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M. Bonnet [a], J. Laugier [b], V. I. Ovcharenko [b c], Y. Pontillon [a], E. Ressouche [a], P. Rey [b], P. Schleger [a d] & J. Schweizer [a]

[a] CEA Grenoble/DRFMC / SPSMS or SCIB

[b] CENG, 17 rue des martyrs, 38054, Grenoble Cedex 9, France

[c] International Tomography Center, Institutskaya 3a, Novosibirsk, Russia

[d] ILL 156X, 38042, Grenoble Cedex 9, France

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SPIN DENSITY IN AN ENAMINOCETONE NITROXIDE COPPER COMPLEX

M. BONNET[1], J. LAUGIER[2], V.I. OVCHARENKO[2]*, Y. PONTILLON[1], E. RESSOUCHE[1], P. REY[2], P. SCHLEGER[1]** AND J. SCHWEIZER[1]

CEA Grenoble/DRFMC / SPSMS[1] or SCIB[2], CENG, 17 rue des martyrs, 38054 Grenoble Cedex 9, France

* Present adress: International Tomography Center, Institutskaya 3a, Novosibirsk, Russia

** Present adress: ILL 156X, 38042 Grenoble Cedex 9, France

Abstract The copper complex $C_{18}H_{28}O_2N_2Cu(NO)_2$ is a molecule which carries three spins S=1/2. It crystallizes in the monoclinic space group Pc, with two molecules in the asymetric unit. Its χT starts to increase when the temperatures decreases, indicating ferromagnetic intramolecular coupling, and then, below T=40K, it completely collapses, showing negative coupling between molecules. We have investigated its spin density with polarized neutrons at T=40K and T=4.10K. At the higher temperature, the spin density is well localized on the Cu atom and the two NO groups of each molecule. At the lower temperature, the spin density exists, for each molecule, on the Cu atom and on one of the two NO groups only. There is a quasi dimerization on two NO groups, belonging to the different molecules, facing each other, and distant only by 3.40 Å.

INTRODUCTION

The design of high spin molecular based species is highly dependent on the ability of organic groups linking the spin carriers to mediate strong magnetic interactions. We have used the 3-imidazoline radicals as spin carriers in metal-organic molecular materials as their organic chemistry is well documented and as functionalization towards chelating species has been developed[1]. Although their chemical structure is closely related to that of imino-nitroxides, the imidazoline free radicals have a dramatically different electronic

structure, involving one unpaired electron localized on the NO group which is included in an unconjugated backbone. Recently, the investigation of the magnetic properties of copper(II) complexes, including these free radicals as ligands[2], have shown that coordination to the imino nitrogen atoms provides a fairly efficient pathway mediating sizable ferromagnetic interactions between imidazoline nitroxides and metal ions.

We report here the crystal structure, the magnetic properties and the spin density investigation of the copper(II) complex of 4-(1-ethenyl-2-oxyato)-2,2,5,5-tetramethyl-imidazoline-1-oxyl : of formula $C_{18}H_{28}O_2N_2Cu(NO)_2$, a molecule with three spins S=1/2 which is represented in Figure 1.

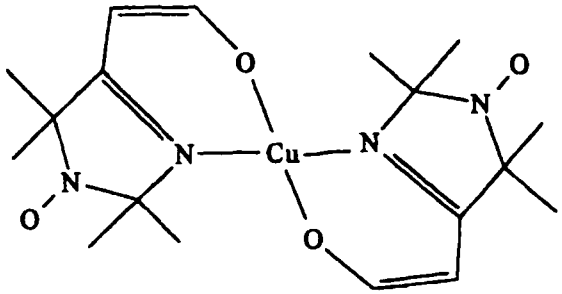


FIGURE 1 The enaminocetone nitroxide copper complex

CRYSTAL STRUCTURE

The synthesis of this molecule was already described[1]. Crystals, suitable for X-ray study were obtained by cooling down of the ethanol solution. Preliminary Weissenberg photographs showed that the system is monoclinic. A crystal of approximate dimensions 0.2x0.2x0.2 mm^3 was mounted on an Enraf-Nonius four-circle CAD-4 diffractometer, equipped with a graphite-monochromatized Mo radiation. The unit cell parameters, as determined with X-rays at room temperature, are a=11.398Å, b=11.492Å, c=16.720Å, β=110.82°. Intensity data were corrected for Lorentz and polarization factors, but not for absorption.

The Pc space group was established from systematic absences and the structure was solved by the standard heavy-atom method, using the SHELX76 package of structure determination[3]. Difference Fourier maps revealed electron density contributions appropriately located. These were refined with anisotropic temperature factors, except for hydrogens.

As for a spin density polarized neutron investigation it is necessary to know the crystal structure at low temperature, including the hydrogen positions and the temperature

factors, we have made a low temperature crystal structure experiment with unpolarized neutrons. A large crystal, with the shape of a platelet of dimensions 7.2x4.6x1.6 mm^3 was mounted on the 4-circle neutron diffractometer DN4 at the reactor Siloe. The crystal was cooled down to T=9K, and the intensities of 3574 reflections were recorded with a wavelength λ=1.179Å. The unit cell parameters, as determined at this low temperature, are a=11.18Å, b=11.35Å, c=16.56Å, β=111.5°. After correction of the absorption (μ=0.232 mm^{-1}), the position parameters and the anisotropic temperature factors were refined with the ORXFLS programme[4] down to an agreement factor of 5.6% and a chi 2 factor of 2.2.

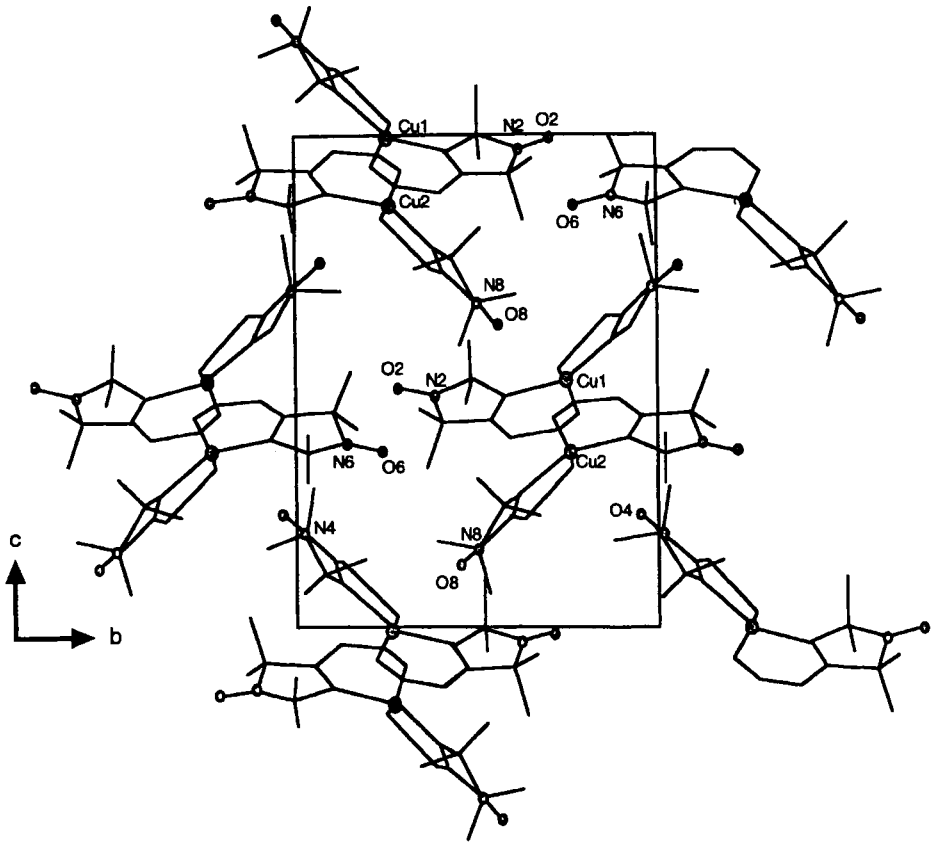


FIGURE 2 Projection of the crystal structure along the $\vec{a}$ axis

The crystal structure, projected along the $\vec{a}$ axis, is represented in Figure 2. The familiar bis-chelate structure is confirmed, slightly complicated by the presence of two molecules in the asymetric unit. The two molecules, A (Cu1) and B (Cu2), are arranged in such a way that one of the planar ligand in A is parallel to the corresponding ligand in B. The two other ligands are nearly perpendicular. The two molecules are close enough to bring the two copper ions at 4.02 Å.

More important from the point of view of the magnetic properties, the NO groups N2O2 of molecule A and N6O6 of molecule B form a parallelogram such that the distance O2-O6 is 3.40 Å only .

In the two molecules the copper ions are four-coordinated by two oxygen and two nitrogen atoms, in a trans but not symmetrical arrangement. The molecules have no element of symmetry and all the binding distances are different. For both molecules, neither the four coordinated atoms are coplanar nor correspond to a regular tetrahedron. The situation is intermediate between these two idealized patterns.

MAGNETIC MEASUREMENTS

The magnetic susceptibility of a powder sample of this copper complex has been measured by use of a SQUID magnetometer between 300K and 2K, in a field of 0.5 Tesla. The temperature dependence of the product χT is diplayed in Figure 3. The room

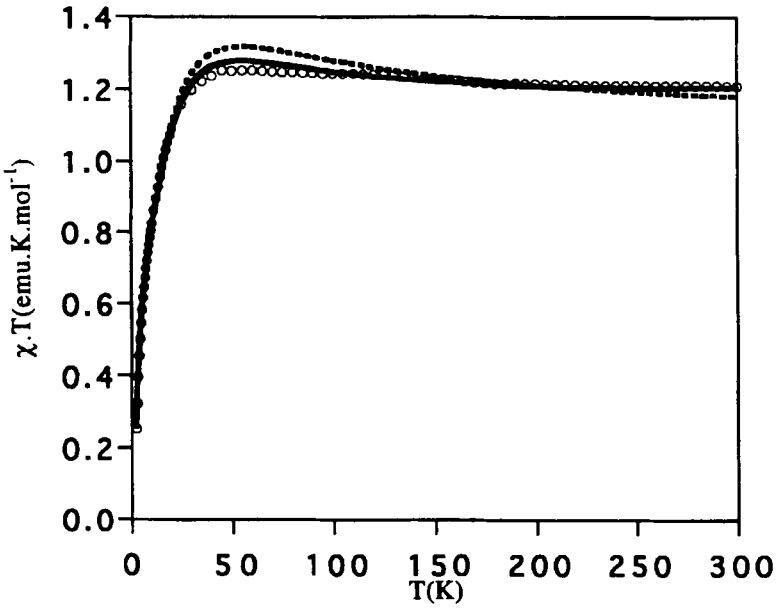


FIGURE 3 Termal variations of the χT product: experimental data (circles), 3 spin model with a negative molecular field (dashed line), 6 spin model with a negative J_{34} interaction (continuous line)

temperature of this product (1.21 emu.K.mole^{-1}, 3.11μ_B) is very close to that expected for three S=1/2 independent spin system. On decreasing the temperature, one observes a slight increase of χT (1.26 emu.K.mole^{-1} at 45 K), and then a drop down to 0.255

emu.K.mole^{-1} at 2 K. The increase of χT between 300 K and 45 K is the signature of ferromagnetic coupling, very likely intramolecular in nature, while the drop below 45 K points to intermolecular antiferromagnetic interactions. We fit these data considering a symmetrical three spin model with a positive $J_{Cu\text{-}NO}$ interaction and a negative molecular field corresponding to J_{inter}. The best fit values are g= 2.123, $J_{Cu\text{-}NO}$=24.8 K and J_{inter}=-7.2 K. The agreement with the experimental χT is represented in Figure 3 by the dashed line.

The magnetic susceptibility has also been measured on solutions, down to 6 K. The product χT increases continually when the temperature decreases, and reaches 1.74 emu.K.mole^{-1} at 6 K. This absence of low temperature decrease confirms the intermolecular nature of the negative interactions in the solid.

The magnetization as a function of the applied field has also been investigated for the solid, up to 5 Tesla in the SQUID magnetometer, and up to 9 Tesla in a magnetometer using an axial extraction method. In the conditions of the polarized neutron experiments, we have found:

H=8.0 Tesla, T=4.10 K, M=1.590 μ_B/molecule
H=5.0 Tesla, T=40.0 K M=0.285 μ_B/molecule

SPIN DENSITY MEASURED BY POLARIZED NEUTRON DIFFRACTION

The polarized neutron diffraction technique applies to magnetic materials which present a long range magnetic order. This is the case of ferromagnets below their Curie temperature, but it is also the case of paramagnets with their magnetic moments aligned by a strong external magnetic field.

The neutron-matter interaction is of two types: a nuclear interaction between the neutron and the nuclei of the atoms, and a magnetic interaction between the neutron magnetic moment and the magnetic moments due to the spins of the unpaired electrons. These two interactions are expressed in terms of nuclear and magnetic structure factors.

The nuclear structure factors are the Fourier components of the atomic nuclei in the unit cell:

$$F_N(\vec{K}) = \sum_j b_j \, e^{i\vec{K}\vec{r}_j} \, e^{-W_j} \qquad (1)$$

where b_j is the scattering amplitude of the nucleus of atom j, and W_j a thermal factor.

The magnetic structure factors are the Fourier components of the spin density:

$$F_M(\vec{K}) = \int_{cell} s(\vec{r}) \, e^{i\vec{K}\vec{r}} \, d\vec{r} \qquad (2)$$

In the polarized neutron diffraction technique, a monochromatic neutron beam is elastically scattered by a single crystal of the material to investigate, and the different Bragg reflections (hkl) are measured. A magnetic field is applied in the vertical direction, and this field aligns the magnetic moments (the spin density). The polarization of the neutron beam is also aligned vertical, parallel to the field, and can be oriented either upwards or downwards. If one restricts the collection of Bragg reflections to horizontal scattering vectors (in the horizontal plane), the intensity of such a reflection can be written very simply as:

$$I^{\pm}(\vec{K}) = \left|F_N(\vec{K}) \pm F_M(\vec{K})\right|^2 \tag{3}$$

The neutron spins are polarized alternatively up and down, and one measures the flipping ratio:

$$R(\vec{K}) = \frac{I^+(\vec{K})}{I^-(\vec{K})} = \frac{\left|F_N(\vec{K}) + F_M(\vec{K})\right|^2}{\left|F_N(\vec{K}) - F_M(\vec{K})\right|^2} \tag{4}$$

For centric structures, both F_N and F_M are real quantities. The measurement of the flipping ratios and the knowledge of the nuclear structure yields the magnetic structure factors $F_M(\vec{K})$. As these are the Fourier coefficients of the spin density distribution, the latter can be reconstructed.

In the general case of acentric structures, both FN and F_M are complex quantities:

$F_N = F'_N + iF''_N$

$F_M = F'_M + iF''_M$

Equation (4), extended to Bragg reflections with scattering vectors out of the horizontal plane, must then be written:

$$R = \frac{F'^2_N + F''^2_N + 2\sin^2\alpha\,(F'_N F'_M + F''_N F''_M) + \sin^2\alpha\,(F'^2_M + F''^2_M)}{F'^2_N + F''^2_N - 2\sin^2\alpha\,(F'_N F'_M + F''_N F''_M) + \sin^2\alpha\,(F'^2_M + F''^2_M)} \tag{5}$$

where α is the angle between the scattering vector $\vec{K}$ and the direction of the magnetic field. In the horizontal plane, $\sin^2\alpha = 1$.

Contrarily to the case of centric structures, when the structure is acentric, it is not possible, knowing the nuclear structure (which means knowing F'_N and F''_N) to obtain the complex magnetic structure from the measured flipping ratio: the application of formula (5) consists in one equation with two unknown quantities: F'_M and F''_M. Informations concerning the spin density distribution are nevertherless contained in the flipping ratios, but to retrieve this distribution, another way has to be used, which extracts these informations directly from the flipping ratios.

POLARIZED NEUTRON EXPERIMENTS

Two experiments were performed with polarized neutrons: one at T = 4.10 K, on the DN2 diffractometer at the Siloe reactor, and one at T = 40 K, on the 5C1 diffractometer at the Orphee reactor. Both diffractometers have the same features: a polarized neutron monochromatic beam, a vertical field provided by a cryomagnet, and a lifting counter which allows to collect Bragg reflections above the horizontal plane. Both experiments were carried out with the same crystal (7.2x4.6x1.6 mm^3), which was used with unpolarized neutrons to refine the nuclear structure, and both experiments were performed in the same way. In a first orientation, the 7.2 mm edge, which is parallel to [100], was aligned vertical, in order to measure (0kl), (1kl), (2kl) and (3kl) reflections. Then the crystal was turned by 90° and the 4.6 mm edge, parallel to (012) was aligned along the field, which allowed to measure another set of reflections, corresponding to a slice of the reciprocal lattice orthogonal to the slice measured with the first orientation. The wavelengths were 1.20 Å on DN2 and 0.84 Å on 5C1.

DATA TREATMENT

There are two ways of retrieving the spin density distribution from polarized neutron data[5]. The first one is a model-free way in that sense that the distribution is reconstructed with no assumption on its nature. Opposed to it, the second way assumes a certain knowledge on the spin density, based, for instance, on chemical grounds, and the experimental data allow to determine the parameters which describe the model.

A model-free reconstruction: the maximum entropy (MaxEnt) method

The magnetic structure factors F_M being the Fourier coefficients of the periodic function spin density s(r), the most direct way is to use the Fourier inversion series to obtain the spin density. However, in the case of acentric structures, we have seen that the real and the imaginary parts of the magnetic structure factors $F_M(\vec{K})$ cannot be determined directly from the experimental flipping ratios $R(\vec{K})$, and another way has to be followed.

Recently a new method has appeared, which is based on the theory of information and the bayesian probabilities[6], and which was just recently extended to the case of acentric structures[7]: the maximum entropy method. The principle is the following: among all the maps of the spin density distribution which fit the data, that means for which $R_{cal}(\vec{K})$-$R_{obs}(\vec{K})$ is in the range of the experimental error, the method chooses that one which has the highest intrinsic probability to exist. Here is introduced the idea of entropy:

the highest probability corresponds to the highest entropy, the entropy of a map being defined as:

$$S = -\sum_i p_i \, \mathrm{Log}(p_i) \tag{6}$$

where the sum $\sum$ is taken over all the pixels of the map, and where p_i is the density at pixel i, normalized over all the cells:

$$p_i = \frac{s_i}{\sum_j s_j} \tag{7}$$

In the case of centric structures, the quality of the reconstruction is tremendously improved, compared to the Fourier inversion. For acentric structures, it is the only method which allows to get a spin density distribution without any assumption on the distribution.

Figures 4 and 5 represent the spin density distributions obtained by the maximum entropy method and projected along the $\vec{a}$ axis, at temperatures 4.10 K and 40 K respectively.

At T=40 K, one clearly sees localized spin densities on the Cu and NO atoms of each molecule: Cu1, N2O2 and N4O4 for molecule A, Cu2, N6O6 and N8O8 for molecule B. Out of these atoms, no spin density is visible.

The striking fact at T=4.10 K is the practical disappearance of the spin density on the two groups N2O2 and N6O6. On all the other Cu atoms or NO groups, the spin density is reinforced, compared to 40K.

Modeling the spin density

Another approach to process the polarized neutron data models the spin density, knowing that it results from the presence of unpaired electrons. One can write the magnetic molecular wave function as a linear combination of atomic orbitals centered on the atoms of each magnetic group.

$$|\psi\rangle = \sum_{\text{atom i}} A_i \, \phi_i \tag{8}$$

where the ϕ_i are the usual s, p, or d atomic orbitals which can be represented by the Slater functions, with their radial and with their angular parts. The spin density, in a restricted Hartree-Fock scheme correspond to:

$$s(r) = \langle\psi|\psi\rangle = \sum_{\text{atom i}} M_i \langle\phi_i|\phi_i\rangle \tag{9}$$

where M_i is the spin population on atom i

The flipping ratios $R(\vec{K})$, through the real and imaginary parts $F'_M(\vec{K})$ and $F''_M(\vec{K})$ of the magnetic structure factors $F_M(\vec{K})$, are then analytical functions of the spin populations M_i and of the angular parts of the orbital coefficients Ai. Using

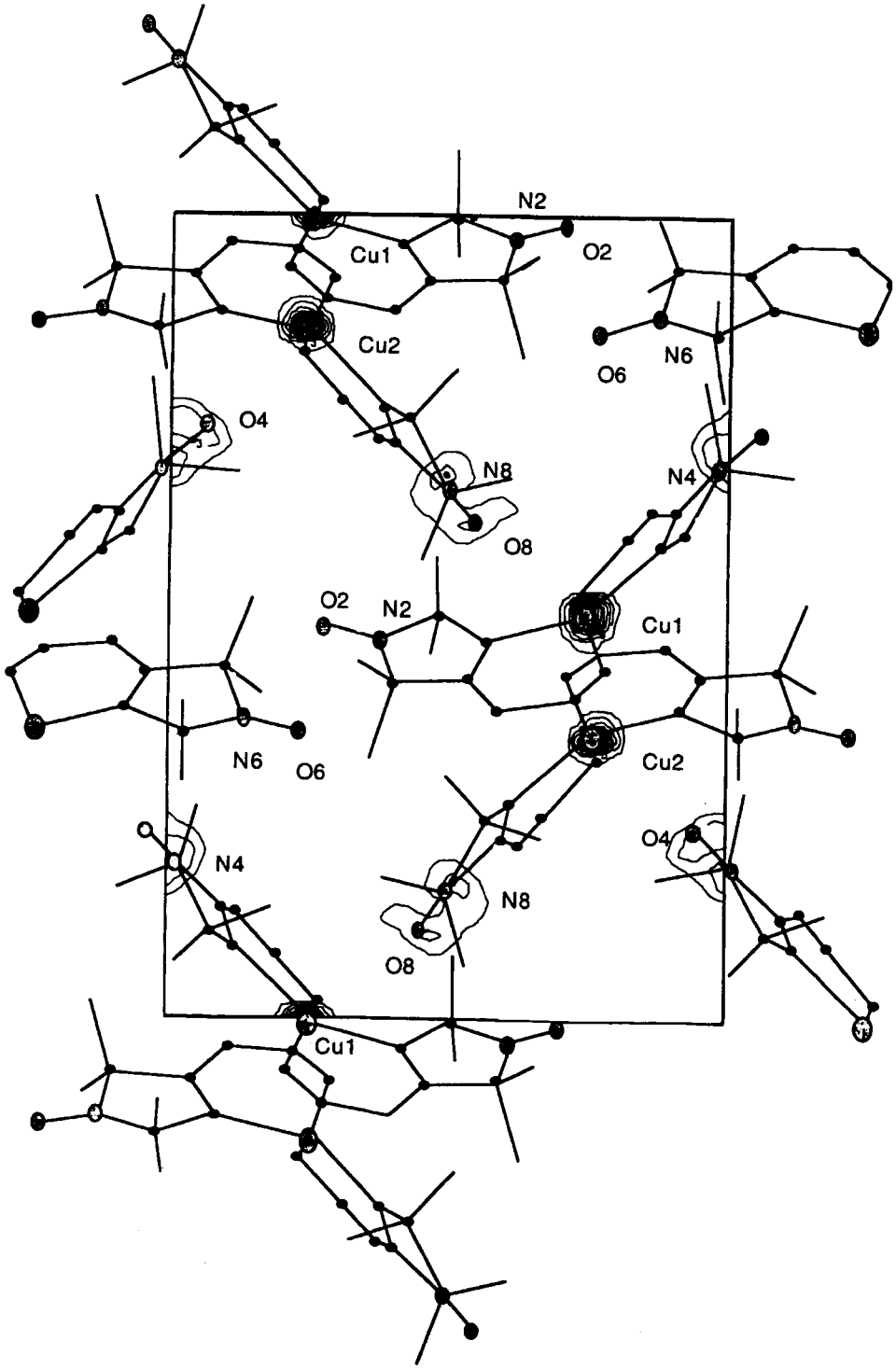


FIGURE 4 Spin density obtained at T=4.10K by MaxEnt and projected along the ã axis

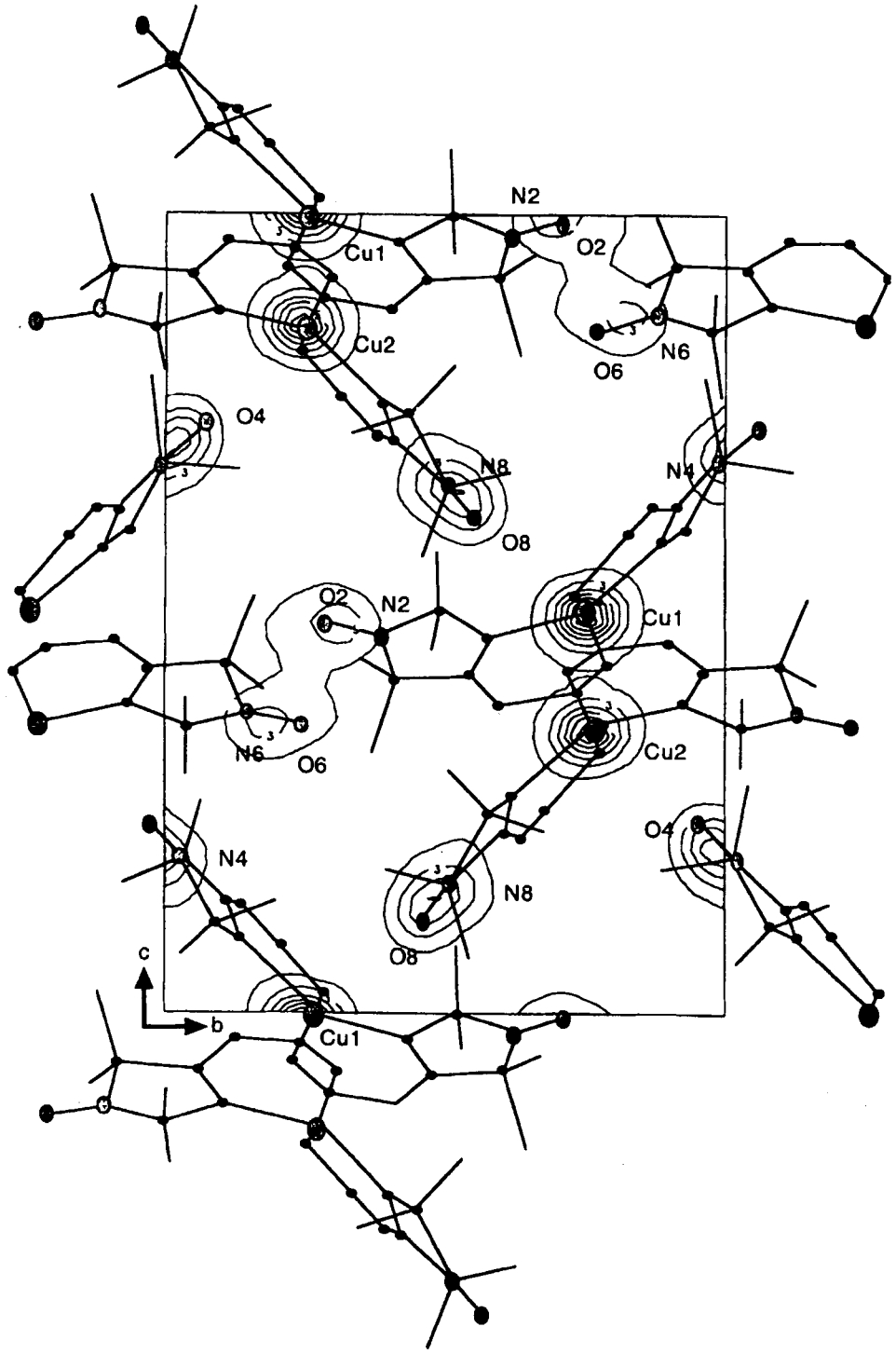


FIGURE 5 Spin density obtained at T=40K by MaxEnt and projected along the $\vec{a}$ axis

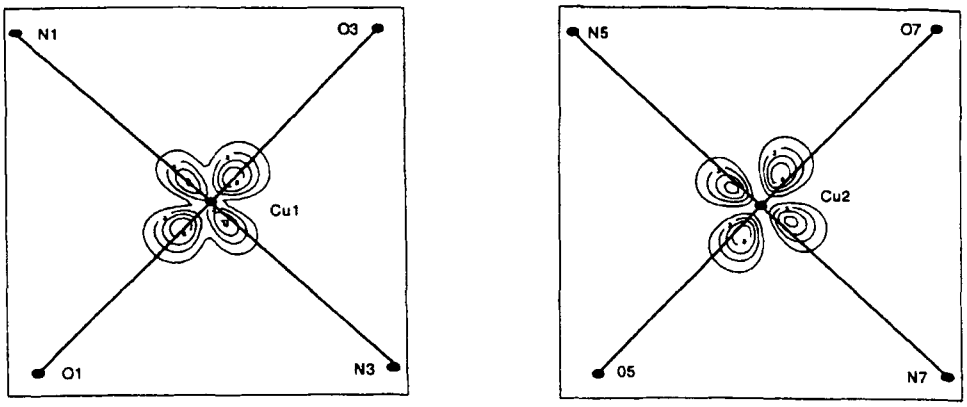
equations (5), (8) and (9), it is possible to refine these coefficients with a least square method, and determine that way the molecular magnetic wave function and the corresponding spin density, as refined from the polarized neutron data.

The spin populations of orbitals p for N and O atoms, and orbitals d for Cu atoms, are reported in Table I. For the spin populations, as expected from the maximum entropy reconstruction, those found at T=4.10 K for the p orbitals of atoms N2, O2, N6 and O6 are much less than the spin populations of other "magnetic" atoms. Furthermore, at this temperature of 4.10 K, the direction of the p orbitals on atoms N4, O4, N8 and O8 were not found to deviate significantly from the z direction, where z is the normal to the CNC plane.

TABLE I Spin populations (in μ_B) obtained by modeling the spin density

	T = 4.10 K H = 8.0 T	T = 40 K H = 5.0 T
N2	- 0.001 (46)	0.039 (10)
O2	0.018 (43)	0.047 (8)
Cu1	0.544 (39)	0.118 (9)
N4	0.339 (50)	0.075 (13)
O4	0.298 (44)	0.065 (12)
N6	0.196 (44)	0.054 (10)
O6	0.082 (44)	0.018 (8)
Cu2	0.772 (40)	0.091 (9)
N8	0.519 (49)	0.045 (13)
O8	0.392 (44)	0.027 (12)

The spin density of the d orbitals of atoms Cu1 and Cu2, as refined from the data at T=4.10 K, are represented in Figures 6 and 7 respectively. Having in mind that the environment of these two copper sites is intermediate between the tetrahedral and the planar environment, it is clear that the wave function of the unpaired electron on both copper sites are the usual $3d_{x2-y2}$ orbitals which would exist in an idealized planar environment.



FIGURES 6 and 7 Spin density of the d orbital on Cu1 and Cu2, as refined from the data at T=4.10K

At T=40K, the magnetic signal is much weaker than at T=4.10 K, as a smaller part of the magnetization was aligned by the field. Therefore we refined the populations M_j but made no attempt to refine the angular parts of the orbitals, and kept those which were determined at the lower temperature. The spin populations are much weaker than at 4.10 K. The magnetic moments found on the N and O atoms of the different NO groups are all of the same order of magnitude.

DISCUSSION

We have summarized on Table II the magnetization found on the three magnetic groups NO/Cu/NO of each molecule. The main point to discuss is the relative disappearance, at low temperature of the spin density on the groups N2O2 and N6O6. From the susceptibility measurements, we have concluded to a positive intramolecular coupling, and to a negative coupling between the molecules. The disappearance of the spin density on the NO groups of the two molecules which are facing each other, at a distance O2O6 of 3.40Å, looks like a dimerization, and indicates that the negative coupling is not a general coupling between the molecules, but a well localized negative coupling between the N2O2 and the N6O6 groups. We have then reanalyzed the magnetic susceptibility in a six spin model, with two types of interactions: a positive intramolecular $J_{Cu\text{-}NO}$ interaction, and a negative $J_{N2O2\text{-}N6O6}$ interaction. The best fit values have been obtained for g=2.08, $J_{Cu\text{-}NO}$=24.8K and $J_{N2O2\text{-}N6O6}$=-18.5K. The agreement with the

experimental data is represented in Figure 3 by the continuous line. One can see that this model fits the data better than the first model.

TABLE II Spin densities calculated in the 6 spin model, and taken from the experiment after normalization

	6 spin model T = 0 H = 8.0 T	T = 4.10 K H = 8.0 T	T = 40 K H = 5.0 T
N_4O_4	0.479	0.402(42)	0.483(62)
Cu_1	0.426	0.344(25)	0.407(31)
N_2O_2	0.093	0.011(40)	0.296(45)
N_6O_6	0.093	0.176(39)	0.248(45)
Cu_2	0.426	0.488(25)	0.313(31)
N_8O_8	0.479	0.576(42)	0.248(62)

We have carried out a little further the idea of "dimerization" between the spins N2O2 and N6O6 in the frame of the 6 spin model corresponding to two molecules, with $J_{12}=J_{23}=J_{45}=J_{56}=J_{Cu\text{-}NO}=24.8K$ for the four interactions between Cu and NO, and the negative $J_{34}=J_{N2O2\text{-}N6O6}=-18.5K$ interaction between the NO groups, facing each other, and belonging to the two different molecules. If we define

$$\vec{S}_{34}=\vec{S}_{N2O2}+\vec{S}_{N6O6}$$

in the absence of any applied field, the ground state of the six spin system is $E_0=-35.78K$, and:

$<\vec{S}_{34}{}^2>=0.323$ as compared to 2 for a spin S=1.

Without an applied fied, we have obviously for the z component

$<\vec{S}_{34\ z}>=0$

When, as in the low temperature polarized neutron experiment, a 8 Tesla field is applied, the ground state of the six spin system is $E_0=-54.26K$. The individual values of the z component of the spin $<S_{iz}>$ are reported in Table VII. For the compound spin $\vec{S}_{34}$ we have:

$<\vec{S}_{34}{}^2>=0.375$ as compared to 2 for a spin S=1, practically the same value as without any applied field

$<\vec{S}_{34\ z}>=0.188$ as compared to 1 for a spin S=1

We can see that in this six spin system, the negative interaction between N2O2 and N6O6 is strong enough to provoke an almost complete dimerization of these two central spins, while the four other spins, as shown in Table II, are only slightly affected.

CONCLUSIONS

The determination of the spin density in this enaminocetone nitroxide copper complex has been realized by polarized neutron diffraction. This problem may be considered as rather difficult to solve for two reasons:

-it concerns two non equivalent molecules, each of them including three magnetic groups, non related by symmetry element

-the crystal structure of the compound is acentric, which reduces the amount of information contained in the measurements.

Nevertherless, the main features of the spin density have been determined, and in particular the nature of the magnetic wave function on the different atoms. Furthermore, it has been shown that the main characteristic of this six spin system is the negative interaction between two NO groups, facing each other at a short distance, and belonging to two different molecules, interaction which produces a quasi dimerization of these two spins.

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