Cu^{2+}-doped $K_2Zn(H_2O)_6(SO_4)_2$.

The behavior of the g tensors of the complexes $Cu(NH_3)_2Cl_4^{2-}$ and $Cu(NH_3)(H_2O)Cl_4^{2-}$ is quite similar to that reported for the CuF_6^{4-} ion doped into Ba_2ZnF_6[44] and K_2ZnF_4.[15] All four species have axially symmetric g tensors, suggesting compressed tetragonal ligand coordination geometries, but while $Cu(NH_3)_2Cl_4^{2-}$ and Cu^{2+}-doped Ba_2ZnF_6 have $g_{\parallel}$ values very close to that expected for an electron in a pure d_{z^2} orbital and EPR parameters that vary very little with temperature, $Cu(NH_3)(H_2O)Cl_4^{2-}$ and Cu^{2+}-doped K_2ZnF_4 both have $g_{\parallel}$ shifted substantially from the expected value, with this deviation increasing as the temperature is raised. Apparently, the two former species have potential surfaces with steep minima, while the two latter have potential surfaces that rise only slightly in energy as the ligands move from a tetragonal to an orthorhombic arrangement. An important distinction between the species in Cu^{2+}-doped NH_4Cl and those in the above Zn^{2+} host lattices is that the anisotropy of the bond strengths causing the perturbation of the basic warped Mexican hat potential surface of each system is due to different ligands in the former case but to host lattice packing effects in the latter. Perhaps the most pleasing feature of the present model is that in every case the perturbation deduced from the behavior of the EPR parameters has been found to agree with the expectations of simple bonding theory and with the structural properties of the host lattices.

It would clearly be of interest to try to interpret the behavior of the centers formed when Cu^{2+} is doped into NH_4Br by using the present model, for comparison both with the results of Sorokin and Chirkin[18] and with those of the NH_4Cl systems, and a study of this kind is under way in our laboratories. However, the increased covalency and large spin-orbit coupling constant of the halide are expected to complicate the interpretation of the g values of the bromide complexes. The present results confirm other work[26,45,46] which suggests that fluxional behavior due to vibronic coupling is a fairly common feature of copper(II) chemistry. It has even recently been shown that certain copper(II) complexes of biological importance have temperature-dependent EPR parameters indicative of dynamic structural changes,[47] and it was suggested that this might play a role in their biological activity. It may be noted that the simplest means by which dynamic behavior may be detected is via the temperature dependence of the EPR spectrum,[48] while the electronic spectrum will generally be rather insensitive to fluxional behavior of the kind discussed here.

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Registry No. *trans*-$Cu(H_2O)_2Cl_4^{2-}$, 20102-44-7; *trans*-$Cu(NH_3)_2Cl_4^{2-}$, 114027-34-8; *trans*-$Cu(H_2O)(NH_3)Cl_4^{2-}$, 113859-50-0; Cu^{2+}, 15158-11-9; NH_4Cl, 12125-02-9.

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Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR,
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Xα–SW Calculations of the Electronic Structure and Magnetic Properties of Exchange-Coupled Transition-Metal Clusters. 2.[1] μ-Carbonato-Bridged Copper(II) Dimers

Carlo Albonico and Alessandro Bencini*

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Symmetrically bridged (μ-carbonato)dicopper(II) complexes are diamagnetic and constitute one of the few examples of diamagnetic copper(II) dimers bridged by polyatomic groups. The self-consistent-field multiple-scattering Xα model has been applied to calculate the magnetic coupling constant, J, of these complexes with the aim of explaining the origin of the observed diamagnetism. A singlet–triplet splitting of $\simeq 4000\ \mathrm{cm^{-1}}$ has been computed and has been related to a strong covalent interaction between the metal d orbitals and p orbitals of the carbonato oxygens with negligible contribution from the carbon atom. The magnetic behavior of other carbonato-bridged copper(II) complexes has been related to their geometrical structure by using an empirical orbital model.

Introduction

The understanding of the orbital mechanisms that determine the isotropic magnetic interaction between the ions forming transition-metal clusters is an actual topic that is attracting the interest of both chemists and physicists.[1-3] At the present stage of knowledge a number of experimental techniques, ranging from the measurement of the temperature dependence of magnetic susceptibility to optical spectroscopy and magnetic resonance techniques, allow one to measure also feeble interactions,[3-6] and several quantum mechanical models can be used to relate the observed interactions to bonding and geometrical parameters.[7-12]

The effect of the isotropic exchange interaction on the energy levels of the cluster is generally represented through the spin Hamiltonian

$$H_{ex} = \textstyle\sum_{a,b} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b \qquad (1)$$

where the sum runs over all the neighboring paramagnetic metal atoms with total spin $\mathbf{S}_i$, and J_{ab} is the exchange coupling constant between atoms a and b, which is evaluated experimentally.[13]

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Table I. Structural and Magnetic Properties of Selected μ-Carbonato–Copper(II) Complexes

compd	type[a]	d(Cu–Cu), Å	magnetic properties	ref
$[(tmpd)CuCl]_2(CO_3)$	I ($\alpha = 91°$)	4.29	diamagnetic[b]	28, 29
$[CuL]_2(CO_3)(ClO_4)_2$	I ($\alpha = 90°$)	4.08	diamagnetic[b]	30
$[(teed)CuCl]_2(CO_3)$	II ($\alpha = 93°$, $\alpha' = 101°$)	4.47	weak antiferromagnetic[c]	32
$Cu(NH_3)_2CO_3$	II	3.5	$J \cong 10$ cm^{-1}	34, 38, 39
$Na_2Cu(CO_3)_2$	III ($\delta \simeq 10°$)	4.89	$J = -8.2$ cm^{-1}	35, 40, 41
$Na_2Cu(CO_3)_2 \cdot 3H_2O$	III[d]		$J = -1.18$ cm	42, 43, 44
$K_2Cu(CO_3)_2$	III ($\delta \approx 70°$)		$J \cong -2.38$ cm^{-1}	36, 44
$[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4$	IV		$J = -9.64$ cm^{-1}	37

[a] α, α', and δ are defined in the text. [b] From EPR spectroscopy. [c] From measurement of the temperature dependence of magnetic susceptibility. [d] Copper is six-coordinate.

Although the form of the Hamiltonian (eq 1) is the same as a direct magnetic coupling between the two spins $\mathbf{S}_a$ and $\mathbf{S}_b$, the interaction is caused by an electronic effect and the actual value of the exchange coupling constant is strongly affected by electronic correlation.

In establishment of the electronic nature of the mechanisms that determine the size and sign of the exchange coupling constants, efforts are currently under way to study dinuclear complexes containing bridging polyatomic anions.[2,14] These studies rely heavily on establishing experimental correlations between geometrical parameters and J values and in justifying these correlations by using molecular orbital theories. Qualitative rationalization of magnetostructural correlations can be achieved with a little computational effort by using extended Hückel[10] or ligand field[9] theories. A quantitative estimate of J, which should complete any attempt to rationalize the magnetic properties of a series of complexes, requires more sophisticated and time-consuming molecular orbital models, which should include configuration interaction at the SCF level.[15,16] In recent years the Xα–valence bond (Xα–VB) model[17,18] was applied with some success to calculate J values in a number of transition-metal dimers.[1,19-22]

Much attention has been focused on discrete copper(II) dimers, not only because they are abundant and represent the simplest of systems but also because magnetically interacting copper(II) dimers have been found in a number of naturally occuring enzymes[23] such as hemocyanines, tyrosinase, and laccase. Most copper(II) dimers are antiferromagnetically coupled; i.e., the singlet state lies at lower energy than the triplet one, the strength of the interaction depending on the nature of the bridge. Strong antiferromagnetic interactions ($J > 300$ cm^{-1}) have been measured, for example, in μ-oxalato-,[24,25] μ-pyridine N-oxide-,[26] μ-azido-,[27] and μ-carbonato-bridged[28] dimers. In a few cases the triplet state is so high in energy that it is completely depopulated even at room temperature: the complexes are diamagnetic. Since diamagnetism is rather unusual for copper(II) dimers, we felt it important to explore its electronic origin at least in one of the observed cases. We wish to report here the results of SCF–Xα–SW–VB and extended Hückel calculations on a series of μ-carbonato-bridged copper(II) dimers with the aim of correlating the observed magnetic properties to geometrical variations and to the bonding ability of the carbonato anion.

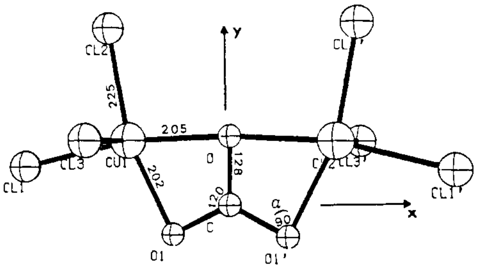
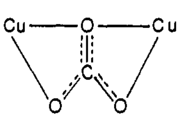


Figure 1. Model type I complex $[Cl_3Cu(CO_3)CuCl_3]^{4-}$ used for the Xα–SW calculations. The y cartesian axis is a C_2 symmetry axis. Bond distances are given in picometers and bond angles in degrees.

Carbonato anions can bridge copper(II) in a number of ways. The most common bonding geometries are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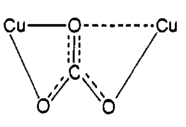
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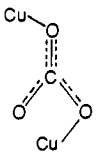
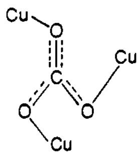

III


IV

Both the sign and the value of J strongly depend on the bonding situation.

Type I complexes can be prepared as isolated dinuclear species possessing a twofold symmetry around the C–O (bridging) bond like $[(tmpd)CuCl]_2(CO_3)$[28,29] and $[LCu]_2(CO_3)(ClO_4)_2$[30] (tmpd = N,N,N',N'-tetramethyl-1,3-propanediamine, L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene). These complexes contain five-coordinated copper(II) ions and are diamagnetic. Some of them are initiators for the oxidative coupling of phenols by dioxygen,[31] and their chemistry has received some attention.[28-33]

Type II complexes have been isolated both as discrete dinuclear units like $[(teed)CuCl]_2(CO_3)$[32] (teed = N,N,N',N'-tetraethyl-1,3-propanediamine) or polymeric materials like $Cu(NH_3)_2CO_3$.[34] The copper ions are generally five-coordinated and weakly antiferromagnetically coupled.

Type III complexes are found as constituent units in polymeric salts, like $Na_2Cu(CO_3)_2$[35] and $K_2Cu(CO_3)_2$,[36] in which copper(II)

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Table II. Atomic Coordinates, Sphere Radii, and α Values Used in the $X\alpha$–SW Calculations

atom[a]	x[b]	y[b]	z[b]	α	radius[b]
outer sphere	0.000	0.000	0.000	0.7257	572.4
Cu_1	−204.8	122.3	0.000	0.7070	119.6
Cl_1	−423.7	70.05	0.000	0.7232	143.0
Cl_2	−245.6	340.4	0.000	0.7232	142.9
Cl_3	−204.8	122.3	230.0	0.7232	144.5
Cu_2	204.8	122.3	0.000	0.7070	119.6
Cl_1'	423.7	70.05	0.000	0.7232	143.0
Cl_2'	245.6	340.4	0.000	0.7232	142.9
Cl_3'	204.8	122.3	−230.0	0.7232	144.5
O_1	−113.1	−57.66	0.000	0.7445	89.65
O_1'	113.1	57.66	0.000	0.7445	89.65
O	0.000	131.0	0.000	0.7445	89.70
C	0.000	0.000	0.000	0.7593	80.18

[a] Atoms are labeled according to Figure 1. [b] The Cartesian reference system is shown in Figure 1. The atomic coordinates and sphere radii are given in picometers.

Table III. Valence Ionization Potentials and Coefficients and Exponents of the Slater Atomic Functions[a] Used in the Extended Hückel Calculations

atom type	orbital	VSIP, eV	c_1	ζ_1	c_2	ζ_2
Cu	3d	−14.0	0.5933	5.95	0.5744	2.3
	4s	−11.4	1.0000	2.22		
	4p	−6.06	1.0000	2.22		
N	2s	−26.0	1.0000	1.95		
	2p	−13.4	1.0000	1.95		
Cl	3s	−27.1	1.0000	2.03		
	3p	−15.6	1.0000	2.03		
C	2s	−22.5	1.0000	1.62		
	2p	−13.7	1.0000	1.62		
O	2s	−29.9	1.0000	2.28		
	2p	−13.3	1.0000	2.28		
H	1s	−13.6	1.0000	1.30		

[a] Double-ζ functions were used for the d copper orbitals.

ions are four-coordinated by carbonato oxygens and weakly ferromagnetically coupled.

Type IV coordination has been found in the trinuclear complex $[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4$ (pip = 2-[[[2-(2-pyridyl)ethyl]imino]ethyl]pyridine) in which the five-coordinated copper(II) ions are weakly ferromagnetically coupled.[37]

The most relevant complexes and their magnetic properties are collected in Table I.

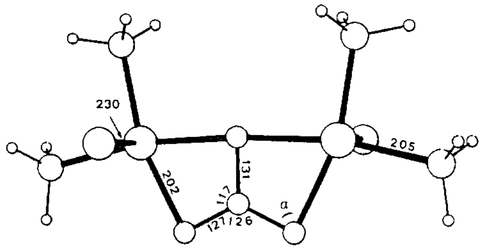
Computational Method

$X\alpha$ Calculations. The calculations were performed in the scattered wave (SW) approximation[45,46] using the computer programs previously described.[47] In all the calculations the SCF procedure was stopped when the relative change in the potential was 10^{-4} and/or the variation of the energy levels was not more than 0.0002 Ry. The virial ratio, $-2T/V$, was 1.0007 ± 0.00005.

Energy levels and eigenvectors were computed for the complex $[Cl_3Cu(CO_3)CuCl_3]^{4-}$ by using the geometrical configuration and the bonding parameters shown in Figure 1. Restricted Hartree–Fock–Slater (RHFS) calculations were performed on the triplet state using real spherical harmonics spanning the A and B irreducible representations of the $C_2(y)$ molecular point group giving two 37 × 37 secular matrices. Maximum l values in each atomic region were 1 for chlorine, carbon, and oxygen and 2 for copper. A maximum l value of 3 was used in the outer-sphere region.

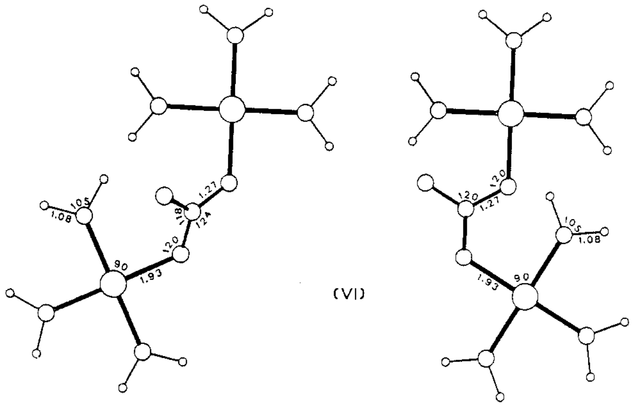
$X\alpha$–SW–VB calculations[17] were performed by using unrestricted Hartree–Fock–Slater theory (UHFS) on a 74 × 74 secular matrix without any symmetry block factorization and imposing a mirror symmetry in the spin up and spin down potentials.

The sphere radii, chosen with the Norman procedure[48] with a reduction factor $R = 0.88$, are shown in Table II. A tangent Watson sphere with +4 charge was used to account for the negative charge of the molecule.[49] The α values computed by Schwartz for the free atoms were used in the atomic regions.[50] For the inter- and outer-sphere regions an average of the atomic α values according to the valence electron number was used.



(V)

Figure 2. Model type I complex $[(NH_3)_2ClCu(CO_3)CuCl(NH_3)_2]$ used in the extended Hückel calculations. The reference system is the same as in Figure 1. Bond distances are given in picometers and bond angles in degrees.



(a) (b)

Figure 3. (a) Model type III complex $[(H_2O)_3Cu(CO_3)Cu(H_2O)_3]^{2+}$ used in the extended Hückel calculations. (b) Model type IV complex $[(H_2O)_3Cu(CO_3)Cu(H_2O)_3]^{2+}$ used in the extended Hückel calculations. Bond distances are given in picometers and bond angles in degrees.

Extended Hückel (EH) Calculations. The calculations have been performed by using the FORTICON program properly modified to include a fragment molecular orbitals basis.[51] The nondiagonal elements H_{ij} of the Hückel matrix have been computed through the relation $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$, where S_{ij} is the overlap integral between the φ_i and φ_j atomic orbitals. Atomic orbitals of the Slater type were used by taking single ζ radial functions for all the atomic orbitals except 3d copper functions for which a double ζ basis was used. The calculations were performed on $[(NH_3)_2ClCu(CO_3)CuCl(NH_3)_2]$ (V) and $[(H_2O)_3Cu(CO_3)Cu(H_2O)_3]^{2+}$ (VI) complexes by using several geometrical parameters as discussed below. The actual values of VSIP and coefficients and exponents of Slater functions are collected in Table III. In the calculations performed on V we fixed the Cu–N, Cu–Cl and Cu–O_1 bond distances to the values shown in Figure 2, which correspond to values usually found in the crystal structures of the complexes shown in Table I. The overall symmetry of the molecule is C_2. The geometry of the CO_3^{2-} ion is distorted from a regular D_{3h} symmetry to mimic the situation

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observed in the crystal structures.[28-30] Calculations of the energy levels and eigenvectors of V were made by varying the value of the C–O$_1$–Cu bond angle, α, from 90 to 130° while preserving an overall C_2 symmetry of the molecule.

The EH calculations on VI were performed by using the bond distances and geometrical conformations shown in Figure 3. The energy levels and eigenvectors of VI in the configuration shown in Figure 3a were computed by varying the dihedral angle δ between the CuO$_4$ and CO$_3$ planes from 0 to 90°, the two CuO$_4$ moieties being always kept coplanar. This variation mimics the geometrical situation observed in the crystal structures of the complexes reported in Table I.

Orbital Interpretation of the Magnetic Properties of Copper(II)-Carbonato Polynuclear Complexes

Within the orbital model of the isotropic exchange interaction[10-12] the overall value of the exchange coupling constant, J, arises from the sum of two opposite contributions, one ferromagnetic, J_F, and the other antiferromagnetic, J_{AF}. In the simplest form of the model the ferromagnetic term is given as a sum of exchange integrals between localized molecular orbitals containing the unpaired electrons (the magnetic orbitals), and the antiferromagnetic contribution to J, J_{AF}, is related to the energy difference between the molecular orbitals containing the unpaired electrons. In the case of a dinuclear complex with two unpaired electrons we are interested in two molecular orbitals, φ_1 and φ_2, which originate from the two magnetic orbitals φ_a, φ_b, and J_F and J_{AF} take the form

$$J_F = -K_{ab} \tag{2}$$

$$J_{AF} = (\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab}) \tag{3}$$

where ϵ_i is the HF energy of the ith orbital obtained from an SCF calculation on the triplet state and K_{ab}, J_{aa}, and J_{ab} are exchange and Coulomb integrals.[10] The energy difference $\epsilon_1 - \epsilon_2$ can be easily evaluated within the extended Hückel[10] or the ligand field[9] framework for any set of geometrical and bonding parameters, and assuming that the ferromagnetic contribution and the other quantities in eq 2 and 3 do not vary appreciably along the series, this can be assumed to mimic the magnetic behavior of the substances.

In order to rationalize the magnetic properties of polynuclear complexes of copper(II) with bridging carbonato groups of structural types I–IV we performed EH calculations on the model complexes V and VI shown in Figures 2 and 3.

Geometrical variations on V have been performed by varying the Cu–O$_1$–C angle α from 90 to 130° to reproduce structural types I and II. For α = 90° we have the symmetrically bridged diamagnetic dimer. From Table I we learn that when the α angle is increased from 90 to 110°, the compounds become weakly antiferromagnetic. The actual structures[32] observed in these complexes show that the CO$_3^{2-}$ anion bridges the copper atoms in an unsymmetrical fashion as soon as $\alpha \neq 90°$. The Cu–O$_1$ and Cu–O distances remain similar to those observed at α = 90° for one of the two copper atoms with a Cu–O$_1$–C angle at ≃93°, while the Cu–O distance for the other copper atom significantly increases together with the Cu–O$_1$–C angle. In order to apply the orbital model in the simplest of the forms, we kept in all the calculations an overall C_2 symmetry of the molecule, probably overestimating the effect of the angular variation.

The computed energy of the two highest occupied molecular orbitals, φ_a and φ_s, is shown in Figure 4 as a function of the α angle. The labels s and a refer to the symmetric and antisymmetric molecular orbitals spanning the A and B irreducible representations of the C_2 point group. For α = 90° we computed the largest splitting (0.38 eV). The energy difference between them $|\epsilon_1 - \epsilon_2|$, decreases on increasing α, but the two levels never cross and the splitting remains significant at any value of α ($|\epsilon_1 - \epsilon_2|$ = 0.11 eV for α = 115°). In order to give an orbital explanation for this effect we performed EH calculations on a fragment basis[51] with $[(NH_3)_2CuClClCu(NH_3)_2]^{2+}$ and CO$_3^{2-}$ as fragments. The LCAO composition of the HOMO's of the two fragments is shown in Figure 5 together with their interaction diagram. The HOMO's of the metal fragment are linear combinations of mainly d$_{xy}$ and d$_{x^2-y^2}$ copper orbitals, which we have labeled d$_a$ and d$_s$ to reflect their symmetry properties. The corresponding orbitals in the carbonato molecule are labeled p$_a$ and p$_s$ and correspond to antibonding linear combinations of oxygen p orbitals with no contributions from the carbon atom. In the free ion these orbitals are the highest occupied molecular orbitals split by 0.06 eV on account of the deviation of the molecule from the D_{3h} symmetry. The p$_a$ orbital is 77% p$_x$ of O and 26% of p$_x$ and p$_y$ of O$_1$ (net atomic orbital populations) and p$_s$ is 20% p$_y$ of O and 40% p$_y$ of O$_1$. From the interaction of these fragment molecular orbitals with d$_a$ and d$_s$, the two most destabilized molecular orbitals result. The variation of the overlap populations p$_s$–d$_s$ and p$_a$–d$_a$ with α is shown in Figure 6. It is apparent that the main interaction responsible for the energy splitting $|\epsilon_1 - \epsilon_2|$ is the p$_a$–d$_a$ overlap, which shows the largest variation with α, while the p$_s$–d$_s$ overlap is much less sensitive to the geometrical deformation.

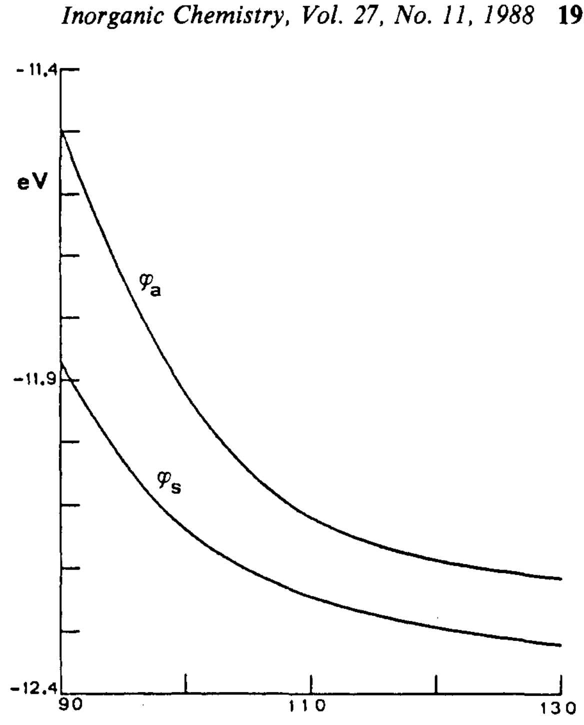

Figure 4. Variation of the energy of the two highest occupied molecular orbitals with the angle α (see text) computed by extended Hückel calculations on the model type I–II complex. φ_a and φ_s represent antisymmetric and symmetric linear combinations with respect to the C_2 symmetry of the molecule.

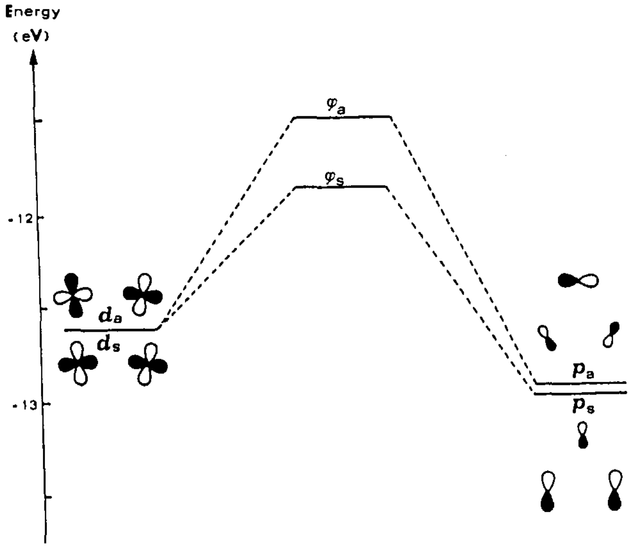

Figure 5. Interaction diagram of the highest occupied molecular orbitals for the model type I complex. The HOMO's of the $[(NH_3)_2CuCl]_2^{2+}$ fragment are shown on the right, the HOMO's of the whole complex on the center, and the HOMO's of the CO$_3^{2-}$ fragment on the left.

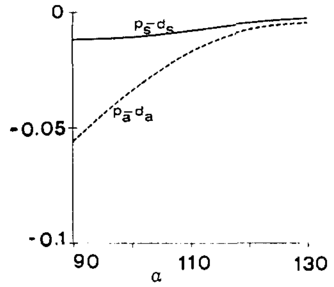

Figure 6. Computed variation of the p_s–d_s and p_a–d_a overlap populations with α for the model type I–II complex.

The above results show that the strongest antiferromagnetic interaction is expected when CO_3^{2-} is bridging at $\alpha = 90°$ than in the case when $\alpha > 90°$. Furthermore since no crossing of the energy of the HOMO's is computed we can expect that the overall interaction remain still antiferromagnetic. The magnitude of the interaction at $\alpha = 90°$ will be estimated as follows by using the Xα–VB model.

The energy splitting $|\epsilon_1 - \epsilon_2|$ drastically decreases when CO_3^{2-} is bridging as a monodentate ligand. For the geometrical configurations shown in Figure 3, in fact it is about 0.05–0.1 eV, and it is not very sensitive to the dihedral angle δ between the CuO_4 and CO_3 planes. These facts can rationalize the weak ferromagnetism observed in a number of complexes in which CO_3^{2-} molecules bridge as monodentate ligands like those reported in Table I.

It has to be noted to this point that a small $|\epsilon_1 - \epsilon_2|$ does not necessarily cause a ferromagnetic interaction. In order to have a negative J (ferromagnetic interaction), K_{ab} must be different from zero. Since in the present complexes the bridging carbonato ion is strongly involved in the bonding, causing a delocalization of the electronic cloud onto the bridging group, a sizable overlap density between the magnetic orbital can be expected, resulting in a K_{ab} value different from zero.[27] Also higher order terms[15,27] should be included in eq 2 and 3, corresponding to double-spin polarization, metal–ligand and ligand–metal charge transfer, etc. Among these higher order terms the double-spin polarization term was found negative in μ-azido–copper(II) complexes[27] thus contributing to the ferromagnetic term. The estimate of these contributions to J_F has been performed with ab initio calculations[15,16] on some copper dimers. Within the Xα–SW formalism the direct calculation of J_F has not yet been tried due to the intrinsic complication caused by the intersphere charge and still remains an open problem. For the present complexes, since the ferromagnetic interaction is very weak ($|J| < 10$ cm^{-1}), we can expect that the Xα–SW model is inaccurate to describe the interaction, and we have not tried the direct calculation of J for these complexes.

OMOs and Singlet–Triplet Splitting in Symmetrically Bridged Complexes

RHFS and UHFS Xα–SW calculations[45,46] have been performed on the model complex shown in Figure 1 on the triplet and $M_s = 0$ state using the parameters given in a previous section. The overall $C_2(y)$ molecular symmetry was used throughout all the calculations and the Xα determinant was factorized into two 37×37 determinants according to the irreducible representations of the C_2 symmetry group. The molecular potential of the $M_s = 0$ state at a partial convergence in the SCF procedure was then used as the starting potential of the broken symmetry state after imposing a left–right specular symmetry to the spin-up and spin-down densities. The Xα energies on the broken symmetry state were found by solving a single 74×74 determinant. In Table IV and V the energies of the highest occupied and lowest unoccupied one-electron levels for the triplet and broken symmetry state, respectively, are reported together with their charge distribution. Before discussing these figures, it is convenient to look at some features of the RHFS and UHFS results on the triplet and $M_s = 0$ states. In Figure 7 the energies of the highest occupied molecular orbitals are shown. The triplet $S = 1$ state is represented in the RHFS formalism by a Slater determinant containing double-occupied MO's up to 23b and 23a, which are singly occupied. These two orbitals are mainly in plane d copper orbitals with relevant contributions from chlorine p orbitals and oxygen p orbitals of the CO_3^{2-} anion as shown in Figure 8. The Xα energies of the 23b and 23a orbitals are strongly influenced by interelectronic exchange effects as clearly shown by the UHFS calculations (Figure 7c) where the spin-up orbitals are largely stabilized by spin polarization effects.

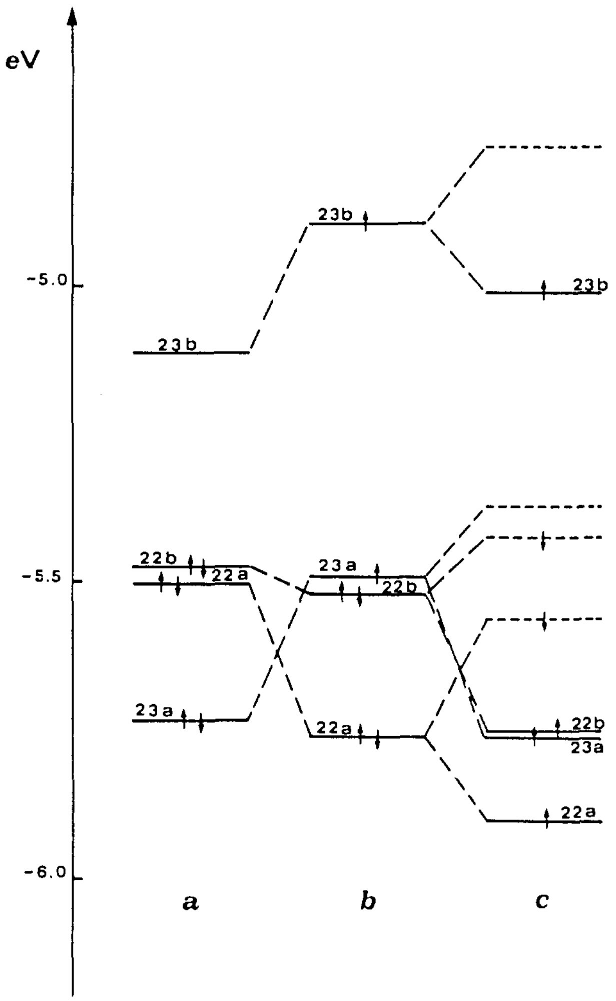

Figure 7. Highest occupied and lowest unoccupied Xα energy levels for $[Cl_3Cu(CO_3)CuCl_3]^{4-}$: (a) RHFS calculations on the $M_s = 0$ Slater determinant; (b) RHFS calculation on the $S = 1$ Slater determinant; (c) UHFS calculation on the $S = 1$ Slater determinant (full lines correspond to spin-up orbitals; broken lines correspond to spin-down orbitals).

Exchange effects also determine the energy level ordering obtained in the RHFS $M_s = 0$ state. This state is represented by a Slater determinant with all the one-electron orbitals doubly occupied up to the 23b one, which is empty. The 23b and 23a orbitals are strongly stabilized with respect to the $S = 1$ state, and a level crossing also occurs between the 23a and 22a orbitals. The same level ordering is found in the UHFS-broken symmetry calculations. The actual solutions of the RHFS and UHFS calculations on the $M_s = 0$ state are very similar both in the energy of the levels (they differ less than 0.003 eV) and in total energies, which are −12 596.036 Ry and −12 596.037 Ry respectively, but differ in the space distribution of the electronic charge.

The contour maps of some of the highest occupied MO's and of the lowest unoccupied MO obtained form the broken symmetry calculations are shown in Figure 9. They result localized on the left, right, and central part of the complex. This localization, which is due to the specular symmetry of the spin-up–spin-down potentials, strongly depends on the covalency of the Cu–CO_3 interaction. Strong covalency results in a small localization of the molecular orbitals. From Table V and Figure 9 it is apparent that the LUMO's, 46↓ and 46↑, and the 43↓ and 43↑ orbitals are

Table IV. Highest Occupied Energy Levels and Percent Charge Distribution for $[Cl_3Cu(CO_3)CuCl_3]^{4-}$ Obtained from RHF Calculations on the Triplet State

level[a]	energy, eV	% charge distribn									% Cu anglr contribn
		Cu_1	Cl_1	Cl_2	Cl_3	O_1	O	C	int[b]	out[b]	
23b[c]	−4.896	44	13	10	0	16	11	0	6	0	100 d
23a[c]	−5.489	42	6	16	17	10	0	0	8	0	3 p; 96 d
22b	−5.522	34	7	5	41	4	1	0	9	0	1 s; 6 p; 93 d
22a	−5.658	35	27	2	26	1	0	0	8	0	6 p; 94 d
21b	−6.392	1	13	3	68	1	3	0	11	0	
21a	−6.451	2	1	7	72	6	0	0	12	0	
20b	−6.454	5	1	5	73	4	0	0	12	0	
20a	−6.512	5	15	3	64	1	0	0	12	0	
19b	−6.685	17	60	5	3	5	0	0	10	0	2 p; 98 d
19a	−6.729	21	59	3	1	5	0	0	10	0	1 p; 99 d
18b	−6.878	33	44	3	7	1	3	0	10	0	100 d
18a	−6.880	31	21	2	6	30	0	0	11	0	100 d
17a	−6.945	32	26	16	5	10	0	0	10	0	99 d
16b	−7.033	22	7	58	1	0	4	0	8	0	2 p, 98 d
17b	−7.243	43	2	45	0	1	0	0	9	0	99 d
16a	−7.251	25	7	55	2	1	0	0	10	0	2 p; 98 d
15a	−7.539	12	5	41	0	26	0	0	15	0	4 s; 5 p; 91 d
15b	−7.569	15	14	3	1	19	35	0	13	0	1 s; 1 p; 98 d

[a] The energy levels are labeled according to the $C_2(y)$ point group. [b] int = intersphere charge; out = outer-sphere charge. [c] Singly occupied levels.

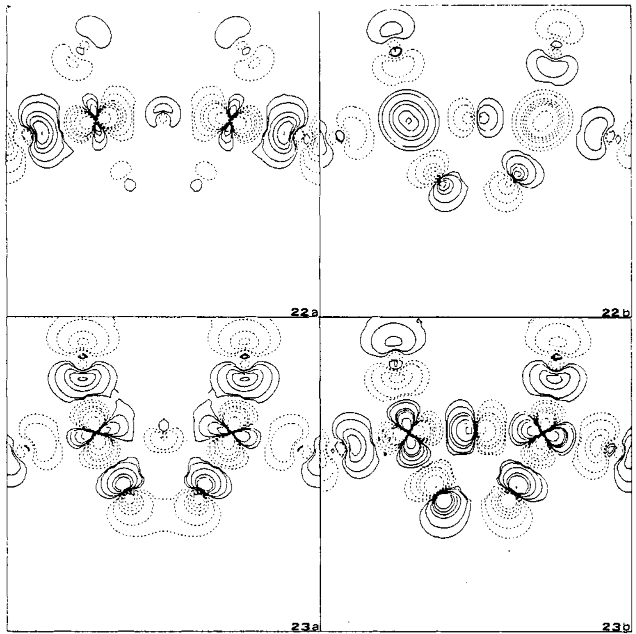

Figure 8. Contour maps of the highest occupied molecular orbitals obtained from RHF-Xα-SW calculation on $[Cl_3Cu(CO_3)CuCl_3]^{4-}$ in the triplet state. Contour values are 0.015, 0.030, 0.06, 0.08, 0.1, 0.125, and 0.25. The levels are numbered in Table IV.

strongly delocalized over the whole complex. These MO's derive from the 23b and 23a orbitals in the C_2 description and are the orbitals responsible for the magnetic properties of the dimer. It must be noted that in the most destabilized orbitals, 46↑ and 46↓, 25% of the electronic charge is delocalized onto the carbonato oxygens, 10% of this charge being on the bridging oxygen. In the 45↑ and 45↓ orbitals only 4% of the charge is on the carbonato oxygens. This figure suggests that the exchange pathway is going through the p oxygen orbitals of the bridging carbonato group, the strongest interaction being through the bridging oxygen.

The large delocalization of the magnetic orbitals and the strong similarity between the RHFS and UHFS calculations show that in the present case we are dealing with largely overlapping Xα–VB orbitals near the molecular orbital limit. For small values of the overlap, $S_{ab} \ll 1$, the singlet–triplet separation, J, can be computed through the relationship[17]

$$J = 2[E(S = 1) - E_B] \qquad (4)$$

where $E(S = 1)$ and E_B are the Xα energies of the triplet and broken symmetry state, respectively. In the limit of fully overlapping magnetic orbitals, $S_{ab} = 1$, the energy of the broken symmetry state is given by[52]

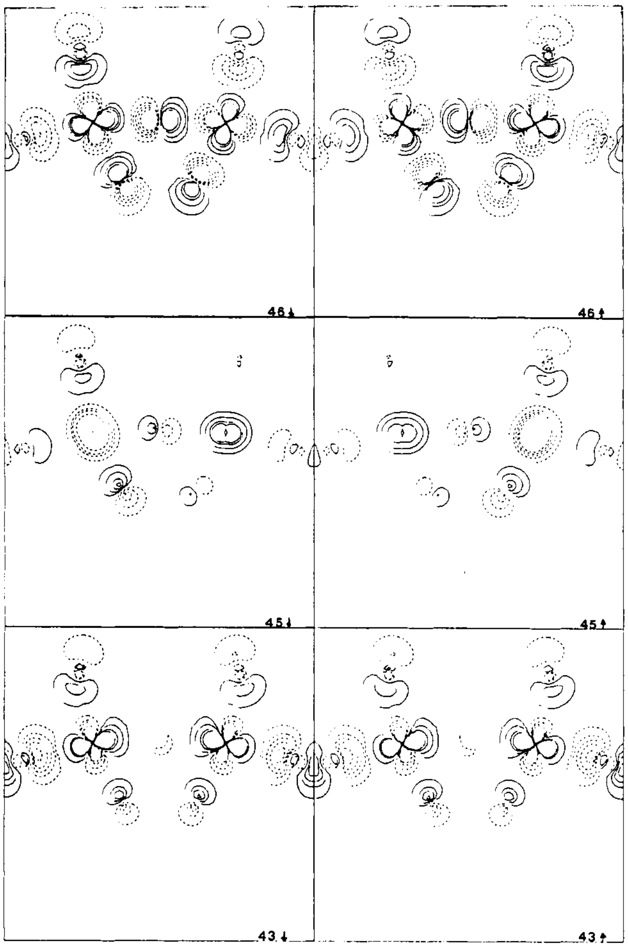

Figure 9. Contour maps of the lowest unoccupied and some of the highest occupied molecular orbitals obtained from broken symmetry Xα–SW calculations on $[Cl_3Cu(CO_3)CuCl_3]^{4-}$. Spin-up levels are shown on the right, spin-down levels on the left. The levels are numbered in Table V.

$$E_B = E(S = 0) \qquad (5)$$

and the singlet triplet separation is

$$J = [E(S = 1) - E_B] \qquad (6)$$

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(52) Noodleman, L.; Norman, J. G., Jr. *J. Chem. Phys.* **1979**, *70*, 4903.

Table V. Lowest Unoccupied and Highest Occupied Energy Levels and Percent Charge Distribution for $[Cl_3Cu(CO_3)CuCl_3]^{4-}$ Obtained from Broken Symmetry Calculations

level	energy, eV	% charge distribn														% Cu_1 anglr contribn
		Cu_1	Cu_2	Cl_1	Cl_1'	Cl_2	Cl_2'	Cl_3	Cl_3'	O_1	O_1'	O	C	int[a]	out[a]	
46↓[b]	-5.113	21	23	6	7	5	6	0	0	7	8	10	0	5	1	100 d
46↑[b]	-5.113	23	21	7	6	6	5	0	0	8	7	10	0	5	1	100 d
45↓	-5.474	8	22	2	4	1	5	12	34	1	2	1	0	9	0	
45↑	-5.474	22	8	4	2	5	1	34	12	2	0	1	0	9	0	7 p; 93 d
44↓	-5.502	23	9	2	1	8	4	30	8	4	2	0	0	9	0	6 p; 94 d
44↑	-5.502	9	23	1	2	4	8	8	30	2	4	0	0	9	0	
43↓	-5.730	19	17	15	14	4	4	9	8	1	1	0	0	7	1	4 p; 96 d
43↑	-5.730	17	19	14	15	4	4	8	9	1	1	0	0	7	1	4 p; 96 d
42↓	-6.203	1	1	3	3	1	2	35	40	1	1	2	0	12	0	
42↑	-6.203	1	1	3	3	2	1	40	35	1	1	2	0	12	0	
41↓	-6.235	3	0	1	0	3	0	71	6	2	0	0	0	13	0	
41↑	-6.235	0	3	0	1	0	3	6	71	0	2	0	0	13	0	
40↓	-6.240	2	0	0	0	4	0	72	5	3	1	0	0	13	0	
40↑	-6.240	0	2	0	0	0	3	5	72	1	3	0	0	13	0	
39↓	-6.338	4	4	4	4	2	2	35	32	0	0	0	0	12	0	
39↑	-6.338	4	4	4	4	2	2	32	35	0	0	0	0	12	0	
38↓	-6.848	5	10	23	37	3	4	0	0	3	4	0	0	10	0	
38↑	-6.848	10	5	37	23	4	3	0	0	4	3	0	0	10	0	3 p; 97 d
37↓	-6.903	12	9	37	22	2	1	0	0	4	2	0	0	10	0	1 p; 99 d
37↑	-6.903	9	12	22	37	1	2	0	0	2	4	0	0	10	0	
36↓	-7.029	8	20	13	36	2	6	1	2	0	0	1	0	10	0	
36↑	-7.029	20	8	36	13	6	2	2	1	0	0	1	0	10	0	100 d
35↓	-7.057	10	15	14	29	0	0	1	1	10	9	0	0	11	0	100 d
35↑	-7.057	15	10	29	13	0	1	1	1	9	10	0	0	11	0	100 d
34↓	-7.067	17	14	10	2	15	13	1	1	9	8	0	0	10	0	100 d
34↑	-7.067	14	17	2	10	13	15	1	1	8	9	0	0	10	0	100 d
33↓	-7.082	10	11	2	2	29	33	0	0	0	0	3	0	9	0	1 p; 99 d
33↑	-7.082	11	10	2	2	33	29	0	0	0	0	3	0	9	0	1 p; 99 d

[a] int = intersphere charge; out = outer-sphere charge. [b] Unoccupied levels; all the other levels are singly occupied.

In the general case the true J value will range between the two limiting cases (4) and (6).

Equation 4 has been successfully applied to a number of weakly coupled dinuclear complexes.[1,19-22] The energy difference in (4) and (6) can be accurately computed by using a Slater transition state from the broken symmetry solution, in which 0.5 electron is moved from 43↓ (43↑) to 46↑ (46↓). This procedure yields $J = 9420$ and 4710 cm^{-1} from (4) and (6), respectively. Since the calculations show that the broken symmetry and the MO solutions are almost equal, the second figure is a better estimate of J for the present case. The value of 4710 cm^{-1} clearly accounts for the observed diamagnetism of the symmetric μ-carbonato-bridged copper(II) complexes.

Conclusions

The present Xα calculations show that carbonato ions are very efficient in transmitting exchange interactions between transition-metal ions when bonding two metals in a symmetrical bidentate fashion (type I complexes). The exchange interaction is strongly antiferromagnetic when CO_3^{2-} is bridging two copper(II) ions, and the present calculations give a singlet–triplet splitting of the order of magnitude of thousands of wavenumbers. Although the calculations have been performed on model complexes, which contain Cl atoms to replace the more complex ligands of the actual complexes, the order of magnitude of the interaction should be correct since it mainly depends on the strong covalent bond formed by the carbonato group. This interaction is most efficient in the symmetric complex (I), and any deviation from the regular structure (I) causes a less effective exchange pathway. As a matter of fact all the other complexes reported so far show only weak exchange coupling between the metal centers.

It is apparent from this and previous studies[1] the intercorrelation between empirical molecular orbital models and SCF calculations. Only by combining both methods of calculation can one have a full insight into the electronic structure of complexes. With empirical models one can easily find qualitative correlations between experimental data and geometric and bonding parameters that form the starting point for the quantitative description of the electronic structure of the complexes which can be obtained only by using calculations at the SCF level. The present calculations show, in particular, that spin-polarization effects can severely alter the electronic energy levels depending on the spin state of the system because of the difference in the orbital parts of spin-up and spin-down electrons.

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Registry No. $[Cl_3Cu(CO_3)CuCl_3]^{4-}$, 112398-34-2.