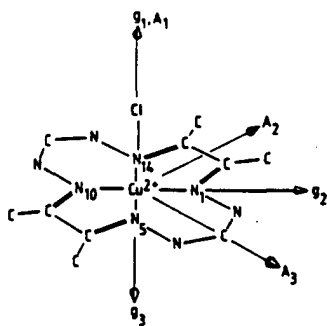


CRYSTALLOGRAPHIC AND ESR STUDY OF THE TETRAIMINE MACROCYCLIC Cu(II) COMPLEX  
PURE AND DILUTED IN THE ISOMORPHIC Ni(II) COMPLEX.

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The single crystal ESR spectrum of the tetra-  
imine macrocyclic Cu(II) complex  
 $\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_8)\text{Cl}_2$ , pure and diluted in the ana-  
logous Ni(II) complex as well as the crystal  
structures of these two compounds have been de-  
termined.

Both crystallize in the triclinic system (Space  
Group P 1) with  $Z = 2$  and the following param-  
eters:

$[\text{Ni}(\text{C}_{10}\text{H}_{20}\text{N}_8)\text{Cl}]_2\text{Cl}_2$  :  $a = 7.523$  ,  $b = 9.502$  ,  $c =$   
 $11.447$  Å,  $\alpha = 95.82$ ,  $\beta = 108.01$ ,  $\gamma = 98.62^\circ$   
 $[\text{Cu}(\text{C}_{10}\text{H}_{20}\text{N}_8)\text{Cl}]_2\text{Cl}_2$  :  $a = 7.574$  ,  $b = 9.548$  ,  $c =$   
 $11.469$  Å,  $\alpha = 96.31$ ,  $\beta = 107.19$ ,  $\gamma = 99.67^\circ$

Due to the presence in the crystallographic cell of only two molecules re-  
lated 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 eigen-  
vectors directed  $\sim$  along the bond directions.

The  $g$ -values found in the magnetically diluted complex (prepared with the  
 $^{63}\text{Cu}$  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  $^{63}\text{Cu}$  nucleus could be  
measured:  $A_1 = 175$ ,  $A_2 = 48$ ,  $A_3 = 22$  gauss and also the superhyperfine in-  
teraction with the four nitrogen ligands:  $A_1 = 16$ ,  $A_2 = 14$ ,  $A_3 = 13$  gauss.

The  $g$ -eigenvectors are  $\sim$  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:

$(e_\sigma)_{\text{N}_{1,10}} = 7680 \text{ cm}^{-1}$ ,  $(e_\sigma)_{\text{N}_{5,14}} = 8000 \text{ cm}^{-1}$ ,  $(e_\sigma)_{\text{Cl}} = 2000 \text{ cm}^{-1}$ ,  $(e_\pi)_{\text{N}_i} =$   
 $1000 \text{ cm}^{-1}$ ,  $(e_\pi)_{\text{Cl}} = 500 \text{ cm}^{-1}$ ,  $\zeta_{\text{Cu}} = 500 \text{ cm}^{-1}$ ,  $P = 300 \cdot 10^{-4} \text{ cm}^{-1}$  and

$\kappa = 0.3$ .