Formation of Sulfur−Sulfur Bonds in Copper Complexes

Gabriel Aullón*[a] and Santiago Alvarez[a]

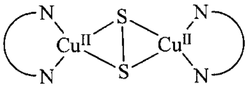
Keywords: Copper-sulfur complexes / Ligand−ligand bonds / Density functional calculations / Through-ring bonding / Electronic structure

The recently reported dinuclear complexes $[Cu_2(\mu\text{-}S_2)(\text{diketiminato})_2]$ that have short S–S distances across their Cu_2S_2 rings are theoretically studied with the help of density functional calculations and a topological analysis of the electron density. The possibility of obtaining the isomeric form without a S–S bond is explored by comparing the structure and bonding with its oxo analogue. A study of the influence of several terminal-chelating ligands on the relative stability of the sulfido- and the disulfido-bridged forms is also presented. The only way to stabilize a sulfido-bridged isomer is found to be via two-electron reduction, whereas chemical substitutions are not able to produce the cleavage of the S–S bond.

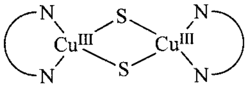
Introduction

The rich chemistry of copper-oxygen compounds is dramatically modified when we move to the sulfur analogues, limited to a few examples in biological chemistry, such as cupredoxins[1] and metallothioneins.[2] An example is provided by the so-called Cu_A dinuclear center, active in electron transfer processes, and present in heme-copper oxidases and also nitrous oxide reductases.[3] Its basic unit is a Cu_2S_2 ring in which two cysteine ligands bridge the two copper atoms, whose coordination sphere is completed with two terminal histidine and methionine residues. In such compounds both the oxidation states I and II are available for the metal atoms.

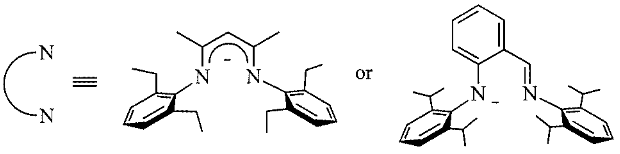
A recently reported reaction of a β-diketiminato Cu^{II} complex with $(TMS)_2S$ or a Cu^I analog with S_8 yields the disulfido Cu^{II} complexes of type **1a**.[4] One can in principle expect an alternative structure for the same compounds, schematically represented in **1b**, formally a sulfido/Cu^{III} complex with a long through-ring S···S distance, similar to what is found for oxygen-bridged copper complexes, for which equilibria between the peroxo and oxo-bridged forms have been well characterized.[5,6] We asked ourselves two questions that we tried to answer by performing a theoretical study: Could the sulfido-bridged Cu^{III} isomer **1b** be isolated? What could be made to favor the formation of that isomer? These compounds belong to a wider family represented by **2a** and **2b**, and challenge our understanding of the electronic structure and bonding of double bridged dinuclear complexes, since the framework electron counting rules[7,8] predict it to present the regular ring structure **2b**, with no S−S bonding interactions across the ring, in clear disagreement with the experimental result. Therefore, understanding the structural preferences of these compounds is a relevant task considering the importance of copper complexes in several biological processes.[9]



1a



1b



2a **2b**

To the best of our knowledge, the only structurally characterized copper compound with unsubstituted bridging sulfur atoms is the disulfido-bridged complex $[Cu_2(\mu\text{-}S_2)(HB\{3,5\text{-}iPrpz\}_3)_2]$, which also has a rather short S−S

---

[a] Departament de Química Inorgànica and Centre de Recerca en Química Teòrica, Universitat de Barcelona,
Avda. Diagonal 647, 08028 Barcelona, Spain

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200400206

distance (2.07 Å) across the $\{Cu_2S_2\}^{2+}$ unit.[10] Other Cu_2S_2 cores either correspond to thiolato bridges or belong to cubane-type Cu_4S_4 structures. Examples of square-planar complexes of d^8 ions of the type $[L_2M(\mu\text{-}XR_n)_2ML_2]$, with dialkylphosphido or thioether bridges (XR_n = PR_2, SR_2) are known and they all have regular M_2X_2 rings without bonding interactions across the diamond (2.82−2.90 and 2.92−3.06 Å, respectively), whereas a silylene bridged compound (XR_n = SiR_2) has a short Si···Si distance (≈ 2.6 Å).[7] Recently, we have studied the possibility of ring isomers for $[M_2(\mu\text{-}X)_2(PR_3)_4]$ complexes with square-planar metals, where M and X are group 10 and 16 elements, respectively.[11]

We attempt here to extend these theoretical studies to copper-sulfur complexes in order to understand their structural behavior and to compare them with the important analogous oxo-bridged compounds.[8,12] In particular we would like to find out whether the alternative structure **1b** for a copper-sulfur core could be obtained by an adequate choice of terminal ligands. To that end, we report calculations based on density functional theory for $[Cu_2(\mu\text{-}O)_2(dki)_2]$ and $[Cu_2(\mu\text{-}S)_2(dki)_2]$, as well as for the reduced species $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$ and for several related complexes $[Cu_2(\mu\text{-}S)_2(chel)_2]$, where chel stands for a variety of bidentate ligands and dki represents a β-diketiminato ligand.

Results and Discussion

Optimized Structures: The main results of our DFT calculations for complexes of formula $[Cu_2(\mu\text{-}X)_2(chel)_2]$ (X = O or S) are reported in Table 1 and the optimized structures are shown in Figure 1. The atomic coordinates of structures corresponding to calculated energy minima are supplied as Supporting Information (see footnote on the first page of this article). We discuss here the diketiminato complexes and defer the analysis of the results with other terminal ligands to a later section. For $[Cu_2(\mu\text{-}O)_2(dki)_2]$, two minima are found that correspond to different through-ring O−O distances (2.36 and 1.44 Å, respectively), in agreement with previous results for a related simpler model $[Cu_2(\mu\text{-}O)_2(NH_3)_6]$[12] and with the existence of structurally characterized compounds with either structure (Table 2). The existence of an energy minimum at a long O−O distance agrees well with the prediction of the FEC rules for d^8 transition metals with square-planar coordination and O^{2-} as bridging ligands. Other optimized structural data (e.g., O···O and Cu−O distances of 2.36 Å and 1.81 Å, respectively) are in good agreement with experimental results for related complexes (2.26−2.35 and 1.80−1.86 Å, respectively, see Table 2) and for the infinite chains of CuO_2^- present in solid state compounds (2.45−2.51 and 1.82−1.85 Å). All these data for the isomers of type **2b** are consistent with their formulation as Cu^{III} compounds[13] for which planar rings can be expected.[14]

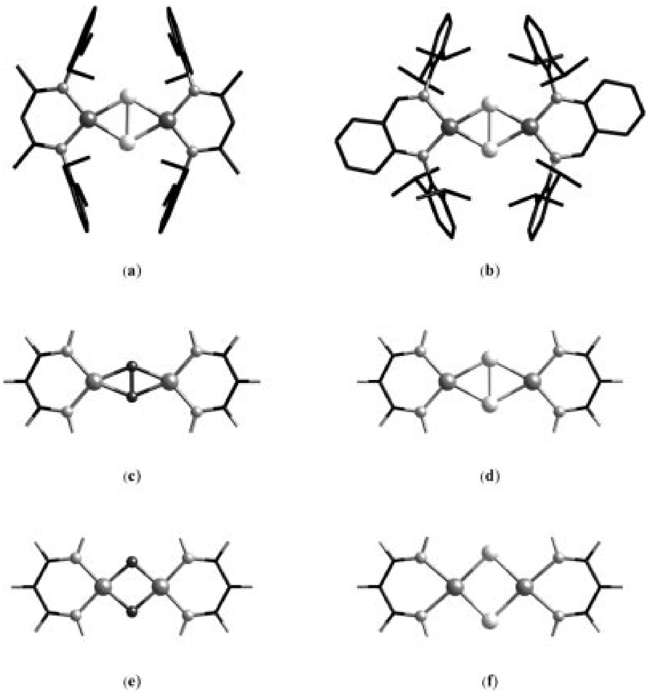


Figure 1. Experimental structures[4] of $[Cu_2(\mu\text{-}S_2)(dki)_2]$ (**a** and **b**), and optimized structures of $[Cu_2(\mu\text{-}O_2)(dki)_2]$ (**c**), $[Cu_2(\mu\text{-}S_2)(dki)_2]$ (**d**), $[Cu_2(\mu\text{-}O)_2(dki)_2]$ (**e**) and $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$ (**f**)

A geometry of the type **2a**, such as that with a short O−O distance found here for $[Cu_2(\mu\text{-}O)_2(dki)_2]$, has recently been analyzed in related compounds of group 10 metals.[11] In that study, the isoelectronic oxo complexes having Pd_2O_2 and Pt_2O_2 cores always produce the two minima that

Table 1. Optimized data for the two isomers (**2a** and **2b**) of diketiminate complexes with $Cu_2(\mu\text{-}X)_2$ core (X = O or S). Distances in Å, angles in degrees and energies in kcal·mol^{-1}.

Compound	Isomer	X···X	Cu−X	Cu−L	X−Cu−X	L−Cu−L	Energy
$[Cu_2(\mu\text{-}O)_2(dki)_2]$	**2a**	1.443	1.944	1.933	43.6	96.7	+0.7
	2b	2.359	1.808	1.897	81.4	92.3	0.0
$[Cu_2(\mu\text{-}S)_2(dki)_2]$	**2a**	2.178	2.313	1.928	56.2	97.2	0.0
	2b	3.238[a]	2.307	1.924	89.1	92.9	+21.4
$[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$	**2a**	2.178[a]	2.516	2.103	51.3	87.6	+7.0
	2b	3.238	2.321	2.142	88.5	81.0	0.0

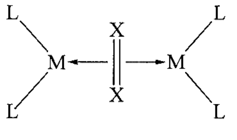
[a] Parameter frozen in the geometry optimization.

Table 2. Main structural parameters for experimental structures of $[\mathrm{Cu_2}(\mu\text{-}X)_2L_4]$ complexes (X = O, S) and of inorganic solids of formula $\mathrm{ACuX_2}$ (A = alkaline cation)

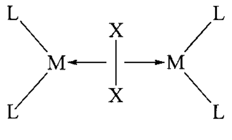
Compound	X···X	Cu−X	X−Cu−X	Cu−L	L−Cu−L	Ref.	Code[a]
Isomer **2a**							
$[\mathrm{Cu_2S_2}(N,N'\text{-Ar-NC}_6\mathrm{H_4CH{=}N})_2]$	2.166	2.206	58.8	1.901	97.7	[4]	–
$[\mathrm{Cu_2S_2}(N,N'\text{-Ar-1,3-Me-dki})_2]$	2.201	2.195	60.2	1.908	99.3	[4]	–
$[\mathrm{Cu_2S_2}(\mathrm{HB}\{3,5\text{-}i\mathrm{Pr\text{-}pz}\}_3)_2]$[b]	2.072	2.265	54.5	2.018	93.3	[10]	LEJBOR
$[\mathrm{Cu_2O_2}(\mathrm{HB}\{3,5\text{-}i\mathrm{Pr\text{-}pz}\}_3)_2]$ [b]	1.413	1.913	43.3	1.997	92.6	[15]	KECZEK10
$[\mathrm{Cu_2O_2}(\{6\text{-Me-py}_2\mathrm{CHpy}\}_2\mathrm{C_2H_4})]^{2+}$ [b]	1.486	1.908	45.8	1.995	91.6	[16]	GUGPUT
Isomer **2b**							
$[\mathrm{Cu_2O_2}(N,N'\text{-Ar-1,3-Me-dki})(\mathrm{C_3H_6}\{\mathrm{NMe_2}\}_2)]^{2+}$	2.259	1.818	76.8	1.943	98.7	[17]	OGIXAD
$[\mathrm{Cu_2O_2}(\text{9ane-BzN}_3)_2]^{2+}$ [b]	2.287	1.806	78.6	1.986	88.9	[18]	ZOSXIO10
$[\mathrm{Cu_2O_2}(\{\mathrm{pyCH_2}\}\{6\text{-Me-pyCH}_2\}_2\mathrm{N})_2]^{2+}$ [b]	2.323	1.803	80.2	1.940	87.0	[19]	QIDBUA
$[\mathrm{Cu_2O_2}(\{\text{9ane-}i\mathrm{PrN_3}\}_2\mathrm{C_2H_4})]^{2+}$ [b]	2.352	1.827	80.1	1.991	88.0	[20]	RENZEP
$[\mathrm{Cu_2O_2}(\mathrm{C_6H_{10}}\{\mathrm{NMeEt}\}_2)_2]^{2+}$	2.344	1.807	80.8	1.938	89.6	[21]	NUWDAK
$[\mathrm{Cu_2O_2}(t\mathrm{Bu_2P}\{\mathrm{NSiMe_3}\}_2)_2]$	2.339	1.865	77.7	1.978	77.4	[22]	WOMVOJ
$\mathrm{LiCuO_2}$	2.469	1.836	84.5	1.836	84.5	[23]	074978
$\mathrm{NaCuO_2}$	2.446	1.839	83.4	1.839	83.4	[24–26]	203080
$\mathrm{KCuO_2}$	2.460	1.829	84.5	1.829	84.5	[26–28]	203081
$\mathrm{RbCuO_2}$	2.500	1.845	85.3	1.845	85.3	[27]	015096
$\mathrm{CsCuO_2}$	2.511	1.849	85.5	1.849	85.5	[27]	015097

[a] Alphanumerical code for CSD[29] or ICSD[30]. [b] The terminal ligand acts as tridentate.

we have also observed for Cu. This second isomer can be formulated as either having two d^{10} transition metal atoms bridged by a side-on bridging dioxygen molecule (**3a**), or two d^9 $\mathrm{Cu^{II}}$ ions, side-on bridged by a peroxo group (**3b**). As found earlier,[11] the Cu−O edges of the diamonds in the complex with structure **2a** (1.94 Å) are significantly longer than in the **2b** isomer (1.81 Å). Such distances, as well as the O−O one (1.44 Å) are in excellent agreement with those experimentally found in complexes that present this structural motif (≈ 1.91 and 1.41−1.49 Å, respectively, see Table 2).



3a



3b

When oxygen atoms are replaced by sulfur, an important change is produced,[12] since only one minimum with a short S−S distance (2.18 Å) is found for $[\mathrm{Cu_2}(\mu\text{-S})_2(\mathrm{dki})_2]$. Such a distance is consistent with the experimental values (2.16 and 2.20 Å) in the complexes prepared by Tolman et al.[4] and somewhat longer than in the other known compound with bare sulfur atom bridges, $[\mathrm{Cu_2}(\mu\text{-S}_2)(\mathrm{HB}\{3,5\text{-}i\mathrm{Prpz}\}_3)_2]$ (2.07 Å).[10] This behavior is remarkably different from that found earlier for isoelectronic complexes of group 10 metals with sulfur bridging atoms, since the two minima (**2a** and **2b**) were found for the $\mathrm{Pd_2S_2}$ core, whereas $\mathrm{Ni_2S_2}$ and $\mathrm{Pt_2S_2}$ compounds are predicted to only have structure **2b**.[11]

Since it is well known that $\{\mathrm{Cu_2}(\mu\text{-O})_2\}^{2+}$ species acting as mild two-electron oxidants are reduced to $\{\mathrm{Cu_2}(\mu\text{-O})_2\}^0$,[5,31] it seemed interesting to explore the hypothetical reduced sulfur complex $[\mathrm{Cu_2}(\mu\text{-S})_2(\mathrm{dki})_2]^{2-}$. For this compound the **2b** isomer appears to correspond to an energy minimum (see Figure 1). The structural data (e.g., S···S = 3.24, Cu···Cu = 3.34 and Cu−S ca. 2.32 Å) are in excellent agreement with those in two structurally characterized isoelectronic $\mathrm{Cu^{II}}$ compounds with thiolato bridges (Cu···Cu = 3.34 and Cu−S = 2.33 Å).[32] It is remarkable that the Cu−N distances increase upon reduction from 1.93 to 2.14 Å, in contrast with what happens with the Cu−S distances, that are practically unaltered. Other bond lengths are practically unaffected by reduction, except for a decrease of the bite distance (N···N) of the bidentate dki ligand (≈ 0.1 Å shorter) concomitant with the increased Cu−N distance. Alternatively, in agreement with the framework electron counting rules,[7] a second structure for the reduced complex $[\mathrm{Cu_2}(\mu\text{-S})_2(\mathrm{dki})_2]^{2-}$ with tetrahedrally coordinated copper atoms and a short S−S distance (2.31 Å) is found as an energy minimum, only a few kcal·mol^{-1} above the **2b** isomer. Given the small energy difference between alternative geometries, one can anticipate that both could be obtained experimentally.

Cross sections of the potential energy surfaces for the O- and S-bridged complexes $[\mathrm{Cu_2}(\mu\text{-X})_2(\mathrm{dki})_2]$ are presented in Figure 2, where the calculated energy is plotted as a function of the normalized X···X distance. For the $\mathrm{Cu_2S_2}$ core the minimum is found at a normalized distance of 1.07 (i.e., a S−S distance that is practically twice the sulfur atomic radius[12]). Upon reduction, the minimum is shifted to 1.59 (**2b**), a geometry that is 21 kcal·mol^{-1} above the minimum for the neutral species. For the analogous complex with a

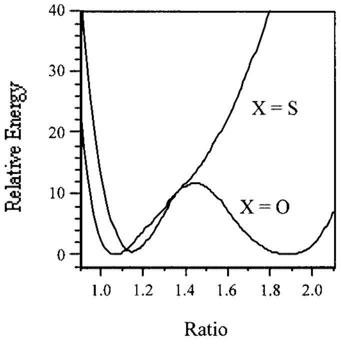


Figure 2. Relative energy (in kcal·mol^{-1}) as a function of the normalized X···X distance for complexes [$Cu_2(\mu\text{-}X)_2(dki)_2$] (X = O or S). The normalized distance is defined as the ratio between the X···X distance and twice the atomic radius of X

Cu_2O_2 core, two nearly isoenergetic minima appear with O···O distances at 1.15 and 1.87 times the atomic radii sum and the transition state can be estimated to appear near 1.45 with an approximate barrier of 11.8 kcal·mol^{-1}. These results are in agreement with the equilibrium between two isomers recently proposed for the activation of O_2 by β-diketiminatocopper(I),[33] but the evaluation of the energy difference between the oxo- and peroxo-bridged forms of copper complexes is not straightforward and the reader is referred to a recent study by P. Siegbahn[34] for a more detailed discussion.

Orbital Analysis: In an attempt to understand the different behaviors of the oxo and sulfido-bridged complexes, we report here on an analysis of the corresponding molecular orbitals. In the oxo isomer with a regular ring **2b**, the bonding within the $\{Cu_2X_2\}^{2+}$ core can be associated with four framework bonding molecular orbitals (a_g, b_{1u}, b_{2g} and b_{3u} in Figure 3). For the Cu^{III}/O^{2-} compound, these four orbitals are occupied, whereas the framework antibonding orbitals (only two out of four are shown as the uppermost orbitals in Figure 3: $2b_{2g}$ and $2b_{3u}$).

As the rhombus distorts and the two oxygen atoms approach each other, the energies of the framework orbitals change due to the interplay of the through-ring σ overlap and the metal-bridging ligand overlap. Since two occupied framework orbitals are stabilized and two are destabilized upon distortion, two minima appear, separated by a low barrier resulting from the crossing between the two b_{3u} orbitals. Additionally, an important change in composition of the framework orbitals is induced by the approach of the two oxygen atoms, the occupied bonding b_{3u} combination becoming localized at the Cu atoms and the empty antibonding one at the bridging O atoms.[7,8,11,12] The outcome of such an orbital localization is that the two b_{3u} electrons

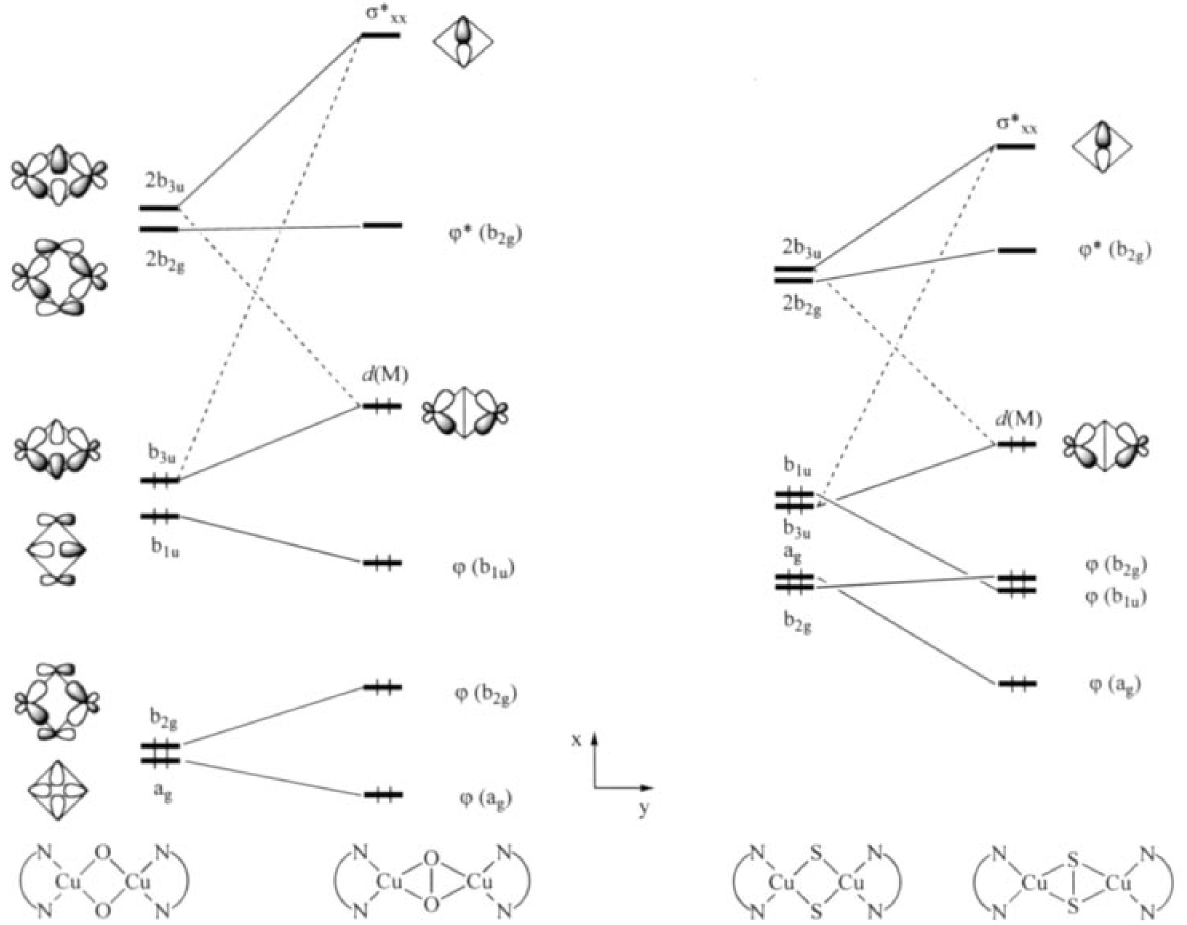


Figure 3. Simplified orbital diagram for the compounds [$Cu_2(\mu\text{-}O)_2(dki)_2$] (left) and [$Cu_2(\mu\text{-}S)_2(dki)_2$] (right)

are transferred from the Cu_2O_2 framework to the metal d orbitals, the copper atoms becoming formally Cu^{II} and the bridging oxo ions forming a peroxo bridge (notice the loss of σ* character of the occupied b_{3u} orbital in the **2a** form), which is the reason why the framework electron counting rule[7,8,11,12] fails. It must be noted that a strong antiferromagnetic coupling should be expected between the two Cu^{II} ions.[35] Such a description of the electronic structure of the **2a** form is consistent with the results of a natural bond order (NBO)[36] analysis, that indicates a net charge transfer of about 0.4 e^- from each sulfur atom to copper and the terminal ligands when going from **2b** to **2a**. It is also seen that such a charge transfer occurs mainly between the p_x orbitals of the bridges and the d_{xy} orbitals of the copper atoms, as would be expected from the change in the composition of the b_{3u} framework orbital.

For the analogous sulfur complex, a similar orbital picture should apply (Figure 3), but in fact we find only the disulfido-bridged compound **1a**, both theoretically and experimentally. The main difference between the two Walsh diagrams can be found in the occupied b_{2g} orbital, which is significantly stabilized when the two bridges are taken apart for X = O, but is practically insensitive to the bridge-bridge distance for X = S. The analysis of the composition of that orbital (Figure 4) clearly shows that in the sulfido-bridged compound there is little contribution from the metal to this molecular orbital, thus accounting for its nearly constant energy throughout the **2a** $\leftrightarrows$ **2b** interconversion path. It is likely that the lesser mixing of the metal xy and the sulfur p orbitals in b_{2g} for the sulfido bridges compared with the oxo ones should be attributed to the less electronegative character of sulfur. A similar effect was previously observed for isoelectronic square-planar Pt complexes with XH_2 bridges,[7] for which increasing orbital localization and decreasing through-ring X···X distances (S > P > Si) were found for different bridging atoms. Since the degree of mixing is likely to be affected by the basis set used, this finding could provide a rationale for the strong effect that the basis set has on the calculated relative energies of isomers **2a** and **2b** in other cases, as recently reported by Siegbahn.[34] Also the different behavior of related Ni, Pd and Pt complexes found recently by us[11] might be related to this subtle orbital effect.

Upon two-electron reduction of the sulfido complex, the structure is dramatically modified and the regular Cu_2S_2 ring with a long S···S distance is obtained. From Figure 3 it is clear that such a geometry change must be associated with the occupation of the high lying (framework antibonding) b_{3u} orbital. The proximity of b_{2g} and b_{3u} suggests an open shell ground state for this compound. Indeed our broken symmetry calculations indicate open shell singlet and triplet states to be close in energy, with the former being more stable (by 240 cm^{-1}), indicating antiferromagnetic coupling of the two Cu^{II} ions, in good agreement with the observed line broadening in the ^1H NMR spectrum and the EPR-silent nature of the experimentally known analogues.[32] All these results are consistent with the formal description of the reduced compound as Cu^{II}/S^{2-}, although the increase in Cu−N distances upon reduction is indicative of significant delocalization throughout the $\{Cu_2S_2\}$ core.

Analysis of the Electron Density: To further characterize the electronic structure of the studied compounds, we carried out a topological analysis of the electron density ρ(*r*) for the optimized geometries, according to the "Atoms in Molecules" theory.[37] According to Bader, the main properties of the electron density can be summarized in terms of critical points. A bond critical point corresponding to two negative and one positive curvatures, is also referred to as a (3, −1) critical point, and is taken as an indication of the presence of a chemical bond. On the other hand, ring

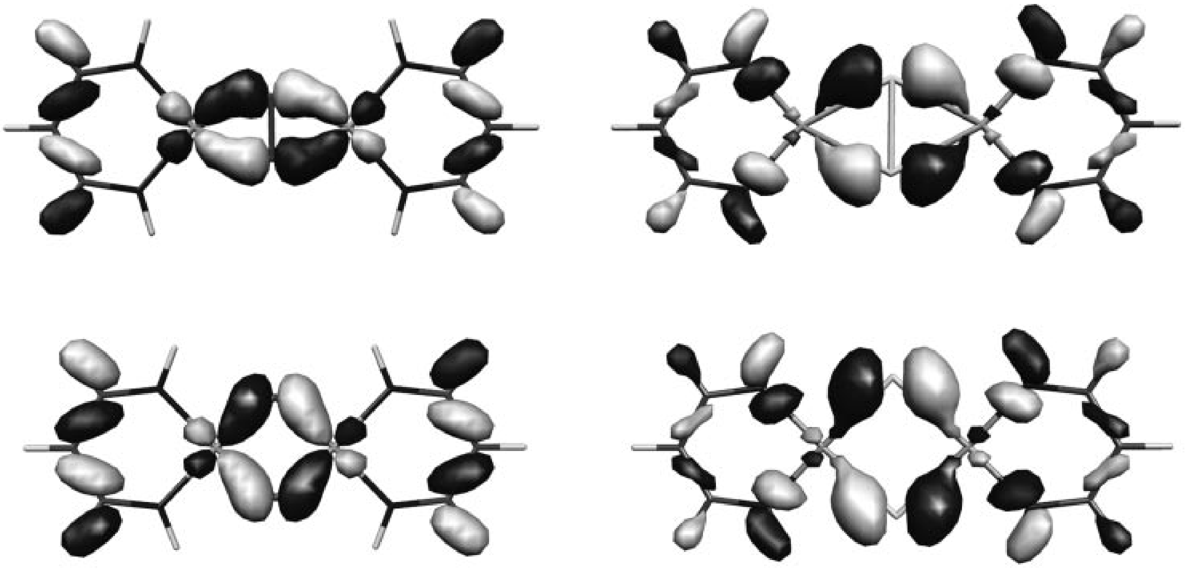


Figure 4. Composition of the occupied b_{2g} molecular orbital in the $[Cu_2(\mu\text{-}X)_2(dki)_2]$ complexes with X = O (left) and S (right) in the **2a** (top) and **2b** (bottom) geometries

critical points (3, +1) are characterized by a single negative curvature and are taken as an indication of a cyclic path of chemical bonds around it.

For the $[Cu_2(\mu\text{-}X)_2(dki)_2]$ compounds (X = S, O) with geometries **2a** and **2b** we have found four bond critical points between each Cu−X pair (Figure 5), consistent with the presence of four Cu−X single bonds, according to their ellipticities ($\varepsilon < 0.06$ for X = S and $\varepsilon < 0.10$ for X = O). The positive values of $\nabla^2\rho(r)$ ($\approx$ 0.20 and 0.55−0.65 for sulfur and oxygen complexes, respectively), point to shared interactions characteristic of donor-acceptor Cu−X bonds and indicate a stronger covalent character for the Cu−S bonds compared to the Cu−O ones.

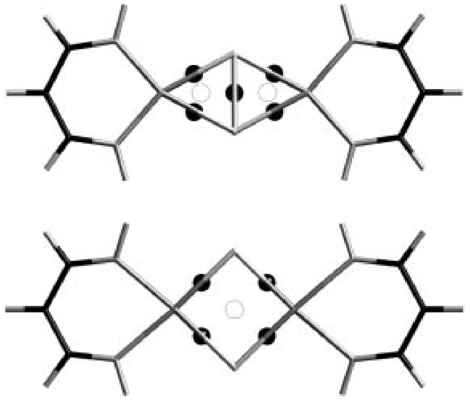
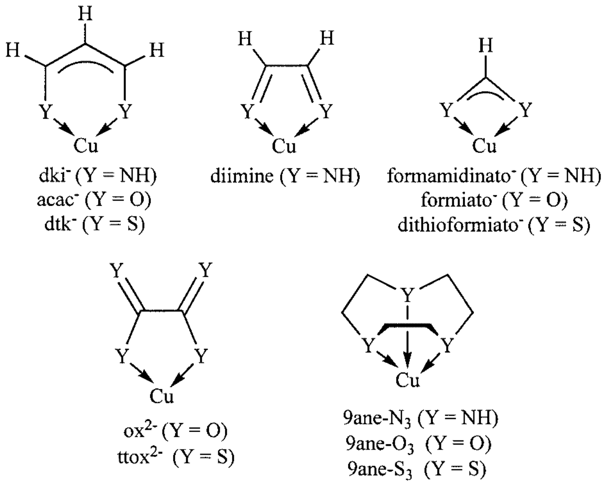


Figure 5. Localization of the critical points in Cu_2S_2 diamonds of the optimized complexes $[Cu_2(\mu\text{-}S_2)(dki)_2]$ (top) and $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$ (bottom). The bond critical points (3,-1) are represented by black circles, ring critical points by white circles

The optimized structures **2a** present an extra (3, −1) bond critical point between the two bridging atoms, consistent with the existence of X−X bonds (Figure 5, top). The negative value of $\nabla^2\rho(r)$ at this critical point indicates their covalent nature, and its ellipticity ($\varepsilon \approx 0.2$) shows a weak π character due to the non-negligible contribution of the Cu^I/S_2 alternative description.[11] As expected, two (3, +1) ring critical points are also found at the center of each CuS_2 ring in this case. In contrast, for structures **2b** (optimized for X = O, frozen for X = S) of $[Cu_2(\mu\text{-}X)_2(dki)_2]$, only one (3, +1) ring critical point appears at the center of the Cu_2X_2 core, consistent with the absence of through-ring bonding interactions. Similarly, the reduced sulfido bridged complex $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$ has, in its optimized structure, a ring critical point at the center of the Cu_2S_2 ring, as shown in Figure 5 (bottom).

Effect of the Peripheral Ligands

Now that we know, from calculations, that $[Cu_2(\mu\text{-}S)_2(dki)_2]$ is unlikely to have the **1b** structure, we wish to explore the possibility of stabilizing a Cu_2S_2 core with that geometry by using different peripheral ligands in which we can vary the nature of the donor atoms and bite of the bidentate ligand (see Scheme 1). The results (Table 3) reveal the following trends: (*a*) two minima appear for $\{Cu_2O_2\}^{2+}$ cores whereas only the **2a** isomer is found to correspond to an energy minimum for the related $\{Cu_2S_2\}^{2+}$ complexes;[12] (*b*) changes in the L−Cu−L bite angles within the 66−107° range do not significantly stabilize the sulfido-bridged structure; (*c*) the negatively charged ligands stabilize isomer **2b** relative to **2a** to a certain extent, the former appearing some 30−40, 21−31 and 11−18 kcal·mol^{-1} higher for neutral, monoanionic and dianionic ligands, respectively; (*d*) the tridentante macrocyclic ligands explored destabilize isomer **2a** and show a marked preference for a pseudotetrahedral coordination sphere of the copper atoms, with the sulfur-sulfur bond occupying one of the coordination sites at short S−S distances,[8,12,38] as observed in the experimental compounds cited in the introductory section.



Scheme 1

It is noteworthy that the sulfido-bridged complexes with tridentate terminal ligands (Table 3, last three entries) all give rather short S−S distances (2.06−2.13 Å), as does the tris(pyrazolyl)borato complex of Kitajima (2.07 Å). This is probably an indication of the important contribution of the Cu^I/S_2 form (**3a**), which is favored in the pseudotetrahedral environment provided by a tridentate ligand and the side-on bonded S_2 molecule.[12]

Conclusions

A theoretical study on $[Cu_2(\mu\text{-}X)_2(dki)_2]$ complexes (X = O, S) indicates that two isomers are attainable for X = O, corresponding to peroxo- and oxo-bridged structures **2a** and **2b**, in agreement with the experimental structural data available for a variety of copper-oxygen compounds. The compound with X = S, in contrast, seems to give only the disulfido-bridged isomer **2a**. The reason for the different behavior has been found to be the different mixing of the atomic $p_y(X)$ and $d_{xy}(Cu)$ orbitals in the framework bonding orbital of B_{2g} symmetry, that is stabilized in the oxo-bridged form **2b** with an O−Cu−O bond angle of 44°, but

Table 3. Optimized data for the two isomers (**2a** and **2b**) of complexes with $Cu_2(\mu\text{-}X)_2$ core (X = O or S) and bidentate terminal ligands shown in Scheme 1; distances in Å, angles in degrees and energies in kcal·mol^{-1}

Compound	X···X	Cu−X	Cu−L[a]	L−Cu−L[a]	Energy
$[Cu_2(\mu\text{-}O)_2(acac)_2]$	1.443	1.936	1.927	99.0	
	2.190	1.804	1.908	96.1	+11.7
$[Cu_2(\mu\text{-}O)_2(dtk)_2]$	1.435	1.967	2.276	106.7	
	2.380	1.821	2.278	100.2	+12.5
$[Cu_2(\mu\text{-}S)_2(acac)_2]$	2.175	2.312	1.929	99.5	
	3.238[b]	2.313	1.933	96.7	+28.5
$[Cu_2(\mu\text{-}S)_2(dtk)_2]$	2.146	2.372	2.281	107.7	
	3.238[b]	2.321	2.315	99.6	+26.5
$[Cu_2(\mu\text{-}S)_2(diimine)_2]^{2+}$	2.134	2.330	2.025	81.8	
	3.238[b]	2.309	2.010	81.2	+37.2
$[Cu_2(\mu\text{-}S)_2(ox)_2]^{2-}$	2.225	2.312	1.921	88.4	
	3.238[b]	2.309	1.916	87.0	+17.5
$[Cu_2(\mu\text{-}S)_2(ttox)_2]^{2-}$	2.204	2.368	2.303	91.9	
	3.238[b]	2.304	2.326	87.4	+11.2
$[Cu_2(\mu\text{-}S)_2(HC\{NH\}_2)_2]$	2.173	2.301	2.002	67.2	
	3.238[b]	2.282	2.004	66.6	+24.4
$[Cu_2(\mu\text{-}S)_2(HCO_2)_2]$	2.166	2.308	2.046	65.9	
	3.238[b]	2.296	2.039	65.9	+30.1
$[Cu_2(\mu\text{-}S)_2(HCS_2)_2]$	2.172	2.339	2.384	76.8	
	3.238[b]	2.293	2.393	75.1	+22.9
$[Cu_2(\mu\text{-}S)_2(9ane\text{-}N_3)_2]^{2+}$	2.133	2.353	2.063, 2.180	87.6, 84.7	
	3.238[b]	2.324	2.051, 2.222	86.8, 82.7	+31.3
$[Cu_2(\mu\text{-}S)_2(9ane\text{-}O_3)_2]^{2+}$	2.059	2.443	2.086, 2.152	80.8, 79.2	
	3.238[b]	2.352	2.065, 2.200	80.3, 77.3	+37.8
$[Cu_2(\mu\text{-}S)_2(9ane\text{-}S_3)_2]^{2+}$	2.100	2.407	2.376, 2.477	94.4, 91.9	
	3.238[b]	2.338	2.399, 2.569	91.6, 87.8	+39.9

[a] Parameter frozen in the geometry optimization. [b] For tridentate ligands, the first value corresponds to the basal distance or angle, the second value to the apical one.

not in the sulfido-bridged analogue. The use of other terminal ligands with different donor atoms and a variety of bite angles proved theoretically not to be a good strategy to stabilize the sulfido-bridged isomer in dinuclear copper complexes. The use of tridentate terminal ligands results in shorter S−S distances, due to an enhanced contribution of the Cu^I/S_2 resonance form. Two-electron reduction of the disulfido-bridged complex results in the cleavage of the S−S bond and a Cu^{II}/S^{2-} dinuclear complex.

Appendix

Computational Details: Density functional calculations were carried out using the GAUSSIAN98 package[39] with the UB3LYP hybrid method that applies the Becke three parameters exchange functional[40] and the Lee−Yang−Parr correlation functional.[41] The basis set of valence double-ζ quality and effective core potentials to represent the innermost electrons of the metal atoms (LANL2DZ) was used for Cu atoms.[42] A similar description was used for S atoms,[43] supplemented with extra d-polarization functions.[44] The light elements were described with the 6−31G (C and H of ligands[45]) and 6−31G* (N and O directly attached to the metal[46]) basis sets. Since it has been recently shown that in Cu complexes with two bridges such as those studied here the choice of basis set for the bridging atoms may strongly influence the calculated relative energies of the two isomers,[34] we have performed a series of tests with different basis sets for $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$. The use of the same basis set described above without polarization functions gave a S−S bond length (2.66 Å) that was too long when compared with the experimental value (2.20 Å), and similar results were obtained with a 6−31G* basis set that includes polarization functions for all atoms (2.60 Å). On the other hand, both the triple-ζ TZV basis set and the one discussed in the previous paragraph were found to give excellent agreement with the experimental S−S distance for the new compound (2.23 and 2.18 Å, respectively), and the calculated energy difference between the two isomers was also similar in both cases (18.3 and 21.4 kcal/mol, respectively). These tests allowed us to conclude that the basis set chosen, with a polarization function only for those atoms directly attached to the metal, provide a description of the electronic structure practically as good as a triple-ζ basis set. For the dinuclear Cu^{II} complex $[Cu_2(\mu\text{-}S)_2(dki)_2]^{2-}$, the evaluation of the singlet-triplet energy gap has been carried out by using nonprojected DFT calculations using the methodology described elsewhere.[47] The reported exchange coupling constant corresponds to the spin hamiltonian $H = -J\, S_1 \cdot S_2$. For the topological analysis of the electron density, critical points have been generated with the *Xaim* routine.[48]

Structural Analysis: The structural data were retrieved with the help of the Cambridge Structural Database (Version 5.25, November 2003),[29] including in our search all compounds with Cu_2X_2 cores, X being a group 16 element. Additional crystallographic data has been obtained from the Inorganic Crystal Structure Database (Release 2003),[30] searching for ternary compounds of general formula $ACuX_2$. When more than one structure determination was available for the same compound, the one with the lowest *R* factor was selected.

Acknowledgments

Financial support for this work was provided by the Dirección General de Investigación Científica (MCyT) through grant BQU2002−04033-C02−01 and by Comissionat per a Universitats i Recerca (Generalitat de Catalunya) through grant 2001SGR-0044. The computing resources at the Centre de Supercomputació de Catalunya (CESCA) were made available in part through a grant of Fundació Catalana per a la Recerca (FCR) and Universitat de Barcelona. G. A. thanks a Ramón y Cajal research contract. The authors thank W. Tolman for providing them with experimental information prior to publication and for helpful discussions, and C. Bo (URV) for the Xaim graphical interface.

---

[1] Y. Lu, in *Comprehensive Coordination Chemistry II* (Ed.: T. J. Meyer), Elsevier, Amsterdam, **2004**, vol. 8, pp. 91−122.

[2] P. González-Duarte, in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, vol. 8, pp. 213−228.

[3] B. G. Malmstrom, P. Wittung-Stafshede, *Coord. Chem. Rev.* **1999**, *185*/*186*, 127−140.

[4] E. C. Brown, N. W. Aboelella, A. M. Reynolds, G. Aullón, S. Alvarez, W. B. Tolman, *Inorg. Chem.* **2004**, *43*, 3335−3337.

[5] W. B. Tolman, *Acc. Chem. Res.* **1997**, *30*, 227−237.

[6] A. G. Blackman, W. B. Tolman, *Struct. Bonding (Berlin)* **2000**, *97*, 179−211.

[7] G. Aullón, P. Alemany, S. Alvarez, *J. Organomet. Chem.* **1994**, *478*, 75−82.

[8] S. Alvarez, A. A. Palacios, G. Aullón, *Coord. Chem. Rev.* **1999**, *185*/*186*, 431−450.

[9] [9a] N. Kitajima, *Adv. Inorg. Chem.* **1992**, *39*, 1−77. [9b] E. I. Solomon, M. J. Baldwin, M. D. Lowery, *Chem. Rev.* **1992**, *92*, 521−542. [9c] S. Fox, J. A. Potenza, S. Knapp, H. J. Schugar, in *Bioinorganic Chemistry of Copper* (Ed.: Z. Tyeklar), Chapman & Hall, New York, **1993**, pp. 34−47.

[10] K. Fujisawa, Y. Moro-oka, N. Kitajima, *J. Chem. Soc., Chem. Commun.* **1994**, 623−624.

[11] G. Aullón, M. Hamidi, A. Lledós, S. Alvarez, *Inorg. Chem.* **2004**, *43*, 3702−3714.

[12] X.-Y. Liu, A. A. Palacios, J. J. Novoa, S. Alvarez, *Inorg. Chem.* **1998**, *37*, 1202−1212.

[13] J. L. DuBois, P. Mukherjee, A. M. Collier, J. M. Mayer, E. I. Solomon, B. Hedman, T. D. P. Stack, K. O. Hodgson, *J. Am. Chem. Soc.* **1997**, *119*, 8578−8579.

[14] G. Aullón, G. Ujaque, A. Lledós, S. Alvarez, P. Alemany, *Inorg. Chem.* **1998**, *37*, 804−813.

[15] [15a] N. Kitajima, K. Fujisawa, Y. Moro-oka, *J. Am. Chem. Soc.* **1989**, *111*, 8975−8976. [15b] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 1277−1291.

[16] M. Kodera, K. Katayama, Y. Tachi, K. Kano, S. Hirota, S. Fujinami, M. Suzuki, *J. Am. Chem. Soc.* **1999**, *121*, 11006−11007.

[17] N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 10660−10661.

[18] [18a] J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young Jr., L. Que Jr., A. D. Zuberbühler, W. B. Tolman, *Science* **1996**, *271*, 1397−1400. [18b] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. Pan, X. Wang, V. G. Young Jr., C. J. Cramer, L. Que Jr., W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 11555−11574.

[19] H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, T. Kitagawa, *J. Am. Chem. Soc.* **2000**, *122*, 2124−2125.

[20] S. Mahapatra, V. G. Young Jr., S. Kaderli, A. D. Zuberbühler, W. B. Tolman, *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 130−133.

[21] V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon, T. D. P. Stack, *J. Am. Chem. Soc.* **1997**, *119*, 11996−11997.

[22] B. F. Straub, F. Rominger, P. Hofmann, *Chem. Commun.* **2000**, 1611−1612.

[23] R. Berger, L.-E. Tergenius, *J. Alloys. Compd.* **1994**, *203*, 203−207.

[24] K. Hestermann, R. Hoppe, *Z. Allg. Anorg. Chem.* **1969**, *367*, 261−269.

[25] J. Pickardt, W. Paulus, M. Schmalz, R. Schöllhorn, *J. Solid St. Chem.* **1990**, *89*, 308−314.

[26] N. E. Brese, M. O'Keeffe, R. B. von Dreele, V. G. Young Jr., *J. Solid St. Chem.* **1989**, *83*, 1−7.

[27] K. Hestermann, R. Hoppe, *Z. Allg. Anorg. Chem.* **1969**, *367*, 249−260.

[28] M. T. Weller, D. R. Lines, *J. Solid St. Chem.* **1989**, *82*, 21−29.

[29] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31−37.

[30] *ICSD*, Gmelin-Institut für Anorganische Chemie and Fachinformationzentrum (FIZ), Karlsruhe, **1995**.

[31] [31a] V. Mahadevan, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *J. Am. Chem. Soc.* **1999**, *121*, 5583−5584. [31b] S. Itoh, in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, vol. 8, pp. 369−393.

[32] [32a] R. P. Houser, J. A. Halfen, V. G. Young Jr., N. J. Blackburn, W. B. Tolman, *J. Am. Chem. Soc.* **1995**, *117*, 10745−10746. [32b] Y. Ueno, Y. Tachi, S. Itoh, *J. Am. Chem. Soc.* **2002**, *124*, 12428−12429.

[33] X. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998−1999.

[34] P. Siegbahn, *J. Biol. Inorg. Chem.* **2003**, *8*, 577−585.

[35] P. K. Ross, E. I. Solomon, *J. Am. Chem. Soc.* **1990**, *112*, 5871−5872.

[36] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899−926 and references cited therein.

[37] [37a] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893−928. [37b] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, **1995**.

[38] P. L. Holland, W. B. Tolman, *Coord. Chem. Rev.* **1999**, *190*−*192*, 855−869.

[39] *Gaussian 98 (Revision A.7)*: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1998**.

[40] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[41] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.

[42] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299−310.
[43] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298.
[44] A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegman, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 237−240.
[45] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257−2261.
[46] [46a] P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta* **1973**, *28*, 213−222. [46b] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654−3665.
[47] [47a] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297−1303. [47b] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* **1999**, *20*, 1391 − 1400. [47c] E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, in *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, vol. 2, pp. 227−279.
[48] *Xaim*; J. C. Ortiz, C. Bo, Departament de Química Física i Inorgànica (Universitat Rovira i Virgili), Tarragona (Spain), **1998**.

Received March 15, 2004
Early View Article