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Framework Bonding and Coordination Sphere Rearrangement in the M_2X_2 Cores of Synthetic Analogues of Oxyhemocyanin and Related Cu and Pt Complexes

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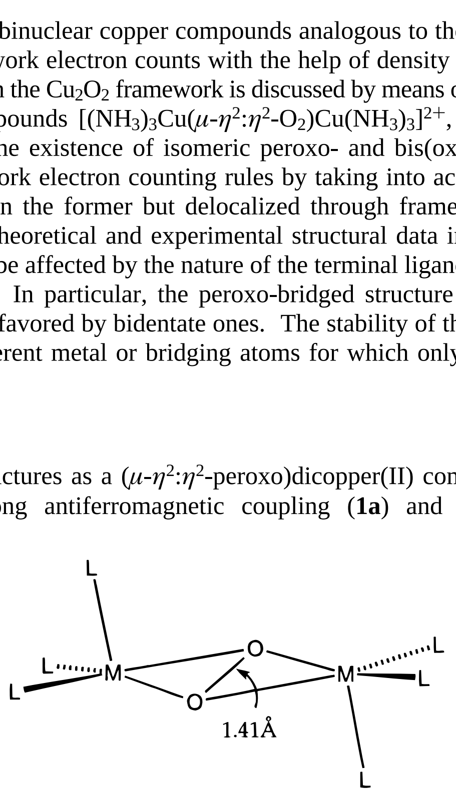
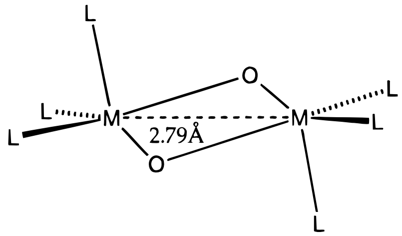
The electronic structures of oxo- and peroxo-bridged binuclear copper compounds analogous to the active site of oxyhemocyanin are analyzed in terms of their framework electron counts with the help of density functional and extended Hückel calculations. Through-ring bonding in the Cu_2O_2 framework is discussed by means of a topological analysis of the electron density for the model compounds $[(NH_3)_3Cu(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)Cu(NH_3)_3]^{2+}$, $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$, and $[(PH_3)_2Cu(\mu\text{-}H)_2Cu(PH_3)_2]$. The existence of isomeric peroxo- and bis(oxo)-bridged Cu complexes can be rationalized in light of the framework electron counting rules by taking into account that two electrons can be localized in the metal 3d orbitals in the former but delocalized through framework bonding molecular orbitals in the latter. An analysis of the theoretical and experimental structural data indicates that a reorganization of the Cu coordination sphere that can be affected by the nature of the terminal ligands is important for the relative stability of the two isomeric forms. In particular, the peroxo-bridged structure is favored by tridentate ligands, whereas the oxo-bridged isomer is favored by bidentate ones. The stability of the two isomers is also compared for analogous complexes with different metal or bridging atoms for which only one isomeric form is known.

One of the most interesting results in the field of model compounds of bioinorganic interest is the recent discovery of binuclear copper compounds with a side-on (μ-η^2:η^2) bridging peroxo group, obtained by reacting $[L_3Cu^IL']$ (L_3 is a tridentate, N-donor ligand, and L′ is a labile ligand such as acetonitrile) with oxygen,[1−9] closely related to the structure of the subunit II of *Limulus polyphemus* oxyhemocyanin.[10,11] Not only the existence and reactivity of these compounds, but also the discovery by Tolman and Que et al. that the oxygen−oxygen bond can be reversibly cleaved while the M_2X_2 framework is kept intact is interesting.[3,12] All of the available experimental data points to a formal description of the two alternative structures as a (μ-η^2:η^2-peroxo)dicopper(II) compound with a strong antiferromagnetic coupling (**1a**) and a bis(μ-oxo)-dicopper(III) complex (**1b**). A structural database search[13] reveals the existence of three analogous complexes of Cu or Ni with dichalcogenide bridges (X = S, Te)[14−16] with a structure of type **1a** for which the corresponding **1b** isomers are not known. Conversely, there are many compounds of the general formula $[L_2M(\mu\text{-}X)_2ML_2]$ (M = Rh(I), Ir(I), Pd(II), Pt(II),



1a



1b

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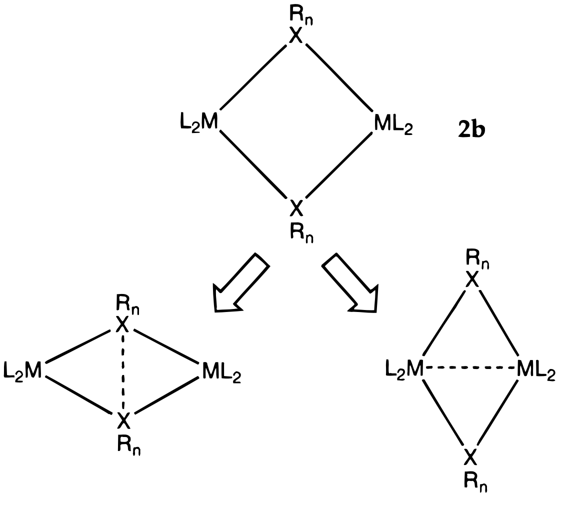
Au(III); X = Cl, Br, S, Se, Te)[17-21] which crystallize in structures of type **1b** but whose **1a** isomers are not known. In this contribution, we wish to take a qualitative, delocalized view of the bonding and electronic structures of these compounds in order to understand the existence of isomerism in the copper-oxygen compounds, the analogies and differences with other existing dichalcogenide-bridged compounds, and the influence of several structural parameters on the isomerization process.

In recent years, we have established simple rules to determine whether a through-ring interaction (**2**) should be expected for the M_2X_2 rings in bis(bridged) binuclear complexes of the late transition-metal ions of the type $[L_2M(\mu\text{-}XR_n)ML_2]$ (n = 0-3).[22-24] In essence, our approach consisted of considering the M_2X_2 framework as a whole and studying its delocalized molecular orbitals in order to account for the possibility of squeezing the M_2X_2 core to get a short through-ring distance as in **2a** or **2c**. It was found that the number of valence electrons available for the σ M-X bonds (i.e., the *framework electron count*, abbreviated FEC from here on) determines the existence or not of a through-ring bonding interaction. In the case of a compound of d^8 metal ions in square planar or of d^{10} ions in tetrahedral L_2X_2 environments, the FEC is just the number of electrons donated by the two XR_n bridges. We will show in the next section that, for the vacant octahedral coordination of Cu in the compounds of type **1**, one can apply the same FEC rules as for d^8 metal ions in a square planar environment. Hence, for **1a**, which can be formally described as a peroxo Cu(II) complex, each d^9-Cu(II) ion contributes one electron to the FEC. The O_2^{2-} bridge, with 14 valence electrons, has four lone pairs pointing away from the ring, and six electrons are left for the framework bonding (including the O-O and Cu-O bonds). In summary, **1a** has a FEC of eight, and no through-ring bonding should be expected. In the case of **1b**, formally a Cu(III) oxo-bridged complex, the copper ions have no electrons available for the framework bonding, but the oxo ions provide four electrons each, since two lone pairs at each oxo ion are pointing away from the ring. Hence, regardless of the convention adopted for the oxidation state of the copper and oxygen atoms in these compounds, they should be considered as systems with eight framework electrons and no net through-ring bonding should be expected, which is in clear disagreement with the experimental structure **1a**. All of this makes these compounds worthy of a theoretical study to find out whether they represent some special class of compounds that constitutes an exception to the FEC rules. Alternatively, one should consider whether these rules should be modified to account for the existence of a quite short O-O distance in **1a**.



2b

2a

2c

Several theoretical studies have been devoted to oxyhemocyanin models and its synthetic analogues[1,25-29] as well as to the interconversion of the two isomeric compounds **1**.[28] In a previous work, Cramer, Smith, and Tolman have shown the existence of two minima in the potential energy surface[28] corresponding to the two experimentally characterized isomers via geometry optimizations at the RHF/STO-3G level. Single-point energy calculations at the CASPT2 level for the optimized structures gave a small energy difference between the two geometries (0.3 kcal/mol). The same authors[5] showed that the anti configuration for the two apical ligands is more stable than the syn one in the oxo-bridged structure **1b**. On the other hand, Bernardi et al. have shown that DFT calculations give a good description of similar compounds when compared with CASPT2 calculations.[27] There are, however, some interesting points to be addressed: Is there some direct Cu···Cu bonding in the μ-oxo form **1b**? If there is no Cu···Cu bonding, how do the four Cu-O bonds of isomer **1b** develop into five bonds in isomer **1a**? How can the bonding situation in this case (FEC = 8) be compared to that in the electron-deficient analogues (FEC = 6)? Is such behavior specific of oxygen, or can it be expected for other group 16 bridges? Is the presence of tridentate terminal ligands an important factor to determine the stability of the oxygenated dimer **1a** and/or its easy interconversion with **1b**? In this paper we try to answer these questions by looking at the qualitative delocalized molecular orbital description of the M_2X_2 cores in the complexes of types **1** and **2** with the help of extended Hückel and density functional (DFT) calculations.

Framework Orbitals

Since the delocalized framework orbitals will be very useful for the discussion of the electronic structure and bonding in the two isomers of **1**, we present here a brief summary of the topologies and bonding characteristics of such orbitals for the general case of an $[L_yM(\mu\text{-}XR_n)_2ML_y]$ complex. We consider as framework orbitals those which are essentially localized at the M_2X_2 ring and have bonding or antibonding M-X characteristics. Since each ML_y or XR_n fragment contributes two

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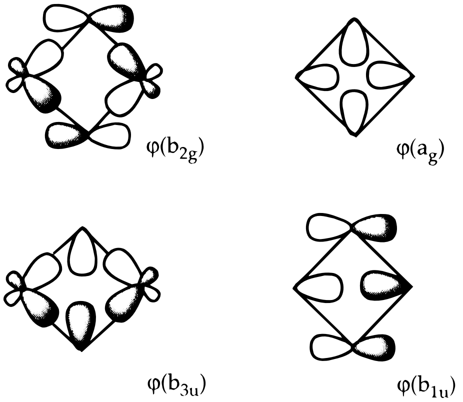
fragment orbitals to the framework, there are eight molecular orbitals involved in framework bonding. For simplicity, we will label these orbitals according to their symmetry in the D_{2h} point group. Four of these orbitals have M−X bonding character (labeled φ in what follows and sketched in **3**) and correspondingly four are M−X antibonding (φ*, not shown in **3**). If the four φ orbitals are occupied (i.e., FEC = 8), they account for the four M−X bonds and a "regular" framework without through-ring interaction (**2b**) is expected, as in cyclobutane. Although these orbitals also bear through-ring M−M and X−X bonding or antibonding characteristics (e.g., a_g is X−X bonding, b_{3u} is X−X antibonding a_g is metal−metal bonding, and b_{1u} is metal−metal antibonding, and similarly for the π characteristics), the net M···M and X···X bond orders are 0 for a FEC of 8. However, for a FEC of 6 (or 4), one (or two) of the φ orbitals is (are) empty, which is either X···X or M···M antibonding, resulting in a net through-ring bonding interaction, and an X···X (**2a**) or M···M (**2c**) short distance should be expected, as in the case of diborane. Only in the case of silylene-bridged Pt compounds[30,31] can one find a short X···X through-ring distance for a system with apparently a FEC of 8, a system that was the subject of a cursory analysis in our previous work.[23] One needs to have two electrons less (FEC = 6) in order to obtain Te−Te or As−As through-ring bonds (**2a**) in Pd and Pt compounds of the type $[L_2M(\mu\text{-}X)ML_2]$.[20,32]



3

In principle, one can consider the coordination sphere of the copper ions in compounds **1a** and **1b** as derived from the square planar one by adding an extra axial ligand to each metal atom. Such extra ligands affect neither the energy nor the occupation of the acceptor orbitals of the metal atoms that participate in the framework bonding (**3**). Therefore, the FEC rules for M_2X_2 rings with vacant octahedral d^8-ML_3 groups are the same as for the square planar d^8-ML_2. Consequently, the fact that the peroxo-bridged compound **1a** with eight framework electrons presents a through-ring oxygen−oxygen bond calls for a revision of the electron-counting rules. We devote the theoretical study in the next sections to that goal. First, we wish to obtain a molecular wave function for the two isomers that correctly reproduce the geometry, stability, and ease of interconversion by using DFT calculations. We will also explore the structure of the transition state for such processes. Then we will analyze the bonding characteristics of the two isomers and the transition state to check whether the relatively short Cu−Cu distance in **1b** is indicative of a Cu···Cu bonding interaction. In a later section we will go back to the general qualitative view of the framework bonding and try to offer an explanation for the noncompliance with the FEC rules.

Exploration of the Potential Energy Surface

Different from previous work by Cramer, Smith, and Tolman,[5,28] who evaluated the geometries and energetics of the oxo and peroxo isomers of **1** (by means of RHF calculations with a single-ζ basis set, complemented with a CASPT2 evaluation of the energies of the two minima), we are more concerned with the topological analysis of their electron densities and with the changes in bonding along the core isomerization process. Therefore, we have carried out density functional calculations at the B3LYP level with a double-ζ basis set (see Computational Details for more information) to optimize the geometries of the model compound $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$. At the optimized geometries, the relative energies were re-evaluated by performing a calculation with a triple-ζ basis set including polarization functions at the Cu and O atoms. In a later section we will present also a study of related compounds in which either the bridging or the metal atoms are changed, using the same level of theory.

The geometry optimization showed the presence of two minima separated by a transition state. The geometry of one of the minima is that represented by **1a** and was found to be 12.6 kcal/mol more stable than the minimum corresponding to **1b** (cf. 0.3 kcal/mol in a previous work[5,28]). On the other hand, the transition state connecting structures **1a** and **1b** was calculated to be 17.0 kcal/mol above the optimized structure **1a**, that is, within the range of thermal energies. These energy values should be taken as orientative only, since they correspond to a simplified model in which the donor atoms are much more flexible than they are in the tridentate ligands of the experimental compounds. Besides, calculations at a higher accuracy level can give different numerical values of the calculated energies. In summary, the numerical values given here provide only a qualitative idea of the energies of the two model isomers, in the sense that their stabilities are not very different and that they can be interconverted without a high-energy barrier.

Rather than analyzing the relative energies of the two isomeric forms, we find it interesting to analyze their calculated structures in order to obtain some clues on which ligands should be expected to favor a particular isomer. In Table 1 we present the structural data for the optimized geometries of the **1a** and **1b** isomers, for the transition state connecting the two minima, for a model of the initial stage of the reaction between two $[Cu(NH_3)_3]^+$ groups and O_2 (with the O−O distance frozen at 1.207 Å), both in the triplet and singlet states, and for a hypothetical oxo-bridged complex with only two terminal NH_3 ligands per copper atom. Available experimental data for related compounds are presented in Table 2, together with those for Cu(II) alkoxo-bridged compounds with analogous structures,[33−35] and will be discussed later on. The agreement of the calculated geometries for the two minima with the experimental data is good, except for slightly large through-ring distances. The

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Table 1. Main Structural Parameters (**4**) for the Theoretically Optimized Structures of Compounds $[L_3Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)CuL_3]^{2+}$ (**1a**), $[L_3Cu(\mu\text{-}O)_2CuL_3]^{2+}$ (**1b**), and $[(NH_3)_2Cu(\mu\text{-}O_2)Cu(NH_3)_2]^{2+}$, for the Transition State between **1a** and **1b**, and for the Adduct Formed by Two $Cu(NH_3)_3^+$ Groups with an O_2 Molecule in Its Triplet and Singlet States[a]

compound[b]		α	β	γ	θ	δ	O···O	Cu···Cu	Cu−O	Cu−N$_{eq}$	Cu−N$_{ax}$
ideal tetrahedron			109.5	19.5	70.5	0				d	d′ = d
$\{[(NH_3)_3Cu]^+\}_2 + O_2$ ($S = 1$)		29	109	0	55	6	1.207[b]	4.634	2.395	2.066	2.091
($S = 0$)		34	108	6	40	16	1.207[b]	3.948	2.064	2.059	2.167
$[(NH_3)_3Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)Cu(NH_3)_3]^{2+}$	(**1a**)[c]	45	104	8	32	19	1.515	3.668	1.985	2.055	2.220
	(**1a**)[d]						1.324	3.758			
transition state[d]		59	101	10	24	24	1.853	3.268	1.853	2.043	2.297
$[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$	(**1b**)[c]	77	99	9	17	29	2.288	2.869	1.835	2.003	2.381
	(**1b**)[e]	80					2.281	2.734	1.780	1.996	2.207
ideal vacant octahedral			90	0	∼0	≥35				d	d′ > d
$[(NH_3)_2Cu(\mu\text{-}O)_2Cu(NH_3)_2]$		77	100		0		2.275	2.838	1.819	1.979	∞
ideal square planar			90		0	90					∞

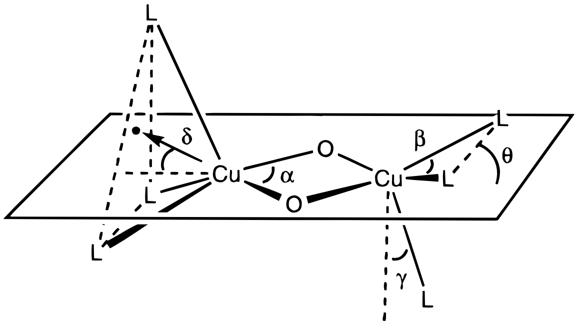
[a] The expected parameters for several idealized structures are also given for comparison. [b] O···O distance kept constant. [c] This work. [d] Reference 28. [e] Reference 5.

Table 2. Main Structural Parameters (**4**) for the Experimentally Characterized Structures of Peroxo- and Bis(oxo)-Bridged Cu Compounds with Structures **1a** and **1b** and for Related Hydroxo-Bridged Cu(II) Complexes

compound[a]	α	β	γ	θ	δ	O···O	Cu···Cu	Cu−O	Cu−N$_{eq}$	Cu−N$_{ax}$
$[(TPB)Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)Cu(TPB)]^{2+}$ (**1a**)[b]	43	93	15	22	17	1.413	3.560	1.915	1.997	2.258
oxyhemocyanine[c]	42	96	10	44	12	1.4	3.6	2.0	2.1	2.4
$[(TIP)Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)Cu(TIP)]^{2+}$ (**1a**)[d]	52					1.72	3.48	1.94	2.05	2.30
$[(TACN)Cu(\mu\text{-}O)_2Cu(TACN)]^{2+}$ (**1b**)[e]	79	89	17	14	27	2.287	2.794	1.803	1.986	2.297
$[L_3Cu^{II}(\mu\text{-}OH)Cu^{II}L_3]$ [f]	77−86	74−105	11−15	9−23	15−41	2.39−2.68	2.87−3.02	1.93−1.96	2.32−2.45	1.96−2.01

[a] TPB = tris(3,5-diisopropylpyrazolyl)borate, TACN = 1,4,7-tribenzyl-1,4,7-triazacyclononane, TIP = tris(imidazolyl)phosphine. [b] Reference 1. [c] Reference 10. [d] Reference 2. [e] Reference 3 and 5. [f] Data obtained from the Cambridge Structural Database.[13]

largest deviations correspond to those parameters that are constrained in the experimental structures due to the tridentate nature of the terminal ligands (β, γ, and θ, see **4**) but unconstrained in our model calculations, in which the chelating ligands were substituted by ammonia molecules.

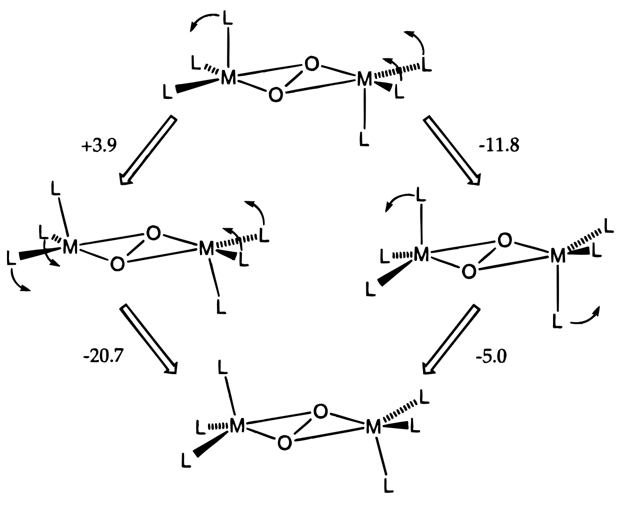


4

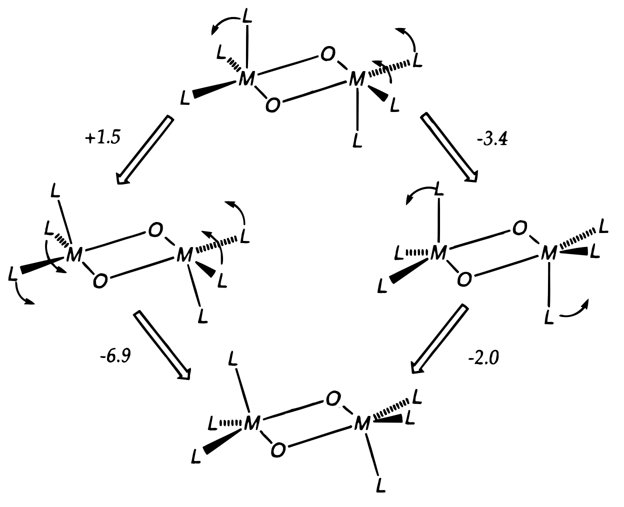
Let us discuss first our computational results for the isomers **1a** and **1b** of $[(NH_3)_3CuO_2Cu(NH_3)_3]^{2+}$ and for the transition state of the interconversion pathway. We wish to stress the prediction of structural changes associated with the isomerization process. Since the structural parameters for the transition state are practically midway between those of the two minima, we limit the discussion to these two structures (**1a** and **1b**, Table 1). It is worthy of note that the Cu_2O_2 framework remains planar throughout the isomerization process. The through-ring Cu−Cu and O−O distances change as expected for the different degrees of ring squeezing (angle α in **4**). In contrast, the Cu−O bond distances undergo an important shortening when going from the peroxo- to the oxo-bridged form. As for the terminal ligands, the Cu−N$_{eq}$ distances are practically unchanged whereas the Cu−N$_{ax}$ distances increase from **1a** to **1b**. Finally, both the N$_{eq}$−Cu−N$_{eq}$ (β, Table 1) and N$_{ax}$−Cu−N$_{eq}$ angles decrease from **1a** to **1b**.

Other than differences in bond distances and angles between **1a** and **1b**, there are important changes in spatial orientation of the terminal ligands that have not been previously noted and can provide some hints to understand the different behavior of the compounds with TACN or TPB ligands. The equatorial donor atoms approach the plane of the Cu_2O_2 core on going from **1a** to **1b** (i.e., a decrease in θ by 15°, Table 1), while the axial ligand is much less affected ($\gamma = 8°$ for **1a**, 9° for **1b**). Nevertheless, the position of the equatorial ligands is in some way affected by the axial ligand, since optimization of the model compound in the absence of axial ligands, $[(NH_3)_2Cu(\mu\text{-}O)_2Cu(NH_3)_2]^{2+}$, results in two perfectly planar isomers (i.e., $\theta = 0°$), analogous to **1a** and **1b**, with O−O = 1.547 Å and Cu−Cu = 2.850 Å, respectively. To better calibrate the relative importance of these two parameters, we have modified the structures of the two optimized minima by independently replacing the axial and equatorial terminal ligands to the vacant octahedral positions, while keeping the rest of the structure untouched. The results, schematically shown in **5** (energy differences given in kcal/mol), indicate that it is the joint motion of the three ligands that stabilizes the molecule upon bending. Bending of the equatorial ligands appears to be more important than that of the axial ones, and the effect is much less important for the oxo than for the peroxo isomer.

All of these results suggest that the isomerization process cannot be correctly described by considering only the changes in the Cu_2O_2 core. To verify the importance of the structural parameters asociated with the spectator ligands, we squeezed the optimized structure **1a** along the Cu···Cu vector (by increasing α) while keeping the rest of the structure untouched. In this process, the calculated energy increases and no minimum is found for larger α values. A similar squeezing of the optimized structure **1b** along the O···O vector (decreasing α) fails to yield the second minimum with a short O−O distance. Hence, a reorganization of the metal coordination sphere is of the utmost importance for the interconversion of the two isomers. Comparison with the experimental data is presented in a later section, and a simple qualitative model will be presented to account for the changes in the structural parameters.



5a

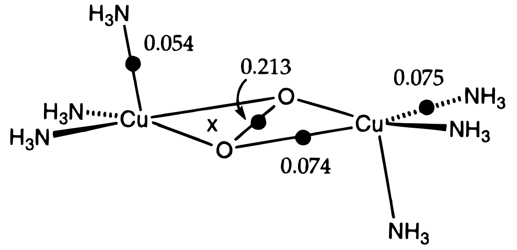


5b

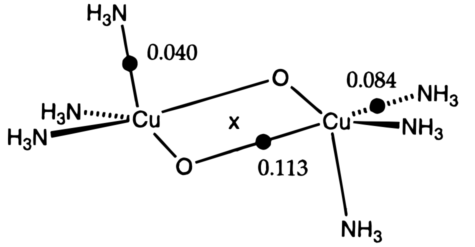
Topological Analysis of the Electron Density

One might be tempted to infer that some through-ring Cu···Cu bonding interaction exists in the open form **1b**, as found for rings with FEC = 4 or 6, given the relatively short Cu···Cu distance (2.794 Å, Table 1). However, since the Cu···Cu bonding, $\varphi(a_g)$ and $\varphi^*(a_g)$, and antibonding orbitals, $\varphi(b_{1u})$ and $\varphi^*(b_{1u})$, have the same overall occupation, no net Cu···Cu bonding interaction is expected. Hence, we would predict that the short Cu···Cu distance is just the result of the geometrical constraints in a ring system with short edges (Cu−O = 1.92 Å). To verify the non existence of a bonding copper−copper interaction, we have carried out a topological analysis of the electron density of **1b** and related structures,[36] and the results are presented in this section.

The results of the Bader analysis of the electron density for $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$ in its two isomeric forms are presented in **6**. There, the bond critical points are indicated by a black circle (only one bond of each type is marked for simplicity) and the ring critical points by a cross. In both cases, the numerical values of the electron density at the bond critical points are indicative of a weak covalent or dative character for the Cu−O and Cu−N bonds, which is consistent with the expectations for metal−ligand bonds. For the isomer **1a**, there is a clear correspondence between the bond critical points (**6a**), the qualitative bonding description, and the structural data. It is worth noting that there are two ring critical points consistent with the Lewis structure **1a**. In contrast, for the **1b** isomer, no bond critical point and only one ring critical point appears in the center of the M_2X_2 framework (**6b**), clearly confirming the nonexistence of Cu···Cu bonding as suggested by our qualitative discussion above. It is also of interest that the electron density in the Cu−O bonds is much smaller in **1a** than in **1b**, which is in agreement with the electron-deficient nature of those bonds in the former case.

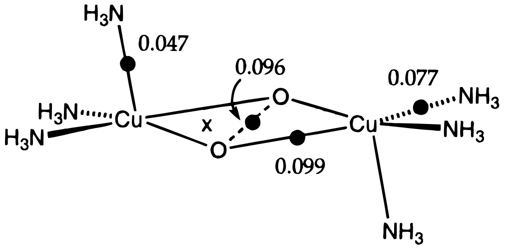


6a



6b

A topological analysis of the electron density was also carried out for the calculated transition state and the results are schematically presented in **6c**. The most interesting result is that a weak oxygen−oxygen bond is already present in the transition state, as indicated by the bond critical point at the center of the Cu_2O_2 diamond and two ring critical points at the center of the CuO_2 triangles. The electron densities calculated for the different bond critical points are intermediate between those calculated for the two end products.



6c

transition state

To further verify that no Cu···Cu bonding should be ascribed to structure **1b**, we have carried out a Bader analysis of the similar compound $[(PH_3)_2Cu(\mu\text{-}H)_2Cu(PH_3)_2]$ for which Cu···Cu bonding should be expected. In effect, it is sensible to consider this compound as formed by Cu(I) ions and hydrido bridges, with a tetrahedral coordination geometry around the copper atoms. For tetrahedral ML_2 fragments, the FEC rules consider an sp^3 hybridization, hence a d^{10} ion contributing with no electrons to the framework bonding. One is left with the four electrons provided by the hydrido bridges to fill two framework bonding orbitals, that is, the FEC is four in this case. Hence,

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(36) Bader, R. F. W. *Atoms In Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

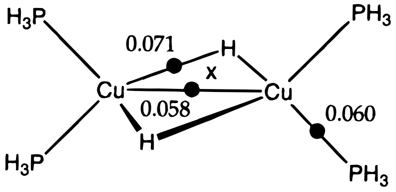
Table 3. Structural Data (see **4** for Definitions) for the $[L_nM(\mu\text{-}X)_2ML_n]$ Complexes (X = H, S) at the Optimized Geometry and at an Alternative Geometry with a Frozen X···X Distance, Together with Experimental Data for Similar Compounds[a]

compound	type	α	β	γ	θ	δ	X···X	M···M	M−X	E_{rel}	ref
$[(PH_3)_2Cu(\mu\text{-}H)_2Cu(PH_3)_2]$	**1b**	98	111				2.603	2.281	1.731		
$[Cu_2\{\eta^2\text{-}MeC(CH_2PPh_2)_3\}_2(\mu\text{-}H)_2]$[b]	**1b**	94					2.54	2.371	1.810, 1.661		37
$[(NH_3)_3Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)Cu(NH_3)_3]$	**1a**	59	102	12	32	16	2.329	4.130	2.370	0	
$[(NH_3)_3Cu(\mu\text{-}S)_2Cu(NH_3)_3]$[c]	**1b**	93	95	12	23	21	3.5	3.312	2.410	32.7	
$[(TPB)Cu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)Cu(TPB)]$[b]	**1a**	54	90	20	20	19	2.072	4.027	2.265		16
$[(PH_3)_2Pt(\mu\text{-}S)_2Pt(PH_3)_2]$	**1b**	84	100		0		3.227	3.615	2.423	0	
$[(PH_3)_2Pt(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)_2Pt(PH_3)_2]$[c]	**1a**	48	118		0		2.1	4.755	2.599	52.9	
$[(PpyPh_2)_2Pt(\mu\text{-}S)_2Pt(PpyPh_2)_2]$[b]	**1b**	80	103		4		3.004		2.326		38

[a] The energy of the two calculated isomeric structures is given in kcal/mol, relative to the minimum. [b] Experimental data. [c] Not a minimum; X···X distance frozen.

a through-ring Cu···Cu bonding interaction should be expected for this compound.[22] Indeed, a similar compound, $[Cu_2\{\eta^{2-}\text{-}MeC(CH_2PPh_2)_3\}_2(\mu\text{-}H)_2]$, with phosphine terminal ligands has been structurally characterized and found to have a short Cu−Cu distance of 2.371 Å.[37] The optimized structure (Table 3) shows the expected trends: the copper ions are tetrahedrally coordinated, the Cu−Cu distance is short (2.223 Å), and the H−Cu−H bond angle is large enough (94°) to indicate the tendency of the two copper ions to approach each other beyond the geometrical constraints imposed by the short Cu−H bridging distances.

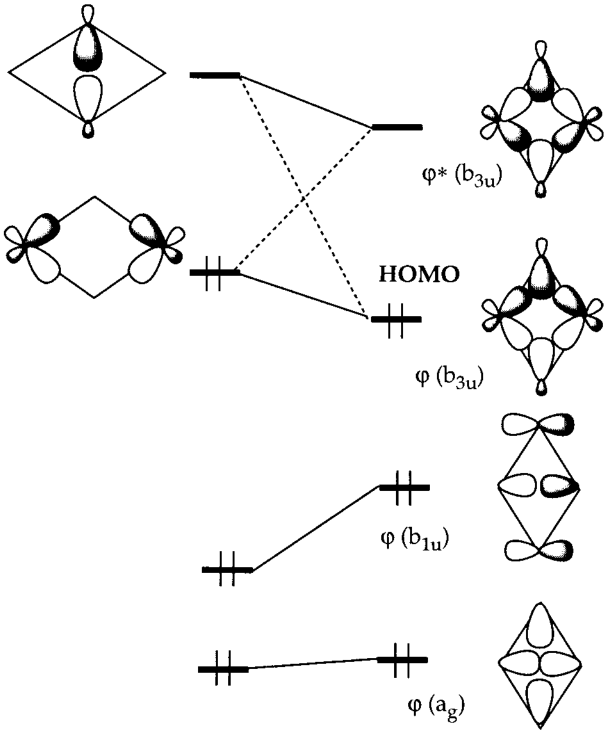
The results of the topological analysis of the electron density of $[(PH_3)_2Cu(\mu\text{-}H)_2Cu(PH_3)_2]$ are summarized in **7**, where the bond critical points are indicated by a black dot and the electron density corresponding to each critical point is given. The most relevant feature for the present discussion is that Cu−Cu bonding appears, in contrast with **6b**, for which no such bonding interaction was found.



7

Walsh Diagram for the Isomerization of $[(NH_3)_3Cu(O)_2Cu(NH_3)_3]$

To offer a qualitative explanation for the structural reorganization induced by the core isomerization process **1a** → **1b** and for the apparent inconsistencies in their framework electron count, we need first to briefly discuss a simplified Walsh diagram (**8**). Let us focus first on the $\varphi(a_g)$ and $\varphi(b_{3u})$ orbitals. For the regular ring of the μ-oxo structure (**1b**), both the σ(O−O) and σ^*(O−O) combinations participate in the occupied framework bonding orbitals $\varphi(a_g)$ and $\varphi(b_{3u})$. Hence, a 0 bond order results for the O−O bond in **1b**. This situation is in agreement with the formal description of this ring as formed by O^{2-} bridges and Cu(III) ions. When the ring is squeezed to obtain the peroxo-bridged structure **1a**, the HOMO should be expected to increase its antibonding character with a subsequent dramatic increase in energy. This does not happen; only a smooth increase in energy of this orbital results from our B3LYP calculations. $\varphi(b_{3u})$ remains the HOMO by losing its σ^*(O−O) contribution and becomes practically a Cu-centered nonbonding orbital. This qualitative picture is consistent with the results of Cramer, Smith, and Tolman, if one disregards the participation of the copper 4p orbitals in $\varphi^*(b_{3u})$ at the shortest O−O distances.



8

The important point is that, in the **1a** → **1b** transformation, two electrons are transferred from localized metal 3d orbitals to delocalized framework orbitals, while simultaneously populating the σ^*(O−O) orbital. Moreover, such localization of the $\varphi(b_{3u})$ orbital in **1a** implies that it is no longer a framework bonding orbital (**8**, left); hence the framework electron count is reduced to six and the existence of a through-ring bond is in agreement with the simple electron-counting rules previously presented by us.[22,23] The change in the O−O bonding is clearly illustrated by the changes in the population of the σ(O−O) and σ^*(O−O) fragment orbitals (EH calculations): the former has 2.00 electrons in **1a** and 1.92 in **1b**, whereas the latter changes its occupation from 0.21 (in **1a**) to 1.83 electrons (in **1b**). All of these results are consistent with the formal description of **1a** as a Cu(II) peroxo species and of **1b** as a Cu(III) oxo compound, supported by a variety of experimental techniques. The small energy difference between the $\varphi(b_{3u})$ and $\varphi^*(b_{3u})$ orbitals makes it a symmetry-allowed process. At the same time, the small gap is associated with strong nondynamical correlation effects which stabilize the structure of the μ-oxo compound, as pointed out by Cramer, Smith, and Tolman.[28]

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(37) Goeden, G. V.; Juffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 2484.

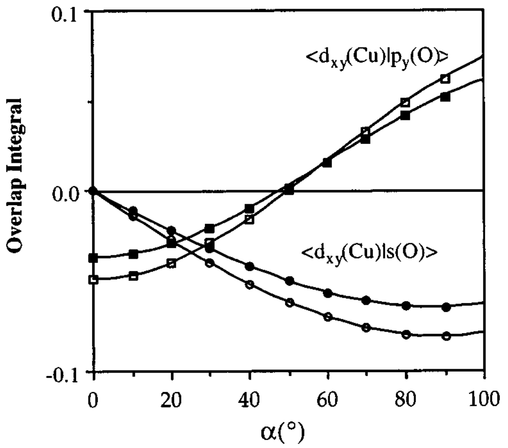
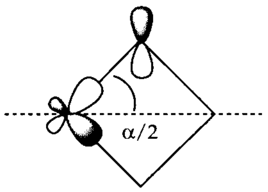
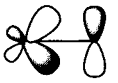


Figure 1. Overlap integrals (EH) between Slater atomic orbitals of Cu and O as a function of α (see **4**). Points represented by open symbols were calculated at Cu−O = 1.81 and those represented by closed symbols at Cu−O = 1.92 Å.

Since the localization of the b_{3u} orbitals in the squeezed structure **1a** is important for the determination of the formal oxidation state of Cu and for the similar stability of the two isomers, it is worth making a digression from our study of the Walsh diagram to offer a simple explanation for such localization effects. When the angle α is varied, as happens when going from **1a** to **1b** or vice versa, the overlap between the d_{xy} orbital of Cu and p_y of the oxygen-bridging atom (**9a**) changes as represented in Figure 1, a behavior that can be understood considering that for the extreme case of $\alpha = 0$ the overlap integral is negative (**9b**) whereas at larger values (e.g., $\alpha/2 \approx 60°$) it is positive. Hence, at $\alpha \approx 50°$ that overlap integral is negligible, and there is no interaction between the d_{xy} and p_y(O) orbitals. Of course the participation of the oxygen 2s orbitals in the b_{3g} orbitals can somewhat modify the angle at which the minimum interaction (maximum localization) appears. In summary, the b_{3g} orbitals can no longer participate in the framework (Cu−O) bonding, and they become therefore localized as in **8**, trying to make $\varphi^*(b_{3u})$ as antibonding as possible and $\varphi(b_{3u})$ as stable as possible. Let us notice in passing that the behavior of the $\langle d_{xy}|p_y\rangle$ overlap integral in the Cu_2O_2 cores has also been blamed for the change in their magnetic properties from antiferro- to ferromagnetic as a function of α.[39]



9a



9b

Continuing now with the analysis of the Walsh diagram, another important orbital is $\varphi(b_{1u})$, whose energy evolves in the opposite way to that of the HOMO. A look at the topology of that orbital (**3**) indicates that, upon increasing α (thus approaching the two Cu atoms), its Cu−O overlap decreases and a strong σ^*(Cu$\cdots$Cu) interaction develops. This orbital is therefore strongly destabilized along the core isomerization pathway **1a** → **1b**. Finally, the third framework orbital having through-ring σ character, $\varphi(a_g)$, increases its energy along the reaction path. This is due to the loss of σ(O−O) bonding interaction, compensated only in part by a gain in σ(Cu$\cdots$Cu) bonding, since the more diffuse Cu orbitals overlap less efficiently than those of oxygen. In summary, it is the combined effect of the b_{3u}, b_{1u}, and a_g orbitals that results in the double minimum at the potential energy surface.

Given that the stabilization of the isomer **1a** is related to the localization of the b_{3u} orbital discussed above, it is appealing to try to extrapolate the overlap argument to other M_2X_2 rings. In that way, one could eventually establish the geometric requirement to reduce the FEC of a ring from 8 to 6 by localizing two electrons at the metal atoms and favor the formation of a through-ring bond. We assume that the crossover point for the integral overlap appears roughly at the same value of α for the different M/X pairs (this was in fact corroborated by EH calculations on Cu/O, Cu/S, and Pt/S pairs). What changes for the different combinations of M and X are the bonding distances M−X and X−X needed for a structure like **1a**. Through elementary trigonometry one can deduce that the angle α, compatible with the simultaneous existence of M−X (framework) and X−X bonds, is related to the covalent radii of M and X in the following way:

$$\alpha \approx 2\arcsin\left(\frac{r_X}{r_M + r_X}\right) \tag{1}$$

For instance, in the Cu_2O_2 rings, if we take $r_O \approx 0.73$ Å and $r_{Cu} \approx 1.10$ Å, the optimum value of α is 47°, amazingly close to that required for 0 overlap. An analysis of the atomic radii for a variety of late transition metals and main group elements of groups 15, 17, and 18 indicates that there are many combinations which comply with eq 1 for angles close to the 0 overlap point. We will come back to this problem later and try to explore the possibility for other complexes to present the two isomers.

Reorganization of the Coordination Sphere of the Cu Atom

We have seen above that the structural parameters that define the position of the terminal ligands (Cu−N_{ax}, θ, γ, and α) in the model compound vary along the **1a** → **1b** transformation. In the model compound, the independent monodentate terminal ligands can easily adapt to the local stereochemistry required by the Cu atoms. However, in the experimental systems, with tridentate terminal ligands bearing bulky substituents, such geometrical parameters are constrained and the relative stability of the two isomeric forms can be significantly altered by the nature of the ligand. Hence, it is important to discuss the correlation found in our model calculations between the changes in the structural parameters of the Cu_2O_2 core and those affecting the terminal ligands.

In a simplified approach, we first discuss the structural changes by just considering the orientation of each CuN_3 trigonal pyramid as a whole. Their orientation relative to the central Cu_2O_2 core is thus defined by δ, the angle between the vector from the Cu atom to the centroid of the three N atoms and the Cu$\cdots$Cu vector (**4**). We distinguish two ideal geometries: (a) that with the axis of the pyramid strictly perpendicular to the O−O bond ($\delta = 0°$), in which the metal ion is tetrahedrally coordinated by three N atoms, with the centroid of the two oxygen atoms occupying the fourth coordination site; (b) that

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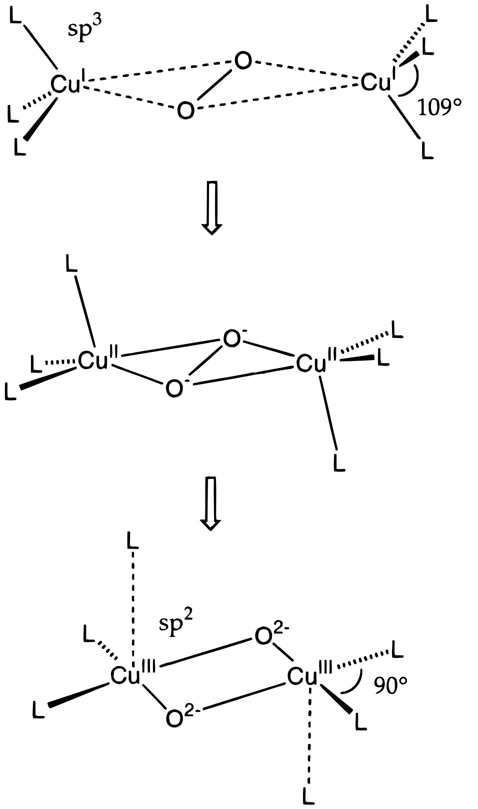
(38) Yam, V. W.-W.; Yeung, P. K.-Y.; Cheung, K.-K. *J. Chem. Soc., Chem. Commun.* **1995**, 267.

(39) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

corresponding to a vacant octahedron with two oxygen atoms occupying cis basal sites, for which δ is expected to be 35° if the three Cu−N distances are the same or to be larger if the $Cu-N_{ax}$ distance is longer than the Cu_{eq} ones. The two ideal geometries are schematically represented in **10**. The *tetrahedral* structure (**10a**) is expected for a d^{10} ion such as Cu(I) if the O_2 molecule were acting as a two-electron donor. A square pyramidal structure (**10b**) with two independent oxo ligands would be consistent with the stereochemistry found in many Cu(II) complexes. For a Cu(III) ion with a d^8 electron configuration, a square planar stereochemistry is expected, that is, geometry **10b** with a very long $Cu-N_{ax}$ distance. This case would be characterized by $\delta \approx 90°$ if one assumes that there is a fifth ligand at a very long distance, or by $\theta = 0°$. In brief, all possible combinations of the formal oxidation states for the Cu atoms and the O_2 group, Cu(I)/O_2, Cu(II)/O_2^{2-}, and Cu(III)/$(O^{2-})_2$, and intermediate situations can be associated with the value of the parameter δ.



10a

10b

The analysis of the optimized δ value for the model compound with different Cu_2O_2 core structures illustrates the differences in their electronic structures. Hence, when the frozen O_2 molecule (i.e., O−O distance kept constant, triplet state) is left to associate with the two $[Cu(NH_3)_3]^+$ groups, the optimized structure ($\delta = 6°$) is close to that of the ideal tetrahedron ($\delta = 0°$). Once the O−O bond is relaxed, the minimum corresponding to a peroxo-bridged structure (**1a**) modifies the orientation of the CuN_3 pyramid, adopting a δ value (19°) intermediate between those for tetrahedral and vacant octahedral conformations. The δ value of 29° found for the bis(oxo)-bridged minimum (**1b**) practically corresponds to an ideal vacant octahedral structure.

Before comparing the structural experimental data, we wish to show that the different values of δ found for the two model isomers can be explained by a simple orbital model. In effect, given the tridentate nature of the terminal ligands, the copper acceptor orbital of σ type participating in $\varphi(a_g)$ and $\varphi(b_{1u})$ is an sp^3 hybrid directed along the trigonal axis of the L_3 group. Hence, for the vacant octahedral geometry, this hybrid orbital is not well-oriented toward the bridging oxygen donor orbitals, and overlap can be improved upon bending. This is shown in Figure 2, where we represent the overlap integrals between the corresponding orbitals of the O_2 and Cu_2L_6 fragments (EH calculations) as a function of the joint displacement of all terminal ligands, measured by δ (taking $\gamma = \theta$). Opposing the bending distortion are the framework orbitals with participation of the copper d_{xy} atomic orbital, $\varphi(b_{2g})$ and $\varphi(b_{3u})$. In this case, the acceptor orbital is coplanar with the equatorial terminal ligands.[40] Hence, the overlap with the oxygen donor orbitals is better in the vacant octahedral geometry, as seen in Figure 2. The final geometry in the isomer **1b** is a compromise between the tendency to bend (i.e., small δ values), favored by the a_g and b_{1u} framework orbitals, and the preference for the vacant octahedral geometry (large δ values) dictated by b_{2g} and b_{3u} (calculated $\delta = 29°$). On the other hand, in the peroxo-bridged isomer **1a** the b_{3u} orbital is no longer involved in Cu−O bonding and an increased tendency for bending results, as seen in the smaller values of δ (Table 1).

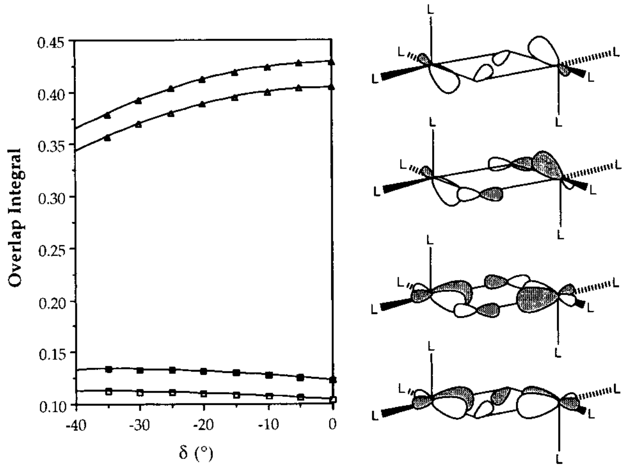


Figure 2. Evolution of the overlap integrals between the σ (upper curves) and d_{xy} (lower curves) acceptor orbitals of the CuL_3 fragments and the donor orbitals of O_2 in the model compound $[H_3Cu(\mu\text{-}O_2)CuH_3]^{4-}$ as the terminal ligands are tilted from the vacant octahedral geometry (see **4** for the definition of the angle δ).

The tridentate ligands in the structurally characterized synthetic compounds with structures of types **1a** and **1b** should have no problems in following the electronically driven position of their donor N atoms, except for those derived from bulky substituents. Interestingly, the experimental δ values (Table 2) are relatively small for the peroxo-bridged compounds: 12° and 17° for oxyhemocyanin and its synthetic model with a tris(pyrazolyl)borato (TPB) ligand, respectively, compared with a calculated value of 19° for the model compound. In contrast, the oxo-bridged complex with a triazacyclononane (TACN) ligand presents a larger δ value (27°), in excellent agreement with the calculated value of 29°. The analysis of other structurally characterized compounds of first-row transition metals with a framework of type **1a** (Table 4) also shows that the metal coordination spheres significantly deviate from the idealized vacant octahedral geometry as reflected by the relatively small values of δ defined in **4**. These structural

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(40) Albright, T. A.; Burdett, J. K.; Whangbo, W.-H. *Orbital Interactions in Chemistry*; J. Wiley: New York, 1985; p 298.

Table 4. Structural Data for Other Compounds of Type $[L_3Cu(\mu\text{-}\eta^2{:}\eta^2\text{-}X_2)CuL_3]$ (**1a**), L_3 Being a Tridentate Ligand

M	X	L_3	α	β	γ	θ	δ	X···X	ref
Ni	S	TPPE	60	92	30	35	3	2.209	14
Cu	S	HTPB[a]	54	93	20	20	19	2.072	16
Ni	Te	TPPE[b]	66	94	28	38	2	2.802	15

[a] HTPB = hydrogen tris(3,5-diisopropyl-1-pyrazolyl)borato. [b] TPPE = 1,1,1-tris(diphenylphosphinomethyl)ethane.

effects, associated to the first coordination sphere of the Cu atoms, may be in part affected in the experimental systems by the steric bulk of the substituents at the multidentate ligands. It is worth stressing that as a result of all these geometrical changes, the ligands suffer important displacements from the initial Cu(I) to the peroxo-bridged Cu(II) and the oxo-bridged Cu(III) species, a result that might be of interest for the understanding of the cooperative effect of oxygen uptake by hemocyanin,[41] whose exact mechanism is not well-understood.[11]

Not only the orientation of the CuN_3 pyramids but also their internal structure (i.e., Cu−N bond distances and N−Cu−N bond angles) changes from **1a** to **1b**. The variations found for these parameters in our calculations can also be associated with the differences in electronic structure (**10**). Thus, the calculated values of β decrease on increasing δ (i.e., going down in Table 1), as should be expected when moving from an sp^3 to an sp^2 hybridization at the Cu atoms. The rigidity of the multidentate ligand can in this case favor a different β angle than that preferred by the Cu atom. In this regard, the two ligands used in the synthetic models of hemocyanin studied here are quite different, as revealed by a structural database analysis[13] of their Cu complexes. TPB seems to be a quite flexible ligand ($80.4° < N{-}Cu{-}N < 103.0°$ for 133 bond angles from 48 structures) and should have no problems in adapting to the β angles required by the local stereochemistry of Cu in the two isomers. Consequently, the energy order found in the calculations with monodentate ligands should prevail, and the peroxo isomer **1a** would be predicted to be more stable, in good agreement with the experimental finding. In contrast, TACN is a much more rigid ligand ($79.5° < N{-}Cu{-}N < 87.6°$ for 66 bond angles from 48 crystal structures). It is thus clear that this ligand must be highly strained to form a peroxo isomer, and the energy difference between the two isomers should be smaller than the values calculated for the monodentate NH_3 ligands, in agreement with the experimental identification of the two isomers of $[(TACN)CuO_2Cu(TACN)]$.

To complete the picture of the ligand sphere reorganization, we optimized the structure of the peroxo complex in both its triplet and singlet states (Table 1), keeping the O−O distance frozen at its value in the free molecule in order to simulate an early stage of the complex formation reaction (a discussion of the early stages of the reaction and of the triplet−singlet intersystem crossing was presented by Bernardi et al.[26]). It is interesting to note that the optimized Cu···Cu distance in the triplet state of the incipient dioxygen complex is identical (4.6 Å) to that found between the two three-coordinate Cu atoms in the structure of the deoxygenated active site of *L. polyphemus* hemocyanin.[42]

Similarities and Differences with Related Compounds

We have seen above that a simple geometrical analysis suggests other combinations of metal and bridging atoms as candidates to give the two isomers of type **1a** and **1b**. In fact other structures of type **1a** or **1b** are known. Several compounds of the general formula $[L_3M(\mu\text{-}\eta^2{:}\eta^2\text{-}X_2)ML_3]$ present short through-ring distances between the bridging atoms (Table 4). Two common features of these molecules and the μ-peroxo complex are the presence of a tridentate ligand L_3 and a large deviation from the vacant octahedral geometry, as reflected by the small angle δ (Tables 1−4). On the other hand, a few structures have been determined for analogous systems $[L_2M(\mu\text{-}X)_2ML_2]$ with no through-ring interactions: Te···Te = 3.258 Å (M = Pt),[17] Te···Te = 3.066 Å (M = Pd),[18] Te···Te = 3.465 Å (M = Pt),[19] Te···Te = 3.263 Å (M = Pt),[20] and S···S = 3.004 Å (M =Pt).[38] In the latter case, L_2 represents either a bidentate diphosphine or two monodentate phosphines and the coordination geometry of the metal atoms is square planar. There are a few other compounds with short X···X through-ring distances, but these have a different electron count (FEC = 6) and are not directly comparable to those under study.[20,32] What appears to be unique for the compounds reported by Kitajima and Tolman is that a slight modification of the tridentate ligand results in important changes in reactivity which allowed Tolman and co-workers to unambiguously identify either or both of the isomers with the same ligand. One can reasonably ask whether the noncharacterized isomers for the other compounds reported in the literature are attainable, and we explore such possibilities in this section.

We focus on two examples to study this problem, one with a short and another one with a long through-ring S···S distance: $[(TPB)Cu^I(\mu\text{-}S_2)Cu^I(TPB)]$, where TPB stands for the tris(3,5-diisopropyl-1-pyrazolyl)borate anion,[16] and $[(dppe)Pt(\mu\text{-}S)_2Pt(dppe)]$, where dppe stands for 1,1,2,2-bis(diphenylphosphino)ethane).[38] We have carefully analyzed the potential energy surface of the two model compounds $[(NH_3)_3Cu(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)Cu(NH_3)_3]$ and $[(PH_3)_2Pt(\mu\text{-}S)_2Pt(PH_3)_2]$. In both cases, only one minimum could be found, with structures close to the experimental ones (see Table 3 for calculated and experimental structural data). It thus appears that the M_2X_2 systems are quite capricious, and one can obtain either one of the two alternative structures **1a** or **1b** or both by modifying the bridging atoms or the metal atoms. Why does each one of the three compounds studied behave in the way it does? A careful analysis of the wave functions (at both the EH and the DFT levels of theory) obtained for the optimized and alternative structures (i.e., with fixed S···S distances) allows us to obtain some hints to answer this question:

(1) First, there is a geometrical effect present when we compare the isomers with short X···X distances (**1a**) in compounds with the same metal atom (Cu) and bridging atoms of different sizes (O or S). For the larger-bridging S, the two metal atoms are separated by a larger distance (4.03 Å experimentally, 4.13 Å computationally) than they are for the smaller bridging O (3.56 Å experimentally, 3.67 Å, computationally). As a result, the b_{1u} orbital (**8**) is more stabilized in the Cu−S system and the conformer **1a** becomes much more stable than the **1b** one, which is no longer a minimum.

(2) Because of the larger electronegativity of the O atom compared to S, at large X···X distances the $\varphi(b_{3u})$ orbital (**8**, right) appears at lower energy in the oxygen-bridged compound. At short X···X distances, however, that orbital has essentially Cu-3d character and similar energies in compounds with X = O and X = S. Consequently, $\varphi(b_{3u})$ is much more stabilized

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at long X⋯X distances (from left to right in **8**) in the oxygen-bridged than in the sulfur-bridged complex, accounting for the appearance of the second minimum (**1b**), as recognized earlier by Cramer, Smith, and Tolman.[28]

(3) The Pt−S system, with only two terminal ligands per metal atom, cannot undergo the ligand reorganization described above for the ML_3 fragments that stabilizes the **1a** isomer. Let us recall that for the Cu−O case we have found that ligand reorganization accounts for a stabilization of the form **1a** by some 17 kcal/mol. Hence, only one minimum corresponding to geometry **1b** appears in this case. In this regard it is pertinent to note that the reaction of O_2 with a Cu(I) complex having a coordinated bidentate amine[43] directly gives an oxo-bridged trinuclear compound, in agreement with our conclusion that the tricoordinate ligands contribute to the stability of the peroxo-bridged structure **1a**, although the steric bulk of the substituents might also be important for the stabilization of such a structure.

Concluding Remarks

The molecular structures of two isomers of $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$ (**1a**,**b**) and of the transition state for their interconversion reaction have been optimized by means of density functional calculations. The peroxo-bridged isomer **1a** is calculated to be slightly more stable than the bis(oxo)-bridged isomer **1b** (13 kcal/mol), and the barrier for the isomerization process has been estimated to be 17 kcal/mol. The topological analysis of the calculated electron densities indicates the existence of oxygen−oxygen bonding in the peroxo-bridged complex **1a** and in the transition state but no through-ring bonding in the μ-oxo complex **1b**. In contrast, a Cu⋯Cu through-ring bond can be detected in the topological analysis of the electron density of $[(PH_3)_2Cu(\mu\text{-}H)_2Cu(PH_3)_2]$, a model for the experimentally characterized molecule $[MeC(CH_2PPh_2)_3\text{-}Cu(\mu\text{-}H)_2CuMeC(CH_2PPh_2)_3]$, in which four electrons participate in the Cu_2H_2 framework bonding (FEC = 4). The existence of a through-ring O−O bond in **1a** is associated to the presence of six Cu_2O_2 framework electrons and a d^9 configuration of the Cu atoms. On the other hand, the absence of through-ring bonding in **1b** is associated with a copper d^8 configuration and a square pyramidal coordination sphere having eight framework electrons.

The interconversion of the peroxo- and bis(oxo)-bridged forms of $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]$ cannot be adequately described by considering only the changes in the Cu_2O_2 core. A rearrangement of the coordination sphere of the Cu atoms accompanies the core isomerization. At the early stages of the reaction of O_2 with $[Cu(NH_3)_3]^+$, the terminal ligands occupy the base of a tetrahedron and the bridging η^2-O_2 ligand occupies the apical position. The changes in the structural parameters from such incipient triplet complexes to peroxo-bridged isomers **1a** to the oxo-bridged compounds **1b** can be schematically described (**10**) by a gradual change from an idealized tetrahedral geometry around Cu(I) ions (sp^3 hybridization) to a nearly square planar geometry with a weakly bound axial ligand for the Cu(III) ions in the oxo complexes (sp^2 hybridization).

The number of terminal ligands and the nature of the bridging atoms are also crucial to determine the structure of the M_2X_2 cores. Theoretical and experimental structural data for several compounds with M_2X_2 cores (M = Cu, Ni, Pt; X = O, S, Te) indicates that the presence of three terminal ligands per metal atom, together with the larger bridges (S, Te), favors the isomer **1a** with a d^9 configuration and an X−X bond. In contrast, the presence of two terminal donors per metal atom and the smaller electronegative bridging oxygen atom favors structure **1b** corresponding to a d^8 configuration of a copper atom and no X−X bond. In this regard it is interesting to notice that Eisenstein et al. recently found[29] that the presence of four terminal nitrogen donors favors an end-on bis(monodentate) coordination of the O_2 molecule, as experimentally found by Karlin and Zubieta et al.[44] Apparently, the combination of bridging oxygen atoms with the rather rigid tridentate triazacyclononane ligands results in the ability of the M_2X_2 core in the compounds synthesized by Tolman and co-workers (and possibly in the active site in oxyhemocyanin) to appear in the two isomeric forms.

Appendix: Computational Details

All DFT calculations have been performed with the Gaussian94 program.[45] Local spin density calculations were carried out using the Slater exchange[46] and Vosko, Wilk, and Nusair correlation[47] functionals. Generalized gradient corrections have been introduced using the Lee, Yang, and Parr correlation part[48] and the adiabatic connection method with three parameters proposed by Becke (abbreviated B3LYP)[49] to incorporate the Hartree−Fock exchange contribution. A double-ζ basis set with pseudopotentials for all but the outermost core orbitals proposed by Hay and Wadt (LANL2DZ basis set)[50] was used for $[(PH_3)_2Pt(\mu\text{-}S)_2Pt(PH_3)_2]$. For all other compounds, the VDZ basis set of double-ζ quality was used.[51] The character of minimum of all the optimized structures was verified by performing frequency calculations. Similarly, a frequency calculation was carried out for the structure presented as the transition state, and the only negative frequency found was one connecting the two minima. A semiquantitative estimate of the relative energies of the two minima and the transition state for $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$ was obtained by using a triple-ζ basis set including polarization functions for the Cu and O atoms.[52] Although it is not clear presently that a broken-symmetry treatment can be consistently applied to study a system in which no broken-symmetry solution exists in different parts of the potential energy surface, we have evaluated the effect that a broken-symmetry[53,54] (BS) solution would have on the calculated energies by performing single-point double-ζ calculations at the optimized structures for the peroxo isomer and for the transition state of $[(NH_3)_3Cu(\mu\text{-}O)_2Cu(NH_3)_3]^{2+}$. The BS energy of the peroxo isomer is decreased by 12.6 kcal/mol, and that of the transition state is lowered by only 0.8 kcal/mol. No BS solution could be found for the oxo isomer, in keeping with its closed-shell nature. The topological analysis of the B3LYP wave functions (double-ζ basis set) was carried out using the PROAIM[55] program and the Gaussian94 options[56] to carry out an "atoms in molecules" (AIM) analysis.[36]

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The qualitative orbital analysis has been performed with the help of the extended Hückel[57,58] molecular orbital calculations, carried out with the CACAO[59] and YAeHMOP[60] programs and using the modified Wolfsberg−Helmholz formula[61] and standard atomic parameters. The following models with three or two terminal ligands per metal atom were used: $[(NH_3)_6Cu_2O_2]^{2+}$, $[(NH_3)_4Cu_2O_2]^{2+}$, $[H_6Cu_2O_2]^{4-}$, and $[H_4Cu_2O_2]^{2-}$. An idealized vacant octahedral geometry assumed for the Cu ions (i.e., L−Cu−L bond angles of 90°) was modified as explained in the text for the study of the effect of angles α, γ, and θ. The following bond distances were used: $Cu{-}N_{ax} = 2.30$ Å, $Cu{-}N_{eq} = 2.00$ Å, $Cu{-}O = 1.98$ Å, and $Cu{-}H_{ax} = Cu{-}H_{eq} = 1.62$ Å.

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