CRYSTALLOGRAPHIC AND ESR STUDY OF THE TETRAIMINE MACROCYCLIC Cu(II) COMPLEX PURE AND DILUTED IN THE ISOMORPHIC Ni(II) COMPLEX.

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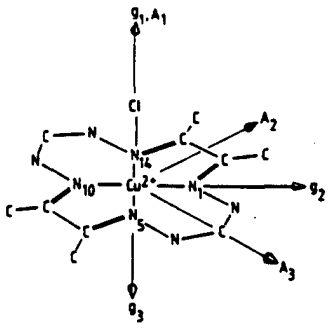

The single crystal ESR spectrum of the tetraimine macrocyclic Cu(II) complex $Cu(C_{10}H_{20}N_8)Cl\ Cl$, pure and diluted in the analogous Ni(II) complex as well as the crystal structures of these two compounds have been determined.
Both crystallize in the triclinic system (Space Group P $\bar{1}$) with Z = 2 and the following parameters:
$[Ni(C_{10}H_{20}N_8)Cl]Cl$: a = 7.523 , b = 9.502 , c = 11.447 Å, α = 95.82, β = 108.01, γ = 98.62 °
$[Cu(C_{10}H_{20}N_8)Cl]Cl$: a = 7.574 , b = 9.548 , c = 11.469 Å, α = 96.31, β = 107.19, γ = 99.67 °

Due to the presence in the crystallographic cell of only two molecules related by a centre of inversion, the molecular g-values could be directly determined from the single crystal measurement of the pure copper complex. One finds : $g_1 = 2.183$, $g_2 = 2.066$, $g_3 = 2.047$ with the corresponding eigenvectors directed ~ along the bond directions.

The g-values found in the magnetically diluted complex (prepared with the ^{63}Cu isotope) are practically the same, within experimental error : $g_1 = 2.178$, $g_2 = 2.066$, $g_3 = 2.048$.
Here, moreover, the hyperfine interaction with the ^{63}Cu nucleus could be measured: $A_1 = 175$, $A_2 = 48$, $A_3 = 22$ gauss and also the superhyperfine interaction with the four nitrogen ligands: $A_1 = 16$, $A_2 = 14$, $A_3 = 13$ gauss.

The g-eigenvectors are ~ along the bond directions whereas the hyperfine eigenvectors are oriented along the bissectors of the bonds in the basic plane of the coordination pyramid.
The measured values of the ESR quantities could be reproduced theoretically in the frame of an AOM model with the following parameter values:
$(e_\sigma)_{N_{1,10}} = 7680\ cm^{-1}$, $(e_\sigma)_{N_{5,14}} = 8000\ cm^{-1}$, $(e_\sigma)_{Cl} = 2000\ cm^{-1}$, $(e_\pi)_{N_i} = 1000\ cm^{-1}$, $(e_\pi)_{Cl} = 500\ cm^{-1}$, $\zeta_{Cu} = 500\ cm^{-1}$, $P = 300.10^{-4}\ cm^{-1}$ and $\kappa = 0.3$.