Ground State Wave Function and Superexchange Interaction in $CuCl_2 \cdot 2NC_5H_5$

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A model of superexchange, which takes into account the contributions of the polar states, is applied to the case of $CuCl_2 \cdot 2\,NC_5H_5$. As pointed out in a preceding paper, the experimental exchange constant J_{eff} can be fitted in a reasonable range of parameters of the ground state wave function, which, on the other hand, is tested by means of ESR experimental data. The results are compared with those obtained for $CuCl_2 \cdot 2\,H_2O$ and the approximations introduced are discussed and justified.

Introduction

Several authors [1–4] have studied, in recent years, the magnetic properties of Copper Dichloride Dipyridine (CDP), which is a well known example of an $S = 1/2$ antiferromagnetic Heisenberg linear chain.

In fact, the exchange hamiltonian for CDP is usually assumed as

$$\mathscr{H}_{\text{ex}} = -\,2\,J_{\text{eff}} \sum_{i=1}^{N} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}\,, \tag{1}$$

where the value of the intrachain effective exchange constant is $J_{\text{eff}} = -9.3\ \text{cm}^{-1}$, as deduced from susceptibility and specific heat measurements [3, 4], and from neutron scattering experiments on deuterated CDP [5].

This antiferromagnetic coupling is ascribed to a superexchange interaction via the chlorine ions, which are the "bridging" ligands of two adjacent units in the chain [2, 6] (Figure 1). Actually, this is the most relevant magnetic interaction in CDP, because the interchain exchange constant, as inferred from the ordering temperature T_N [3] and from ESR linewidth studies [1], is about two orders of magnitude smaller than the intrachain constant J_{eff}.

In this work, we give an interpretation of the superexchange mechanism by means of a suitable LCAO-MO ground state wave function of the single complex ion in the chain, built up taking into account the available ESR data.

In a previous paper [7], hereafter referred as I, one of us (G.A.) has proposed a formalism by which it is possible to obtain quantitative information about the most important contributions to J_{eff} for a pair of $S = 1/2$ complex ions. In particular, this theoretical approach takes into account the polar states corrections to J_{eff}, which may become important when the pure Heitler-London contributions tend to balance each other to give a net exchange interaction of the same order of the ionic terms. This was actually the case of $CuCl_2 \cdot 2\,H_2O$ [7], which is, on the other hand, very similar to CDP, from the point of view of the magnetic behaviour. In fact, the most relevant magnetic interaction in $CuCl_2 \cdot 2\,H_2O$ is an antiferromagnetic

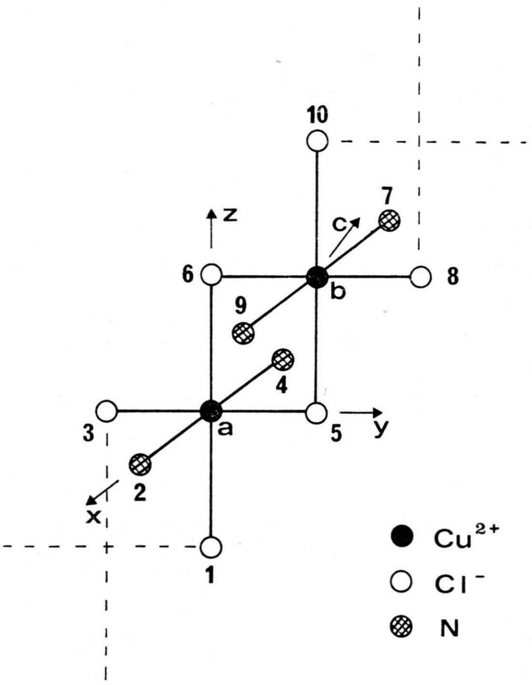

Fig. 1. A segment of a linear chain parallel to the c axis in CDP.

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coupling, with $J_{\mathrm{eff}} = -4.71\ \mathrm{cm}^{-1}$ [8], along the chain of $S = 1/2$ Cu^{2+} complex ions lying on the c-axis. Moreover, the chain structure is practically the same in CDP and $CuCl_2 \cdot 2\,H_2O$ (Fig. 1), differing only in the bond lengths and in the nature of the ligands on the x-axis (N in CDP, O in $CuCl_2 \cdot 2\,H_2O$). It must be noted that, in CDP, the out-of-plane Cu-Cl bond is not exactly orthogonal to the coordination plane (the deviation is $\sim 2°$ [6]). However, we have assumed an orthogonal reference frame, to avoid unnecessary complications: in fact, the inherent error is far within the approximations used.

Therefore we have applied the theoretical treatment of I to the case of CDP, bearing in mind that, since we are concerned with the detailed calculation of the superexchange interaction within a chain, it is possible to deal with a single pair of adjacent complex ions only [9].

On the other hand, in the present case of CDP no information was available about the hyperfine tensor **A**, the knowledge of which is useful to determine the parameters of the ground state wave function. This was due to the difficulty to find an isostructural diluent crystal and to the fact that liquid solvents strongly modify the surrounding of the Cu^{2+} ion. Therefore we have considered A_z as a parameter and carried out the calculations for different assumed values of A_z. We have chosen a range of values for A_z between $-190 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $-110 \times 10^{-4}\ \mathrm{cm}^{-1}$, which are typical values for a Cu^{2+} ion with a surrounding, in the coordination plane, of four nitrogen and four chlorine ions, respectively.

In Sect. 1, the proper g-tensor for the single unit in the CDP chain is calculated from the experimental mean tensor, and then some covalency coefficients of the ground state wave function are determined by fitting the ESR data.

In Sect. 2, the theoretical formalism for the evaluation of J_{eff} is briefly recalled and applied to the case of CDP.

In Sect. 3, the numerical results are given and discussed. The most important molecular integrals and parameters used are listed in the Appendix.

1. Ground State Wave Function and g-Tensor

The ground state wave function for a single distorted octahedron in the CDP chain can be written as (see I)

$$\psi^a_{0\sigma} = \alpha\, d^a_{x^2-y^2} + \xi\, d^a_{z^2} - \frac{\gamma}{\sqrt{2}}\left(-\sigma_x{}^2 + \sigma_x{}^4\right) - \frac{\delta}{\sqrt{2}}\left(\sigma_y{}^5 - \sigma_y{}^3\right) - \sqrt{2}\,\varepsilon\left(-\sigma_z{}^6 + \sigma_z{}^1\right) \qquad (2\mathrm{a})$$

with

$$\sigma^i = n\,p^i \mp (1 - n^2)^{1/2} s^i\,, \qquad (2\mathrm{b})$$

where the upper sign refers to ligands on the positive x, y and z axes and n is the hybridization parameter, for which the usual value $(2/3)^{1/2}$ has been taken [7, 10].

The form of the function (2a) derives from the assumption of D_{2h} symmetry for the CDP complex ion, as evident from the presence of a d_{z^2} mixing [11]. This is in disagreement with the previous assumptions [1, 3] of an axial g-tensor. On the other hand, such mixing is necessary to have the right connexion in the superexchange path. Moreover, an accurate decomposition of the mean experimental g-tensor allows to point out the rombic character of the coordination plane. In fact, assuming the bond directions as the principal axes of the single ion g-tensor, we can evaluate the principal values g_x, g_y and g_z in the usual way [11], from the relations

$$g_i{}^2 = g_x{}^2 \cos^2 \widehat{g_i x} + g_y{}^2 \cos^2 \widehat{g_i y} + g_z{}^2 \cos^2 \widehat{g_i z}\,, \quad i = 1, 2, 3\,. \qquad (3)$$

The directions of the principal axes and the principal values g_1, g_2 and g_3 of the experimental mean tensor are given in Tab. V of Ref. [3]. From these data, we obtain

$$g_x = 2.036, \quad g_y = 2.075, \quad g_z = 2.252\,. \qquad (4)$$

Actually, as already said in the preceding Section, the out-of-plane Cu-Cl bond (that is the assumed g_z direction) is not exactly perpendicular to the x-y plane, but this introduces an uncertainty on the values (4) smaller than the experimental one on g_1, g_2 and g_3, and therefore negligible. It is worthy to note that our g_z and mean value of g_x and g_y are in substantial agreement with the values of $g_{\parallel}$ and $g_{\perp}$ previously calculated [3].

The coefficients α and ξ, appearing in the wave function (2) can be evaluated by means of a best fit procedure on the g principal values, for fixed values of the hyperfine parameter A_z in the quoted range ($-190 \times 10^{-4} \div -110 \times 10^{-4}\ \mathrm{cm}^{-1}$). To carry out the calculations we have used a simplified form of the general expressions (5a, b, c, f) of Ref. [11], obtained for a planar complex with rombic symmetry. In fact, assuming a perturbative d_{z^2} mixing, as in (2), the contributions to the expressions of the g and A components from the out-of-plane ligands are of higher order and therefore the terms in ε can be dropped. Moreover, the parameters γ and δ have a little influence on the g values (whilst they are essential, together with ε, to account for J_{eff}), so that we have modified the quoted expressions introducing a mean in-plane covalency coefficient α' and a mean overlap integral S_{xy}. In such a way, we are left with a greater flexibility as regards the values of the individual parameters γ and δ, in the best fit procedure for J_{eff}. This approximation is justified also by the fact that the in-plane g anisotropy is mostly due to the parameter ξ, that is to the d_{z^2} mixing in the ground state. Finally, we have neglected the small $T(n)$ contributions to the g components, because their effect may be included in the uncertainty of the crystal field splittings.

Therefore, we have used the reduced expressions

$$g_x = 2.0023 - \frac{2\lambda_0 \beta'^2}{\Delta yz} \cdot [\alpha + \sqrt{3}\,\xi][\alpha + \sqrt{3}\,\xi - 2\alpha' S_{xy}]\,, \tag{5a}$$

$$g_y = 2.0023 - \frac{2\lambda_0 \beta^2}{\Delta xz} \cdot [\alpha - \sqrt{3}\,\xi][\alpha - \sqrt{3}\,\xi - 2\alpha' S_{xy}]\,, \tag{5b}$$

$$g_z = 2.0023 - \frac{8\lambda_0 \beta_1^2}{\Delta xy}\,\alpha[\alpha - 2\alpha' S_{xy}]\,, \tag{5c}$$

$$\begin{aligned} A_z = P\Big\{ &- \alpha^2\left(\frac{4}{7} + k_0\right) + \xi^2\left(\frac{4}{7} - k_0\right) - \frac{8\lambda_0}{\Delta xy}\,\alpha^2\beta_1^2 - \frac{1}{7}\frac{\lambda_0}{\Delta xz}(\alpha - \sqrt{3}\,\xi) \\ &\cdot (3\alpha + \sqrt{3}\,\xi)\,\beta^2 - \frac{1}{7}\frac{\lambda_0}{\Delta yz} \\ &\cdot (\alpha + \sqrt{3}\,\xi)(3\alpha - \sqrt{3}\,\xi)\,\beta'^2 \Big\}\,, \end{aligned} \tag{5d}$$

and the ground state wave function normalization condition

$$\alpha^2 + \xi^2 + 2\alpha'^2 - 4\alpha\alpha' S_{xy} = 1\,, \tag{5e}$$

where for λ_0, P and k_0, which have the usual meaning, we have assumed the values $-828\ \text{cm}^{-1}$, $0.036\ \text{cm}^{-1}$ and 0.43 respectively [11, 12]. The parameters β_1, β and β' are the covalency coefficients appearing in the expressions of the $\psi_{B_{1g}}$, $\psi_{B_{2g}}$ and $\psi_{B_{3g}}$ excited states respectively [11].

S_{xy} is defined as [13]

$$S_{xy} = \tfrac{1}{2}(S_{24} + S_{53}) \tag{6a}$$

with

$$S_{24} = \sqrt{2}\,\langle d_{x^2-y^2} | -\sigma_x{}^2 \rangle\,, \tag{6b}$$

$$S_{53} = \sqrt{2}\,\langle d_{x^2-y^2} | \sigma_y{}^5 \rangle\,. \tag{6c}$$

For the optical splitting Δxy, Δxz and Δyz, we have assumed, from the available optical data [14], the common value $14300\ \text{cm}^{-1}$. On the other hand, taking into account that such splittings appear in (5) in the ratios of the type β^2/Δ^2 only, we can include a possible spread of the energies of the π states in the covalency parameters. Therefore, we have not taken the fixed values $\beta' = \beta = 1$ as in [11], but the condition $\beta' = \beta$ only. This is reasonable, for the two more excited states, and moreover allows to obtain a very good fitting of the g-values from Eqs. (5) with the only unknowns α, ξ, α', β_1 and β. This fitting has been performed numerically in a self-consistent way [11, 12], taking into account that α and β_1 are well defined from the values of A_z and g_z, while ξ and β are the preponderant parameters in the fitting of the in-plane g anisotropy $(g_y - g_x)$ and mean value $(g_y + g_x)/2$ respectively, and α' can be deduced from the normalization condition (5e).

The values of the parameters, obtained in this way for every fixed value of A_z, are listed in Table 1. We note that ξ, although slowly increasing in modulus with A_z, is of the same order as in $CuCl_2 \cdot 2\,H_2O$ (where $\xi = -0.064$), in agreement with the similar in-plane g anisotropy in the two compounds. The parameter α increases, following A_z, as evident from Eq. (5d), while α' simultaneously decreases, owing to the condition (5e). As regards β_1 and β, one can see that it is always $\beta_1 > \beta$. This is not unusual and can be understood taking into account that the experimental ratio

Table 1. Values of the parameters α, ξ, α', β_1 and β obtained by a best fit procedure from Eqs. (5), for fixed values of A_z (in cm^{-1}).

$A_z \cdot 10^4$	α	ξ	α'	β_1	β
− 110	0.781	− 0.0807	0.474	0.996	0.903
− 130	0.814	− 0.0845	0.445	0.950	0.862
− 150	0.845	− 0.0884	0.413	0.909	0.825
− 170	0.875	− 0.0921	0.377	0.873	0.792
− 190	0.905	− 0.0957	0.337	0.840	0.762

between the spin-orbit corrections to g_z and to $(g_y+g_x)/2$, as from (4), is greater than 4 and observing that the same ratio, as given by (5a, b, c), is about $4\beta_1{}^2/\beta^2$. Therefore, we obtain a greater covalency for d_{xz} and d_{yz} π-states or, alternatively, a greater energy shift for these states than for d_{xy} state.

The small values of β_1 and β (particularly of β) and the relatively large value of $|\xi|$, in correspondence to the maximum value of A_z, show that the fit of the ESR data is more critical in this case. This suggests that the value of A_z in CDP can not be very different from that of $CuCl_2 \cdot 2\,H_2O$.

2. Numerical Calculation of J_{eff}

The expression for J_{eff}, in the limit of small overlap between the two interacting complex ions, is, as given in I,

$$J_{\text{eff}} = J_{\text{eff}}^{\text{H-L}} + \Delta J\,, \tag{7a}$$

where

$$J_{\text{eff}}^{\text{H-L}} = J_2 - C_2\,S^2 + J_1 - C_1\,S^2 \tag{7b}$$

is the effective exchange constant for the Heitler-London approach, and

$$\Delta J = -\frac{2}{F_2 - C_2}\,[C_2\,S - M_2 + \Delta_0(1+S^2)]^2 \tag{7c}$$

is the correction to $J_{\text{eff}}^{\text{H-L}}$, due to the presence of ionic configurations. Δ_0 represents half the splitting between the lowest bonding and antibonding states of the dimeric system, that is

$$\Delta_0 = \frac{1}{2}\left[\frac{(C_1 - J_1)\,S}{1-S^2} - \frac{J_1}{S}\right]. \tag{8}$$

Equations (7) and (8) contain the usual one- and two-body molecular integrals, which we rewrite for convenience

$$F_2 = \langle\psi_0{}^a(1)\,\psi_0{}^a(2)|\,r_{12}^{-1}\,|\psi_0{}^a(1)\,\psi_0{}^a(2)\rangle\,, \tag{9a}$$

$$M_2 = \langle\psi_0{}^a(1)\,\psi_0{}^a(2)|\,r_{12}^{-1}\,|\psi_0{}^a(1)\,\psi_0{}^b(2)\rangle\,, \tag{9b}$$

$$J_2 = \langle\psi_0{}^a(1)\,\psi_0{}^b(2)|\,r_{12}^{-1}\,|\psi_0{}^a(2)\,\psi_0{}^b(1)\rangle\,, \tag{9c}$$

$$C_2 = \langle\psi_0{}^a(1)\,\psi_0{}^b(2)|\,r_{12}^{-1}\,|\psi_0{}^a(1)\,\psi_0{}^b(2)\rangle\,, \tag{9d}$$

$$S = \langle\psi_0{}^a(1)\,|\,\psi_0{}^b(1)\rangle\,, \tag{9e}$$

$$J_1 = 2S\,\langle\psi_0{}^a(1)|\left[V^a_{\text{Cu}}(1) + \sum_{\{a\}}{}' V^a_{\text{lig}}(1)\right]|\psi_0{}^b(1)\rangle\,, \tag{9f}$$

$$C_1 = 2\,\langle\psi_0{}^b(1)|\left[V^a_{\text{Cu}}(1) + \sum_{\{a\}}{}' V^a_{\text{lig}}(1)\right]|\psi_0{}^b(1)\rangle\,, \tag{9g}$$

where $\psi_0{}^a$ is the single unit ground state wave function (2), (1) and (2) is a short notation for $(\boldsymbol{r}_1)$ and $(\boldsymbol{r}_2)$ and the sum for the one-body potential is extended to all the ligands of the unit a, except for those which are common to the two units.

In the LCAO-MO scheme, the triplet state is identical to that of the pure Heitler-London treatment, while the lowest singlet, which is shifted in energy by $2\,J_{\text{eff}}$, is a combination of the Heitler-London one and of the polar states wavefunction, that is

$$\psi^-(1,2) = b^-_{\text{HL}}\,\psi_{\text{HL}}(1,2) + b^-_{\text{PS}}\,\psi_{\text{PS}}(1,2)\,, \tag{10}$$

where, a part from the usual normalized singlet spin term,

$$\psi_{\text{HL}}(1,2) = \frac{1}{\sqrt{2(1+S^2)}} \cdot [\psi_0{}^a(1)\,\psi_0{}^b(2) + \psi_0{}^b(1)\,\psi_0{}^a(2)]\,, \tag{11a}$$

$$\psi_{\text{PS}}(1,2) = \frac{1}{\sqrt{2(1+S^2)}} \cdot [\psi_0{}^a(1)\,\psi_0{}^a(2) + \psi_0{}^b(1)\,\psi_0{}^b(2)]\,. \tag{11b}$$

The coefficients b^-_{HL} and b^-_{PS} were defined in I, and the superscript means that $\psi^-(1,2)$ is the eigenfunction belonging to the eigenvalue E^- of the 2×2 non-diagonal block of the energy matrix. It results that the polar states contribution is smaller the greater is the energy difference $(F_2 - C_2)/(1-S^2)$, between the lowest and the first excited singlets, compared with $2\,J_{\text{eff}}$. It will be shown that $\psi^-(1,2)$ is practically a Heitler-London singlet, and nevertheless the little mixing of polar states is foundamental to obtain a correct value for J_{eff}.

As in I and Ref. [10], some assumptions have been made to calculate the integrals (9). First of all, V^a_{Cu} and V^a_{lig} have been approximated as $-Z^{\text{Cu}}_{\text{eff}}/r_a$ and $-Z^{\text{lig}}_{\text{eff}}/r_{\text{lig}}$ respectively. Moreover, the pure ionic values $Z^{\text{Cu}}_{\text{eff}} = +3$, $Z^{\text{Cl}}_{\text{eff}} = -1$ and $Z^{\text{N}}_{\text{eff}} = 0$ have been assumed for the effective charges. In fact, as pointed out in I, the value of J_{eff} is not very sensitive to $Z^{\text{lig}}_{\text{eff}}$, while its dependence on $Z^{\text{Cu}}_{\text{eff}}$ is stronger. On the other hand, since in the calculation of the molecular integrals we take into account all the contributions deriving from the electron delocalization, we can avoid to deal with screening factors for $Z^{\text{Cu}}_{\text{eff}}$, due to the presence of the ligands [10, 15]. The reliability of the results obtained with this assumption supports once more the picture of a pair of complex Cu^{2+} ions as a sort of diatomic molecule, in which delocalization effects are properly taken into account.

As usual, the calculation of molecular integrals has been carried out in the charge cloud approximation scheme for the multi-center contributions [16], while the most important one- and two-center integrals were directly calculated by means of computer programs [17].

In particular, following Ref. [16], the pure ionic Cu^+ value 0.942 a.u. has been taken for F_2, while for M_2 we have used the value $2S/R_{ab}$ (see I), taking into account that in these cases to disregard the electron delocalization and to use the charge cloud approximation leads to an inaccuracy of few percent only [16].

The details for the computation of S, J_1, J_2, C_1 and C_2 are given in I and in [10]. The only difference is, in the present case, a more complete evaluation of the largest two-center integrals appearing in J_2, by means of the computer program QCPE 277 [18], translated for the CDC 7600 system. Some of these integrals are listed in the Appendix, together with the one-center exchange integrals, which account for at least 2/3 of the J_2 value. The nuclear attraction integrals, which are the most important contributions to the resonance integral appearing in the expression of J_1, are also listed in the Appendix. As regards C_1 and C_2, their calculation is accurate enough using the charge cloud approximation and taking into account the electron delocalization. However, the values calculated in this way are not very different from those obtained following the point charge approximation.

3. Results and Discussion

The results of the calculations are summarized in Fig. 2, where the curves connecting the points of the plane δ, $|\varepsilon|$ for which one obtains exactly the experimental value of J_{eff} are plotted, for $|A_z|$ increasing from the right to the left [19]. The dashed curves are the loci of the points for which $\gamma = \delta$, so that $\delta > \gamma$ at the right of each curve. To have a direct comparison with the case of $CuCl_2 \cdot 2\,H_2O$, $J_{\mathrm{eff}}^{\mathrm{HL}}$, ΔJ and S are given in Table 2a, for some points of the curve corresponding to $A_z = -130 \times 10^{-4}\ \mathrm{cm}^{-1}$, together with the values of the terms appearing in (7b). As usual, we have chosen these points so that the pairs of δ and ε values are consistent with the previous fitting of the ESR data and with the perturbative character of our theory. In particular, $|\varepsilon|$ can be neither greater than $|\xi|$, nor too small, in which case the superexchange interaction would be effective for unreasonable values of δ only and moreover the computational approximations, quoted in the preceding Section, would become critical. For example, as $|\varepsilon|$ decreases, according to Table 2a, the contribution to J_2 due to the one-center integrals on the common ligands goes from $\sim 82\%$ to $\sim 67\%$ of the total, owing to the less important role of the out-of-plane ligands in the exchange mechanism. As regards the consistency with ESR data, one can note, from Table 2b, that the g values calculated with the formulas (5a, b, c), extended to the case $\gamma \neq \delta$ and $S_{24} \neq S_{53}$, may vary within $1^0/_{00}$ only with respect

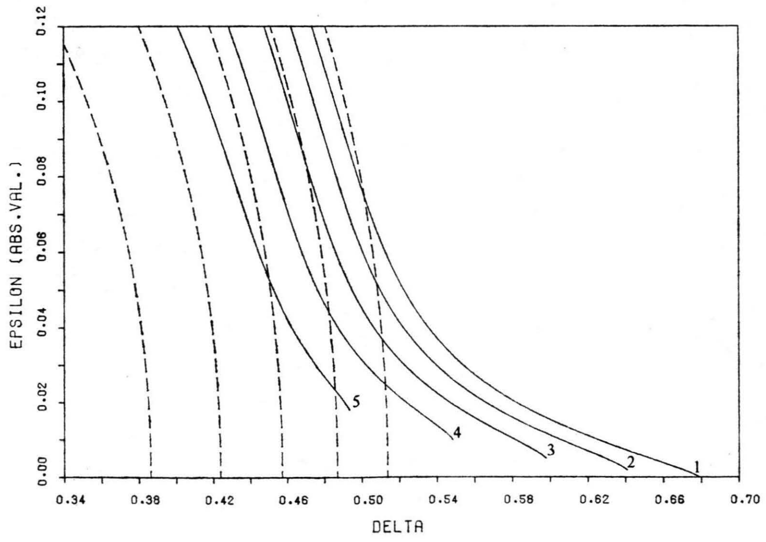

Fig. 2. Level curves in the δ, $|\varepsilon|$ plane, connecting points for which $J_{\mathrm{eff}} = -9.3\ \mathrm{cm}^{-1}$, each one for a fixed value of A_z. Numbers from 1 to 5 refers to $A_z = (-110, -130, -150, -170, -190) \times 10^{-4}\ \mathrm{cm}^{-1}$ respectively. The dashed curves are the loci of points for which $\gamma = \delta$ for the quoted values of A_z and in the same order. In the region at the right of each dashed curve $\delta > \gamma$ for the corresponding value of A_z.

Table 2a. Values of $J_{\mathrm{eff}}^{\mathrm{H-L}}$ and ΔJ (in cm^{-1}), of overlap S and of the various contributions to $J_{\mathrm{eff}}^{\mathrm{H-L}}$, for five points of curve 2 in Fig. 2, corresponding to $A_z = -130 \cdot 10^{-4}$ cm^{-1}. The related covalency parameters are shown.

δ	ε	γ	$S \cdot 10^2$	J_1	J_2	$-C_1 S^2$	$-C_2 S^2$	$J_{\mathrm{eff}}^{\mathrm{H-L}}$	ΔJ
0.500	-0.0605	0.453	1.627	-74.45	59.74	24.67	-7.73	2.23	-11.53
0.520	-0.0413	0.439	1.188	-41.58	30.79	13.11	-4.10	-1.78	-7.52
0.540	-0.0297	0.416	0.932	-26.89	17.74	8.07	-2.52	-3.60	-5.70
0.560	-0.0218	0.387	0.767	-19.22	10.90	5.48	-1.71	-4.55	-4.75
0.580	-0.0159	0.352	0.653	-14.71	6.86	4.00	-1.24	-5.09	-4.21

Table 2b. Values of M_2, $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm^{-1}), of the coefficient $b_{\overline{\mathrm{PS}}}$ and the calculated g components in the same cases as in Table 2a.

δ	ε	M_2	$2\Delta_0$	$\frac{F_2 - C_2}{1 - S^2}$	$b_{\overline{\mathrm{PS}}} \cdot 10^2$	g_x	g_y	g_z
0.500	-0.0605	994.4	3061.1	177627.0	1.1366	2.0362	2.0739	2.2502
0.520	-0.0413	726.4	2395.8	177745.1	0.9197	2.0361	2.0742	2.2502
0.540	-0.0297	569.4	2020.8	177765.4	0.8005	2.0359	2.0746	2.2505
0.560	-0.0218	468.7	1791.5	177750.5	0.7310	2.0357	2.0750	2.2510
0.580	-0.0159	399.0	1640.7	177697.6	0.6880	2.0355	2.0756	2.2517

to the values (4), confirming the hypothesis made in Sect. 1 on the origin of the **g** in-plane anisotropy.

It appears from Fig. 2 that the correct value of J_{eff} can not be obtained unless $\delta > \gamma$ (except for the curve corresponding to the extreme value $A_z = -110 \cdot 10^{-4}$ cm^{-1}, if $|\varepsilon| > 0.075$). This is in agreement with the case of $CuCl_2 \cdot 2\,H_2O$, but the condition is more restrictive for CDP, owing to the greater negative value of J_{eff}. In fact, it may be noted (see also Table 3a of I) that assuming similar values of ε and γ both for $CuCl_2 \cdot 2\,H_2O$ and CDP, the correct value of J_{eff} for CDP is obtained for larger values of δ, as a consequence of a smaller α. This corresponds to a larger overlap S in CDP, in agreement with a stronger antiferromagnetic coupling of the unpaired spins [20, 21].

In this regard, it appears from Table 2b that the splitting $2\Delta_0$ and the polar states coefficient $b_{\overline{\mathrm{PS}}}$, calculated for the same pairs (δ, ε) of Table 2a, are larger than for $CuCl_2 \cdot 2\,H_2O$. In fact, as noted in I, a stronger nuclear attraction, that is a larger Δ_0, favours the antiferromagnetism both by lowering $J_{\mathrm{eff}}^{\mathrm{H-L}}$ and increasing the effect of the polar states, owing to the fact that we can write

$$\Delta J \cong -(M_2 - 2\Delta_0)^2/[2\,(F_2 - C_2)]\,,$$

within the approximation used for M_2. This expression of ΔJ and the data of Table 2a, b show that the polar states contributions vary less rapidly than the single terms of $J_{\mathrm{eff}}^{\mathrm{HL}}$, so that their effect becomes important when the contributions to $J_{\mathrm{eff}}^{\mathrm{HL}}$ tend to balance each other to give a total of the same order of ΔJ. Anyway, the approximations introduced computing F_2 and M_2 are not critical, in this respect.

In Tables 3a and 3b the same parameters of Table 2a, b are reported, but for a fixed value of ε (the central one of the preceding Tables) and for the five A_z values of Figure 2. As regards the calculated g values, the considerations already made for Table 2b are still valid. Except δ and γ, which decrease as $|A_z|$ increases, one can note a weak variation only of the other terms. The parameter γ, which is less involved in the superexchange mechanism, is more sensitive to the increase of α and $|\xi|$, as given in Table 1, and therefore undergoes a larger variation than δ. The relative unsensitiveness of the other terms shows that, in the quoted range, ε is the most crucial parameter for the evaluation of exchange constants. In fact, a variation of ε, as in Table 2a, b, can produce a drastic change in the values of these terms.

We want to remark that the numerical agreement necessary to plot the curves of Fig. 2 is not a critical condition, from a general point of view. In I a possible error of $\pm 20\%$, due to the approximations introduced both in the theoretical expressions and in the computation procedure, was discussed. However, this might be a pessimistic estimation,

Table 3a. Values of $J_{\mathrm{eff}}^{\mathrm{H-L}}$ and ΔJ (in cm^{-1}), of overlap S and of the various contributions to $J_{\mathrm{eff}}^{\mathrm{H-L}}$, for $\varepsilon = -0.0297$ and for the five values of A_z (in cm^{-1}) in Figure 2. The related covalency parameters δ and γ are shown.

$A_z \cdot 10^4$	δ	γ	$S \cdot 10^2$	J_1	J_2	$-C_1 S^2$	$-C_2 S^2$	$J_{\mathrm{eff}}^{\mathrm{H-L}}$	ΔJ
− 110	0.555	0.461	0.933	− 27.41	18.88	7.92	− 2.50	− 3.11	− 6.19
− 130	0.540	0.416	0.932	− 26.89	17.74	8.07	− 2.52	− 3.60	− 5.70
− 150	0.523	0.363	0.930	− 26.30	16.49	8.22	− 2.54	− 4.13	− 5.17
− 170	0.503	0.299	0.928	− 25.62	15.07	8.38	− 2.55	− 4.72	− 4.58
− 190	0.476	0.217	0.926	− 24.78	13.37	8.57	− 2.56	− 5.40	− 3.90

Table 3b. Values of M_2, $2\Delta_0$ and $(F_2 - C_2)/(1 - S^2)$ (in cm^{-1}), of the coefficient $b_{\overline{\mathrm{P}}\mathrm{S}}$ and the calculated g components in the same cases as in Table 3a.

$A_z \cdot 10^4$	δ	M_2	$2\Delta_0$	$\frac{F_2 - C_2}{1 - S^2}$	$b_{\overline{\mathrm{P}}\mathrm{S}} \cdot 10^2$	g_x	g_y	g_z
− 110	0.555	570.4	2088.7	178045.5	0.8340	2.0360	2.0742	2.2507
− 130	0.540	569.4	2020.8	177765.4	0.8005	2.0359	2.0746	2.2505
− 150	0.523	568.3	1945.5	177485.3	0.7619	2.0357	2.0749	2.2505
− 170	0.503	567.1	1858.2	177195.3	0.7180	2.0355	2.0755	2.2515
− 190	0.476	565.8	1751.9	176915.2	0.6630	2.0354	2.0762	2.2526

particularly if we limit the question to the errors in the evaluation of the molecular integrals only, accepting the reliability of the theoretical model.

The effect of an error on the calculation of J_{eff} may be seen as a broadening of each curve of Fig. 2, which becomes a band of possible pairs (δ, ε). This broadening is maximum in the region of $\varepsilon \simeq -0.030$ (where the contributions to J_{eff} are less sensitive to δ, as shown in Table 3a), so that in this range the first three bands are still separated if the error is $\pm 10\%$, but partly overlap (with the fourth band beginning to overlap the third one) when the error is $\pm 20\%$. As pointed out in I, this fact does not affect our conclusions, because we are concerned to find a reasonable range of parameters, which can account both for ESR data and for the antiferromagnetic coupling. In other words, a relatively large error in the computation of J_{eff} would mean that the ranges of the parameters δ and ε could not be separately defined for each value of A_z, but they should be extended to be consistent with a "spectrum" of A_z values. For example, if we consider an error of $\sim \pm 20\%$ on J_{eff}, we find that the ranges $0.48 < \delta < 0.56$ and $0.016 < |\varepsilon| < 0.060$ are consistent with all the values of A_z from $-110 \cdot 10^{-4}$ to $-150 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ and give the correct value of J_{eff} within the hypothized error.

As said in Sect. I, we have assumed for the hybridization parameter of the ligand orbitals the value $n = (2/3)^{1/2}$. Available data for $(\mathrm{CuCl})^{4-}$ complexes [22] would show a smaller amount of s character and moreover a smaller covalency degree for Cl^- ions than in our case. Nevertheless, it must be noted that in CDP the situation may be very different, owing to the adjacent interacting unit. Besides this, as pointed out in a preceding paper [10], the s orbitals of the ligands play an essential role in the superexchange mechanism, although a too small value of n would lead to situations of doubtful physical meaning. In fact, one can see from Fig. 3, where the level curves for $J_{\mathrm{eff}} = -9.3\ \mathrm{cm}^{-1}$ are plotted in the plane n, $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ for the extreme values of the pair (δ, ε) in Table 2a, that a value of the effective charge of Cu^{2+} of $\sim +3$ is always required for $n \leqq (2/3)^{1/2}$, but that beyond this value $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ increases very rapidly, tending asintotically to infinity as n tends to 1. This behaviour shows that for a small amount of s character an unreasonably high value of $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ is necessary to fit the experimental value of J_{eff}.

As regards the ligand covalency parameters, particularly γ and δ, it must be remembered that to decrease δ, and consequently to increase γ, tends to reduce the total overlap between the two interacting units and therefore the antiferromagnetic coupling. This effect may be compensated by increasing $Z_{\mathrm{eff}}^{\mathrm{Cu}}$, as one can see in Fig. 4, where the level curves for $J_{\mathrm{eff}} = -9.3\ \mathrm{cm}^{-1}$ are plotted in the

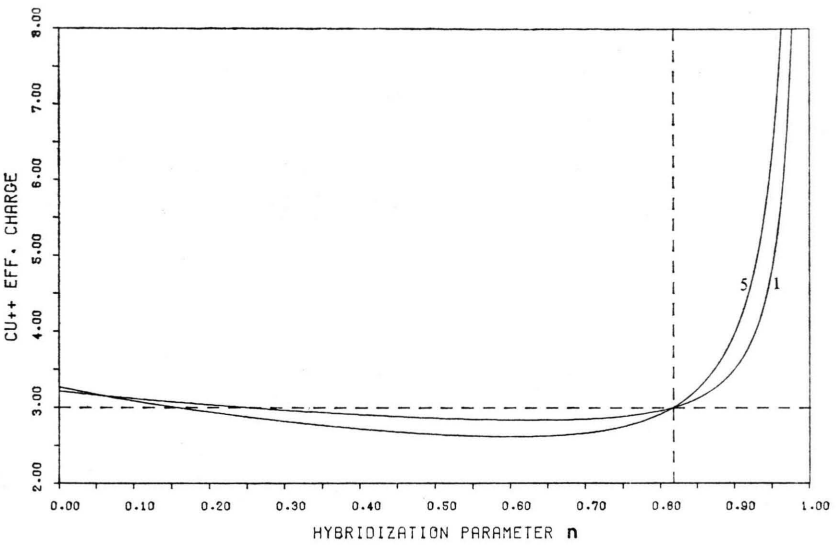

Fig. 3. Level curves in the n, $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ plane, connecting points for which $J_{\mathrm{eff}} = -9.3\ \mathrm{cm}^{-1}$ for the extreme values of the pair (δ, ε) in Table 2a. 1 refers to ($\delta = 0.500$, $\varepsilon = -0.0605$), 5 to ($\delta = 0.580$, $\varepsilon = -0.0159$). In both cases $A_z = -130 \times 10^{-4}\ \mathrm{cm}^{-1}$.

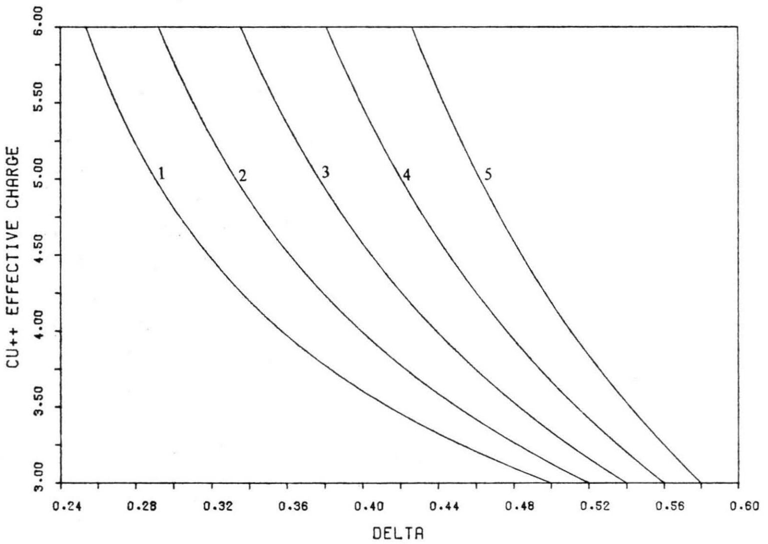

Fig. 4. Level curves in the δ, $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ plane, connecting points for which $J_{\mathrm{eff}} = -9.3\ \mathrm{cm}^{-1}$, for all the values of ε in Table 2a, decreasing in modulus from 1 to 5. In all cases $A_z = -130 \times 10^{-4}\ \mathrm{cm}^{-1}$.

plane δ, $Z_{\mathrm{eff}}^{\mathrm{Cu}}$, for all the values of ε in Table 2a. The variation of $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ with δ must be greater for the lowest value of $|\varepsilon|$, because in this case the contribution of the $d_{x^2-y^2}$ orbital becomes preponderant in the superexchange mechanism while for $|\varepsilon| = 0.0605$ it is sufficient to increase the effective charge from $+3$ to $\sim +3.2$ to obtain the correct value of J_{eff} with $\delta < \gamma$. Such increasing of $Z_{\mathrm{eff}}^{\mathrm{Cu}}$ as δ or $|\varepsilon|$ decrease is consistent with the increased electron spin localization [15].

In conclusion, although our results strongly support the assumptions introduced to carry out the calculations, our theoretical model is sufficiently flexible to account for other possibilities, if direct informations about the covalency parameters should become available. In particular, a greater ionicity of the Cu-Cl bond should lead to a higher value of the Cu^{2+} effective charge.

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Appendix

In Table A1 the distances (in Å) d_x, d_y and d_z relating to Fig. 1 for CDP are reported, from [1].

In Table A2 the overlap integrals, which have been used in formulae (6), are listed.

The one-center and the most important two-center integrals appearing in the expression of J_2 are reported in Table A3, while the nuclear attraction integrals appearing in the expression of J_1 are listed in Table A4.

d_x	d_y	d_z
2.004	2.298	3.026

Table A1. Cu-ligands distances (in Å) for CDP.

Table A2. Single unit overlap integrals appearing in Equations (6).

$\langle d_{x^2-y^2} \| -p_x{}^2 \rangle$	$\langle d_{x^2-y^2} \| s^2 \rangle$	$\langle d_{x^2-y^2} \| p_y{}^5 \rangle$	$\langle d_{x^2-y^2} \| -s^5 \rangle$
0.05739	0.04468	0.04495	0.03006

Table A3. One-center two-body integrals and some two-center two-body integrals (in a.u.) for CDP.

$\langle p_\sigma{}^5(1)\, p_\sigma{}^5(1) \| r_{12}^{-1} \| p_\pi{}^5(2)\, p_\pi{}^5(2) \rangle$	0.43421
$\langle p_\sigma{}^5(1)\, p_\pi{}^5(1) \| r_{12}^{-1} \| p_\sigma{}^5(2)\, p_\pi{}^5(2) \rangle$	$0.26311 \cdot 10^{-1}$
$\langle p_\sigma{}^5(1)\, s^5(1) \| r_{12}^{-1} \| p_\sigma{}^5(2)\, s^5(2) \rangle$	0.10698
$\langle s^5(1)\, s^5(2) \| r_{12}^{-1} \| s^5(2)\, s^5(2) \rangle$	0.56555
$\langle d_\sigma{}^a(1)\, p_\pi{}^5(1) \| r_{12}^{-1} \| d_\sigma{}^a(2)\, p_\pi{}^5(2) \rangle$	$0.77417 \cdot 10^{-4}$
$\langle d_\sigma{}^a(1)\, p_\pi{}^6(1) \| r_{12}^{-1} \| d_\sigma{}^a(2)\, p_\pi{}^6(2) \rangle$	$0.48766 \cdot 10^{-5}$
$\langle d_\sigma{}^a(1)\, s^5(1) \| r_{12}^{-1} \| d_\sigma{}^a(2)\, s^5(2) \rangle$	$0.10700 \cdot 10^{-2}$
$\langle d_\sigma{}^a(1)\, s^6(1) \| r_{12}^{-1} \| d_\sigma{}^a(2)\, s^6(2) \rangle$	$0.52341 \cdot 10^{-4}$
$\langle d_\delta{}^a(1)\, p_\pi{}^5(1) \| r_{12}^{-1} \| d_\delta{}^a(2)\, p_\pi{}^5(2) \rangle$	$0.53005 \cdot 10^{-4}$
$\langle d_\delta{}^a(1)\, p_\pi{}^6(1) \| r_{12}^{-1} \| d_\delta{}^a(2)\, p_\pi{}^6(2) \rangle$	$0.48176 \cdot 10^{-5}$
$\langle d_\delta{}^a(1)\, s^5(1) \| r_{12}^{-1} \| d_\delta{}^a(2)\, s^5(2) \rangle$	$0.45389 \cdot 10^{-4}$
$\langle d_\delta{}^a(1)\, s(1)^6 \| r_{12}^{-1} \| d_\delta{}^a(2)\, s^6(2) \rangle$	$0.20751 \cdot 10^{-5}$

Table A4. Nuclear attraction integrals (in a.u.) for CDP.

$\langle p_\sigma{}^5 \| r_a^{-1} \| s^5 \rangle$	0.05161	$\langle s^5 \| r_a^{-1} \| s^5 \rangle$	0.23022
$\langle p_\sigma{}^6 \| r_a^{-1} \| s^6 \rangle$	0.02999	$\langle s^6 \| r_a^{-1} \| s^6 \rangle$	0.17485
$\langle p_\sigma{}^5 \| r_1^{-1} \| p_\sigma{}^5 \rangle$	0.14479	$\langle p_\pi{}^5 \| r_1^{-1} \| p_\pi{}^5 \rangle$	0.13642
$\langle p_\sigma{}^5 \| r_1^{-1} \| s^5 \rangle$	0.01904	$\langle s^5 \| r_1^{-1} \| s^5 \rangle$	0.13927
$\langle p_\sigma{}^6 \| r_1^{-1} \| s^6 \rangle$	0.00751	$\langle s^6 \| r_1^{-1} \| s^6 \rangle$	0.08743
$\langle p_\sigma{}^5 \| r_3^{-1} \| s^5 \rangle$	0.01302	$\langle s^5 \| r_3^{-1} \| s^5 \rangle$	0.11514

[1] R. C. Hughes, B. Morosin, P. M. Richards, and W. Duffy, Jr., Phys. Rev. B **11**, 1795 (1975).

[2] K. Andres, S. Darack, and S. L. Holt, Solid State Comm. **15**, 1087 (1974).

[3] W. Duffy, Jr., J. E. Veuneman, D. L. Strandburg, and P. M. Richards, Phys. Rev. B **9**, 2220 (1974).

[4] K. Takeda, S. Matsukawa, and T. Haseda, J. Phys. Soc. Japan **30**, 1330 (1971).

[5] Y. Endoh, G. Shirane, R. J. Birgenau, P. M. Richards, and S. L. Holt, Phys. Rev. Lett. **32**, 170 (1974).

[6] J. D. Dunitz, Acta Cryst. **10**, 307 (1957).

[7] G. Amoretti, Z. Naturforsch. **33a**, 130 (1978).

[8] A. C. Hewson, D. Ter Haar, and M. E. Lines, Phys. Rev. **137**, A 1465 (1965).

[9] P. W. Anderson, Solid State Physics **14**, 99 (1963).

[10] G. Amoretti and V. Varacca, J. Chem. Phys. **61**, 3651 (1974), ibid. **65**, 1511 (1976); ibid. **67**, 989 (1977).

[11] E. Buluggiu, G. Dascola, D. C. Giori, and A. Vera, J. Chem. Phys. **54**, 2191 (1971).

[12] D. Kivelson and R. Neiman, J. Chem. Phys. **35**, 149 (1961).

[13] Here and in the following the SCF wavefunctions of Watson et al. [23] for Cu^{2+} and Cl^- and of Clementi et al. [24] for N have been used.

[14] E. König and H. L. Schläfer, Z. Phys. Chem. N.F. **26**, 5371 (1960).

[15] I. G. Ross and J. Yates, Trans. Faraday Soc. **55**, 1064 (1959).

[16] P. A. Van Dalen, in: Magnetic Ordering in Insulating Solids, Thesis, Eindhoven, 1966 and Physica **37**, 349 (1967); P. A. Van Dalen and P. Van der Leeden, Physica **37**, 329 (1967).

[17] The one-center one- and two-body integrals, the overlap and the two-center integrals of the type $\langle \psi_i | r_i{}^{-1} | \psi_j \rangle$, were calculated by means of computer programs kindly supplied by Prof. L. Oleari of the Institute of Physical Chemistry of the University of Parma.

[18] This program computes two-center two-body exchange integrals between linear combinations of Slater-type atomic orbitals, using the method by E. L. Mehler and K. Ruedenberg, J. Chem. Phys. **50**, 2575 (1969).

[19] As $|A_z|$ increases, there is a value of $|\varepsilon|$, below which the experimental value of J_{eff} can not be fitted. This is due to the normalization condition (5e), which lowers the upper limit of the available range of δ values, as α increases.

[20] J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 1, McGraw-Hill Book Company, Inc., New York 1963.

[21] C. Herring, Magnetism **2** B, 1 (1966).

[22] J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, Proc. Phys. Soc. **78**, 1263 (1961).

[23] R. E. Watson, Phys. Rev. **118**, 1036 (1960); R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

[24] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).