Xα-SW Calculations of the Electronic Structure and Magnetic Properties of Weakly Coupled Transition-Metal Clusters. The $[Cu_2Cl_6]^{2-}$ Dimers

Alessandro Bencini* and Dante Gatteschi

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R, Firenze, Italy, and Dipartimento di Chimica, Università di Firenze, Firenze, Italy. *Received August 19, 1985*

Abstract: The self consistent field multiple scattering Xα model has been used to calculate the electronic structure and the magnetic coupling constant, J, of planar and pseudotetrahedral $[Cu_2Cl_6]^{2-}$ complexes with the aim of exploiting the actual possibilities of the model to describe the spectral (electronic and EPR) and magnetic properties of transition-metal polynuclear complexes. The observed variation of J with the degree of tetrahedral distortion has been quantitatively reproduced. The 19 000-cm^{-1} feature characteristic of the electronic spectra of hexachlorodicuprate(II) complexes is computed in the present calculations as a chlorine-to-metal charge transfer.

The exchange interactions between transition-metal ions in orbitally nondegenerate states have been extensively studied in oligonuclear and polynuclear complexes.[1-4] These interactions generate manifolds of closely spaced levels which give the molecule unusual magnetic properties and have attracted the interest of both theoreticians and experimentalists. Two types of interactions can occur. To the first type belong the magnetic interactions which involve the ground states of the ions in the cluster. These are usually the strongest ones and isotropic in space. To the second type belong the interactions involving the excited states of the ions. These are usually less than 1 cm^{-1} and highly anisotropic.

A number of experimental techniques, ranging from the measurement of the temperature dependence of magnetic susceptibility to optical spectroscopy and magnetic resonance techniques, have been employed to measure also very weak interactions involving both the ground and the excited electronic states.[5-8]

Many studies have been devoted to the correlation of the isotopic exchange interaction with the electronic structure and geometry of the complexes.[9] The effect of this interaction on the energy levels of the cluster is generally represented by using a spin Hamiltonian approach through the operator

$$H_{ex} = \sum_{a,b} J_{ab} S_a S_b \qquad (1)$$

where the sum runs all the neighboring paramagnetic metal atoms with total spin S_i, and J_{ab} is the exchange coupling constant between atoms a and b, which is evaluated experimentally.

The J_{ab} values are commonly related to the electronic structure of the polynuclear molecule by using semiempirical methods based on the Anderson theory of superexchange[10,11] or using orbital models which relate the J_{ab} values to overlap and energy differences between molecular orbitals evaluated within Ligand Field[12] or extended Huckel formalisms.[13-15] The use of these models allowed the rationalization of the magnetic properties of series of structurally related complexes, but they did not give any quantitative estimate of the J's.

The actual calculation of the J_{ab} values with more rigorous MO methods is hampered by the necessity of computing energy differences of the order of 10^1–10^2 cm^{-1} which are largely affected by electron correlation. In order to overcome this problem, whose solution requires extensive configuration interactions, a perturbation approach has recently been suggested to calculate J_{ab} with an ab initio approach. Calculations have been performed on copper(II) acetate,[16] oxalate,[17] and di-μ-chloro bridged[18] dimers. The agreement between the experimental and the computed J values was generally satisfactory. By using ab initio models, however, it is not a simple task to compute other physical observables such as electronic transitions and EPR parameters, which constitute a severe test of the applicability of the model to the description of the electronic structure of transition metal clusters. A more approximate method than ab initio but still retaining enough flexibility in the radial wave functions is needed in order to make the problem computationally tractable.

In recent years density functional methods have been shown to give an accurate description of the properties of open-shell transition-metal complexes.[19] In particular the Slater-Johnson Xα-SW model[20-21] has been applied with some success to calculate the electronic structure of several transition-metal complexes.[22-28]

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* Address correspondence to this author at the Institute per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R.

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The success of this method seems to rely in the numerical nature of the radial wave functions, which gives a full radial flexibility to the AO's of a given l value without introducing extended basis sets, and in the use of the Slater transition state formalism[21] which allows an accurate determination of energy differences including electronic relaxation effects.

In order to apply the Xα-SW model to calculate the exchange coupling in weakly coupled polynuclear complexes Noodleman developed a formalism based on the use of localized molecular orbitals which partially includes CI effects and can be applied to either Hartree-Fock theories or spin polarized density functional theories.[29,30] This model, called Xα-Valence Bond (Xα-VB), was applied with some success to the case of polynuclear sulphur bridged iron complexes.[31-34]

Having a comparatively simple model with which to calculate both the magnetic and the spectral properties of weakly coupled dinuclear complexes has been a dream of experimentalists for many years. In particular it would be important to have a model which can relate the energy levels of the dimer to those of the corresponding mononuclear units. We felt that the proposed Xα-VB-SW model might be a candidate to meet this expectation, and we decided to test the actual possibilities of the model by considering a simple system for which many different experimental observables have been measured.

Among the possible systems the $[Cu_2Cl_6]^{2-}$ complexes appear to be tempting. Their geometries are strongly dependent on the nature of the countercation. When small ions like Li^+ or K^+ are used, the coordination around copper is square planar,[35,36] with axial interactions between adjacent molecules; while when bulky groups like Ph_4A (A = Sb, As, P) are used, the coordination around copper is pseudotetrahedral.[37-39] This geometrical variation is accompanied by a large variation of the magnetic properties. In fact, for systems close to the square planar limit the magnetic coupling between the unpaired electrons on the copper atoms has been found to be antiferromagnetic, while pseudotetrahedral species have ferromagnetic coupling.[13] Now it is worth noting that the ferromagnetic coupling is less understood on the basis of simple orbital models as compared to the antiferromagnetic one.[40] Also the ab initio calculations have been performed on antiferromagnetic coupled systems up to now.

Given the current large interest[41,42] in the understanding of the conditions which may determine ferromagnetic coupling, it is extremely important that the theoretical models are tested in their ability to calculate such couplings and also in their sensitivity to geometrical distortions. On this basis $[Cu_2Cl_6]^{2-}$ species appears to be ideal testing grounds.

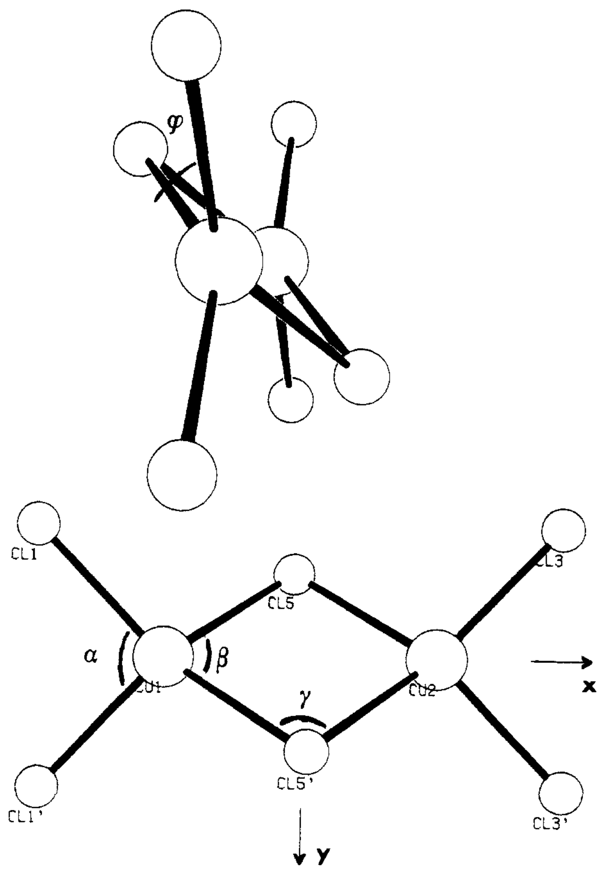

Figure 1. Schematic view of the $[Cu_2Cl_6]^{2-}$ molecule defining the geometrical parameters and reference system used in the calculations. The x axis is parallel to the Cu1–Cu2 direction, and the z axis perpendicular to the Cu1Cl5Cu2Cl5′ plane.

A number of spectral data are available on copper–chloro complexes, including optical and EPR data.[37-39,43,44] The EPR parameters give an accurate description of the nature of the ground state (g values) and information on the delocalization of the unpaired spins on the molecule (A values); the optical transitions give the ordering of the excited states. In particular a band at about 19 000 cm^{-1} observed in the electronic spectrum is characteristic of the dinuclear species and has been assigned by using semiempirical calculations.[43] This is another interesting factor of the $[Cu_2Cl_6]^{2-}$ systems because in several other dinuclear species bands are observed which characterize the dimer, whose nature has not been fully established. Calculating the energies of these bands may yield a relevant contribution to our understanding of the electronic structure of dimers.

To our knowledge it is the first time that a method of calculation is applied to compute both spectral and magnetic observables on dimeric complexes. These calculations constitute a severe test for the usefulness of the Xα model to the description of the electronic structure of transition-metal complexes and a basis for future calculations.

We wish to report here the results of our Xα-SW calculations on $[Cu_2Cl_6]^{2-}$ in three different geometries. The singlet–triplet separation as well as electronic transitions and EPR parameters will be computed and compared to the experimental data.

Computational Method

The standard version of the SCF-Xα-SW method was used.[20] The molecular properties were calculated according to the procedure described by Case and Karplus.[45-47] The calculations were

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performed on a GOULD 72 computer, by using the COOK5/TAMU1 program written by M. Cook, B. Bursten, and G. Stanley, properly modified to suit our machine. To this program we added the molecular properties routine by M. Cook and D. A. Case obtained by QCPE.

In all the calculations the SCF procedure was stopped when the relative change in the potential was 10^{-3} or smaller and/or the variation of the energy levels was not more than 0.0002 Ry. The virial ratio, $-2T/V$, was in any case within the limits 1.0000 ± 0.0004.

In the calculations the bond lengths and angles in the $[Cu_2Cl_6]^{2-}$ molecule were fixed to values obtained by averaging the values observed in the reported crystal structures.[35-39,48,49] The copper–chlorine bond lengths were 226 and 230 pm for the terminal and bridging atoms, respectively. The angles α, β, and γ defined in Figure 1 were 93, 85, and 95°, respectively. The overall geometries of the complexes were D_{2h} and C_{2h} for the planar and pseudotetrahedral cases, respectively. Three geometrical configurations were considered with the ϕ angle (Figure 1) at 0, 45, and 70°, which correspond to an increasing tetrahedral distortion.

The sphere radii were chosen by fixing the relative ratio, R, of the copper to chlorine sphere radii by using the Norman procedure.[50] Temptative calculations of J were made varying R at $\phi = 0°$ and $\phi = 45°$ starting from the value $R = 1$. $R = 0.90$ was chosen since we found a satisfactory agreement between the observed and calculated J values. This ratio was then used for all the other calculations. The corresponding sphere radii are 2.395 au for copper, 2.775 au for terminal chlorine, and 2.640 au for bridging chlorine atoms. These correspond to 21 and 16% copper–chlorine sphere overlap for the terminal and bridging atoms, respectively. A tangent Watson sphere with +2 charge was used to account for the negative charge of the complex.[51]

All the calculations were performed by using basis functions which span the irreducible representations of the C_2 point symmetry group. The α values computed by Schwarz[52] for the free atoms were used in the atomic regions. For the inner- and outer-sphere regions an average of the atomic α values according to the valence electron number was used.

OMO and Exchange Interaction

In the Xα-VB model[29] the calculations are performed on a model state in which the dimer is considered as formed by two identical high spin monomers with opposite spins. This state is represented by a single Slater determinant which is easily built up in a spin unrestricted formalism by lowering the space symmetry of the dimer removing any symmetry element connecting the two halves of the molecule and imposing a mirror symmetry in the spin up and spin down potentials. When the SCF procedure is allowed to converge, a state of lowered space symmetry and mixed spin symmetry is obtained which is called the broken symmetry state. The energy of this state is a weighted average of the energies of the pure spin multiplets which originate from the exchange interaction. The exchange coupling constant for the dimer can be determined from the energy of the broken symmetry state, E_B, and that of the highest spin multiplet, $E(S_{max})$, according to

$$J = 2[E(S_{max}) - E_B]/S^2_{max} \tag{2}$$

where S_{max} is the maximum spin state corresponding to all the unpaired electrons aligned with parallel spins. In the present case the dimer can be viewed as formed by two $CuCl_2$ moieties, each with one unpaired electron, bridged by two chlorine atoms with overall C_2 symmetry. The singlet–triplet splitting, J, can be computed according to eq 2 by

$$J = 2[E(S = 1) - E_B] \tag{3}$$

Table I. Lowest Unoccupied and Highest Occupied Energy Levels and Percent Charge Distribution for $[Cu_2Cl_6]^{2-}$ at $\phi = 0°$

level	energy (eV)	Cu_1	Cu_2	Cl_1	Cl_3	Cl_5	in[a]	out[a]	Cu_1 anglr contrbtns
16b↓[b]	−4.826	44	4	25	4	17	5	1	100% d
16b↑[b]	−4.826	4	44	4	25	17	5	1	
15b↓	−5.217	5	40	4	26	19	5	1	
15b↑	−5.217	40	5	26	4	18	5	1	1% p; 99% d
14b↓	−6.589	0	1	63	23	4	9	0	
14b↑	−6.589	1	0	23	63	4	9	0	
18a↓	−6.594	43	0	46	0	3	7	1	1% p; 99% d
18a↑	−6.594	0	43	0	46	3	7	1	
17a↓	−6.623	36	0	54	0	2	8	0	100% d
17a↑	−6.623	0	36	0	54	2	8	0	
13b↓	−6.691	41	4	33	4	10	7	0	100% d
13b↑	−6.691	4	41	4	33	10	7	0	
12b↓	−6.845	1	1	22	63	2	11	0	
12b↓	−6.845	1	1	63	22	2	11	0	

[a] in = inter-sphere charge; out = outersphere charge. [b] Unoccupied orbitals.

Table II. Lowest Unoccupied and Highest Occupied Energy Levels and Percent Charge Distribution for $[Cu_2Cl_6]^{2-}$ at $\phi = 45°$

level	energy (eV)	Cu_1	Cu_2	Cl_1	Cl_3	Cl_5	in[a]	out[a]	Cu_1 anglr contrbtns
16b↓[b]	−5.159	50	0	28	0	14	6	1	2% p; 98% d
16b↑[b]	−5.159	0	50	0	28	14	6	1	
15b↓	−5.547	0	44	1	31	17	6	1	
15b↑	−5.547	44	0	31	1	17	6	1	3% p, 97% d
14b↓	−6.404	43	1	35	1	13	7	0	2% p, 98% d
14b↑	−6.404	1	43	1	35	13	7	0	
18a↓	−6.451	47	1	37	1	7	6	1	2% p, 98% d
18a↑	−6.451	1	47	1	37	7	6	1	
17a↓	−6.645	40	2	46	2	1	8	0	100% d
17a↑	−6.645	2	40	2	46	1	8	0	
13b↓	−6.670	3	19	28	29	13	8	0	
13b↑	−6.670	19	3	29	28	13	8	0	4% p, 96% d
16a↓	−6.792	10	26	12	37	7	7	1	2% s, 1% p, 97% d
16a↓	−6.792	26	10	37	12	7	7	1	4% p, 96% d

[a] in = inter-sphere charge; out = outersphere charge. [b] Unoccupied orbitals.

Table III. Lowest Unoccupied and Highest Occupied Energy Levels and Percent Charge Distribution for $[Cu_2Cl_6]^{2-}$ at $\phi = 70°$

level	energy (eV)	Cu_1	Cu_2	Cl_1	Cl_3	Cl_5	in[a]	out[a]	Cu_1 anglr contrbtns
16b↓[b]	−5.434	50	1	30	1	12	6	1	4% p, 96% d
16b↑[b]	−5.434	1	50	1	30	12	6	1	
15b↓	−5.831	1	44	1	34	12	6	1	
15b↑	−5.831	44	1	34	1	12	6	1	5% p, 95% d
14b↓	−6.069	49	3	20	0	22	6	0	3% p, 97% d
14b↑	−6.069	3	49	0	20	22	6	0	
18a↓	−6.336	50	4	29	2	9	6	0	3% p, 97% d
18a↑	−6.337	4	50	2	29	9	6	0	
13b↓	−6.458	2	38	6	28	19	7	0	
13b↑	−6.458	38	2	28	6	19	7	0	4% p, 96% d
17a↓	−6.612	40	8	35	6	5	7	0	100% d
17a↑	−6.612	8	40	6	35	5	7	0	
16a↓	−6.683	27	19	21	18	7	7	0	1% s, 99% d
16a↓	−6.683	19	27	18	21	7	7	0	5% p, 95% d

[a] in = inter-sphere charge; out = outer-sphere charge. [b] Unoccupied orbitals.

where $E(S = 1)$ is the energy of the triplet state obtained through an SCF procedure. The energy difference in eq 3 can conveniently be evaluated with a Slater transition-state calculation.

The lowest unoccupied and highest occupied electronic energy levels of the broken symmetry state computed for $[Cu_2Cl_6]^{2-}$ with ϕ = 0, 45, and 70° are shown in Tables I–III together with the charge distribution.[53] Due to the initial symmetry imposed to

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(53) Tables SI–SIII containing the computed energies and charge distribution are available as supplementary materials.

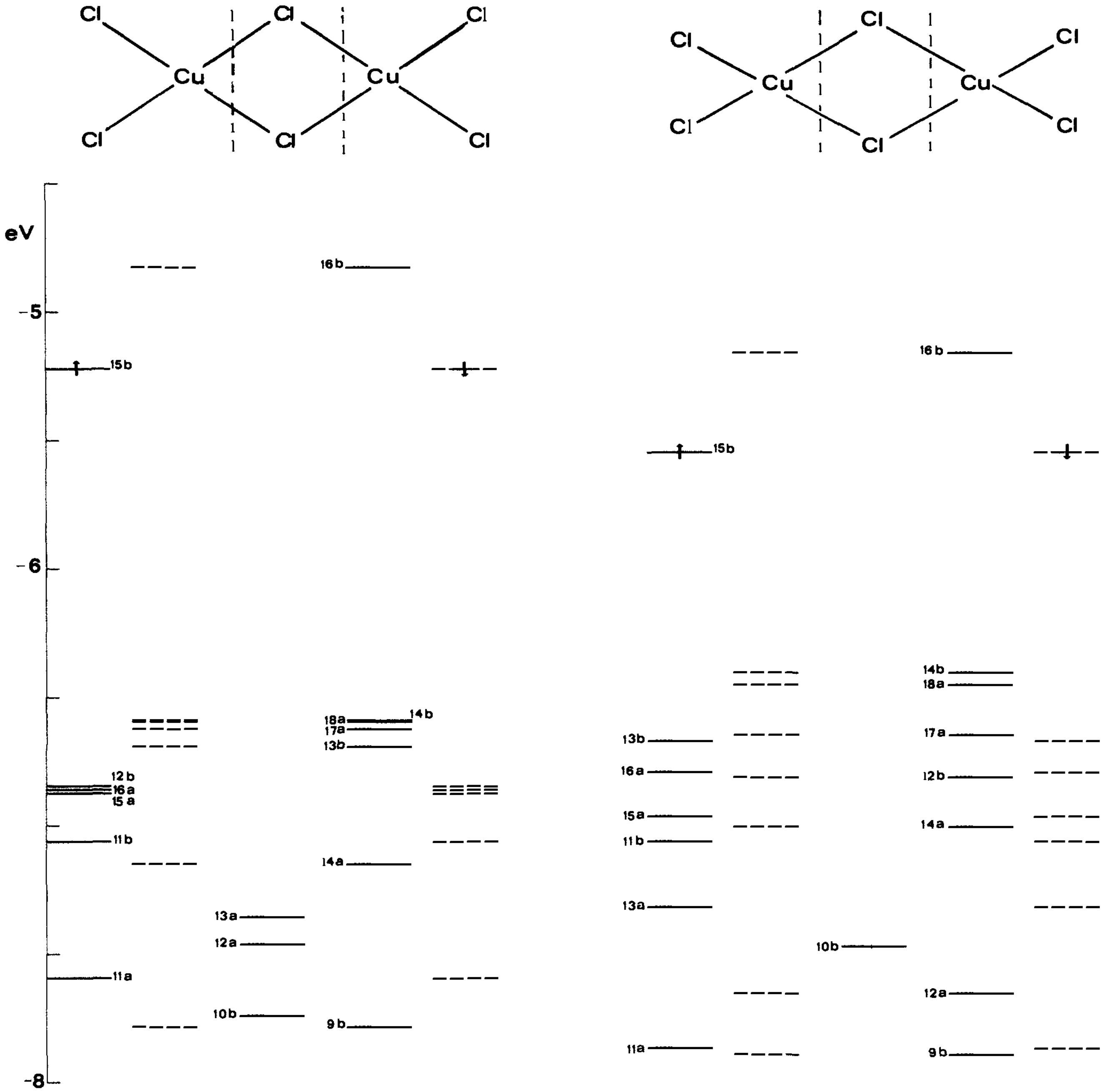

Figure 2. Highest energy levels of $[Cu_2Cl_6]^{2-}$ for $\phi = 0°$ (left) and $\phi = 45°$ (right). The highest occupied molecular orbitals are 15b′ s. Spin up levels are shown with solid lines, spin down with dashed lines. The orbitals are grouped according to their distribution on the left, center, and right part of the molecule.

the potential the energy levels result localized onto two different parts of the molecule. In Figure 2 the highest occupied and the lowest unoccupied energy levels are shown for $\phi = 0$ and 45°. The orbitals are grouped in columns to reflect their localization on the left, middle, and right part of the dimer. Due to the broken state symmetry each spin up (↑) electron on the left is in a level which is energetically degenerate with a mirror image spin down (↓) level on the right.

Spin polarization effects are particularly important for copper d orbitals, determining large splittings in couples of orbitals differing for their spin localized on the same side of the molecule. For example, the x^2-y^2 orbitals on the right copper atom at $\phi = 0°$, 18a↑ and 16a↓ which should be degenerate in a spin restricted description of the molecule, are split by 0.27 eV.

The highest occupied molecular orbitals, 15b↑ and 15b↓, contain the two unpaired electrons and are relevant to the description of the exchange interaction. They are called magnetic orbitals.[11] Contour maps of the magnetic orbitals for $\phi = 0$, 45, and 70° are shown in Figure 3. Three features can be noticed: (a) a large contribution comes from the *xy* orbitals of the copper atoms, although the delocalization of the orbitals onto the terminal and bridging atoms is important; (b) the localization of the orbitals onto the left and right part of the molecule increases on going from $\phi = 0°$ to $\phi = 45°$ and decreases again when $\phi = 70°$; (c) the magnetic orbitals for $\phi = 0$ and 45° represent in phase linear combinations of copper d orbitals compared with an out of phase

Table IV. Observed and Computed J Values for $[Cu_2Cl_6]^{2-}$ Dimers

compound	ϕ (deg)	J_{obsd}	J_{calcd}	ref
$[LiCuCl_3]\cdot 2H_2O$	0	0		35
$[KCuCl_3]$	0	40	98.8	36, 48
$[Me_2NH_2CuCl_3]$	0	3		51
$[(Ph_4Sb)CuCl_3]$	44.4	-90		37-39
	45.0		-210	
$[(Ph_4As)CuCl_3]$	48.2	-80		37-39
$[(Ph_4P)CuCl_3]$	50	-80		37-39
	70		113	

[a] Values in cm^{-1}.

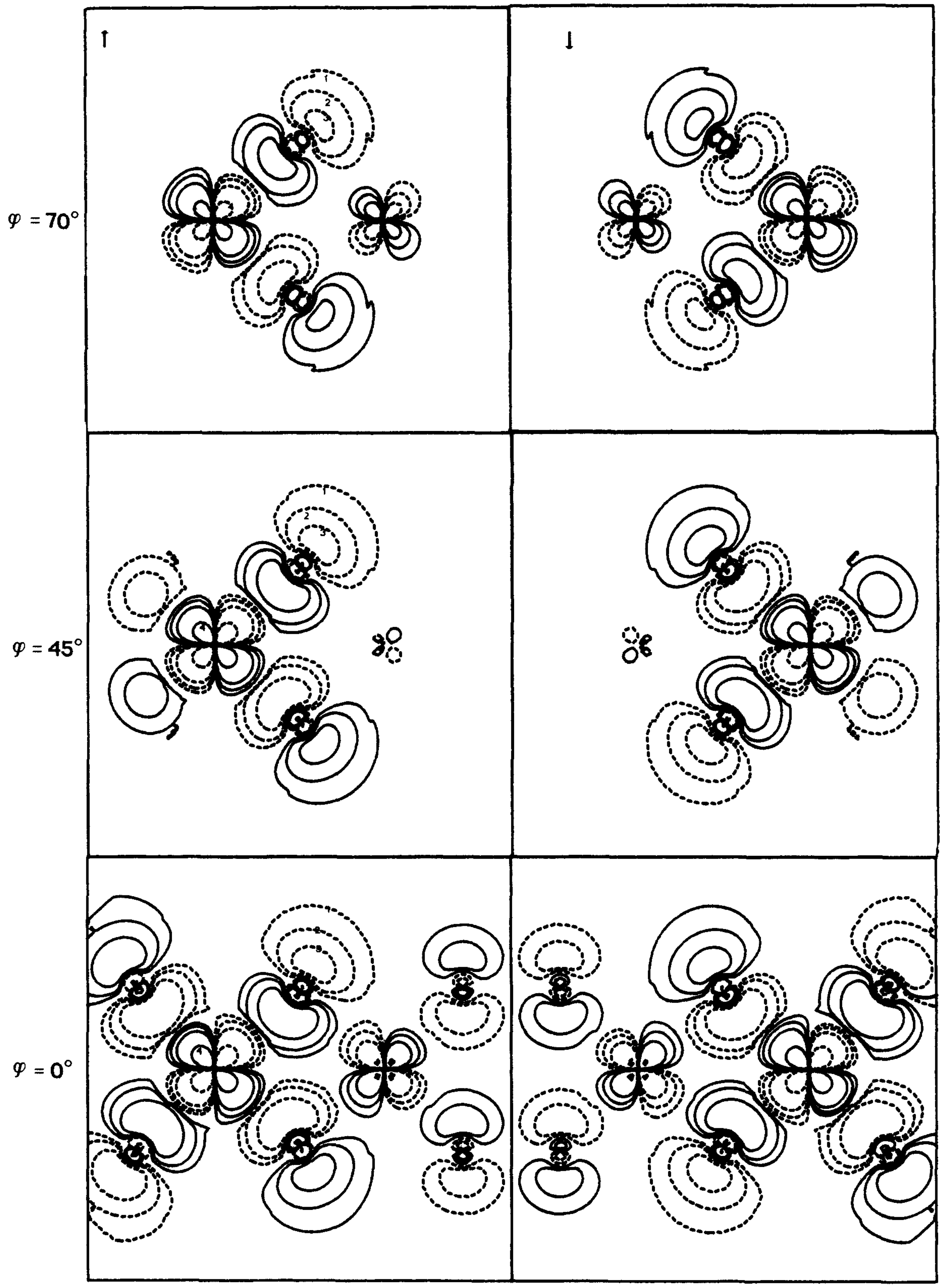

Figure 3. Contour maps of the magnetic orbitals plotted in the xy plane for $\phi = 0°$ (bottom), $\phi = 45°$ (middle), and $\phi = 70°$ (top). Spin up levels are plotted on the left, spin down levels on the right. Contour values in Figures 3 and 4 are +0.015, +0.06, and +0.08, and +0.125.

linear combination for $\phi = 70°$ showing that 16b and 15b cross between 45 and 70°.

The triplet state is obtained by moving the 15b↓ electron into the 16b↑ orbital. To evaluate the singlet–triplet splitting using eq 3 a transition state has been used in which the occupation of the 15b↓ and 16b↑ orbitals is 0.5. The computed J values are shown in Table IV and compared with the available experimental data. It is apparent from the inspection of Table IV that the J values nicely compare with experimental values both in sign and in the order of magnitude. A fairly large antiferromagnetic coupling is also predicted for $\phi = 70°$ in agreement with the results of the orbital model of the exchange interaction.[13] Ab initio calculations are in progress[18] on $[Cu_2Cl_6]^{2-}$ dimers with the same geometrical parameters used in the present calculations, and preliminary results give J values close to those computed with the Xα-VB-SW method. Since it is well-known[54] that the J values

Table V. Computed Electronic Transition Energies for $[Cu_2Cl_6]^{2-}$ Dimers[a]

AO contrbtns	$x^2 - y^2$	yz	xz	z^2	Cl
$\phi = 0°$	18a↓	17a↓	13b↓	14a↓	14b↓
	14647	15000	15100	20433	17525
$\phi = 45°$	18a↓	17a↓	14b↓	14a↓	12b↓
	10500	12100	10108	14200	18400

[a] Electronic energies in cm^{-1} The transitions are one-electron excitations from the indicated level to the 16b↓ orbital. The main orbital contributions to the individual levels are shown in the first line. $x^2 - y^2$, yz, and z^2 refer to the d orbital of copper, and Cl stands for p orbitals on chlorine atoms.

in doubly bridged copper(II) dimers are sensitive not only to the ϕ angle but, for example, also to the γ angle and since we used an average geometry for all the calculations, the agreement of the computed J values with the experimental ones can be considered as satisfactory. In particular the ferro-magnetic coupling in the pseudotetrahedral limit $\phi = 45°$ is satisfactorily reproduced.

Electronic Transitions

The electronic transitions can be computed by using the broken symmetry Xα-SW solution by moving half an electron from an occupied spin up level localized on the right part of the molecule into the empty 16b↑ orbital or equivalently from an occupied spin down level localized on the left into the 16b↓, according to the Slater transition-state theory.[21] The computed transition energies correspond to an average of the singlet–singlet and triplet–triplet transitions and can be directly compared with the experiment. Cross molecule transitions, corresponding to metal–metal charge-transfer and spin up–spin down transitions, corresponding to spin forbidden transitions, were not calculated. The results of these calculations are shown in Table V. Since no $[Cu_2Cl_6]^{2-}$ dimer reported so far has ϕ angles significantly larger than 45°, the calculations of the electronic transitions and EPR parameters for $\phi = 70°$ were not performed.

The electronic spectra of hexachlorodicuprates(II) dimers are characterized by a set of transitions between 8000 cm^{-1} and 13000 cm^{-1}, a maximum around 19000 cm^{-1}, and more intense transitions above 22000 cm^{-1}. The maxima between 8000 and 13000 cm^{-1} are assigned to transitions between antibonding orbitals with large contributions from the d copper orbitals and compare well with those observed in monomeric $[CuCl_4]^{2-}$.[55] This fact indicates that the energy separation between transitions within the singlet and triplet states is small. Also the transitions above 22000 cm^{-1} compare well with analogous transitions observed in the monomeric species[27,55] and are assigned to charge-transfer transitions. The maximum observed around 19000 cm^{-1} is at distinctly lower energy than the first charge-transfer transition observed in monomeric tetrahalocuprates and has been used as a diagnostic of dimer formation.[43] Similar "dimer" bands are known also for other dinuclear copper(II) complexes. A well-known example is the 28000-cm^{-1} band of copper(II) acetate.[56] This transition has been assigned as a charge-transfer transition on the basis of semiempirical molecular orbital calculations.[43] It can be also suspected that this transition is a double electron excitation[57] since it occurs at an energy which is twice the energy of the d–d bands, with a rather small intensity (ϵ = 400 mol^{-1} cm^{-1}), and similar transitions have been already observed in several polynuclear transition-metal complexes.[58] However the experimental result of a decrease in the transition frequency on passing from tetrahedral to square planar complexes is more in line with a CT transition.

The assignment of the d–d transitions in square planar $[CuCl_4]^{2-}$ complexes is not well-settled, also because genuine examples of pure square planar species are very rare.[55] The spectra of $[(PhCH_2CH_2NMeH_2)_2CuCl_4]$ have been assigned[59,60] with the x^2–y^2 → xy transition at 12500, (xz,yz) → xy at 14300, and z^2 → xy at 16900 cm^{-1}. The present calculations at $\phi = 0°$ reproduce the above level ordering with a better agreement than previous Xα-SW calculations,[23a] and the first three bands nicely agree with the experimental ones. The z^2 → xy transition however is computed at 20400 cm^{-1} definitely higher than the experimental one.

On passing from the square planar complex ($\phi = 0°$) to the pseudotetrahedral one ($\phi = 45°$) the computed d–d transitions shift to lower energies, as expected for four coordinate copper(II) complexes.[55] The single-crystal spectrum of $[(Ph_4As)_2Cu_2Cl_6]$ ($\phi = 48.2°$) recorded at 78 K[43] showed two resolved maxima at 8930 and 12200 cm^{-1}. The reflectance spectra of $[(Ph_4A)_2Cu_2Cl_6]$ (A = P, Sb with ϕ = 50 and 44.4°, respectively) were found[38] to be temperature dependent with a broad maximum at room temperature at 11100 cm^{-1} which split into two features at 12600 and 10000 cm^{-1} at 210 K and 13100 and 10100 cm^{-1} at 77 K. The first higher energy band is close to 21000 cm^{-1} for the three complexes.[37,38,43] The transitions computed for $\phi = 45°$ range from 10100–14100 cm^{-1} in nice agreement with the experiment. Two quasidegenerate transitions (10000 and 10500 cm^{-1}) are at lower energy than the other ones, in line with an assignment of the electronic spectra of pseudotetrahedral copper(II) complexes which requires a transition from an e level at lowest energy.[61]

A charge-transfer transition has been computed at 17500 and 18400 cm^{-1} for $\phi = 0$ and $\phi = 45°$, respectively. This can be assigned to the experimental transition at 19000 and 21000 cm^{-1} observed in square planar and pseudotetrahedral $[Cu_2Cl_6]^{2-}$ complexes. This is a ligand-to-metal charge transfer originating from the transition 14b↓ → 16b↓ and 12b↓ → 16b↓ for $\phi = 0$ and 45°, respectively. A contour map of the 14b and 12b orbitals showing the large delocalization of the MOs onto the chlorine atoms is shown in Figure 4.

In the discussion of the spectral properties of weakly coupled dimers it is usual to relate the energies of the transitions of the dimer to those of the corresponding monomers. In order to establish this comparison here a calculation of the first charge-transfer transition was performed for the square planar monomeric $[CuCl_4]^{2-}$ complex with the same geometrical parameters and sphere radii used in the present calculations. The transition was found in this case to be at 21055 cm^{-1}. The high energy shift of this CT transition on passing from dinuclear to mononuclear complexes can be rationalized by using the LCAO description of the bonding in $[CuCl_4]^{2-}$ and $[Cu_2Cl_6]^{2-}$. The overall symmetry of the square planar $[CuCl_4]^{2-}$ complex is C_{2v} and that of the $[Cu_2Cl_6]^{2-}$ dimer is D_{2h}. Labeling the states using the C_{2v} and D_{2h} irreducible representations the 21055-cm^{-1} transition of $[CuCl_4]^{2-}$ is $b_1 \rightarrow b_1$ while the 17500-cm^{-1} transition of $[Cu_2Cl_6]^{2-}$ is $b_{1g} \rightarrow b_{2u}$. There are two main orbital contributions to the b_{1g} orbital, one coming from a bonding linear combination of the copper xy orbital and terminal chlorine p orbitals and the other coming from the linear combination of the bridging chlorine p_x orbitals of b_{1g} symmetry which is antibonding, as clearly shown in Figure 4. In C_{2v} symmetry both contributions are present in the b_1 molecular orbital, but there is also a contribution from a linear combination of bridging chlorine p_y orbitals spanning the b_1 irreducible representation. This interaction with the p_y orbitals is bonding in nature and stabilizes the b_1 level shifting the transition at higher energy.

We understand that these calculations alone cannot be a proof of the goodness of the assignment. Indeed transition intensities calculations for this and for the alternative assignment as a simultaneous pair excitation should be performed, in conjunction with detailed single-crystal experiments. This is what we plan to perform in the next future.

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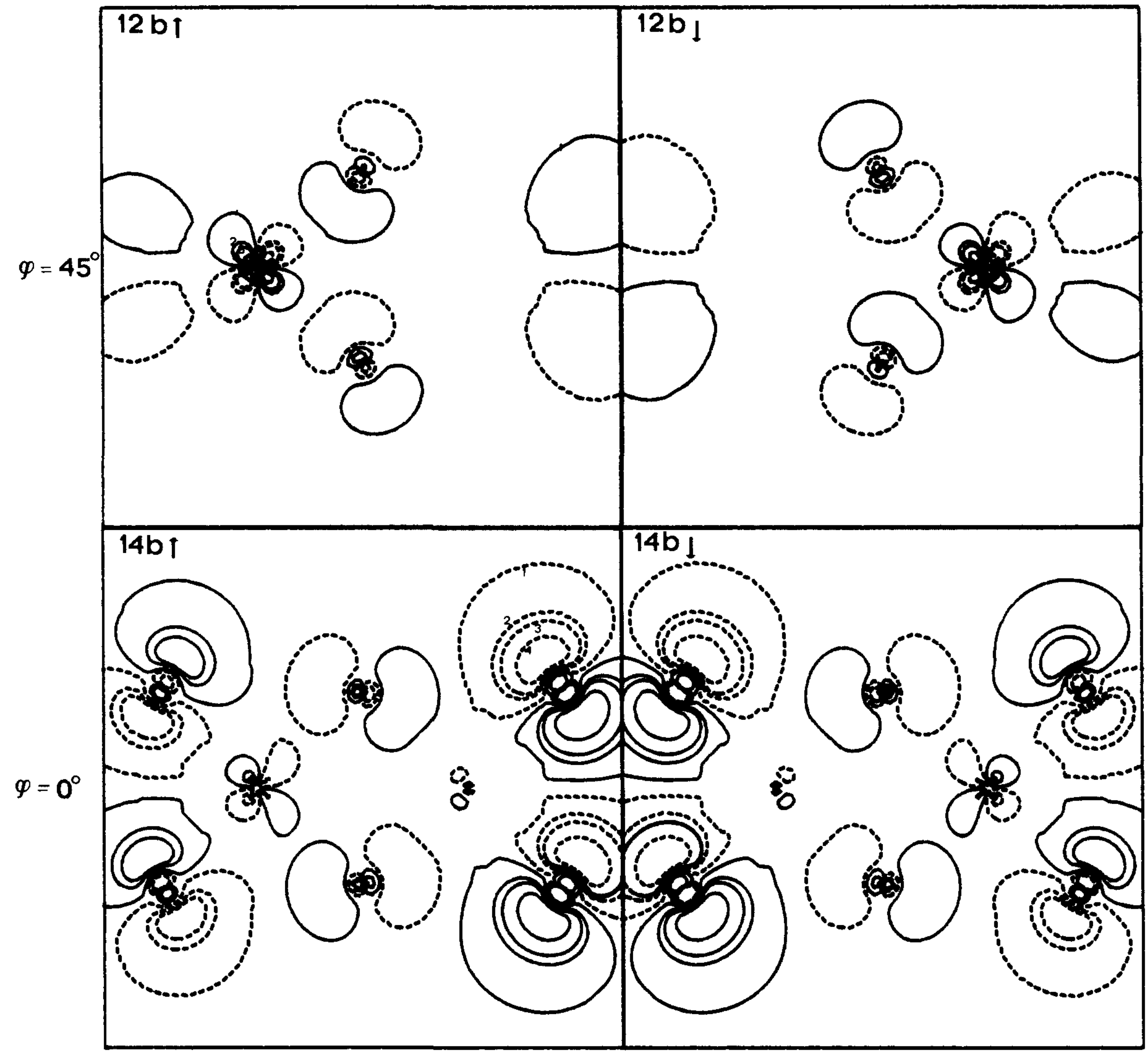

Figure 4. Contour maps of the 14b levels for $\phi = 0°$ (bottom) and 12b levels for $\phi = 45°$ (top). Spin up levels are plotted on the left, spin down levels on the right.

EPR Parameters

The possibility of using the Xα-SW wave functions to calculate the EPR parameters of copper(II) complexes has already been discussed, and the required formalism has been developed.[23,25] Since the broken symmetry state is not a pure spin state, the triplet wave functions, obtained by SCF procedure on the $M_S = 1$ state, have been used in the calculations. The α, β, and γ metal orbital coefficients in the predominantly metal d molecular orbitals are shown in Table VI together with the Δg's computed by using the calculated transition energies and the free ion spin orbit coupling constant. These coefficients have been calculated from the fractional charge associated with the corresponding partial 1 wave of the SCF-Xα-SW orbitals. The Δg values shown in Table VI have been computed assuming axial symmetry by using the average of the γ and γ' coefficients and the average of the computed energies. The observed Δg's for pseudotetrahedral $[(Ph_4A)_2Cu_2Cl_6]$ (A = Sb, P, As) are $\Delta g_z = 0.31, 0.33, 0.32$, $\Delta g_y = 0.04, 0.04, 0.8$, and $\Delta g_y = 0.06, 0.06, 0.11$, respectively.[35,36] The computed values are about 60% smaller than the experimental ones. It has, in fact, often been observed that the Xα wave functions overestimate the covalency of the metal-to-ligand bonds giving g values lower than those experimentally observed. This fact has been accounted for by introducing an empirical correction parameter in the calculation of the g values in $[CuN_2S_2]^{2-}$ chromophores.[62]

Table VI. Metal Orbital Coefficients[a] in the Predominantly Metal d Molecular Orbitals and g Values[b]

ϕ(deg)	$\alpha(xy)$	$\beta(x^2-y^2)$	$\gamma(xz)$	$y'(yz)$	$\Delta g_\perp$	$\Delta g_\parallel$
0	0.656	0.714	0.678	0.678	0.021	0.10
45	0.663	0.678	0.707	0.734	0.034	0.13

[a] Gross atomic orbital population from the fractional charge associated with the partial 1 wave in the molecular orbital. The predominant d metal orbital is shown in parentheses. [b] Computed by using the calculated electronic energies and $\zeta_d = 828$ cm^{-1} with the formulas in ref 36. An average value for the γ and γ' coefficients has been used in the calculation of $\Delta g_\perp$.

A slightly better agreement is obtained for the square planar case. The observed Δg's are $\Delta g_z = 0.21$, $\Delta g_x = 0.06$, and $\Delta g_y = 0.08$ for $KCuCl_3$[63] and $\Delta g_z = 0.24$ and $\Delta g_x = \Delta g_y = 0.05$ for $[(PhCH_2CH_2NMeH_2)_2CuCl_4]$.[64]

The computed principal values of the hyperfine tensor describing the coupling of the unpaired electron with the ^{63}Cu and ^{35}Cl nuclei are shown in Table VII. The Fermi contact contribution, A_F, the spin dipolar contribution, A_D, and $P = g_e g_N \mu_B \mu_N \langle r^{-3} \rangle$ which appear in the calculation of the orbit dipolar contribution, A_L, are also shown.[22,23] Since the A tensor has been computed by using the triplet wave functions and considering the contributions coming from both the symmetric and antisymmetric MOs, the values

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Table VII. Computed **A** Tensor[a] for ^{63}Cu and ^{35}Cl

^{63}Cu	ϕ(deg)	A_F	A_{Dx}	A_{Dy}	A_{Dz}	P'	$A_{L\perp}$	$A_{L\parallel}$	A_x	A_y	A_z
	0	−68.5	63.2	65.6	−128.8	452.0	17.8	104.6	12.5	14.9	−92.7
	45	−61.6	75.5	51.6	−127.1	450.1	21.2	161.1	35.1	11.2	−27.6
^{35}Cl	ϕ(deg)	A_F	A_{Dx}'	A_{Dy}'	A_{Dz}'				A_x'	A_y'	A_z'
C11	0	11.2	−9.0	18.7	−9.6				2.2	29.9	1.6
C15	0	21.8	8.6	4.3	−12.9				30.4	26.1	8.9
C11	45	8.8	−8.9	19.1	−10.2				−0.1	27.9	−1.4
C15	45	16.0	4.4	6.5	−10.9				20.4	22.4	5.1

[a] Values in cm^{-1} × 10^{-4}. The x, y, z axes are defined in Figure 1. The x', y', and z' axes are defined in the text. The copper values have been calculated by using $\Delta g_\parallel = 0.21$, $\Delta g_\perp = 0.05$, and $\Delta g_\parallel = 0.33$, $\Delta g_\perp = 0.06$ for $\phi = 0$ and 45°, respectively.

Table VIII. Computed and Observed Spectromagnetic Properties of $[Cu_2Cl_6]^{2-}$ Dimers[a]

	$\varphi = 0°$		$\varphi = 45°$	
	obsd	calcd	obsd	calcd
J (cm^{-1})	0 + 40	98.8	−80 + −90	−210
elec trans (cm^{-1})				
d–d	12500	14647		10500
d–d	14300	15000	9000	10108
d–d	14300	15100	12000	12100
d–d	17000	20433		14200
LMCT	19000	17525	21000	18400
$g_\parallel$	2.21	2.10	2.31	2.13
$g_\perp$	2.07	2.02	2.06	2.03
$A_\parallel^{Cu}$ (cm^{-1} × 10^{-4})[b]	|163|	−92.7	|25|	−27.5
$A_\perp^{Cu}$	|35|	12.5, 14.9	|48|	35.1, 11.2
$A_\parallel^{Cl1}$	|23|	29.9	|13|	27.9
$A_\perp^{Cl1}$	|5|	2.2, 1.6	|5|	−0.01, −1.4

[a] For references see text. [b] The principal directions of the computed tensors are defined in the text.

obtained correspond to those expected for a monomeric complex and are related to the expected values for a dimer, A_{dim}, through the relationship $A_{dim} = {}^1/_2A$.[65] The principal values of A_L have been computed in axial symmetry. A comparison with experimental data cannot be done directly since no hyperfine splitting has been detected so far in the EPR spectra of dinuclear $[Cu_2Cl_6]^{2-}$ complexes. The copper hyperfine values can be compared, for the square planar case, with those observed for copper(II) doped K_2PdCl_4[63] where $|A_\parallel| = 163 \times 10^{-4}$ and $|A_\perp| = 34.5 \times 10^{-4}$ cm^{-1}. The agreement with the computed values is not perfect, the computed values being always smaller than the observed ones. A comparison with previous calculations[23a] on $[CuCl_4]^{2-}$ complexes shows that we have now computed a smaller dipolar contribution which can probably be ascribed to the geometrical distortion from a pure (D_{4h}) square planar geometry.

On passing to the pseudotetrahedral geometry the computed A_z values decreased, as experimentally observed in mononuclear copper(II) complexes.[66] A comparison with the hyperfine values seen in the copper(II) doped $[Cs_2ZnCl_4]$[67] is rather satisfactory since the values are $|A_\parallel| = 25 \times 10^{-4}$ and $|A_\perp| = 48.5 \times 10^{-4}$ cm^{-1}. The values shown in Table VII have been actually computed by using the average of the g values experimentally observed[38] in $[(Ph_4A)_2Cu_2Cl_6]$ which compare well with the values observed in copper(II) doped $[Cs_2ZnCl_4]$.

Chlorine hyperfine splittings has been measured[63] for copper(II) doped $[K_2PdCl_4]$ as $|A_\parallel^{Cl}| = 23.3 \times 10^{-4}$ and $|A_\perp^{Cl}| = 5.3 \times 10^{-4}$ cm^{-1}. The z direction was assumed parallel to Cu–Cl. These values compare well with the values computed for the terminal chlorine atoms. The y' direction, where the largest hyperfine coupling has been computed, makes an angle of 8° with the Cu–Cl_1 direction, and x' is parallel to Cu–Cu. For the briding chlorines the x', y', and z' axes called in Table VI are parallel to x, y, z as required by the overall symmetry of the complexes. Since the principal directions of the hyperfine tensor of the bridging chlorine atoms are symmetry determined, the A values cannot be directly compared with the values observed in monomeric complexes. It is however apparent that the computed values have the correct magnitude.

Chlorine hyperfine splitting has been recently measured[68] in the pseudotetrahedral copper(II) doped $[(enH_2)_2ZnCl_4]$. The measured values were $|A^{Cl}{}_z| = 13 \times 10^{-4}$, $|A^{Cl}{}_y| = 3.5 \times 10^{-4}$, and $|A^{Cl}{}_x| = 6.5 \times 10^{-4}$ cm^{-1} (values averaged over two inequivalent chlorine atoms). The z direction was found significantly misaligned with respect to the Cu–Cl bond direction making an average angle of 29°. These values nicely compare with the values reported in Table VII as well as with the values previously computed.[23] The z' direction is computed at 13.8° from the Cu–Cl_1 direction.

Conclusions

The Xα-SW model is applied to the calculation of the singlet–triplet splitting, J, electronic transition energies, and EPR parameters of $[Cu_2Cl_6]^{2-}$ dimers. Final comparison between observed and computed quantities is given in Table VIII. The observed order of magnitude of J is reproduced as well as the variation of J with the degree of tetrahedral distortion. The computed values agree well with those obtained by an ab initio calculation which includes CI at second order in perturbation theory. The major advantage of the ab initio method over the Xα-VB-SW one is the decomposition of J into terms directly related to the familiar Anderson picture of superexchange. A similar decomposition of J can be done within the Xα-VB-SW model, but the procedure is cumbersome and has not been attempted here.

With the Xα-SW model it has been possible to compute electronic transitions and EPR parameters of the complexes. From these calculations it is apparent the general agreement between the observed and calculated electronic transitions, and it seems to be possible to assign the 19 000-cm^{-1} feature seen in the electronic spectra of the dimeric unit to a chlorine-to-copper charge transfer. The chlorine hyperfine splitting is correctly described by the Xα wave functions, while a worse fitting of the copper A values has been obtained. This has already been observed in other complexes[19,23b–26] whose electronic structure has been computed with the Xα method. One possible explanation is that the Fermi contact term is uncorrectly calculated since, depending on the value of the wave function on the nuclei, the nonrelativistic radial wave function should be inaccurate. This explanation seems in line with the fact that the chlorine hyperfine splitting is in better agreement with the experimental values than the copper one due to the smaller relativistic effects expected for chlorine atoms.

In the present calculations we have computed a larger covalency of the copper–chlorine bond than that previously calculated for the monomeric $[CuCl_4]^{2-}$ ions.[23] This is certainly due to the smaller copper/chlorine sphere radii ratio used in order to reproduce the J values. It seems now quite a general observation that the Xα wave functions overestimate the covalency of the metal–ligand bonds and consequently give a bad estimate of the g values.

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Supplementary Material Available: Tables SI–SIII containing the complete listing of energy levels and charge distributions (15 pages). Ordering information is given on any current masthead page.

Mechanism of the Diels–Alder Reaction: Reactions of Butadiene with Ethylene and Cyanoethylenes

Michael J. S. Dewar,[*†] **Santiago Olivella,**[‡] **and James J. P. Stewart**[†]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, and Departament de Quimica Organica, Facultat de Quimica, Universitat de Barcelona, 08028 Barcelona, Spain. *Received September 12, 1985*

Abstract: PMO theory suggests that the effects of substituents on the rate of the Diels–Alder reaction between ethylene and 1,3-butadiene cannot be explained on the basis of a synchronous mechanism. Calculations are reported, using the RHF, UHF, and CI versions of MNDO and AM1, for the Diels–Alder reactions of 1,3-butadiene with ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene. The results confirm the PMO conclusions, indicating unambiguously that the reactions involving the cyanoethylenes cannot be synchronous. The evidence suggests that Diels–Alder reactions in general proceed via very unsymmetrical transition states, close to biradicals in structure and with energies differing little from those of the corresponding biradicals. The regioselectivities and rates of Diels–Alder reactions can be predicted on this basis, more simply and more reliably than they can in terms of frontier orbital theory. The mechanism of the simplest example, i.e., the reaction of ethylene with butadiene, remains uncertain.

The mechanism of the Diels–Alder (DA) reaction has been the subject of major interest and controversy, ever since it was discovered 60 years ago.[1] The chemical evidence seemed initially to favor a two-step[2] mechanism, involving a biradical or zwitterionic intermediate, since the regioselectivity of DA reactions can be interpreted very effectively on this basis (see below). It was, however, recognized that the observed stereochemistry is difficult to explain in such terms, DA reactions almost invariably involving exclusive cis addition to the dienophile.

In 1938 Evans and Warhurst[3] pointed out that the cyclic transition state (TS) involved in a synchronous[2] mechanism should be analogous to benzene and hence highly resonance stabilized. They suggested on this basis that DA reactions are in fact synchronous, unlike analogous dimerizations of olefins where the TS would be an analogue of cyclobutadiene. While this work was largely overlooked as a result of World War II and while good evidence for a nonconcerted[2] mechanism was later presented by Woodward and Katz,[4] the investigations of pericyclic reactions by Woodward and Hoffmann[5] revived the synchronous mechanism, and most organic chemists have assumed in recent years that DA reactions in general are not merely concerted[2] but also synchronous.

While the stereospecificity of DA reactions certainly suggests that they are concerted, this argument is not conclusive. The same would be true for a two-step mechanism if the intermediate biradicals or zwitterions collapse to the product faster than they isomerize by internal rotation. Several lines of evidence do, however, show that *both* of the new bonds are formed to significant extents in the TSs of certain specific DA reactions. These, and the properties involved (in parentheses), are as follows: (a) DA reaction of furan with maleic anhydride[6] (kinetic isotope effects); (b) reverse DA conversion of dibenzotricyclo[2.2.2]octadiene to anthracene and ethylene[7] (kinetic isotope effects); (c) DA reactions of diphenylisobenzofuran with methyl and menthyl furmarates[8] (induced optical activity); (d) DA reactions of anthracene and its benzo derivatives with maleic anhydride[9] (comparison of rates with localization and paralocalization energies).

However, contrary to claims in the original papers,[6-9] this evidence does *not* show that any of the reactions in question are synchronous. The arguments to this effect have been given in detail elsewhere[10] and so need not be repeated here. The only new evidence, an addition[11] to (c), is also inconclusive.[12] On the other hand, comparison of the rates of the DA reactions of 1,3-

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[†] University of Texas at Austin.

[‡] University of Barcelona.

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(2) Problems have been caused in the past by loose terminology, the term "concerted" in particular having been used with a variety of meanings. The terminology used here, which now seems to be gaining general acceptance, is as follows. A *concerted* reaction is one which takes place in a single kinetic step. A *two*-step reaction is one which takes place in two distinct steps, via a stable intermediate. A *synchronous* reaction is a concerted reaction in which all the bond-breaking and bond-forming processes take place in parallel, all having proceeded to comparable extents in the TS. A *two-stage* reaction is concerted but not synchronous, some of the changes in bonding taking place mainly in the first half of the reaction, between the reactants and the TS, while the rest takes place in the second half, between the TS and the products. The new features are the precise definition of the term concerted and introduction of the term two-stage. The latter seems to have been first suggested by Goldstein and Thayer (Goldstein, M. J.; Thayer, J. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1925).

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(12) The earlier criticisms[10] apply equally to this work. The experimental results were explained in terms of compensation between two opposing steric effects. There is no reason to suppose that the cancellation may not be almost exact in any given case. The experiment by Tolbert and Ali was what may be termed a "one way" experiment, i.e., an experiment with two possible outcomes, one of which leads to a definite conclusion, whereas the other does not.

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