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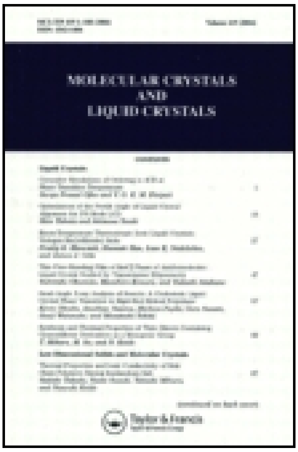

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Spin Densities in Nitronyl Nitroxide Free Radicals

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Spin Densities in Nitronyl Nitroxide Free Radicals.

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Abstract: The spin density distributions of three nitronyl nitroxide (NIT) free radicals have been determined by polarized neutron scattering. For such a determination the neutron is an ideal tool as it is a magnetic probe which feels the spin density at the microscopic level, and also as it is an itinerant probe which sees the spin density everywhere throughout the molecule.

I INTRODUCTION.

Nitroxide free radicals have been widely investigated because of their stability, and also because their simple hyperfine EPR patterns allow them to be used as spin labels for macromolecules. Among them, the nitronyl nitroxides play an important role. Their Lewis formula is represented in figure 1, and shows two N-O groups and one unpaired electron delocalized on the conjugated O-N-C-N-O fragment.

The possibility of varying the substituant R and the various possible couplings that could arise upon coordination to metal centers through the oxygen atoms, allow the synthesis of a large number of nitronyl nitroxide derivatives possessing different properties.

Magnetically, nitronyl nitroxides are free radicals with $S=1/2$. In principle, the unpaired electron is symmetrically distributed on the 2 N-O groups, in an antibonding molecular orbital which presents a node at the central carbon position. Depending on the substituant group and/or the coordinated metal ion, the symmetry is broken, and one can expect a modification of the unpaired electron distribution, modification which reflects the strength of the couplings.

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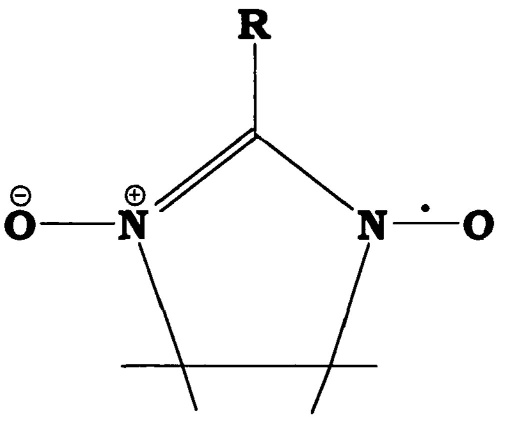

Figure 1 (a) : Lewis formula of Nitronyl Nitroxides (NIT)

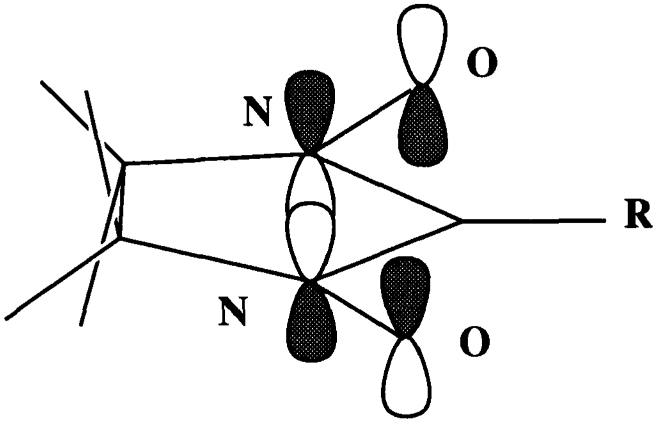

Figure 1 (b) : Schematic view of the π* magnetic orbital in Nitronyl Nitroxide.

In this paper we report the spin density investigation of three species including nitronyl nitroxide radicals, using the technique of polarized neutron diffraction :

-the first is : 2-phenyl-4,4,5,5,-tetramethyl-4,5-dihydro-1,H-imidazol-3-oxide-1-oxyl or (NITphi), the uncoordinated free radical carrying a phenyl ring as the R fragment.

-the second is: catena - (m - 1, 3 -(2 , 4 , 4, 5,5-pentamethyl-4,5-dihydro-1,H-imidazol-3-oxide-1-oxyl)bis(hexafluoroacetylacetonato)copper(II)) or Cu(hfac)$_2$NIT-Me, a chain-like compound where the methyl substituted nitroxide bridges copper(II) ions, the coordination being axial.

-the third is : bis-(2-phenyl-4,4,5,5,-tetramethyl-4,5-dihydro-1,H-imidazol-3-oxide-1-oxyl)copper(II)-chloride, or CuCl$_2$(NITphi)$_2$, where the copper(II) ion is bonded to two Cl atoms and two phenyl substituted nitronyl nitroxides, and where the coordination between the Cu, the Cl's and the NO groups is equatorial.

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II SPIN DENSITY DETERMINATION BY NEUTRON SCATTERING.

While bulk measurements, such as magnetization or susceptibility, integrate the spin density over all the molecules, a microscopic determination of the spin density implies the use of a magnetic probe which interacts with the spin density. In resonance techniques, the magnetic probe is a nuclear spin localized in a particular atomic site which gives a local sight of the spin density. Contrarily, in neutron scattering, the magnetic probe, the neutron with its spin, is itinerant, and measures the microscopic spin density at each point of the molecule.

II-1) Principle.

A neutron diffraction experiment consists in measuring the intensity of a monochromatic neutron beam elastically scattered by a crystal in the different directions corresponding to the Bragg reflections (hkl) with the scattering vectors $\vec{K}$. The neutron-matter interaction is of two types : a nuclear interaction with the nuclei of the atoms and a magnetic interaction with the unpaired electron spin. These two interactions give rise, for each Bragg reflection, to one nuclear and one magnetic amplitude which are expressed in terms of nuclear and magnetic structure factors.

The nuclear structure factors are the Fourier components of the density of atomic nuclei in the elementary cell of the crystal :

$$F_N(\vec{K}) = \sum_{j}^{\text{atoms}} b_j \, e^{i\vec{K}.\vec{r}_j} \qquad (1)$$

where b_j is the scattering length of atom j .

In the same way the magnetic structure factors are the Fourier components of the periodic spin density :

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

In a polarized neutron experiment, the magnetic moments, and therefore the spin density, are aligned by a vertical magnetic field, and the incident neutron beam is polarized either parallel or antiparallel to this magnetic field. The intensity of the Bragg reflection takes the expression :

$$I_{\pm}(\vec{K}) \approx \left|F_N(\vec{K}) \pm F_{M\perp}(\vec{K})\right|^2 \qquad (3)$$

where $F_{M\perp}(K)$ is the component of the magnetic structure factor perpendicular to the scattering vector K. The neutron beam is polarized alternatively up and down, and one determines the flipping ratio between the intensities I+ and I- , at the peaks of the different Bragg reflections :

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

In the case of centrosymmetric crystals, both F_N and F_M are real quantities. The knowledge of the crystal structure implies the knowledge of the nuclear structure factors F_N's, and the resolution of equation (4) provides experimental values for the magnetic structure factors F_M's. In most of the cases, magnetic structure factors are much smaller than nuclear structure factors. With polarized neutrons, as shown by equations (3) and (4), the accuracy in the determination of the magnetic structure factors is enhanced by the nuclear structure factors, which play the role of amplifiers.

II-2)Spin density reconstruction.

The question which arises now is how to determine the spin density from the experimental F_M's. There exist two main approaches to solve this question : one approach is model free and retrieves the spin density from the F_M's uniquely, without any assumption on the density itself. The second involves the refinement of a parametrized model based on the fact that the spin density is due to unpaired electrons.

a) Model-free spin density.

The magnetic structure factors F_M's being the Fourier coefficients of the periodic function $s(\vec{r})$, it is quite natural to use the Fourier inversion to obtain the spin density :

$$s(\vec{r}) = \frac{1}{V} \sum_{\vec{K}} F_M(\vec{K})\, e^{-i\vec{K}.\vec{r}} \tag{5}$$

where V is the volume of the cell, and where Σ implies a summation over all the Bragg reflections. In practice it is not possible to measure all the structure factors, and the series (5) is performed over a limited and somewhat arbitrary number of reflections. The result of this truncation is the following : among all the possible maps which are consistent with the experimental data, the inverse Fourier method chooses that one which corresponds to zero values for the Fourier coefficients which have not been

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measured. Nevertheless this method is the classical reconstruction method and is widely used.

Recently a new method has appeared which is based on the theory of information and the bayesian probabilities : the maximum entropy method (MAXENT). The principle is the following : among all the maps which fit the experimental data, the method chooses that one which has the highest intrinsic probability to exist. Here comes the idea of entropy : the highest intrinsic probability corresponds to the highest entropy, the entropy of a map being defined as :

$$S = - \sum_i p_i \operatorname{Log}(p_i) \qquad (6)$$

where the sum Σ is taken over all the pixels of the map, and where p_i is the density at pixel i, normalized over the cell :

$$p_i = \frac{s_i}{\sum_j s_j} \qquad (7)$$

With this MAXENT method the computing time is much longer, but the quality of the reconstruction is tremendously improved. Moreover in the reconstruction of projected distributions (as for instance the projection of the spin density along the $\vec{c}$ axis), this method makes use of the informations which are contained in all the measured structure factors $F_M(hkl)$, and does not restrict itself to those which are contained in the $F_M(hk0)$ as the Fourier inversion method does.

b) Modeling the spin densities.

Such an approach, which models the spin densities, is based on the knowledge that spin densities result from the presence of unpaired electrons, and the modeling represents the shell nature of these electrons. There are two main ways of modeling : the first one models directly the spin density in a multipolar expansion [1], while the second one models the molecular wave function of the unpaired electron which carries the spin density. We shall develop here this last approach only.

One can write the magnetic molecular wave functions as linear combinations of atomic orbitals centered on the different atoms.

$$|\psi> = \sum_{i}^{\text{atoms}} A_i |\Phi_i> \qquad (8)$$

with

$$\Phi_i = \sum_j a_{ij}\, \varphi_{ij} \qquad (9)$$

where the φ_{ij}'s are the usual 1s , 2s , $2p_x$, ... orbitals which can be represented by the usual Slater functions, with their radial and their angular parts.

The spin density, which, in a restricted Hartree Fock scheme, corresponds to :

$$s(\vec{r}) = <\psi|\psi> \qquad (10)$$

is taken here as :

$$s(\vec{r}) = \sum_{i}^{\text{atoms}} M_i <\Phi_i|\Phi_i> \qquad (11)$$

where M_i, the spin population of atom i, allows, as in an unrestricted Hartree Fock scheme, for a possible negative spin polarization.

The magnetic structure factors $F_M(K)$, which are the Fourier coefficients of $s(\vec{r})$, are then analytical functions of the spin populations M_i, the orbital coefficients a_{ij}, and the exponential coefficients of the radial part of the wave functions. Using equations (9) and (11), it is possible to refine,with a least square method, these coefficients and determine that way the magnetic molecular wave function and then the spin density.

III EXPERIMENTAL PART.

As a polarized neutron experiment consists in measuring the flipping ratios of Bragg reflections, precise nuclear structure factors are required to determine from these flipping ratios accurate magnetic structure factors. Two steps are then necessary : a first type of experiment is carried out with unpolarized neutron (nuclear scattering) to

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determine the low temperature crystal structure of the compound. The second type of experiment is then carried out with polarized neutrons (magnetic scattering), to determine magnetic properties.

III-1) Nuclear scattering.

NITphi : NITphi crystallizes in the monoclinic $P2_1/c$ spacegoup, with two molecules per assymetric unit cell [2]. The low temperature structure was determined on the DN4 diffractometer at the reactor SILOE. A 4x2.5x1 mm^3 crystal was used. 1320 independant reflections with $\sin\theta/\lambda$ up to 0.48 $Å^{-1}$ were collected at T=10K, the incident neutron wavelength being 1.18 Å. The low temperature cell constant are :

a=20.871(33) Å
b=10.150(09) Å β=107.15(10)°
c=12.130(21) Å

Atomic positions were refined using the program ORXFLS [3].

Cu(hfac)2NIT-Me : this axial complex has been reported to crystallize in the triclinic $P\bar{1}$ space group [4]. A 1.6x2.1x1.5 mm^3 crystal was set on the D15 lifting counter diffractometer at the ILL, with $\vec{a}$ axis perpendicular to the equatorial diffraction plane. 616 independant reflections up to $\sin\theta/\lambda$=0.74 $Å^{-1}$ were collected with an incoming neutron wavelength of 1.18 Å at T=10K. Under these temperature conditions, cell parameters are :

a=8.728(21) Å α=81.07(9)°
b=15.988(27) Å β=72.65(11)°
c=9.052(11) Å γ=79.25(13)°

Atomic positions were refined using the program ORXFLS, and complete results of this low temperature structure are reported in ref. [5].

CuCl2(NITphi)2 : the crystal structure of this equatorial complex was determined at room temperature by Laugier et al. [6]. It crystallizes in the monoclinic system, in the space group $P2_1/c$. Two different crystals of size 1.7x1.3x0.5 and 1.2x1x0.6 mm^3 were mounted on the D15 diffractometer with respectively $\vec{a}+\vec{c}$ and $\vec{c}-\vec{b}$ axis vertical. Two sets of 931 and 588 independant reflections were measured with a wavelength of 1.18Å. Atomic positions and thermal parameters were refined using ORXFLS [5].

At T=13K, cell parameters are :

a=11.887(6) Å
b=10.707(6) Å β=128.14(12)°
c=14.215(12) Å

III-2) Magnetic scattering.

NITphi : two series of experiment were carried out on the DN2 polarized neutron diffractometer at SILOE using the wavelength of 1.205Å. In the first series, the 10x4.5x1.3 mm^3 crystal was mounted with the $\vec{c}$ axis vertical and with an applied field of H=8T. In the second series the same crystal was used but it was remounted to set $\vec{b}$ axis vertical; the applied field was in this case 4.65T. 255 independant flipping ratios were collected with $\sin\theta/\lambda$ up to 0.42 Å^{-1}.

Cu(hfac)$_2$NIT-Me : the polarized neutron experiment was performed on the D3 diffractometer (ILL), with a crystal of size 4.8x2.5x2.5 mm^3. One edge of the crystal, corresponding to the $\vec{a}$ axis, was aligned parallel to the 4.65T applied magnetic field. A temperature of 2.5K was chosen to measure the flipping ratios as at lower temperature the magnetic signals decrease, clearly indicating inter-chains coupling. Under these experimental conditions, a set of 162 flipping ratio was collected up to $\sin\theta/\lambda$=0.47 Å^{-1} with a wavelength of 0.84Å.

CuCl$_2$(NITphi)$_2$: this investigation was realized in two steps on the D3 diffractometer. A 6.6x5x1.3 mm^3 crystal was first mounted with $\vec{a}+\vec{c}$ axis collinear to the 4.65T applied field, and then rotated by an angle of 60° for the second part of measurements. For both orientations, the choosen temperature was 13K, temperature where the susceptibility curve reaches a maximum. 227 flipping ratios were measured up to $\sin\theta/\lambda$=0.65 Å^{-1} using the same wavelength as for the previous compound.

III-3) Magnetism.

Susceptibility measurements were performed using a SQUID on the 3 compounds to characterize their magnetic behaviour. Magnetization measurements were also realized to obtain the magnetic structure factor of the (0 0 0) Bragg peak.

NITphi : the compound exhibits typical paramagnetic behaviour with no deviations from the Brillouin susceptibility corresponding to 1μ_B per NITphi formula. At T=5K, the magnetization has been measured at 0.57μ_B per NITphi formula for H=4.65T, and extrapolated to 0.79μ_B at H=8T.

Cu(hfac)$_2$NIT-Me : as expected from geometrical considerations, the magnetic susceptibility as a function of the temperature clearly exhibits a weak ferromagnetic coupling inside the NIT-Cu(hfac)$_2$-NIT-Cu(hfac)$_2$ chains. Below 2.5K, an

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antiferromagnetic coupling between chains appears, forbidding any 3D ferromagnetic ordering of this compound.

$CuCl_2(NITphi)_2$: the strong antiferromagnetic coupling between the 3 fragments of the molecule Nit-CuCl2-Nit which can be predicted by geometrical considerations in term of overlapping of magnetic orbitals has been verified by the variation of the susceptibility with temperature [6]. At low temperature, another mechanism, an antiferromagnetic coupling between neighbouring molecules, gives rise to a decrease of the susceptibility at T<13K. The magnetization at this temperature and in a 4.65T applied field (the polarized neutron experiment conditions) corresponds to $0.08\mu_B$ per $CuCl_2(NITphi)_2$ formula.

IV DATA TREATMENT AND RESULTS.

As pointed out in the first part of this paper, several approaches exist for the reconstruction of the spin density from the experimental magnetic structure factors. We report here the results of magnetic wave function refinement. In this framework, a magnetic wave function is built as a linear combination of Slater type orbital at each magnetic site.

NITphi : the magnetic wavefunction on the nitrogen and oxygen atoms included the $|2p_z>$ (z perpendicular to the the O-N-C-N-O plane) Slater orbital. The phenyl ring contributed six $|2p_{z'}>$, (z' perpendicular to the phenyl ring) orbitals. The spin density on the 3 carbon atoms of the nitronyl group was treated as spherical.

$Cu(hfac)_2NIT\text{-}Me$: the unpaired electron on both copper sites was described by linear combinations of 3d orbitals. The representation $\alpha|2s> + \beta_i|2p_i>$ (i=x,y,z) was adopted for the two N-O groups on the radical fragment. Carbons of the radical backbone and oxygens of the (hfac)'s were reduced to spherical contributions.

$CuCl_2(NITphi)_2$: as the magnetic signal for this compound is weak, more restricted assumptions were included. The contribution on the Cu(II) ion was imposed to be $3dx^2\text{-}y^2$, as expected for a square planar environment. As before, only spherical contributions of the carbons were refined. The same assumption has been used to

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chloro ligands. The 2s contribution in the representation $\alpha|2s> + \beta_i|2p_i>$ has been neglected on both N-O groups.

Coefficients of the projections on the different atomic orbitals were then refined using the program Molly [7], together with Slater radial exponents for compounds 1 and 2. The resulting atomic spin populations are listed in Table I, and the corresponding reconstructed spin density are visualized on figure 1a to 1c as projections along the π^* direction of the NIT radicals.

Table I : spin populations (μ_B) obtained from refinements for the 3 compounds.

Nitϕ	Populations *	Cu(hfac)$_2$ NIT-Me	Populations *	CuCl$_2$ (NITphi)$_2$	Populations *
N1	0.195(5)	N1	0.311(8)	N1	0.017(2)
N2	0.193(5)	N2	0.299(8)	N2	0.018(2)
O1	0.170(5)	O1	0.205(7)	O1	0.000(2)
O2	0.206(6)	O2	0.190(10)	O2	0.019(2)
C1	-0.071(6)	C1	-0.100(9)	C1	-0.010(2)
		Cu1	0.858(9)	Cu	-0.020(2)
		Cu2	0.754(8)		
N3	0.197(5)				
N4	0.195(5)				
O3	0.178(5)				
O4	0.200(5)				
C2	-0.080(6)				

* These populations are normalized to the magnetization values in the experimental conditions (temperature, field).

V DISCUSSION.

In the case of NITphi, the reliability of our experiments is confirmed by the fact that we obtain exactly the same results for the two crystallographically independant molecules (see Table I). The spin distribution shows positive values on the two N-O group and a small but significant negative value on the bridging sp^2 carbon, which can be accounted for by polarization effects. One can see that the two N-O groups carry the same spin. Moreover, the spin density is equally distributed between N and O within each N-O group, as it was already witnessed in a previous polarized neutron experiment on the radical tempone [8].

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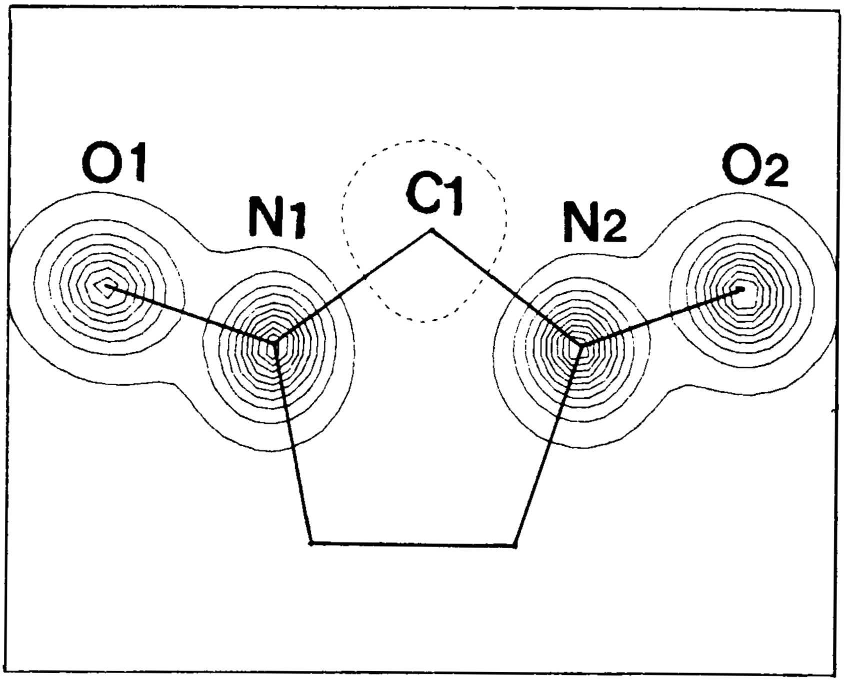

Figure 1-a : Projection of the spin density in the compound NITphi along the π* direction.

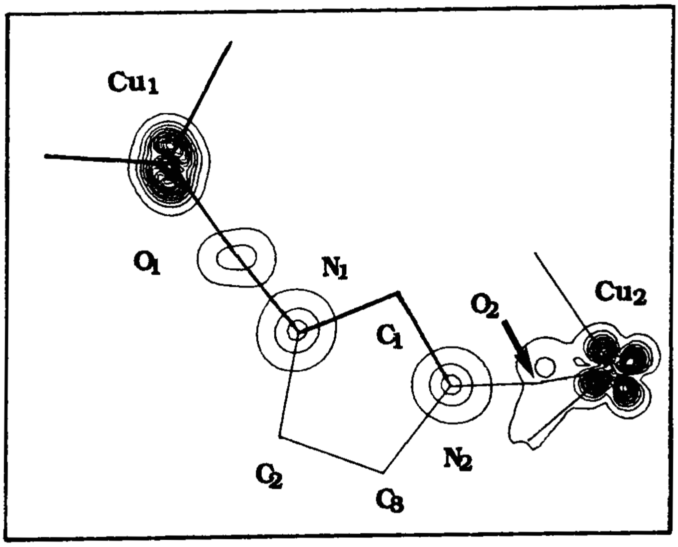

Figure 1-b : Projection of the spin density in the complex Cu(hfac)$_2$NIT-Me along the π* direction.

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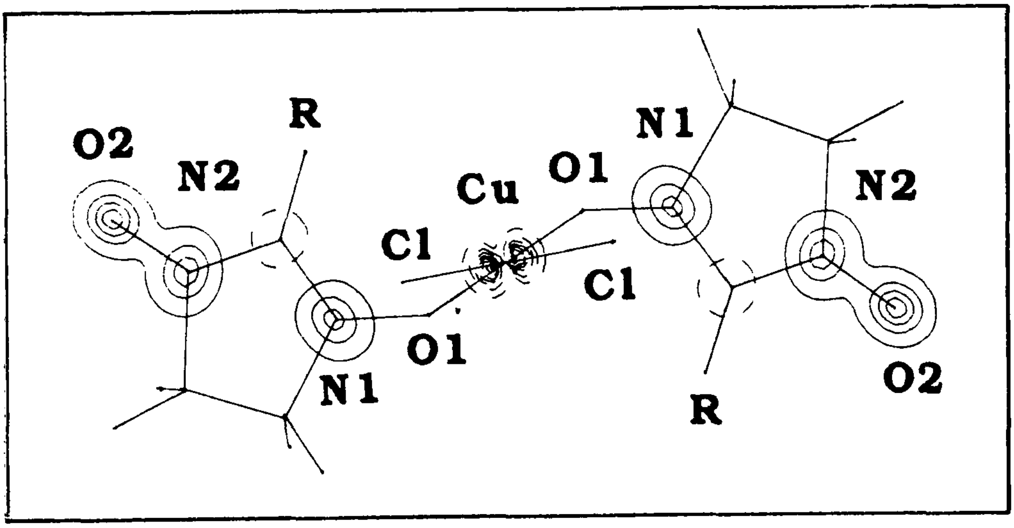

Figure 1-c : Projection of the spin density in the complex $CuCl_2(NITphi)_2$ along the π^* direction.

As expected for a ferromagnetic interaction case, the spin density distribution in the axial complex, $Cu(hfac)_2$NIT-Me, exhibits only positive values except on the central sp^2 carbon. The spin density on the radical is symetrically shared by the two N-O groups, but inside each group one can observe, if we refer to the previous compound, a transfer from oxygen to nitrogen, resulting in a 40%/60% repartition. The weak metal-radical coupling leads to a small transfer from O to N, as it is the case when nitroxydes are involved in weak bonding such as hydrogen bonds [8]. Furthermore, our wave function analysis of unpaired electrons is in good agreement with the scheme of accidental orthogonality of magnetic orbitals [9] that can be used to explain the ferromagnetic behaviour of this compound.

The spin density distribution in the equatorial complex, $CuCl_2(NITphi)_2$, has opposite signs on radical and copper parts as expected for an antiferromagnetic coupling. The negative contribution on the bridging carbon due to polarization effects is still there. What differs drastically from the previous cases is the distribution inside the nitronyl nitroxyde. The two atoms N-O of the uncoordinated bear equal spin populations, as it was the case for the isolated radical (compound 1), whereas dramatic changes occur in the coordinated N-O group. While the nitrogen atom carries a spin population roughly equal to both N and O on the uncoordinated group, no spin density is found on the bridging oxygen. The strong binding with the copper ion results in a complete loss of the spin density on this oxygen.

The absence of spin density on the chloro ligands is the sign of a predominant ionic character of the copper-halogen bond. If we look at spin populations, we can see a repartition of spin density 2/3⇑ on NIT, -1/3⇓ on Cu, 2/3⇑ on the second NIT. This repartition corresponds to one of the two expected doublets of antiferromagnetic coupling of 3 spins s=1/2. Our orbital description in this equatorial complex is also consistent with the scheme of an overlapping of the magnetic orbitals leading to a strong negative interaction [9].

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