

Figure 7. Variable-temperature 50.3-MHz ^{13}C CP/MAS spectra of pyridine adsorbed on silica-alumina; 2000 to 20000 1-s repetitions per spectrum, 1-ms contact time.

γ carbon in experiments without ^1H decoupling during data acquisition implies that other types of motion reduce the dipolar coupling for this carbon as well. The variable contact time experiment suggests that rotation about the C_2 axis is a significant contribution to a complex overall motion. These results and interpretations are consistent with preferential broadening of the γ -carbon signal in the decoupler-off experiment (Figure 5).

A variable-temperature study was made to explore further the pyridine/silica-alumina system. A high level of loading was again used. Spectra, shown in Figure 7, were obtained from 21 to -80°C . The broad, high-shielding signal is due to vacuum line contamination. As the temperature was lowered, the pyridine lines were observed to broaden. Two general types of mechanisms can account for this observation. According to one, molecular motion on the millisecond time scale can interfere with averaging of MAS and/or ^1H decoupling, producing line broadening.²⁹⁻³¹ Since no

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spinning side bands are observed, even at low temperatures, the motionally reduced CSA must remain smaller than the spinning speed; this implies that molecular motion does not interfere with averaging of the CSA. The possibility of motion interfering with decoupling is not as easily dismissed. A more plausible explanation for the increased line width at low temperature is a decrease in chemical exchange rates, approaching coalescence at -80°C . If this is the case, then further decreases in temperature will not yield well-resolved lines until the temperature is low enough to reduce the exchange rates well below coalescence values. Future experiments at lower loading levels, using ^{13}C -enriched adsorbate, and low temperature may be capable of sorting out the individual species. Such species and equilibria have been discussed before in the interpretations of other types of data.^{27,32}

In summary, the combination of ^{13}C and ^{15}N spectroscopy has provided a relatively detailed characterization of the pyridine/silica-alumina system. The data suggest that hydrogen bonding is the dominant interaction for samples with surface coverages of above 0.5 monolayer. The pyridine is very mobile for loading levels this high, and signals from an exchange-averaged species are observed. Rotation about the C_2 axis is one facet of a complex overall motion. ^{13}C spectral evidence suggests that a low-mobility Lewis acid-base complex dominates at lower loading levels. ^{15}N CP/MAS NMR (of enriched samples) provides evidence for two discrete forms of protonated pyridine for HCl pretreated samples. A further indication that ^{15}N NMR is a more promising probe for adsorbed amines than ^{13}C NMR is the fact that some pyridine samples with much higher isotopic enrichment than the 30% used in this work show additional low-intensity ^{15}N peaks, including a signal at 200 ppm, which may be due to slowly exchanging (or nonexchanging) Brønsted complex. The ^{15}N approach is now under further study.

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$X\alpha$ Calculations of the EPR Parameters of Pseudotetrahedral Copper(II) Complexes

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Abstract: The self-consistent-field multiple-scattering $X\alpha$ method has been used to calculate the electronic structure of pseudotetrahedral and square-planar CuCl_4^{2-} ions, with the aim of checking the reliability of the method in the calculation of the spectral (electronic and EPR) properties of transition metal complexes. Several different calculation schemes were used in order to improve the fit to the experimental spectral transitions. Overlapping spheres were found to give the best agreement. The values of g and of the ^{63}Cu hyperfine constant were satisfactorily reproduced, showing that the low value of the latter in the pseudotetrahedral ion is due to covalency effects and not to 4p metal orbital mixing into the ground state.

Introduction

The self-consistent-field multiple-scattering $X\alpha$ (SCF-MS- $X\alpha$) method¹ is widely employed for the calculation of the electronic

structure of transition metal complexes.²⁻⁸ The main advantages of the method lie in the limited computer time required for the

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calculation, as compared with the LCAO-Hartree-Fock, (HF) method, and in the fact that the radial functions are not fixed but are numerically calculated, thus giving a full radial flexibility to the AO's of a given l value without introducing extended basis sets.

In the SCF- $X\alpha$ method many spectral properties of the complexes are easily calculated as well.⁸⁻¹¹ The electronic transitions are obtained through the transition-state formalism, thus taking into account to some extent relaxation effects.¹² The spin-unrestricted formalism makes the calculation of the contact hyperfine contribution to the hyperfine electron-nuclear coupling relatively easy, taking into account spin polarization effects; also, the dipolar contribution to the hyperfine constant is easily calculated.⁹ Perturbative approaches are currently used to calculate those experimental variables which depend on spin-orbit coupling, such as g and the pseudocontact contributions to the hyperfine splitting.

Several authors have calculated one, or all, of these properties for transition metal complexes, using different approaches.¹³⁻¹⁸ In some cases tangent spheres were used, while in some other overlapping spheres were considered; in some cases the molecular coefficients which appear in usual perturbation expressions for g and A were obtained directly from the $X\alpha$ calculation; in other cases the $X\alpha$ charge distribution was compared with extended Hückel or INDO calculations.

Since the calculation of the electronic properties of transition metal complexes appears to be one of the most promising fields of application of the $X\alpha$ method, we felt that it is now time to test the actual possibility of employing it, by considering a simple system, for which many experimental data are available. The calculations should be performed using the various different approaches suggested thus far in order to compare them and choose the best suited to the purpose of calculating electronic properties.

Among the possible systems pseudotetrahedral copper(II) complexes appear to be particularly tempting. Quite a few examples of such complexes are known in the literature and also several metallo enzymes and metallo proteins are reported to have a tetrahedral copper site.¹⁹ Although the electronic d-d transitions of the complexes are reasonably well understood,²⁰ much more controversy is still present for the EPR parameters.²¹ Starting from the earlier studies of Cs_2CuCl_4 ²² it was recognized that

Table I. Ground-State Energy Levels^a (eV) and Charge Distribution for Cs_2CuCl_4 ^b

orbital	energy	charge distribution, %						
		Cu			Cl			
		s	p	d	s	p	inter sphere	outer sphere
4b ₂	-3.835 7		2	61	1	30	4	2
5e	-4.526 9		2	67		26	4	1
2b ₁	-4.944 9			78		18	4	
4a ₁	-5.039 6	1		76		20	3	
1a ₂	-5.986 8					93	6	1
4e	-6.107 6			1		92	7	1
3a ₁	-6.828 2	1		20		71	7	1
3b ₂	-6.833 0		3	3		83	10	1
3e	-6.986 0		1	12		78	9	1
1b ₁	-7.347 9			22		71	7	1
2e	-7.851 0		8	9		72		1
2b ₂	-8.007 1		3	34		61		1
2a ₁	-8.767 8	20		3	3	73		1
1b ₂	-18.197 5		1	3	96			
1e	-18.301 9		3	1	96			
1a ₁	-18.574 3	5			93	1		
Cu 3p	-71.640 8		100					
Cu 3s	-111.162 6	100						
Cl 2p	-190.216 4					100		
Cl 2s	-248.642 1				100			
Cu 2p	-914.416 8		100					
Cu 2s	-1041.021 1	100						
Cl 1s	-2734.189 7				100			
Cu 1s	-8741.529 7	100						

^a The highest occupied level is 4b₂. ^b Non-spin-polarized calculation performed with 14% overlapping spheres.

pseudotetrahedral copper(II) complexes are characterized by high g_{\parallel} values (2.25-2.40) and low A_{\parallel} values (25-100 × 10⁻⁴ cm⁻¹).²¹ In order to justify these values, the symmetry-allowed admixture of 4p orbitals in the ground state was advocated,²² but later other models which ascribed the low A_{\parallel} values to covalency and ligand spin-orbit coupling effects were proposed.²³

We wish to report here the results of our SCF MS $X\alpha$ calculations on pseudotetrahedral $CuCl_4^{2-}$ ions in order to discriminate between the two models. We considered also square-planar $CuCl_4^{2-}$ ions in order to investigate the effects of varying the geometry of the complexes.

Computational Method

The standard version of the SCF MS $X\alpha$ method is used.²⁴ The molecular properties were calculated according to the procedure described by Case and Karplus.⁹ The calculations were performed on a SEL 72 computer, using the Cook5/Tamul 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 or better.

For the pseudotetrahedral $CuCl_4^{2-}$ ion we fixed the geometry assuming D_{2d} symmetry, with average bond length Cu-Cl 223 pm, and large Cl-Cu-Cl angles of 129.2°, according to the structural data.^{25,26} Various calculations have been performed using variable radii ranging from tangent to overlapping spheres. The maximum overlap we considered corresponds to an increase of radii by 34% with respect to the tangent sphere value. This means that 14% of the volume of each chlorine sphere is overlapping with the copper sphere. The sphere radii corresponding to this choice are 137.7 and 161.6 pm for copper and chlorine, respectively. The ratio of the copper and chlorine spheres radii was fixed to the value obtained using the Norman procedure.²⁷ The α values computed by Schwarz for the free atoms were used in the atomic regions.^{28,29}

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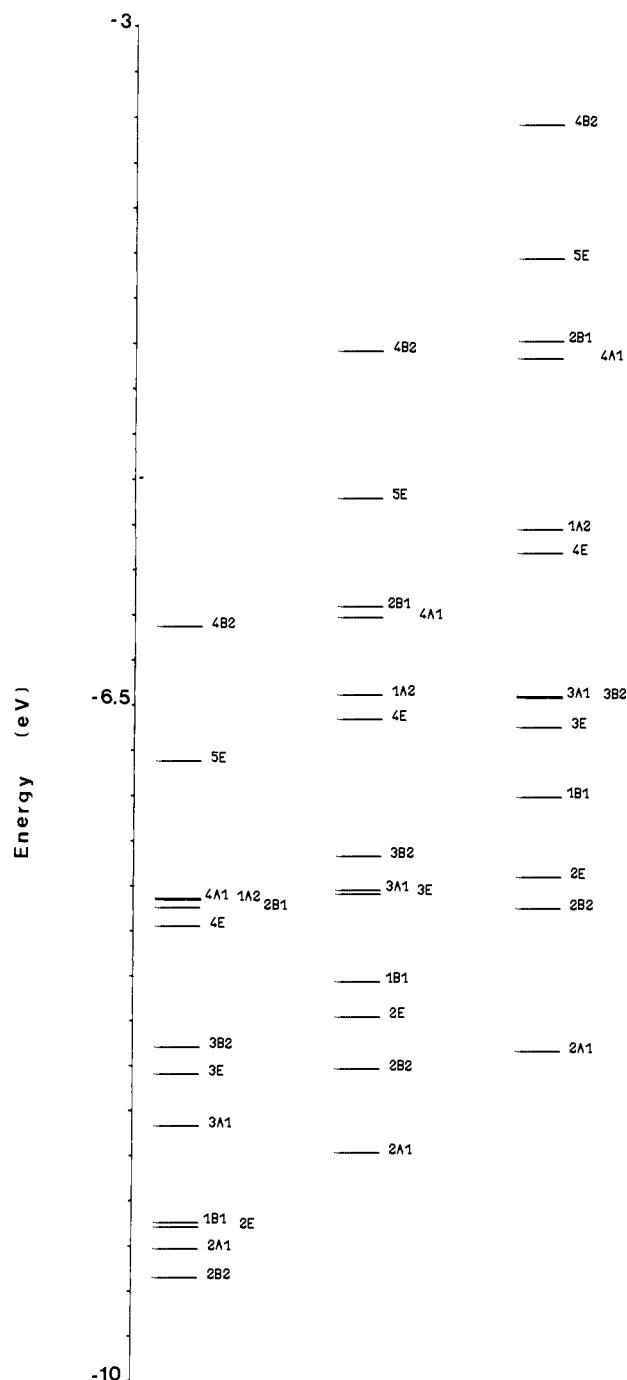


Figure 1. Highest occupied MO's of the pseudotetrahedral CuCl_4^{2-} ion. The MO's are labeled according to D_{2d} symmetry. From left to right the effect of varying the Cu-Cl overlap with $V = 0, 8,$ and 14% , respectively (see text).

For the inter and outer spheres an average value of the atomic values according to the valence electron number was used.

The outer sphere was tangent to the chlorine spheres, and the double negative charge was stabilized using a Watson sphere of opposite charge with the same radius as the outer sphere. In the standard calculations the partial wave expansion was limited at $l = 4$ for the outer sphere, $l = 2$ for copper, and $l = 1$ for chlorine. Atomic coordinates were given in a right-handed Cartesian reference system with x, y, z parallel to the S_4 axes of T_d symmetry, z bisecting the largest Cl-Cu-Cl angle.

For the square-planar CuCl_4^{2-} ion a D_{4h} symmetry was used, with Cu-Cl bond lengths of 226 pm and x and y axes parallel to the bond directions. The sphere radii were fixed at 137 pm for the copper and 160 pm for the chlorine, corresponding to 13% overlap volume of the chlorine sphere.

Table II. Calculated and Experimental Electronic Excitation Energies for Cs_2CuCl_4

transition	type of transition	calcd ^a	exptl ^{a,b}
$5e \rightarrow 4b_2$	d \rightarrow d	5 636	4 800 5 550
$4b_1 \rightarrow 4b_2$	d \rightarrow d	9 348	7 900
$4a_1 \rightarrow 4b_2$	d \rightarrow d	9 962	9 050
$1a_2 \rightarrow 4b_2$ (f) ^c	CT(L \rightarrow M)	30 358	23 000
$4e \rightarrow 4b_2$	CT(L \rightarrow M)	31 967	24 800
$3a_1 \rightarrow 4b_2$	CT(L \rightarrow M)	34 602	34 500
$3e \rightarrow 4b_2$	CT(L \rightarrow M)	35 794	29 000
$3b_2 \rightarrow 4b_2$ (f) ^c	CT(L \rightarrow M)	36 052	
$1b_1 \rightarrow 4b_2$ (f) ^c	CT(L \rightarrow M)	38 140	
$3b_2 \rightarrow 4b_2$ (f) ^c	CT(L \rightarrow M)	39 377	
$2e \rightarrow 4b_2$	CT(L \rightarrow M)	41 567	34 000
$2a_1 \rightarrow 4b_2$	CT(L \rightarrow M)	49 210	42 400

^a Value in cm^{-1} . ^b Experimental values from ref 32.

^c Transition forbidden in D_{2d} symmetry.

Pseudotetrahedral CuCl_4^{2-} Ground State

The electronic energy levels for the pseudotetrahedral CuCl_4^{2-} ion were calculated in the NSP formalism using the geometrical parameters described in the previous section allowing for different overlap, V , between the metal and ligand spheres. The energy levels and the corresponding charge distributions were found to be very sensitive to the overlap. In Figure 1 is shown the variation of the energies of the highest MO's as a function of V ; Figure 2 reports the wave-function contour of the HOMO for $V = 0$ and $V = 14\%$ of chlorine sphere volume, respectively. Our results for $V = 0$ are identical with those previously reported with a 2B_2 ground state.³⁰ In particular, we find that the highest occupied MO is mainly chlorine in nature, while the experimental data²² show that it is mainly metal in character, and that the energies of the $2b_1$ and $4a_1$ orbitals are very close and reversed as compared to the order of the levels found from the electronic transitions. Increasing V decreases the chlorine character of the highest occupied orbitals, as is shown by Figure 2, and gives the correct order for the energy levels. The calculated energy levels, together with the charge distribution, for $V = 14\%$ are shown in Table I; 14% overlap gave better agreement with experimental data.

It is well known that allowing for overlapping spheres reduces to some extent the crudest assumptions of the method.³¹ Overlaps in the range 15–25% seem to be the best compromise between the necessity of letting the spheres overlap and to avoid a too large overlap which makes the method inconsistent. It seems, therefore, that the conclusions,³⁰ according to which the MSX α method is the least consistent of the methods used in studying the copper halides, are not correct, based as they were only on the nonoverlapping sphere model. The four highest MO's are all mainly d metal in character but with substantial chlorine contributions showing that both σ - and π -bonding interactions are relevant in this complex. Another interesting feature is that although the metal 4p orbitals do mix into the two highest MO's, their percent charge distribution, 2%, is much smaller than was anticipated from the analysis of the EPR data.²²

The electronic transitions are compared with the experimental transitions in Table II. The agreement is fairly good for the d-d transitions, certainly better than that found with the tangent spheres calculations.

The energies of the charge-transfer transitions, all ligand-to-metal in nature, agree fairly well with experiment³² if they are calculated as orbital energy differences. If, on the other hand, the supposedly better suited transition-state formalism¹² is used, the first CT transition is predicted at $30\,000\text{ cm}^{-1}$, much higher than experimentally observed. Furthermore, we compute $3e > 3a_1$, while the reverse order was observed experimentally. Similar results were found also with ab initio calculations where the

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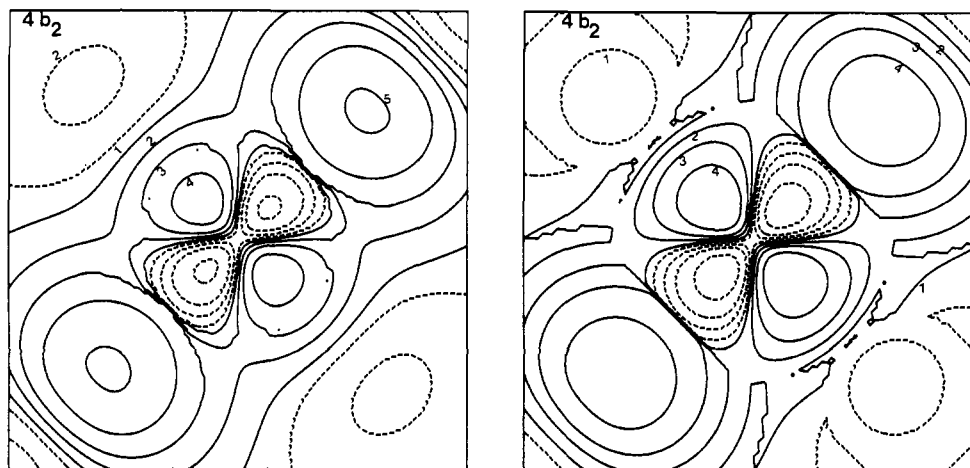


Figure 2. Contour map of the $4b_2$ highest occupied molecular orbital of pseudotetrahedral CuCl_4^{2-} ion. Left $V = 0\%$, right $V = 14\%$. The projection is on the xy plane at $z = 1.7 \text{ \AA}$. The contour values are: (1) 0.004, (2) 0.016, (3) 0.031, (4) 0.062, (5) 0.125 (electrons/bohr³)^{1/2}.

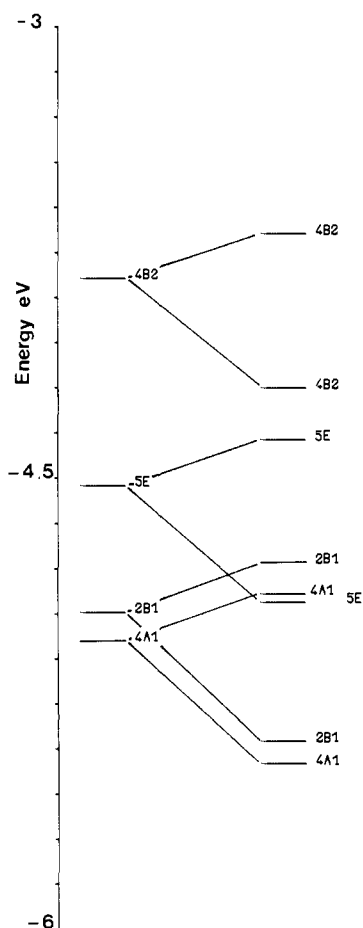


Figure 3. Highest valence energy levels for the pseudotetrahedral CuCl_4^{2-} ion in the NSP (left) and SP (right) formalism.

energies of the transitions were obtained as the difference between the orbital energies computed by independent SCF calculations on excited states and the ground-state, respectively.³³

The calculations were performed also in the SP formalism¹² with the $4b_2$ level accommodating the unpaired electron. In Figure 3 the highest valence energy levels in the SP and NSP formalism are shown. The predominantly copper levels show the largest splitting between their spin-up and spin-down components as expected, but the order of the levels is not changed compared with the NSP case.

Table III. Ground-State Energy Levels^a (eV) and Charge Distribution for Square-Planar CuCl_4^{2-} Ion^b

orbital	energy	charge distribution, %						
		Cu		Cl		inter sphere	outer sphere	
$3b_{2g}$	-3.165 9			56	2	35	4	3
$2b_{1g}$	-4.952 3			80		16	4	
$2e_g$	-4.999 5			73		24	4	
$3a_{1g}$	-5.278 1	4		87		3	6	
$1a_{2g}$	-5.298 1					94	5	1
$3e_u$	-5.781 1		2			90	6	2
$1b_{1u}$	-5.939 3					92	8	1
$1a_{2u}$	-6.670 4		2			84	13	1
$1e_g$	-6.697 4			27		66	7	1
$2e_u$	-7.335 0		3		97			
$1b_{1g}$	-7.495 0			19		72	8	1
$2b_{2g}$	-7.844 6			44		55		1
$2a_{1g}$	-8.751 6	16		8	3	71		2
$1b_{2g}$	-17.781 5			4	96			
$1e_u$	-17.974 2		3		97			
$1a_{1g}$	-18.445 3	4		1	93	1		
Cu 3p	-71.571		100					
Cu 3s	-111.08	100						
Cl 2p	-189.75					100		
Cl 2s	-248.18					100		
Cu 2p	-914.32		100					
Cu 2s	-1040.9	100						
Cl 1s	-2736.7					100		
Cu 1s	-8741.5	100						

^a The highest occupied level is $3b_{2g}$. ^b Non-spin-polarized calculation performed with 13% overlapping spheres.

Square-Planar CuCl_4^{2-} Ground State

The energies and the partial wave composition of the MO's, calculated with $V = 13\%$, are given in Table III. The value of $V = 13\%$ was chosen in order to have maximum copper chlorine overlap, avoiding chlorine-chlorine overlap. All the highest occupied MO's are mainly d-metal in character with the order $3a_{1g} < 2e_g < 2b_{1g} < 3b_{2g}$, the e_g and b_{1g} orbitals being separated by approximately 0.05 eV. The order of the levels is in agreement with previous $X\alpha$ calculations on square-planar CuCl_4^{2-} using tangent spheres.³⁰ On passing from the tetrahedral to the square-planar complex, the HOMO acquires larger chlorine character, and the same is true for MO's which are mainly metal d_{xz} and d_{yz} while for all the other metal orbitals the covalency decreases.

The assignment of the d-d transitions is not very well settled, also because genuine examples of pure square-planar CuCl_4^{2-} complexes are very rare.³⁴ For $(\text{PhCH}_2\text{CH}_2\text{NMeH}_2)_2\text{CuCl}_4$ the

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spectra at 77 K have been assigned^{35,36} with the $b_{2g} \rightarrow b_{1g}$ transitions at 12 500 cm^{-1} , $b_{2g} \rightarrow e_g$ at 14 300 cm^{-1} , and $b_{2g} \rightarrow a_{1g}$ at 16 900 cm^{-1} . If we calculate the energies of the transitions as the difference between the orbital energies, we find $3b_{2g} \rightarrow 2b_{1g}$ at 14 408 cm^{-1} , $3b_{2g} \rightarrow 2e_g$ at 14 790, and $3b_{2g} \rightarrow 3a_{1g}$ at 17 037 cm^{-1} in fair agreement with experiment. If, on the other hand, we use the transition-state formalism we find $3b_{2g} \rightarrow 2e_g$ 15 065 cm^{-1} , $3b_{2g} \rightarrow 2b_{1g}$ at 15 286 cm^{-1} , and $3b_{2g} \rightarrow 3a_{1g}$ at 19 502 cm^{-1} with a slightly worse fitting of the experimental transitions, and also reversing the order of the two lowest transitions.

Calculation of EPR Parameters

Our calculations were performed using the nonrelativistic formalism; therefore, it was possible to calculate g and A values only employing perturbation theory. In particular this approach is required to calculate the deviation of g from the free ion value and the orbit-dipolar contribution²¹ to the hyperfine splitting while the Fermi contact and dipolar contributions can be obtained directly.⁹

The deviation of g from the spin-only value is determined by second-order mixing of excited states through spin-orbit coupling.²¹

A convenient form of the perturbation Hamiltonian is

$$\hat{H} = \sum_{i=1}^N \sum_{M=1}^K \xi_M(r_i) l_i s_i$$

where K is the number of nuclei and N is the number of electrons. The radial functions $\xi_M(r_i)$ are of the form

$$\xi_M(r_i) = \frac{\alpha^2}{2r_i} \frac{dU(r)}{dr_i}$$

where α is the fine structure constant and the potential $U(r)$ is usually approximated by $-Z_M/r$ close to the nucleus so that

$$\xi_M(r_i) \propto r_i^{-3}$$

Different values of the average value of $\xi_M(r_i)$ will be obtained according to the orbitals which are taken into consideration. Therefore, strictly speaking, it is not possible to use the formulas evaluated for minimal basis set LCAO-MO calculations. However, for the present case, $\zeta_d = \langle \xi_M(r_i) \rangle$ is expected to be largely independent of the charge on the copper nucleus⁸ so that it seems safe to use the experimental value 828 cm^{-1} observed for Cu(II).³⁷

In the assumption that the terms containing ligand orbitals can be neglected, simple formulas can be obtained:

$$\Delta g_{\parallel} = \frac{-8\zeta_d \alpha_1^2 \beta_1^2}{\Delta E_{x^2-y^2}}$$

$$\Delta g_{\perp} = \frac{-2\zeta_d \alpha_1^2 \gamma_1^2}{\Delta E_{xz(yz)}}$$

where α_1 , β_1 , and γ_1 are the metal orbital coefficients in the predominantly d_{xy} , $d_{x^2-y^2}$, and d_{xz} MO. The squares of the MO coefficients have been usually identified as the fractional charge associated with the corresponding partial wave of the SCF-MS-X α orbital.^{8,14-16} In principle, there are several objections to the use of this identity. Beyond the fact that LCAO-MO and MS-X α models are quite different from each other and a formal equivalence between, say, the coefficients of the metal d orbitals in the two models can be established only in a loose sense, it must be remembered that the fractional charge in the SCF-MS-X α orbitals corresponds to gross rather than to net atomic orbital populations.

In order to check the validity of this assumption, we projected the highest occupied X α MO's on to LCAO MO's according to the procedure previously reported.^{38,39} The coefficients calculated

Table IV. Comparison between LCAO Coefficients and X α Eigenfunction for $4b_2$ Orbital of Cs_2CuCl_4

function	LCAO ^a	% ^b	X α	% ^b
$3d_{xy}^{\text{Cu}}$	0.813	60	0.782	63
$4p_{xy}^{\text{Cu}}$	0.011	0	0.150	2
$3s_{Cl}^a$	0.059	1	0.102	4
$3p_{xCl}^c$	0.172	10	0.127	7
$3p_{yCl}^c$	-0.172	10	-0.127	7
$3p_{zCl}^c$	-0.246	20	0.207	17

^a The λ and λ^2 coefficients are 1.01 and 1.02, respectively.

^b Percent character referred to the whole molecular orbital.

^c The chlorine contribution refer to the chlorine atom with coordinates 2.6917, -2.6917, 1.8075 using the reference system defined in the text.

in the two methods for the $4b_2$ orbital are shown in Table IV. Although they are sufficiently close to each other, there is a difference which may alter to some extent the calculated values of g .

The g values were calculated for the tetrahedral species using the LCAO coefficients as $\Delta g_{\parallel} = 0.39$ and $\Delta g_{\perp} = 0.13$ in fair agreement with the experimental values of 0.38 and 0.09, respectively.²² If the X α coefficients were directly used, one would find $\Delta g_{\parallel} = 0.34$ and $\Delta g_{\perp} = 0.12$.

Repeating the above calculations for the square-planar species one finds $\Delta g_{\parallel} = 0.21$ and $\Delta g_{\perp} = 0.05$ using LCAO-MO coefficients and $\Delta g_{\parallel} = 0.20$ and $\Delta g_{\perp} = 0.04$ using the X α calculations. The agreement with the experimental values ($g_{\parallel} = 2.24$, $g_{\perp} = 2.05$)^{34,40} is extremely good.

The hyperfine tensor, A , is given by the sum of the three contributions:²¹

$$A = A_F + A_D + A_L$$

where A_F is the Fermi contact contribution, A_D is the spin dipolar contribution, and A_L is the orbit dipolar contribution. A_F is given by the sum of two terms, one relative to the unpaired spin density determined by the unpaired electron in a s orbital and the second relative to the spin polarization of the inner s orbitals.^{41,42} The former can be obtained through both a NSP and a SP treatment and is given by

$$A_{F,1} = \frac{8\pi}{3} P |\psi(0)|_{\text{ns}}^2$$

where $P = g_e g_N \mu_B \mu_N$. In the present case this contribution is zero by symmetry. The second contribution can be calculated only through a SP treatment. It is given by

$$A_{F,2} = \frac{8\pi}{3} P [\rho \uparrow(0) - \rho \downarrow(0)]$$

where $\rho \uparrow(0)$ and $\rho \downarrow(0)$ are the spin-up and the spin-down densities on the nucleus, respectively.

The A_D term is determined by the dipolar interaction between the electron and the nuclear spin. The appropriate operator, for a given nucleus N , is

$$\hat{O}_N = \sum_i \frac{P}{r_i^3} \{ [3(r_i \cdot S^i)(r_i \cdot I_N) / r_i^2] - I_N \cdot S^i \}$$

where the sum is over all the electrons. The dipolar contribution involving electrons on different nuclei can be safely neglected.

The calculation of A_L , which can be performed using the operator

$$\hat{O}_L = \sum_i \frac{P}{r_i^3} I_N \cdot L^i$$

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has the same sort of problems found for g in that it has matrix elements different from zero only if spin-orbit coupling effects are taken into account. In the same approximation used for g the parallel and perpendicular components of A_L are given by:

$$A_{L\parallel} = P(\Delta g_{\parallel} + \frac{3}{7}\Delta g_{\perp})$$

$$A_{\parallel} = P'(^{11}/_{14}\Delta g_{\perp})$$

where $P' = P\langle r^{-3} \rangle$. In the NSP formalism the two components are readily calculated by averaging $\langle r^{-3} \rangle$ within the state corresponding to the unpaired electron. In the SP formalism the corresponding expressions would be much more complicated and it is better to neglect them at this stage.

In the actual calculation of A_F , A_D , and A_L we used two schemes: one in which no redistribution of the intersphere charge was performed and one in which it was partitioned among the spheres proportionally to the overlap surface and the radial function is analytically expanded to account for the extra charge.^{9,11} Essentially no difference was found in the values calculated in the two schemes.

In the calculation of $\langle r^{-3} \rangle$ the problem of the different form of the radial function inside and outside the atomic spheres is overcome by the steep dependence of r^{-3} on the distance, which makes only the contributions from the region close to the nucleus relevant.¹⁷ For the copper atom in the tetrahedral species $A_F = -53.31 \times 10^{-4} \text{ cm}^{-1}$; $A_{L\parallel} = 183.6 \times 10^{-4} \text{ cm}^{-1}$, $A_{L\perp} = 31.02 \times 10^{-4} \text{ cm}^{-1}$; $A_{D\parallel} = -150.09 \times 10^{-4} \text{ cm}^{-1}$, P' being $438.69 \times 10^{-4} \text{ cm}^{-1}$. Summing these contributions one finds $A_{\parallel} = -19.2 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = +52.76 \times 10^{-4} \text{ cm}^{-1}$.

A comparison with the experimental data²² is rather satisfactory since the values are $|A_{\parallel}| = 25 \times 10^{-4} \text{ cm}^{-1}$ and $|A_{\perp}| = 50 \times 10^{-4} \text{ cm}^{-1}$. However, some comments are in order. The experimental values were previously interpreted²² using the ligand field approach which requires

$$A_{\parallel} = P[-K - \frac{4}{7}\alpha_1^2 + \Delta g_{\parallel} + \frac{3}{7}\Delta g_{\perp}]$$

$$A_{\perp} = P[-K + \frac{3}{7}\alpha_1^2 + \frac{11}{14}\Delta g_{\perp}]$$

P' is used as a parameter, whose value is generally taken as $360 \times 10^{-4} \text{ cm}^{-1}$, without much justification.^{41,42} It is worth noting that our calculated value is slightly higher than that. From this expression A_F is evaluated as $A_F = \frac{1}{3}(A_{\parallel} + 2A_{\perp}) - \frac{1}{3}P'(\Delta g_{\parallel} + 2\Delta g_{\perp})$ and α_1^2 is determined accordingly. It is easy to be convinced that these calculated values depend dramatically on P' . Sharnoff²² with this approximation evaluated a very small A_D term, which he attributed to the mixing of metal p orbitals into the ground level, determined by the pseudotetrahedral symmetry. This view has already been criticized²³ on the basis of EPR spectra of other pseudotetrahedral complexes. The present $X\alpha$ calculations do not give any support to the d - p mixing, since the p mixing coefficient in the LCAO projection of the $X\alpha$ wave function is only 0.011.

It is apparent therefore that the main difference between the analysis of the experimental data with our $X\alpha$ results and those based on the ligand field model is mainly in the value of P' which is larger than that calculated for the free ion with the Hartree-Fock method⁴¹ and the Fermi contact term which is smaller than usually anticipated.⁴² Since this seems to be a common characteristics of $X\alpha$ calculations,^{17,45} we tried to verify also if relaxing some of the assumptions used in the calculation determined variations in the A values.

In particular we tried to improve the quality of the function within the copper sphere by using a larger basis, including spherical harmonic expansions with l values larger than 2. In Table V we show the values of A_F , $A_{D,zz}$, and P' calculated including partial

Table V. Variation of the A_F , $A_{D,zz}$, and P' for Cs_2CuCl_4 with l Values Used in the Copper Sphere

l	A_F^a	$A_{D,zz}^a$	P'^a
2	-53.31	-150.1	438.7
3	-58.68	-163.6	439.4
4	-59.49	-165.5	439.6
5	-59.54	-166.1	439.8

^a Values in $\text{cm}^{-1} \times 10^{-4}$.

waves up to $l = 5$ in the copper and outer spheres. The A_F value increases up to $-60 \times 10^{-4} \text{ cm}^{-1}$ while P' varies only slightly.

More complex formulas, which took into account also the chlorine orbitals, were also suggested.²³ Using these formulas the agreement of calculated and experimental g and A values is worse than reported above. It seems that in this case less sophisticated models reproduce better the experimental data, perhaps owing to casual compensation of errors.

The calculated values for ³⁵Cl hyperfine are: $A_F = +6.79 \times 10^{-4} \text{ cm}^{-1}$; $A_{D,zz} = 10.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{D,xx} = -5.37 \times 10^{-4} \text{ cm}^{-1}$, $A_{D,yy} = -5.45 \times 10^{-4} \text{ cm}^{-1}$. The x direction is perpendicular to the Cl-Cu-Cl symmetry plane, while z makes an angle of 20° with Cu-Cl bond direction. In this case no chlorine hyperfine splitting was observed. However, the calculated values appear to be comparable to the experimental values found in other pseudotetrahedral Cu_2Cl_2 chromophores ($A = \text{N, O}$).^{23,46}

On passing to the square-planar case an increase in the calculated A_F value for the copper ion is observed ($-62.3 \times 10^{-4} \text{ cm}^{-1}$). Also in this case a dependence of the calculated value on the wave expansion in the copper and outer spheres was checked. A_F passes to $-68.04 \times 10^{-4} \text{ cm}^{-1}$ when partial waves with l up to 5 are included. The $A_{D,zz}$ term yields -146×10^{-4} and $-157.3 \times 10^{-4} \text{ cm}^{-1}$ in the limited and in the extended basis, respectively, while P' is practically unchanged. The $A_{L\parallel}$ term is thus calculated as $103.2 \times 10^{-4} \text{ cm}^{-1}$ and $A_{L\perp}$ as $16.74 \times 10^{-4} \text{ cm}^{-1}$. The copper hyperfine values are therefore $A_{\parallel} = -105.6 \times 10^{-4}$ and $-122.14 \times 10^{-4} \text{ cm}^{-1}$; $A_{\perp} = 27.7 \times 10^{-4}$ and $38.3 \times 10^{-4} \text{ cm}^{-1}$, respectively. On passing from the tetrahedral to the square-planar species, therefore, one calculates a larger A_{\parallel} and a smaller A_{\perp} as expected.²¹ The difference is given by both a smaller A_D term and a larger A_F term calculated for the square-planar species.

Experimental data are available only for copper-doped K_2PdCl_4 ,⁴⁰ where $A_{\parallel} = 163.6 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 34.5 \times 10^{-4} \text{ cm}^{-1}$. The agreement is good for A_{\perp} , but it is only fair for A_{\parallel} , where we calculate a value which is too small by 25%. It must be mentioned also that for this complex the electronic transitions⁴⁷ have been reported to be at lower energies than those reported for $(\text{PhCH}_2\text{CH}_2\text{NMeH}_2)_2\text{CuCl}_4$.^{35,36} The fact that copper enters as substitutional impurity in the palladium lattice leaves some doubt as to the actual copper-chlorine bond lengths. For the same compound the chlorine hyperfine tensor was reported: $A_{\parallel}^{\text{Cl}} = 23.3 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp}^{\text{Cl}} = 5.3 \times 10^{-4} \text{ cm}^{-1}$. Our calculated values are 24.8×10^{-4} and $5.68 \times 10^{-4} \text{ cm}^{-1}$, respectively, resulting from $A_F^{\text{Cl}} = 12.06 \times 10^{-4} \text{ cm}^{-1}$, $A_{D\parallel}^{\text{Cl}} = -6.38 \times 10^{-4} \text{ cm}^{-1}$.

Conclusions

The MS- $X\alpha$ model has allowed us to calculate with generally fair agreement with experimental data the energies of the electronic transitions, the g and A tensors in tetrahedral and square-planar CuCl_4^{2-} complexes. In particular, the low A_{\parallel} values observed in the tetrahedral species has been justified by a relatively small Fermi contact (smaller than in the corresponding square-planar complex) and by a fairly large P' value (which in this case, however, is very similar to that calculated for the square-planar case) which makes the A_L term more important than was usually anticipated in simplified treatments, where P' is assumed as a parameter and taken to be equal to $360 \times 10^{-4} \text{ cm}^{-1}$. Previous conclusions attributing the low A_{\parallel} values to metal $4p$ mixing into the ground state, therefore, do not find any justification on the

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present calculations, while covalency effects seem to play a major role. This explanation would be also in line with the low A_{II} values observed in blue copper proteins where sulfur donor atoms are known to be present in the copper(II) coordination sphere.⁴⁸⁻⁵⁰

It seems, therefore, that MS-X α is indeed able to describe the spectral properties of transition metal complexes, in a not too time-consuming way. Allowing for overlapping spheres appears to be absolutely necessary to improve the agreement with experimental data, and also the inclusion of higher order spherical harmonics may have a positive influence on the calculated values. However, we did not find improvement better than 10% by including harmonics up to $l = 5$.

At the moment the main limitations for the calculation of the EPR parameters is that the spin-orbit-dependent terms are available only through a perturbation procedure while it would be desirable to use a complete relativistic approach. This does not seem to be possible, in short, but less crude approaches than

the one we also used should be attempted.

Other possible improvements of X α model might be attempted following suggestions which were put forward from the analysis of Fermi contact hyperfine constants in atoms and ions. It was shown for ions, that, the MS-X α model can yield results comparable with those obtained using the HF method either changing the form of the exchange potential or using different α values for different spins.^{45,51-53} While the first type of correction cannot be easily applied to solids, the second might in principle be used. We tried this approach in the present calculation but did not find any substantial improvement, so that we preferred to stay with the traditional α values.

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The 1,2 Hydrogen Shift as an Accompaniment to Ring Closure and Opening: Ab Initio MO Study of Thermal Rearrangements on the C₂H₃N Potential Energy Hypersurface

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Abstract: Ab initio electronic structure calculations employing both 4-31G and DZP (double- ζ plus polarization) basis sets have been made for equilibrium geometries and transition states involved in thermal rearrangements on the C₂H₃N potential energy hypersurface. The principal rearrangements studied are those involving vinyl nitrene, 2*H*-azirine, methyl isocyanide, and acetonitrile. From the computed energies of stationary points and from the pathways connecting these points, several conclusions are drawn. First, singlet vinyl nitrene, although possessing a nonplanar equilibrium geometry, can undergo a ring closure with only a modest activation energy to form 2*H*-azirine. Second, the combined 1,2 hydrogen shift and ring opening required to form acetonitrile from 2*H*-azirine proceeds optimally but indirectly via methyl isocyanide as an intermediate. Thus hydrogen transfer precedes C-N bond breakage, necessitating a subsequent ring closure and reopening. Third, although no direct pathway leading from 2*H*-azirine to acetonitrile was located, there is a higher energy but direct pathway leading to acetonitrile from an excited singlet state of vinyl nitrene.

Introduction

The C₂H₃N molecular system exhibits a number of stable structures (local energy minima) including 1*H*-azirine, 2*H*-azirine, ketenimine, methyl isocyanide, and acetonitrile (methyl cyanide). The rearrangement of methyl isocyanide to acetonitrile has been the subject of numerous theoretical and experimental investigations,¹⁻⁶ and is thus the best understood rearrangement of C₂H₃N. Considerable experimental and theoretical attention has also been given to the photochemical rearrangements of 2*H*-azirine and of substituted azirines.⁷⁻¹² Some related molecular systems which exhibit numerous rearrangements¹³ include the isoelectronic CHNO system,^{14,15} which has been the subject of several theoretical investigations, and the C₆H₃N system,^{16,17} which includes the species phenyl nitrene and cyanocyclopentadiene. The thermal

rearrangements in the latter system resemble those in the smaller C₂H₃N system which is the subject of our present investigation.

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