO's. Except for such cases, the spin delocalization mechanism is generally predominant in intramolecular interactions and the pure polarization model cannot be applied.

In an attempt to establish a link between the Hay–Thibeault–Hoffmann model and the polarization mechanism, we now analyze those systems with no substantial gap between two SOMO's [i.e., in which the second term in Eq. (7) is negligible]. We further restrict our discussion to symmetric systems for simplicity although the effect of asymmetry on the exchange coupling might be important. The first case to consider is that in which the two SOMO's are combinations of orbitals at the two paramagnetic centers that have the same left-right symmetry, such as the degenerate π^* orbitals in the O_2 molecule (**10**). In that case, one cannot obtain localized orbitals by forming the linear combinations ϕ_a and ϕ_b. Therefore, these two orbitals occupy the same region of space (non-disjoint orbitals) and the exchange integral K_{ab} has a large value, resulting in a strong ferromagnetic character. Indeed the O_2 molecule presents the triplet as its ground state, while the $^1\Sigma$ singlet with one electron at each oxygen atom is 155 kJ/mol (13,000 cm^{-1}) higher.

Let us now consider in a qualitative way a symmetric system in which the two SOMO's have different left-right symmetry, such as those sketched in **11**. We recall that, simply speaking, the polarization model implies that ferromagnetism could appear for binuclear (biradical) systems separated by an odd number of atoms, but cannot exist when they are separated by an even number of atoms. Consider first a system with an odd number of spacers linking the two paramagnetic atoms (**12**). The two SOMO's are the symmetry-adapted combinations of the atomic orbitals of the magnetic centers, appropriately mixed with fragment orbitals of the spacers having the same symmetry: a symmetric function, ϕ_S and an asymmetric one, ϕ_A (**13**). Notice that the topology of the fragment orbitals of the spacers is not relevant here; what is important is that ϕ_A has a nodal plane passing through the central spacer, whereas ϕ_S has no nodal plane at the central spacer (the fact that ϕ_S has lower or higher energy than ϕ_A is also irrelevant for the present discussion). If one now

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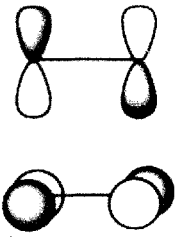

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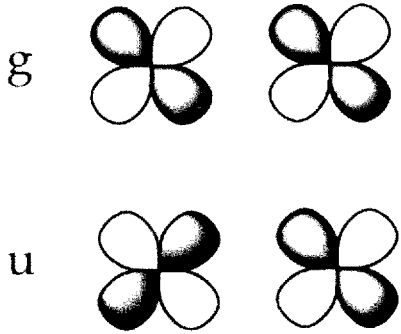

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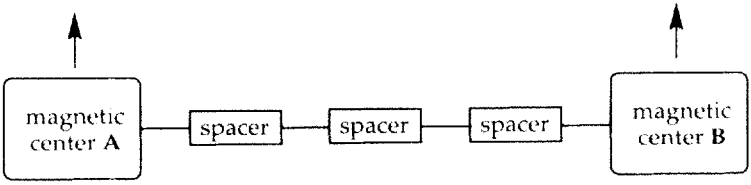

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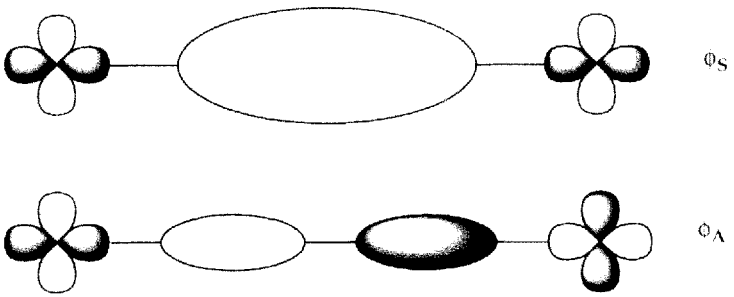

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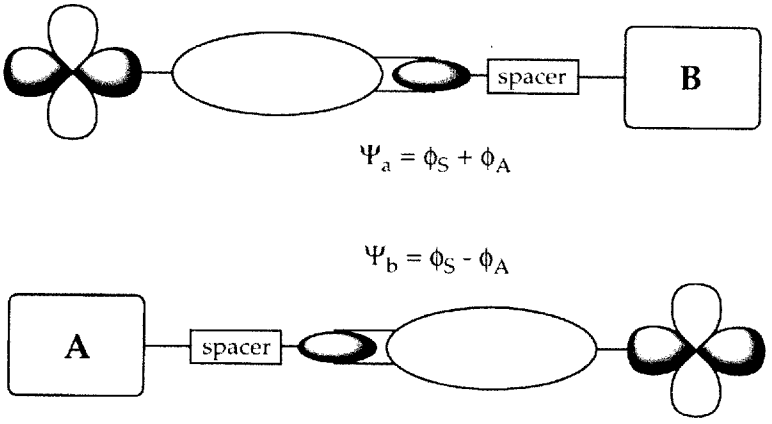
makes combinations of such functions, $\Psi_a = \phi_S - \phi_A$ and $\Psi_b = \phi_S + \phi_A$, both have per force some contribution at the central spacer (**14**). The exchange integral between these two orbitals, K_{ab}, will be non-zero[38] if there is some region of space at which there is a sizable probability for both. In this case, the presence of contributions from both Ψ_a and Ψ_b at the central spacer implies that K_{ab} is non-zero. Consequently, one can predict that in systems with an odd number of spacers there will always be a ferromagnetic contribution, although a ferromagnetic behavior would only result if the antiferromagnetic contribution [second term in Eq. (7)] is comparatively small.

Consider now the case with an even number of spacers. The symmetric and antisymmetric SOMO's, schematically depicted in **15**, present an important difference with the previous case, since ϕ_A has its nodal plane now in the region between the two central spacers. As a result, the combinations of the two SOMO's, Ψ_a and Ψ_b are well localized at the two sides of the molecule (**16**). Since these orbitals are spatially separated (disjoint orbitals), $K_{ab} \rightarrow 0$ and a small ferromagnetic contribution is to be expected. In other words, in symmetric systems with an even number of spacers, weak ferromagnetism can be expected only for molecules with degenerate SOMO's, as happens in the organic biradical tetramethylene-ethylene (TME, **17**).

An example of the ideas just discussed is provided by the hydroxo-bridged binuclear Cu^{2+} compounds with the skeleton sketched in **18**.



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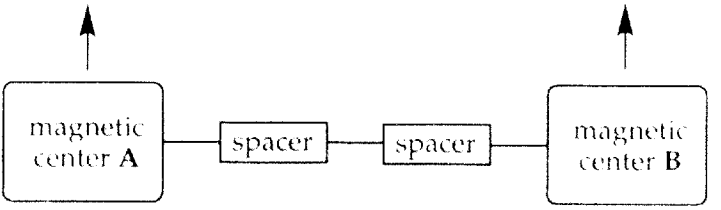

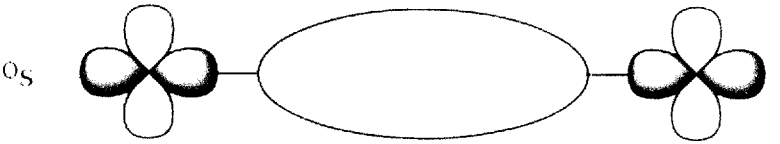

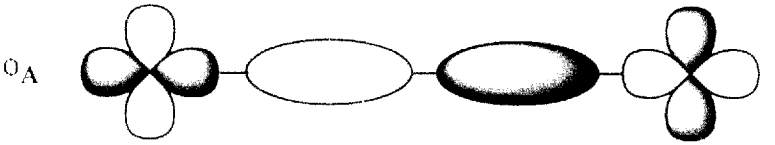

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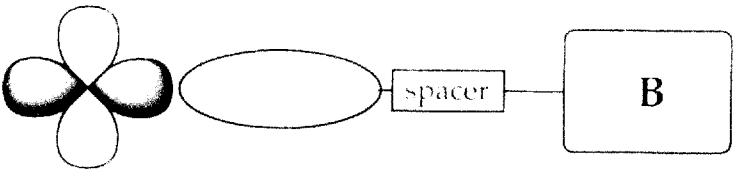
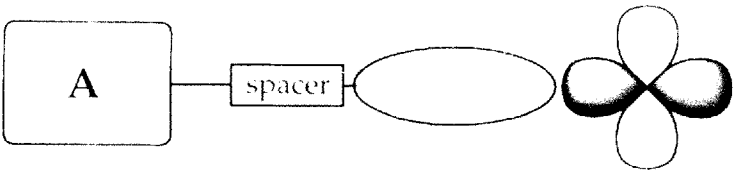


$$\Psi_a = \phi_S + \phi_A$$



$$\Psi_b = \phi_S - \phi_A$$

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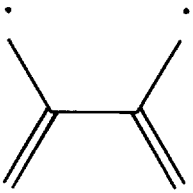

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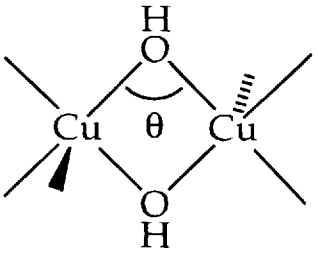

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Since there is an odd number of atoms in each bridge between the Cu^{2+} ions, the spin polarization model would predict a ferromagnetic behavior (**9**). Now we know that this might only be true whenever the gap ($\epsilon_1 - \epsilon_2$) has a small value, which occurs for molecules with small O–Cu–O angles (θ) and a large deviation of the hydroxo H atom from the plane of the Cu_2O_2 core (τ).[36] As an example, calculations for a model system with $\theta = 95°$ and $\tau = 60°$ give a gap between the SOMO's of 0.39 eV (3130 cm^{-1}) and predict a ferromagnetic behavior ($2J_{calc} = +103$ cm^{-1}). In contrast, for $\theta = 99°$ and $\tau = 0°$, a larger gap of 1.14 eV (9190 cm^{-1}) appears, while the K_{ab} term remains practically constant,[36] resulting in a predicted antiferromagnetic behavior ($2J_{calc} = -336$ cm^{-1}). These theoretical results are consistent with the wide range of exchange coupling constants experimentally found for this family of complexes. Another example of molecules with an odd number of spacers that could be antiferromagnetic depending on the molecular structure is given by the family of 1,1-azido-bridged Cu^{2+} binuclear complexes,[39] although all the experimentally characterized compounds have a structure with a small antiferromagnetic contribution and show ferromagnetic behavior.[40,41]

If we go back to the discussion of spin delocalization and spin polarization in mononuclear complexes, and recall that for the unpaired electron in a σ-type orbital a spin delocalization should be expected toward the donor atom, a spin distribution **19** would be predicted for the ferromagnetic hydroxo-bridged Cu^{2+} complexes, rather than the one deduced from a pure spin polarization model (**9a**). Both our calculations and a pnd study of one such complex (having $\theta = 94°$ and $\tau = 68°$)[31] are consistent with the spin distribution **19**. In summary, the application of the spin polarization model to those binuclear complexes with a small gap between the SOMO's should result in a correct prediction of the spin sign at the metal atoms.

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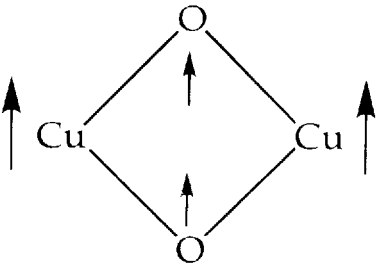

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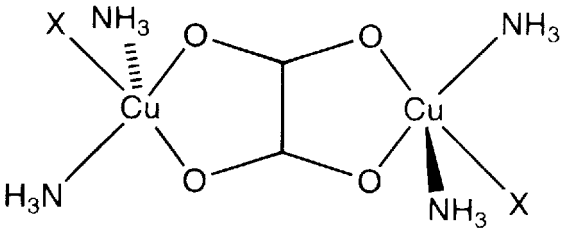

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To get a better feeling for the spin density distribution in binuclear Cu^{2+} compounds, and of its relationship with the sign and magnitude of magnetic coupling, we have carried out several DFT calculations (Table IV). From such calculations we have obtained theoretical estimates of the coupling constant J, as reported elsewhere,[42] as well as the orbital and atomic spin densities for the triplet state. Hence, we studied the series *trans*-$[Cu_2(\mu\text{-}C_2O_4)(NH_3)_2X_2]$, in which X is a halide (**20**), to analyze the effect of the terminal ligand. To the best of our knowledge, pnd studies for binuclear systems with extended bridges have been

TABLE IV

Atomic spin densities calculated for binuclear oxalato-bridged Cu(II) model complexes $[X(NH_3)Cu(\mu\text{-ox})Cu(NH_3)X]$ (X = F, Cl, Br, I).

X	Cu	O_{trans}	O_{cis}	C	Term. Ligands
F	0.692	0.047	0.051	−0.001	0.212
Cl	0.657	0.059	0.052	−0.002	0.234
Br	0.639	0.060	0.052	−0.002	0.252
I	0.608	0.060	0.053	−0.002	0.281

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reported only for an asymmetric oxamido-bridged Cu(II)/Mn(II) complex[33] that will not be considered here since we restrict the present discussion to symmetric systems. The more covalent Cu–X bonds induce a greater delocalization of the x^2-y^2 orbital, leading to a smaller spin density at the Cu atom. At the same time, the more covalent X induces a larger spin delocalization at the trans O-atom. These two variations of atomic spin densities with the electronegativity of X are coupled with the stronger antiferromagnetic coupling previously discussed[43] (see Fig. 3). On the other hand, the compounds with stronger antiferromagnetic interactions are those with smaller spin densities at the Cu atoms. This fact can be understood by taking into account that a stronger delocalization through the terminal ligands induces a larger spin density at the bridging ligand that, in turn, favors a stronger antiferromagnetic coupling.

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CONCLUSIONS

The spin density distribution throughout a molecule of a paramagnetic coordination compound results from the interplay of two mechanisms: spin delocalization and spin polarization. From the point of view of molecular orbital theory, spin delocalization can be explained as a transfer of some unpaired electron density from the metal atom to the ligand donor atoms. The amount of spin density transferred is related to the degree of covalence of the metal–ligand bonds and can be therefore modulated by the choice of the donor atoms (other things being equal, larger spin delocalization is obtained by the less electronegative donors) or of the diffuseness or oxidation state of the metal atom (stronger delocalization for the higher oxidation states and heavier transition metals).

Spin polarization results from the optimization of the exchange and Coulomb terms and induces spin of alternating sign for the successive atoms of a ligand. In the case of unpaired electrons in metal π-type orbitals (e.g., t_{2g}), the spin at the donor atom may be negative due to spin polarization only if the delocalization is very small, as it happens for the most electronegative donors, F and O. In those systems with an unpaired electron in a metal σ-type orbital, the spin delocalization is always the predominant mechanism for the donor atoms, but spin polarization predominates generally for the rest of the atoms in the ligands. The spin density arising from the polarization mechanism is generally smaller in

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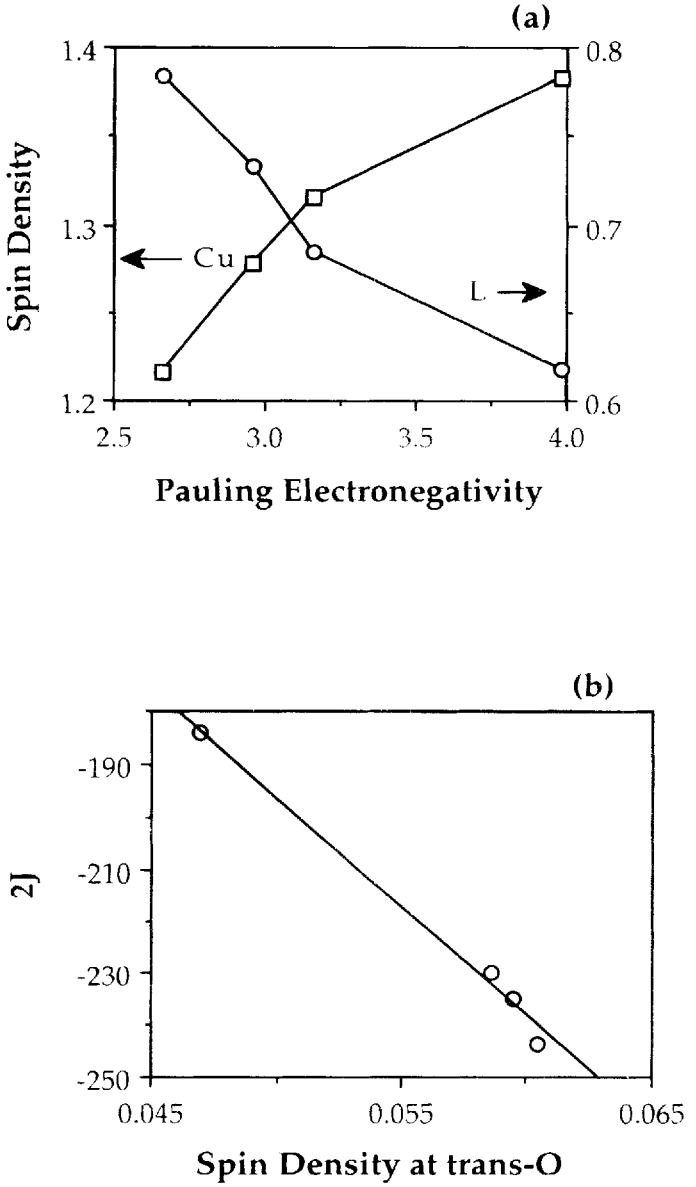

FIGURE 3 (**a**) Calculated spin densities for the Cu atoms (squares) and ligands (circles) in the oxalato complexes **20** as a function of the Pauling electronegativity of the ligand X (X = F, Cl, Br or I). (**b**) Singlet–triplet energy gap ($2J$) as a function of the spin density at the O atom in the oxalato bridge trans to the X ligand.

absolute value than that produced by the delocalization mechanism, and the values of spin density induced by the polarization mechanism are roughly proportional to the number of unpaired electrons.

A necessary, but not sufficient, condition for symmetric binuclear systems to present a ferromagnetic interaction is that an odd number of intervening atoms must exist between the paramagnetic centers. An exception to this rule appears for systems in which the two SOMO's are degenerate. On the other hand, symmetric systems with an even number of spacers can only be weakly ferromagnetic, and the extent of the antiferromagnetic coupling will depend on the HOMO-LUMO gap.

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