J. Am. Chem. Soc. 1986, 108, 2574-2581

Interaction between Copper(II) Ions through the Azido Bridge: Concept of Spin Polarization and ab Initio Calculations on Model Systems

Marie-France Charlot,[†] Olivier Kahn,*[†] Max Chaillet,[‡] and Christiane Larrieu[‡]

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, U.A. n° 420, Université de Paris-Sud, 91405 Orsay, France, and the Laboratoire de Chimie Structurale, U.A. n° 474, Université de Pau et des Pays de l'Adour, 64000 Pau, France.

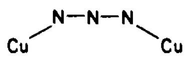
Received May 23, 1985

Abstract: The azido ion N_3^- can bridge two copper(II) ions in three fashions: symmetrical end-to-end (EE), end-on (EO), and unsymmetrical end-to-end. The crystal structure and the magnetic properties of several compounds corresponding to each case have been described. From these investigations, it emerges that the EE bridge favors the antiferromagnetic interaction and the EO bridge the ferromagnetic interaction. As for the third kind of bridge, it leads to either a negligible or a very weakly antiferromagnetic interaction. This last behavior can be easily understood in the framework of models generally utilized to interpret qualitatively the magnetic properties of the coupled systems, but the situation is not the same for the EE and EO cases. It is then necessary to go beyond the approximations on which these models depend and in particular to take into account the role of the Π_g HOMO's of N_3^- which are close in energy to the metal orbitals. For that, we introduce the concept of polarization of the spins of the magnetic electrons induced by the in-plane Π_g orbital of N_3^-. This concept leads to a qualitative interpretation of the specific role of N_3^- according to how it bridges in the EE or the EO fashion. This interpretation is substantiated by a quantitative phenomenological model. Finally, we carry out an ab initio calculation of the singlet–triplet energy gaps in the model systems $(Be_2N_3)^+$ where N_3^- bridges two Be^+ magnetic ions either in EE or in EO. In agreement with the experimental data on the actual copper(II) complexes, the ground state is found to be the singlet in the EE case and the triplet in the EO case. These results only appear after an extended configuration interaction.

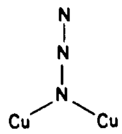
Introduction and Experimental Data

μ-Azido copper(II) bimetallic complexes have been known for about two decades.[1-6] However, the originality and the versatility of their magnetic properties appeared only in the last five years.

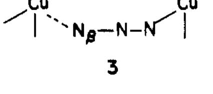
The azido can bridge two copper(II) ions either in a symmetrical end-to-end (EE) fashion **1** or in an end-on (EO) fashion **2**.[4] N_3^- can also bridge in a unsymmetrical end-to-end fashion with a short Cu–N_α bond and a long Cu–N_β bond.[8-9] Such a situation occurs when each metal ion is fivefold coordinated with three coordination sites belonging to terminal ligands, the other positions being occupied by the N_α atom of an azido group and the N_β atom of the other azido group as shown in **3**. When N_3^- bridges as in **1**, the interaction between the copper(II) ions is strongly antiferromagnetic, so that the ground state is a singlet state largely stabilized in energy with regard to the low lying triplet state. A unique complex with a single end-to-end azido bridge has been reported so far.[10] Its structure is shown in Figure 1. In this complex, the singlet–triplet energy gap was found as −308.6 cm^{-1}. A complex with two symmetrical EE azido bridges has also been described. The singlet state is so stabilized with regard to the triplet that even at room temperature only the ground state is thermally populated, and, therefore, the compound appears diamagnetic.[11] Finally, two complexes with the planar bridging network **4** have been synthesized. The bridging oxygen atom belongs either to an alkoxide group[12] or to a phenolato group.[13] Both compounds are also diamagnetic.



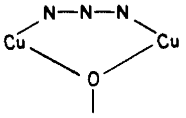
1



2



3



4

When N_3^- bridges as in **2**, the situation is apparently more complicated, and the sign of the interaction actually depends on the nature of the whole bridging network. However, from all the already reported results, it clearly emerges that the EO azido bridge in itself favors the ferromagnetic interaction, i.e., stabilizes the triplet state with regard to the singlet state. Thus, two complexes with two EO azido bridges have been described.[14,15] Their structures are shown in Figure 2. Both exhibit a triplet ground state stabilized with regard to the excited singlet state by 70 ± 20 and 105 ± 20 cm^{-1}, respectively. For this latter compound, a single crystal EPR investigation has also been performed. It unambiguously confirms that the ground state is the triplet state.[16]

[†] Laboratoire de Spectrochimie des Eléments de Transition.

[‡] Laboratoire de Chimie Structurale.

(1) Söderquist, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 450-455.

(2) Agrell, I.; Lamnevik, S. *Acta Chem. Scand.* **1968**, *22*, 2038-2040.

(3) Agrell, I. *Acta Chem. Scand.* **1967**, *21*, 2647-2658.

(4) Dori, Z.; Ziolo, R. *Chem. Rev.* **1973**, *73*, 247-254.

(5) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 481-482.

(6) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1983**, 376-378.

(7) Kahn, O.; Boillot, M. L. In *Biochemical and Inorganic Aspects of Copper Coordination Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1985; Vol 2.

(8) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 444-456.

(9) Bkouche-Waksman, I.; Sikorav, S.; Kahn, O. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 303-310.

(10) Bkouche-Waksman, I.; Boillot, M. L.; Kahn, O.; Sikorav, S. *Inorg. Chem.* **1984**, 4454-4459.

(11) Agnus, Y.; Louis, R.; Gisselbrecht, J. P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93-102.

(12) McKee, V.; Dadgegian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000-7001.

(13) Sorrell, T. N.; O'Connor, C. J.; Anderson, O. P.; Reibenspies, J. H. *J. Am. Chem. Soc.*, in press.

(14) Comarmond, J.; Plumeré, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330-6340.

(15) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490-495.

(16) Boillot, M. L.; Journaux, Y.; Bencini, A.; Gatteschi, D.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 263-267.

0002-7863/86/1508-2574$01.50/0

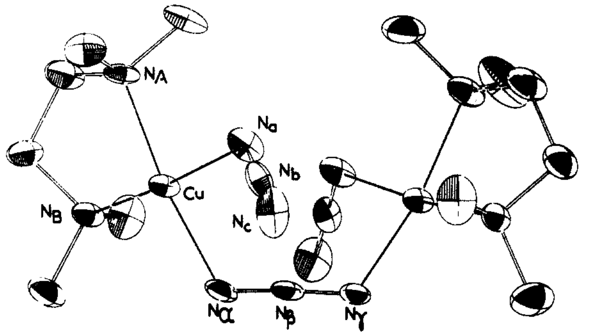


Figure 1. Perspective view of $|Cu_2(tmen)_2(N_3)_3|^+$ with a single EE azido bridge. tmen is *N,N,N′,N′*-tetramethylethylenediamine.

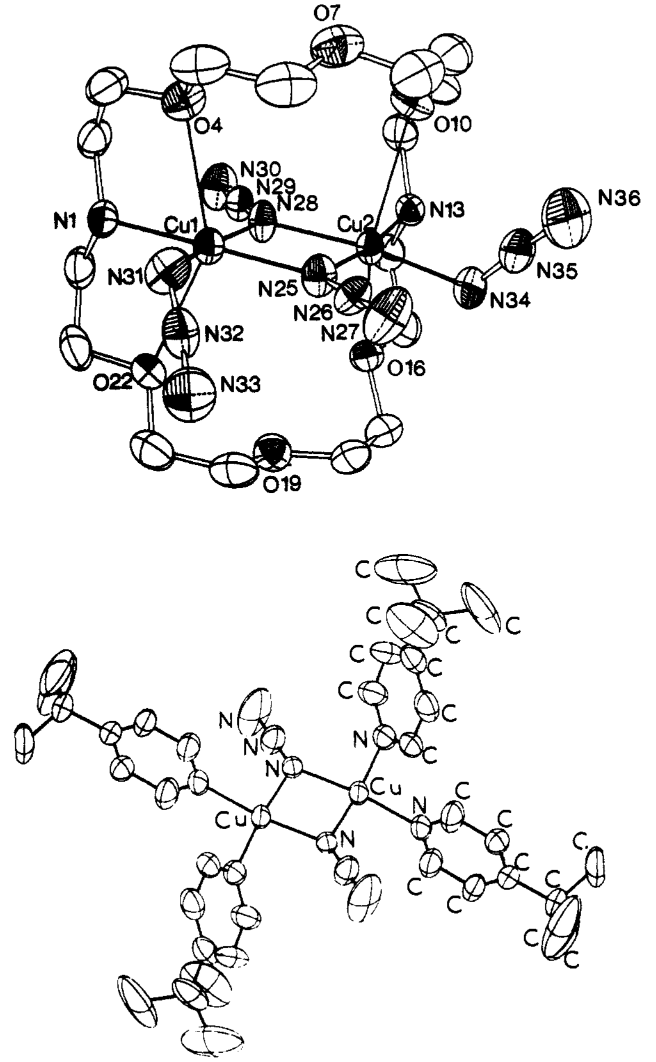


Figure 2. Perspective views of two complexes with two EO azido bridges.

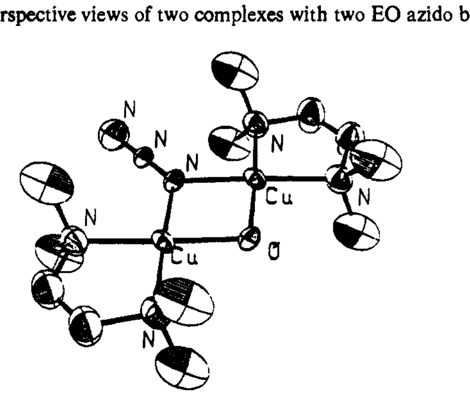


Figure 3. Perspective view of $|Cu_2(tmen)_2(N_3)(OH)|^{2+}$ with an hydroxo bridge and an EO azido bridge.

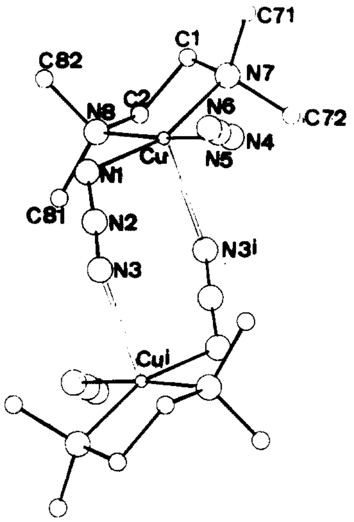
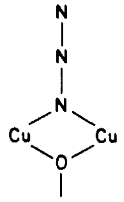


Figure 4. Perspective view of $|Cu(tmen)(N_3)_2|_2$ with two dissymmetrical EE azido bridges.

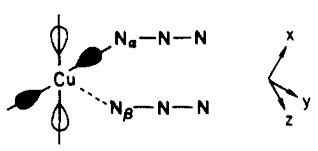
Another ferromagnetically coupled μ-azido copper(II) complex has been described, in which the metal ions are bridged by a hydroxo group in addition to the EO azido group.[17] Its structure is shown in Figure 3. The stabilization of the triplet state for this compound was estimated to be larger than 200 cm^{-1}. The other complexes with the bridging network **5**, where the bridging oxygen atom belongs to a phenolato group are antiferromagnetically coupled.[18,19] In these complexes, the phenolato bridge is known to exert a strong antiferromagnetic contribution,[20] which is not totally compensated by the ferromagnetic contribution exerted by the azido bridge. However, the magnitude of the resulting antiferromagnetic interaction is less pronounced than in any similar complex with N_3^- replaced by any other bridge X, the other ligands remaining the same.



5

As for the complexes with a bridging network like **3**, they exhibit either a negligible interaction when the geometry around the metal is square pyramidal,[9] or a very weak antiferromagnetic interaction when this geometry tends toward the trigonal bipyramid.[8,21] An example of this kind of compound with a negligible interaction is shown in Figure 4.

This latter situation with a bridging network of the type **3** is by far the easiest to understand. Around each copper(II) ion, the unpaired electron is described by a d_{xy}-type magnetic orbital pointing from the metal toward the four nearest neighbor nitrogen atoms, as shown in **6**.[14] The delocalization of such a magnetic



6

---

[17] Kahn, O.; Sikarov, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877-2883.

[18] Boillot, M. L.; Kahn, O.; O'Connor, C. J.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 178-180.

[19] O'Connor, C. J., private communication.

[20] Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683-2686.

[21] Banci, L.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1984**, *23*, 2138-2141.

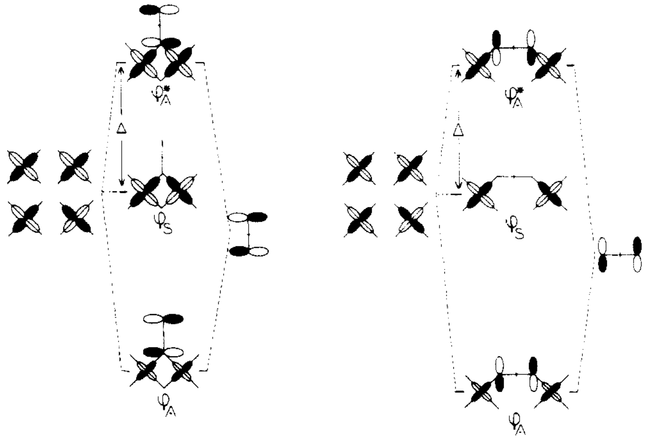


Figure 5. Relative energies of the MO's in EE and EO azido bridged copper(II) binuclear complexes (see text).

orbital toward the N_β atom in apical position is negligible when the environment of the metal is purely square pyramidal. The two magnetic orbitals in the dimeric entity are located in largely separated parallel planes (ca. 5 Å in the compound of Figure 4) and do not interact. When the environment of the metal acquires some trigonal bipyramidal character, this introduces some d_{z^2}-type orbital in the magnetic orbital which now is slightly delocalized toward the N_β atom. Consequently, the two magnetic orbitals may weakly overlap and the interaction no longer be negligible.

Much more difficult and important to understand is the versatility of the magnetic properties of μ-azido copper(II) complexes when N_3^- bridges in an EE or an EO fashion. This paper is devoted to this problem. In the next section, we briefly recall some basic concepts usually utilized to interpret the magnetic properties of copper(II) binuclear complexes, then we shall propose a qualitative interpretation of the specific role of the azido bridge by introducing the concept of spin polarization. This interpretation will be substantiated by a quantitative phenomenological model. Finally, in the hope to understand this specificity of N_3^- in a more thorough manner, we shall present and discuss the results of ab initio calculations with large CI on N_3^- and on the model systems $|Be_2N_3|^+$ where N_3^- bridges two Be^+ ions either in an EE or an EO fashion. A discussion emphasizing both the novel and important aspect of this work and its limits will be also included.

Active Electron Approximation

The goal of this section is to show that the simple concepts[22] used successfully to understand, at least qualitatively, the magnetic properties of most of the copper(II) binuclear complexes are no longer sufficient anymore when the bridge is N_3^- and that it is imperatively necessary to go beyond.

Let us consider a symmetrical copper(II) binuclear complex symbolized by A–X–B where X is the bridging group, and let us assume that the highest occupied molecular orbital (HOMO) of X is low in energy with regard to the d metal orbitals. This assumption is qualitatively valid for most of the usual bridges like halogens or OH^-. In A–X–B, we define two magnetic orbitals centered on A and B, respectively. These magnetic orbitals may be derived in two different ways:[23] (i) either as the HOMO's ϕ_A and ϕ_B for the A–X and X–B fragments, respectively.[24] ϕ_A and ϕ_B are then, of course, strictly localized in the fragments and have, in general, a nonzero overlap integral $S = \langle \phi_A(1)/\phi_B(1) \rangle$ (ii) or from the two singly occupied molecular orbitals γ_1 and γ_2 for the low lying triplet state of A–X–B according to[25,26]

$$\phi'_A = (2^{1/2}/2)(\gamma_1 + \gamma_2)$$
$$\phi'_B = (2^{1/2}/2)(\gamma_1 - \gamma_2) \qquad (1)$$

ϕ'_A and ϕ'_B are then orthogonal but not strictly localized.

In both approaches, the S–T energy gap is expressed as the sum of an antiferromagnetic negative contribution J_{AF} and a ferromagnetic positive contribution J_F. In the former approach, J_{AF} and J_F are given by[22-24]

$$J_{AF} = 4tS = -2\Delta S$$
$$J_F = 2j \qquad (2)$$

with

$$t = \langle \phi_A(1)/h(1) - \alpha/\phi_B(1) \rangle$$
$$\alpha = \langle \phi_A(1)/h(1)/\phi_A(1) \rangle \qquad (3)$$
$$j = \left\langle \phi_A(1)\phi_B(2) \Big/ \frac{1}{r_{12}} \Big/ \phi_A(2)\phi_B(1) \right\rangle$$

Δ is the energy gap between the two molecular orbitals in A–X–B built from ϕ_A and ϕ_B. In the latter approach, we have[25,26]

$$J_{AF} = -\frac{|\epsilon(\gamma_1) - \epsilon(\gamma_2)|^2}{U}$$
$$J_F = 2j' \qquad (4)$$

$\epsilon(\gamma_1)$ and $\epsilon(\gamma_2)$ are the energies of the molecular orbitals γ_1 and γ_2. U is the energy associated to the electron transfer

$$\text{A–X–B} \rightarrow \text{A}^+\text{–X–B}^-$$

and j' is the two-electron exchange integral on the basis of the ϕ'_A and ϕ'_B functions. Two important points emerge from relations (2) and (4): (i) the larger Δ or $\Delta' = \epsilon(\gamma_1) - \epsilon(\gamma_2)$ is the more pronounced magnitude of the antiferromagnetic contribution and (ii) the ferromagnetic contribution is proportional to the self repulsion of the overlap density between the magnetic orbitals. When Δ (or Δ') is zero, the S–T gap reduces to its ferromagnetic contribution, and the triplet state is the lowest. Within the framework of the former approach, this situation corresponds to the accidental orthogonality of the magnetic orbitals which is, for instance, realized in some planar bibridged copper(II) complexes with bridging angles close to 90°.[22,27]

It is clear that the two approaches correspond to the same level of approximation; more precisely, only the two unpaired electrons are explicitly taken into account in the exchange interaction phenomenon. The role of the doubly occupied molecular orbitals is underestimated.

We propose to apply the ideas discussed above to the case of the μ-azido copper(II) complexes and to see whether the observed magnetic properties can be rationalized. We consider a planar complex of this kind with the bridging network **1** or **2**. It has been shown that the Π_g HOMO's of N_3^- are high in energy and largely separated from the occupied molecular orbitals of lower energies[28-33] so that the in-plane Π_g will play the key role in the interaction between the two metal ions. Whatever the nature of the bridge may be, this Π_g orbital is antisymmetric with regard to the mirror plane perpendicular to the molecular plane. It interacts with the antisymmetric combination of the d_{xy} metal orbitals to give a bonding φ_A and an antibonding φ_A^* MO's. As for the symmetric combination φ_S of the d_{xy} orbitals, it is nonbonding, assuming that the direct interaction is negligible. The

---

[22] Kahn, O. In *Magneto Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Nato Asi Series, D. Reidel: Dordrecht, 1984; pp 37–85.

[23] Girerd, J. J.; Journaux, Y.; Kahn, O. *Chem. Phys. Lett.* **1981**, *82*, 534–538.

[24] Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567–576.

[25] Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2–13. Anderson, P. W. In *Magnetism*; Rado, D. T., Suhl, H., Eds.; Academic Press: New York, 1963, Vol. 1.

[26] Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884–4899.

[27] Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J; Jaud, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585–7591.

[28] Clementi, E.; McLean, A. D. *J. Chem. Phys.* **1963**, *39*, 323–325.

[29] Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1967**, *47*, 1953–1966.

[30] Bonaccorsi, R.; Petrongolo, C.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1968**, *48*, 1500–1508.

[31] Wyatt, J. F.; Hillier, I. H.; Saunder, V. R.; Connor, J. A.; Barber, M. *J. Chem. Phys.* **1971**, *54*, 5311–5315.

[32] Archibald, T. W.; Sabin, J. R. *J. Chem. Phys.* **1971**, *55*, 1821–1829.

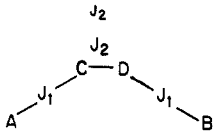
[33] Rossi, A. R.; Bartram, R. H. *J. Chem. Phys.* **1979**, *70*, 532–537.

relative energies of $\varphi_{A'}$, φ_S, and $\varphi_A{}^*$ in the EE and EO cases are schematized in Figure 5. In the active electron approximation, the low lying triplet state derived from the configuration $\varphi_A{}^2\varphi_S\varphi_A{}^*$ and the energy parameter Δ (or Δ') which stabilizes the singlet state is the energy gap between $\varphi_A{}^*$ and φ_S. For both the EE and the EO geometries, Δ is expected to be rather large owing to the $\langle d_{xy}/\Pi_g\rangle$ antibonding overlaps occurring in $\varphi_A{}^*$. This is consistent with the strong antiferromagnetic interaction observed in the EE case but in apparent contradiction with the ferromagnetic stabilization observed in the EO case. The stabilization of the triplet state when $N_3{}^-$ bridges in an EO fashion cannot be understood in the framework of this active electron approximation.

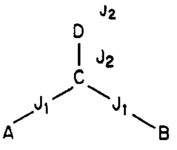
Spin Polarization Effect: Concept and Phenomenological Model

In the previous section, we gave evidence for the necessity to go beyond the active electron approximation to understand the interaction phenomenon in azido bridged copper(II) binuclear complexes. For that, we have to look for the role of the doubly occupied MO φ_A. The in-plane Π_g orbital of $N_3{}^-$ has a node on the central nitrogen atom. In this orbital, at a given instant, an electron with the β spin is localized around one of the terminal nitrogen atoms, and the other electron with the β spin is localized around the other terminal atom. The situation where the two electrons of Π_g are paired around the same terminal nitrogen atom is formally possible in the molecular orbital theory. We shall see further that this polar situation does not play any role in the nature of the interaction. When N_3 bridges in an EE fashion, the α electron is partially delocalized in φ_A toward a d_{xy} metal orbital, and the β electron is symmetrically delocalized toward the d_{xy} orbital centered on the other metal ion. Therefore, in φ_A, we have an instantaneous density of α spin in a d_{xy} orbital and of β spin in the other d_{xy} orbital. To obey the Pauli principle locally, the unpaired electrons occupying the magnetic orbitals will have a probability of β spin larger than $^1/_2$ around the former metal center and of α spin larger than $^1/_2$ around the latter metal center, which favors the singlet state. When $N_3{}^-$ bridges in an EO fashion, the electron on the bridging nitrogen atom, say with the α spin, is partially delocalized in φ_A toward the two d_{xy} metal orbitals. This gives an instantaneous density of α spin on the two metal centers. Therefore, each unpaired electron occupying its magnetic orbital will have a probability of β spin larger than $^1/_2$, which favors the triplet state. This role of φ_A is defined as a spin polarization effect and is schematized in Figure 6. If the two electrons of Π_g are paired around the same terminal nitrogen atom in an ionic form, there is no spin density transferred towad the metal centers, hence no spin polarization effect.

The polarization of the spins of the two active electrons by the in-plane Π_g orbital of $N_3{}^-$ may be described phenomenologically by a simple model using the Heisenberg formalism.[34] We consider the two networks **7** and **8** where A and B stand for the metal centers and C and D for the terminal nitrogen atoms of $N_3{}^-$. On each site, we have a $^1/_2$ spin, noted $\hat{S}_A$, $\hat{S}_B$, $\hat{S}_C$, and $\hat{S}_D$, respectively. $\hat{S}_C$ and $\hat{S}_D$ are strongly antiferromagnetically coupled ($J_2 < 0$), so that, in free C–D, the $S_C - S_D = 0$ state is stabilized by $-J_2$ with regard to the $S_C + S_D = 1$ state. J_2 symbolizes the energy gap between the singlet ground state of $N_3{}^-$ arising from the configuration $(\Pi_g)^4$ and the first triplet excited state arising from the configuration $(\Pi_g)^3(\Pi_u)^1$. In **7**, $\hat{S}_A$ and $\hat{S}_C$ on the one hand and $\hat{S}_B$ and $\hat{S}_D$ on the other hand are weakly coupled in an antiferromagnetic manner ($J_1 < 0$), so that along both A–C and B–D, the paired state is stabilized by $-J_1$ with regard to the unpaired state. J_1 measures the polarization of the spins of the active electrons due to the delocalization of the electrons of Π_g toward the metal centers. More precisely, if we cut the A–C and B–D bonds, the spins $\hat{S}_A$ and $\hat{S}_C$ (and $\hat{S}_B$ and $\hat{S}_D$) are totally uncorrelated and J_1 is zero. At the opposite, if the φ_A MO is very bonding, the delocalization of the electrons of Π_g toward the copper(II) ions is important, giving a large probability of α spin on a metal center and of β spin on the other metal center. Owing to the Pauli principle, this tends to align $\hat{S}_A$ and $\hat{S}_C$ (and $\hat{S}_B$ and $\hat{S}_D$) in an antiparallel way, which corresponds to a negative J_1 value. In the same way, in **8**, $\hat{S}_A$ and $\hat{S}_C$ on the one hand and $\hat{S}_B$ and $\hat{S}_C$ on the other hand are antiferromagnetically coupled with again a J_1 coupling parameter. The phenomenological spin Hamiltonian appropriate to calculate the energies of the spin state for **7** is



7



8

$$\mathcal{H} = -J_1(\hat{S}_A\cdot\hat{S}_C + \hat{S}_B\cdot\hat{S}_D) - J_2\hat{S}_C\cdot\hat{S}_D \qquad (5)$$

The Hamiltonian for **8** is

$$\mathcal{H} = -J_1(\hat{S}_A\cdot\hat{S}_C + \hat{S}_B\cdot\hat{S}_C) - J_2\hat{S}_C\cdot\hat{S}_D \qquad (6)$$

In both cases, for $|J_2| \gg |J_1|$, we have two low-lying states, a singlet and a triplet, and four states around the energy $-J_2$, a singlet, two triplets, and a quintet. The energies of these states can be calculated by using standard techniques. The full results are given in appendix. If we define the energy gap between the singlet and triplet low lying states by J, we have

$$J/|J_1| = \tfrac{1}{2}(-1 - (4 - 2\rho + \rho^2)^{1/2} + (1 + \rho^2)^{1/2}) \text{ for } \mathbf{7} \qquad (7)$$

$$J/|J_1| = \tfrac{1}{4}(1 - 2\rho + (9 - 4\rho + 4\rho^2)^{1/2}) \text{ for } \mathbf{8} \qquad (8)$$

with

$$\rho = J_2/J_1$$

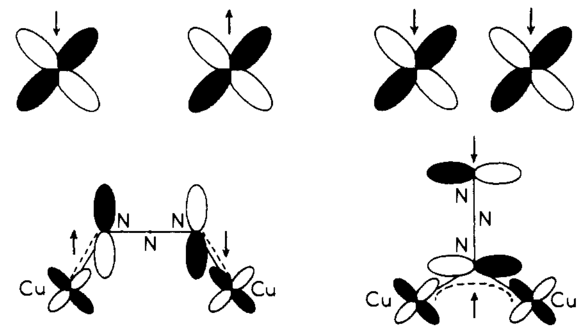


Figure 6. Schematic representation of the spin polarization effect (see text).

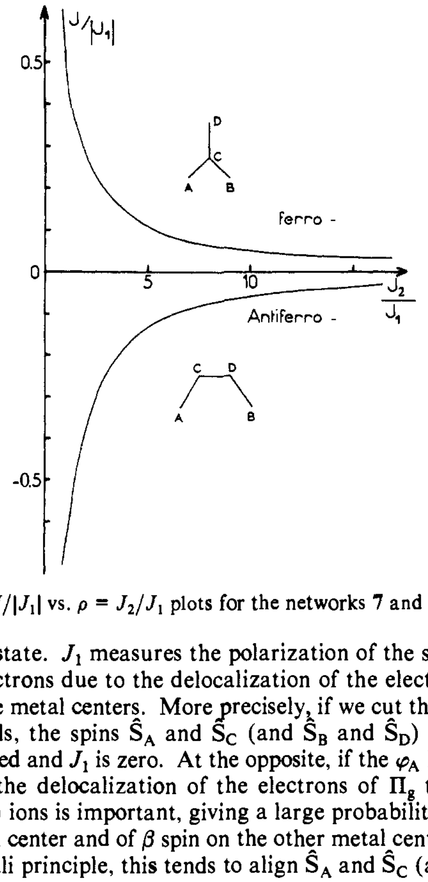


Figure 7. $J/|J_1|$ vs. $\rho = J_2/J_1$ plots for the networks **7** and **8** (see text).

---

(34) Heisenberg, W. *Z. Phys.* **1928**, *38*, 411–420.

Table I. Energies (in au) at the SCF Level and After CI for the Lowest States of N_3^-

	E_{SCF}	E_{IC}
$1\ \Sigma_g^+$	-163.1904	-163.5892
$3\ \Sigma_u^+$	-163.0654	-163.4266
$3\ \Delta_u$	-163.0439	-163.4018
$3\ \Sigma_u^-$	-163.0224	-163.3914
$1\ \Sigma_u^-$	-163.0224	-163.3846
$1\ \Delta_u$	-163.0084	-163.3805
$1\ \Sigma_u^+$	-162.6318	-163.3914

The $J/|J_1|$ vs. J_2/J_1 plots are shown in Figure 7. For **7**, $J/|J_1|$ is negative; the ground state is a singlet, and the effective coupling between $\hat{S}_A$ and $\hat{S}_B$ is antiferromagnetic. For **8**, $J/|J_1|$ is positive with a triplet ground state and a ferromagnetic effective coupling between $\hat{S}_A$ and $\hat{S}_B$.

Ab Initio Calculations on N_3^- and on Model Systems $(Be_2N_3)^+$

Methodology. The theoretical results presented in this section arise from an ab initio treatment with a large CI. The SCF calculations for the model systems $(Be_2N_3)^+$ were performed with a STONG ($N = 4$) basis of Pople[35] including a p polarization orbital for beryllium (exponent $\alpha = 0.2$). The study of N_3^- was performed with a more extended basis, of the double-ζ type in the valence region. This basis is made up of (9s, 5p) Gaussian functions of Huzinaga,[36] contracted in (4s, 2p) by Dunning.[37] We checked that this basis is adequate to describe N_3^- which actually is found to be stable with regard to $N_2 + N + e^-$ of 0.044 au. All the geometries for $(Be_2N_3)^+$ were optimized at the SCF level by using the gradient method. For the triplet states, this optimization was carried out on the UHF function. The CI was performed in the framework of the CIPSI method.[38] In this algorithm, for each spectroscopic state, the most important contribution of the determinants built from the SCF MO's are treated in a variational way, whereas the less important contributions are treated by second order perturbation theory. The variational space includes about 2500 determinants, and for each state the convergence of the perturbational series is obtained by the method of Peyerimhoff.[39] The number of involved determinants is then around half a million. With such a process, the uncertainty on the S–T gaps is estimaed to be less than 5×10^{-4} au (10^2 cm^{-1}).

Electronic Structure of N_3^-. Several theoretical studies of the electronic structure of N_3^- have already been published,[28-33,40] the most recent being that of Rossi and Bartram[33] who carried out an ab initio SCF calculation with (9s, 5p) Gaussian functions of Husinaga[36] contracted in (3s, 2p) by Dunning and Hay,[41] including a d polarization orbital. We reinvestigated the electronic structure of the azido ion. The occupied MO's at the SCF level are schematized in Figure 8 where we also indicated their energies. The energies of the ground and first excited states both at the SCF level and after CI are given in Table I. These calculations were performed for the optimized geometry of the ground state ($N - N = 2.241$ au). In other words, the energy gaps between the states correspond to the vertical transitions. For the $^1\Sigma_g^+$ ground state arising from the closed shell configuration $|-(\Pi_g)^4|$, our results are close to those of Wyatt et al.[31] and of Rossi and Bartram,[33] with, however, a slight stabilization of the Π_g HOMO's in our case.

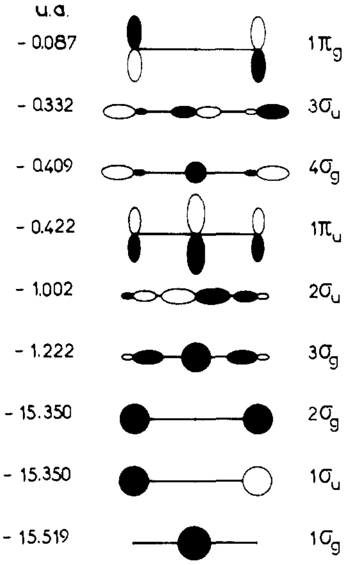
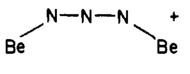


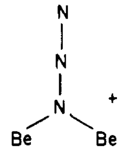
Figure 8. Shapes and energies of the occupied MO's for N_3^-.

The first singlet and triplet excited states arise from the $|-(1\Pi_g)^3(2\Pi_u)^1|$ configuration at the zeroth order which leads to the $^{1,3}\Sigma_u^+$, $^{1,3}\Sigma_u^-$, and $^{1,3}\Delta_u$ states. The CI does not modify the relative order of these states but, as expected, stabilizes the ground state with regard to the excited triplet states. Accordingly, the energy gap between the ground state and the first triplet state, $^3\Sigma_u^+$, is found as 0.162 au, instead of 0.133 au by Rossi and Bartram. Our study locates the first allowed transition $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ at 0.350 au instead of 0.412 au for Rossi and Bartram,[33] which value is still too high to attribute this transition to one of the bands observed in the near UV. As for the two forbidden transitions $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$ and $^1\Sigma_g^+ \rightarrow {}^1\Delta_u$ they are calculated at 0.206 and 0.210 au, respectively, in a region of the spectrum where a weak band is effectively observed, both in solution and in the solid state.[42-45] It must be noticed, however, that Ballard et al. recently attributed the band observed at 0.206 au in solution to an electron transfer to the solvent.[46]

Ab Initio Calculations on Model Systems $(Be_2N_3)^+$. In the hope to understand in a more thorough manner this versatility of the azido bridge to transmit the electronic effects between two copper(II) ions, we performed very accurate ab initio calculations on the two model systems **9** and **10**. The choice of these models deserves some explanations. Indeed, at the first view, a Be^+ ion may seem to be quite inappropriate to simulate a Cu^{2+} ion in a tetragonal environment, and in no way do we suggest that the S–T splitting in **9** and **10** could be quantitatively similar to those observed in the actual azido bridged copper(II) complexes. However, according to the concept of spin polarization presented in the previous section, the nature ferro- or antiferromagnetic of the interaction between two local spin doublets through the azido ion only depends on the symmetry EO or EE of the bridge, provided that the interacting centers have a singly occupied orbital close in energy to the Π_g HOMO's of N_3^-. In other words, the idea of spin polarization is not related to the specificity of the transition ions with their d valence shell. In this respect, we can



9



10

---

(35) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571–572.

(36) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293–1302.

(37) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823–2833.

(38) Huron, B.; Malrieu, J. P.; Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745–5759. Rancurel, P.; Huron, B. *Chem. Phys. Lett.* **1972**, *13*, 515–520. Rancurel, P.; Huron, B.; Praud, L.; Malrieu, J. P.; Berthier, C. *J. Mol. Spectrosc.* **1976**, *60*, 259–276. Oliveros, E.; Riviere, M.; Teichteil, C.; Malrieu, J. P. *Chem. Phys. Lett.* **1978**, *57*, 220.

(39) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta (Berlin)* **1975**, *39*, 217–228; **1974**, *35*, 33–58.

(40) Gora, T.; Kemmey, P. J. *J. Chem. Phys.* **1972**, *57*, 3579–3581.

(41) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 2.

(42) Closson, W. D.; Gray, H. B. *J. Am. Chem. Soc.* **1963**, *85*, 290–294.

(43) Burak, I.; Treinin, A. *J. Chem. Phys.* **1963**, *39*, 189–196.

(44) Deb, S. K. *J. Chem. Phys.* **1961**, *35*, 2122–2127.

(45) McDonald, J. R.; Rabalais, J. W.; McGlynn, S. P. *J. Chem. Phys.* **1970**, *52*, 1332–1339.

(46) Ballard, R. E.; Jones, J.; Sutherland, E.; Chun, B. L. *Chem. Phys. Lett.* **1983**, *97*, 413–417.

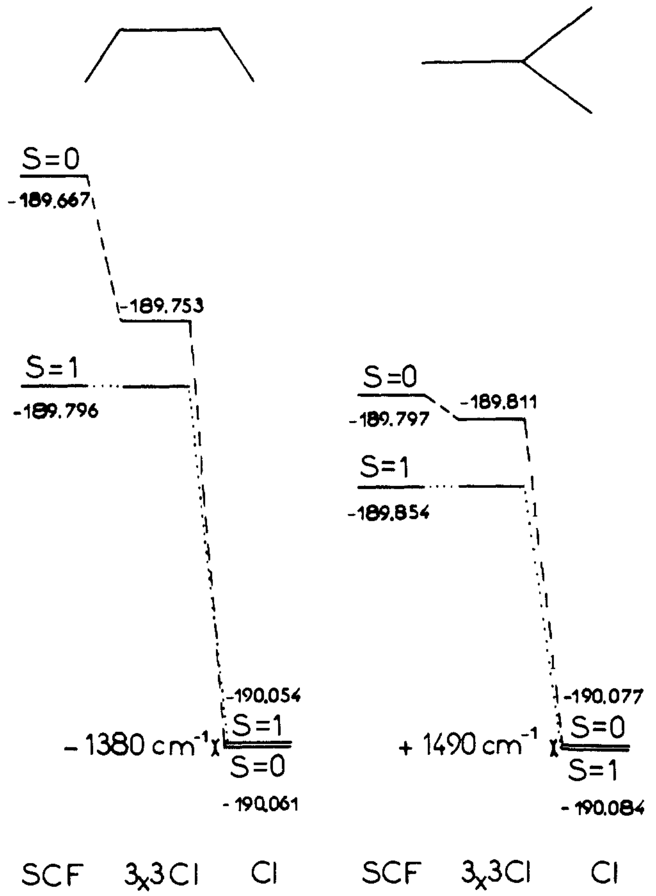


Figure 9. Steps of the calculation of the energies (in au) of the low-lying S and T states for EE and EO $(Be_2N_3)^+$.

notice that the singly occupied 2s orbital of Be^+ is reasonably close in energy to the singly occupied d_{xy}-type orbital of a $Cu(II)N_4$ planar chromophore. Both are slightly above the energy of the Π_g HOMO's of N_3^-.[47] To justify in one sentence our approach, we can say that if the concept of spin polarization is appropriate to understand the magnetic properties of the azido bridged copper(II) complexes, it must be also valid for the model systems **9** and **10** and lead to a singlet ground state in **9** and a triplet ground state in **10**. A rather similar idea of spin polarization has already been proposed in the theoretical study of the organic diradicals and substantiated by ab initio calcuations including extended CI.[56] The choice of the model systems **9** and **10** also results from two other considerations: (i) These systems are cationic as most of the azido bridged copper(II) complexes. Moreover, it is well-known that for a given basis set the description of the electronic structure is easier and in general more accurate with cationic systems than with anionic ones. (ii) Our systems are relatively simple in terms of the number of nuclei and electrons involved; this allows us to take into account all the electrons with an extended basis set and to perform an extended CI in a rigorous way.

The different steps of our calculations are the following: first, we optimized the geometries of **9** and **10** for both the SCF low-lying singlet and triplet states; then, we performed a 3 × 3 CI for the description of the singlet state, which is consistent with the active electron approximation. Finally, we carried out an extended CI involving all the determinants built from the 25 MO's of each system.

We propose now to examine in detail each step of these calculations, of which the results are schematized in Figure 9.

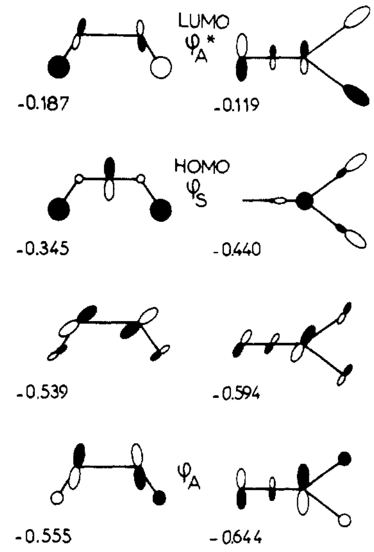


Figure 10. Last three occupied MO's and lowest unoccupied MO for the singlet states of EE and EO $(Be_2N_3)^+$; the energies are in au.

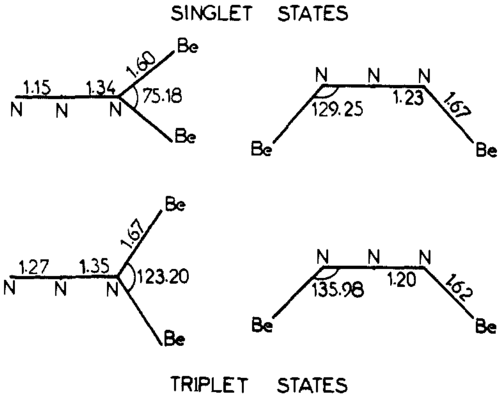


Figure 11. Optimized geometries for EE and EO $(Be_2N_3)^+$.

Molecular Orbitals at the SCF Level. The last three occupied MO's and the lowest unoccupied MO for the closed shell singlet state of each system are represented in Figure 10, and their energies are specified. In this Figure 10, one recognizes the $\varphi_A(b_1)$, $\varphi_S(a_1)$, and $\varphi_A^*(b_1)$ MO's considered in the second section and in addition, between φ_A and φ_S, a b_2 MO which is antisymmetric with regard to the molecular plane. The Δ energy gap between φ_A^* and φ_S is 0.158 au in the EE case and 0.322 au in the EO case.

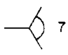
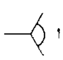
The MO's calculated for the closed shell singlet state form a reasonably good basis for the CI; on the other hand, they lead to a one determinant description which is only a poor approximation for the triplet state. The Nesbet type calculations are, in principle, better adapted to describe the triplet states. So, we carried out such calculations for the optimized geometries (see below). The energies of the MO's are only slightly modified except for φ_A^* and φ_S. The Δ energy gaps are 0.028 au instead of 0.158 au for the EE case and 0.029 au instead of 0.322 au for the EO case.

Optimized Geometries. For the EE case, the optimized geometries of the SCF singlet and triplet states are rather close to each other with BeN bond lengths of 1.67 and 1.62 Å and BeNN bridging angles of 129 and 135°, respectively. In contrast, the geometry of the triplet state for the EO case is very different from that of the singlet state, with a much more open BeNBe bridging angle, 123° instead of 75°. This situation is evidently due to the Be–Be direct interaction. We shall discuss further this geometry effect in the EO case. These optimized geometries are schematized in Figure 11. In the two geometries and for both singlet and triplet states the computed charges are close to $[Be^{+0.5}]_2[N_3]^0$. The electron transfer from the azido ligand toward the beryllium magnetic centers is of the same nature as what would be expected

---

(47) Extended Hückel calculations with charge iteration and correction of the energy shift due to the charge were carried out on N_3^-, the model systems $(Be_2N_3)^+$, and the planar complexes $[(NH_3)_2Cu(N_3)_2Cu(NH_3)_2]^{2+}$. The energy of the Π_g HOMO's of N_3^- was found equal to −13.26 ev. At the convergence, the H_{ii}'s were found in the ranges −9.3, −9.6 ev for the 2s orbital of Be and −10.8, −11.6 ev for the 3d orbitals of Cu.

Table II. Polarization Energies for the Triplet States[a]

structures	energies (au)
 75°	-189.7548 E_{pol} = -0.0449
 124°	-189.7548 E_{pol} = -0.0186
	-189.7550 E_{pol} = -0.0202

[a] In each case, the reference noted with a continuous line corresponds to the one determinant description.

in the actual copper(II) complexes.

S–T Splitting at the SCF Level. At the SCF level, for both the EE and the EO cases, the triplet state at its equilibrium geometry is the lowest. The closed shell singlet state is located 28 270 cm^{-1} above in the EE case and 12 310 cm^{-1} above in the EO case. At this level of approximation, the interaction for the two geometries appears ferromagnetic, the effect being more pronounced with the 1,3-azido bridge. This first result is clearly in complete contradiction with the experimental results concerning the actual copper(II) complexes.

In order to specify the role of the geometric factors, we also calculated the energies of the SCF triplet states with the equilibrium geometries of the SCF singlet states. For the EE case, the triplet state remains the lowest. On the other hand, for the EO case, this triplet state is now destabilized by 3330 cm^{-1} with regard to the singlet state.

Limited Configuration Interaction. It is now well-established that when the energy gap Δ between the HOMO and the LUMO of a molecular system with an even number of electrons is small, the low lying singlet state is poorly described by the single determinant $|\cdots(\mathrm{HOMO})^2|$. This is typically the case for the coupled magnetic systems with singlet and triplet states thermally accessible. In the active-electron approximation presented in section 3, this low lying singlet state is described by the interaction of the two determinants $|\cdots(\mathrm{HOMO})^2|$ and $|\cdots(\mathrm{HOMO})^0(\mathrm{LUMO})^2|$ and the triplet state by the single determinant $|\cdots(\mathrm{HOMO})^1(\mathrm{LUMO})^1|$. We performed such a 3 × 3 CI in order to see whether this would stabilize sufficiently the singlet state and would give S–T splittings qualitatively in agreement with the experimental evidences. In the EE case, the $S = 0$ state is stabilized by 18 790 cm^{-1}, but the triplet remains the lowest with a S–T splitting of 9480 cm^{-1}. In the EO case, the stabilization of the singlet state due to this 3 × 3 CI is 3030 cm^{-1}, and the resulting S–T splitting is 9280 cm^{-1}. To sum up, at this level of approximation which conceptually corresponds to the active-electron approximation, the interaction is found ferromagnetic for the two systems with nearly the same S–T splitting. This confirms the necessity to go beyond this conceptual framework.

Extended CI. We then carried out an extended CI. In both cases, the CI stabilizes the singlet state more than the triplet state. In the EE case, the order of the singlet and triplet states is reversed, and the singlet becomes lower with a S–T splitting of −1380 cm^{-1}. In other words, the interaction is finally found antiferromagnetic, as expected from all the experimental data on copper(II) complexes. As for the EO case, the triplet state remains lower after CI with a S–T splitting of 1490 cm^{-1}. The interaction is actually ferromagnetic.

The energy lowering resulting from CI does not have the same meaning for S and T states. Indeed, the one determinant representation of the triplet state can get stabilization by interaction with all monoexcited configurations. This effect gives the so called polarization energy which is identically zero for the SCF representation of the singlet state. It seemed to us interesting to evaluate this polarization energy for the EE and EO triplet states and study the influence of the geometry relaxation. The results are reported in Table II. For the equilibrium geometries, the polarization energies in the EE and EO cases are nearly equal. On the other hand, the opening of the bridging angle in the EO case when going from the S to the T states leads to an important variation of this term, which seems related to the geometry relaxation.

Discussion and Conclusion

The study of the magnetic properties of μ-azido copper(II) binuclear complexes revealed quite a surprising and striking result: the end-to-end bridge strongly favors the antiferromagnetic interaction, and the end-on bridge favors the ferromagnetic interaction. The question at hand was to understand why such a versatility was observed. In a natural way, we initially attempted to explain this behavior by working in the framework of the qualitative models which were proving successfull for most of the coupled systems. Clearly, these models did not allow to rationalize the experimental data. In particular, the ferromagnetic interaction observed in EO azido bibridged copper(II) dimers cannot be explained in a satisfying way by the accidental orthogonality of the magnetic orbitals.[22,27,28] Such an orthogonality is destroyed by a small structural modification, for instance, a variation of the bridging angle. This does not seem to occur with the EO azido bridges.

In the second step of our work, we attempted to specify the approximations used in these qualitative models that are no longer valid with the azido bridged complexes. In both the models proposed by Hay et al.[26] and by Kahn et al.,[22,50] it is implicitly assumed that the HOMO of the bridges is much lower in energy than the d metal orbitals. This leads to the so called active electron approximation.[22] This approximation is qualitatively valid with very electronegative bridges like halogeno or hydroxo, but the situation is dramatically different with the azido bridge for which the Π_g HOMO's are nonbonding and close in energy to the metal orbitals.

In a subsequent step, we sought a simple model pointing out the role of the in-plane Π_g orbital of the azido bridge in the interaction phenomenon, and we proposed the concept of spin polarization. Of course, the physical reality is much more subtle than what this concept suggests. In a certain sense, one could say that the active electron approximation underestimates the role of the Π_g HOMO's of N_3^-, whereas, the concept of spin polarization focuses on these MO's in an excessive manner. This concept, however, has the advantage to emphasize the difference between EE and EO bridges in quite a simple way. A phenomenological model based on spin Hamiltonians reinforces the idea of polarization of the spin of the magnetic electrons by the electrons of the in-plane Π_g of N_3^- and points out the role of the singlet–triplet energy gap in N_3^- (noted $-J_2$) in the effective interaction between the metal centers. This suggest new experiments in which N_3^- would be replaced by the isoelectronic cyanato bridge NCO^-; indeed, the energy gap between the ground singlet state and the first excited state is larger in NCO^- than in N_3^-.

The final step of this work was to obtain a more rigorous approach of the interaction through the azido bridge. Two possibilities offered themselves to us; either to work with actual copper(II) complexes and to use a simplified development of the CI or to work with much simpler model systems and to perform an extended CI in a rigorous way. Two reasons led us to choose the latter option: (i) Three calculations of the former kind recently appeared,[51-53] one of them concerning the μ-azido, μ-hydroxo complex of which the structure is shown in Figure 3.[53] The method used is based on a perturbational development of the CI, and our opinion is that the convergence problem is not yet fully resolved. Moreover, with azido bridges, the magnetic orbitals are strongly delocalized toward these bridges owing to the weak energy difference between ligand and metal orbitals, and, in this case, the

---

(48) Kahn, O. *Comments Inorg. Chem.* **1984**, *3*, 105–132.

(49) Van Kalkeren, G.; Schmidt, W. W.; Block, R. *Physica B + C (Amsterdam)* **1979**, *97B*, 315–337.

(50) Kahn, O.; Briat, B. *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 268, 281.

(51) De Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007–4016.

(52) Charlot, M. F.; Verdaguer, M.; Journaux, Y.; de Loth, P.; Daudey, J. P. *Inorg. Chem.* **1984**, *23*, 3802–3808.

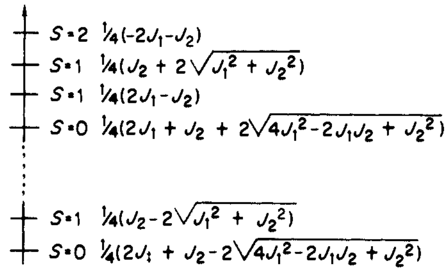
(53) Daudey, J. P.; de Loth, P.; Malrieu, J. P. In *Magneto Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Nato Asi Series, D. Reidel: Dordrecht, 1984; pp 87–104.

choice of the partition of the exact Hamiltonian is still questionable.[54] (ii) According to the concept of spin polarization, the nature of the interaction between two single ion doublet states through the azido bridge does not depend on the surroundings of the magnetic ions but only on the fashion N_3^- bridges, provided that the energy of the magnetic orbitals is close to that of the HOMO's of N_3^-. It was then tempting to modelize the magnetic ions by entities as simple as possible and to see whether an accurate ab initio calculation would give the expected signs for the S–T splittings. The model systems $(Be_2N_3)^+$ fulfilled these conditions, and the nature of the interaction was actually found as expected, namely antiferromagnetic with EE bridge and ferromagnetic with EO bridge. It is essential to note here that this result is achieved only after an extended CI. At both the SCF level and the level of the active electron approximation, the interaction was found ferromagnetic to whatever the geometry of the bridge might be. A point particularly deserves to be discussed, namely the opening of the BeNBe angle between the singlet and the triplet states in the EO case. This effect is essentially due to the overlap between the 2s orbitals of Be and is expected to be much more pronounced than in the actual copper(II) complexes. Indeed, the overlap between the 3d copper orbitals is one order of magnitude weaker than between 2s beryllium orbitals. It would be, however, very interesting to check whether, in the compounds of Figure 2, the value of the CuNCu bridging angle is effectively larger in the ground triplet state than in the excited singlet state. It must be noticed that this effect, if it did exist, would not be of the same nature as the one put into evidence by Hatfield and Hodgson.[54] These authors showed that in a given series of di-μ-hydroxo copper(II) dimers, the sign of the S–T splitting depended on the (average) value of the bridging angle but did not discuss the variation of geometry between the two low lying states for a given compound.

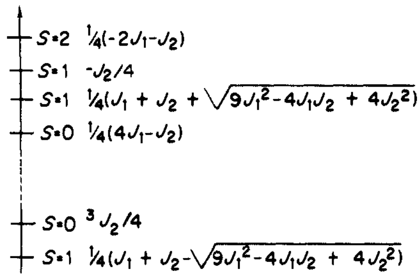
In spite of the simplicity of the model systems $(Be_2N_3)^+$, the ab initio calculation of the S–T splittings keeps some character of black box. We hoped to obtain more quantitative information on the role of the HOMO's of N_3^- and maybe to specify the concept of spin polarization, particularly in the CI process. In fact, this calculation confirms that the geometry of the azido bridge plays an essential part in the nature of the interaction; it also shows that it is necessary to go up to the term of the CI process to obtain the proper relative order of the low-lying states. It suggests an interesting geometry relaxation between these low-lying states in the EO case. However, it cannot be considered as a tool for the experimentalists attempting to design polymetallic systems exhibiting expected magnetic properties.[55] In contrast, the rather naive concept of spin polarization and the phenomenological model which accompanies it could be useful to the experimentalists. This dichotomy confirms that in the field of the interaction between magnetic centers in coupled systems what is gained in mathematical rigor is often lost in heuristic character.

Appendix

Energies of the spin states for the Networks **7** and **8**
For **7**:



For **8**:



Registry No. $(Be_2N_3)^+$, 101225-34-7; N_3^-, 14343-69-2.

---

[54] Crawford, W. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110.

[55] Kahn, O. *Angew. Chem., Int. Ed. Engl.*, in press.

[56] Borden, W. T.; Davidson, E. R. *Ann. Rev. Phys. Chem.* **1979**, *30*, 125–153. Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69–76.