LOCAL STRUCTURE OF THE $\text{CuCu}(\text{EDTA})(\text{H}_2\text{O})_2, 2\text{H}_2\text{O}$ AMORPHOUS COMPLEX: A JOINT MAGNETIC, LAXS, AND MOLECULAR MECHANICS INVESTIGATION

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LOCAL STRUCTURE OF THE $\text{CuCu(EDTA)(H}_2\text{O)}_2 \cdot 2\text{H}_2\text{O}$ AMORPHOUS COMPLEX :
A JOINT MAGNETIC, LAXS, AND MOLECULAR MECHANICS INVESTIGATION

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Résumé - L'ordre local dans le matériau amorphe $\text{CuCu(EDTA)(H}_2\text{O)}_2 \cdot 2\text{H}_2\text{O}$ est étudié par diffusion des rayons X aux grands angles (LAXS) et par la mécanique moléculaire. Trois conformations énergétiquement équivalentes sont mises en évidence. Deux d'entre elles participent à la structure de la phase amorphe.

Abstract - The short range order in the amorphous $\text{CuCu(EDTA)(H}_2\text{O)}_2 \cdot 2\text{H}_2\text{O}$ is studied by Large Angle X-ray Scattering (LAXS) and molecular mechanics. Three conformations of the complex molecule are shown to be energetically equivalent, two of which are simultaneously present in the amorphous material.

Due to their ability to provide outstanding models for experimental and theoretical investigations, the structurally one-dimensional compounds have been thoroughly investigated.

A series of polymeric compounds, $\text{MM'(EDTA)(H}_2\text{O)}_4 \cdot 2\text{H}_2\text{O}$ with $\text{MM}' = \text{Co, Ni, Mn, Cd...}$ have been investigated both in the crystalline and in the amorphous state, and their magnetic versus structural properties established (1-4). The amorphous $\text{CuCu(EDTA)(H}_2\text{O)}_2 \cdot 2\text{H}_2\text{O}$ term exhibits a different behaviour, i.e. a magnetic susceptibility following a Curie law between 4 K and 300 K, implying no magnetic coupling of the Cu(II) ions suggesting a local structure built up by dimeric entities $(\text{H}_2\text{O})\text{Cu(EDTA)Cu(H}_2\text{O)}$ as in the crystalline phase (5).

A LAXS (Large Angle X-ray Scattering) study has been performed giving the typical experimental radial distribution curve indicated in Figure 1 (full line). It has not been possible to fit such curve using the molecular model extracted from the crystal structure.

Investigation by molecular mechanics was then decided in order to find some "reasonable" molecular conformations, i.e. of similar energy and easy to reach. This has been realized with the help of the sophisticated program MM2 by Allinger et al. (6) within the assumption that in the molecule the two fused-ring moieties were rather rigid, at least around the copper atoms.

Figure 1. Comparison between experimental (full line) and theoretical (dotted line) RDF.

Using the "driver" facility of the program, we moved to the dihedral angles θ_1 (Cu(1)-N(1)-C(1)-C(2)) and θ_2 (C(1)-C(2)-N(2)-Cu(2)) and optimized the constraint energy while the other geometrical parameters were left to adjust to the minimization requirements.

For the purpose of comparison, the conformation found in the crystal was allowed to "relax", i.e. to minimize similarly its constraint energy, thus freeing the isolated molecule from the distortions caused by the packing forces. The geometry did not change much and the constraint energy converged on the value 18.84 kcal.mole⁻¹ for the conformation 1 ($\theta_1 = 65.4^\circ$ and $\theta_2 = -64.1^\circ$) (Figure 2).

Two conformations are found very close in energy: conformation 2 ($\theta_1 = 63.6^\circ$, $\theta_2 = -178.9^\circ$, $E_c = 18.92$ kcal.mole⁻¹) and conformation 3 ($\theta_1 = 179.4^\circ$, $\theta_2 = -178.1^\circ$, $E_c = 19.22$ kcal.mole⁻¹).

In order to examine if these conformations were accessible, the rotation barriers around the N(1)-C(1) and C(1)-C(2) bonds were estimated by simulation. For $\theta_1 = 63^\circ$ (fixed) the barrier around C(1)-C(2) was found to be 5.6 kcal.mole⁻¹ while for $\theta_2 = 120^\circ$ (variable) and for $\theta_2 = 180^\circ$ (fixed) the barrier around N(1)-C(1) was 5.8 kcal.mole⁻¹ for $\theta_1 = 120^\circ$ (variable) too.

These results indicate a possible way - two steps at least - which allows conformational transformation with low energy consumption.

Several combinations of these three conformations were tested. The best fit was obtained using conformations 2 and 3. In no case is the broad peak centred at $r \approx 7$ Å explained. It was then thought of building a model implying a stacking of the

Figure 2. ORTEP drawings of preferred conformations for the $\text{Cu}_2\text{EDTA}(\text{H}_2\text{O})_2$ dimer.

molecules in conformation 3. This assumption has been tested by calculating the constraint energy and the optimal relative disposal of two molecules. A stabilization energy due to attractive Van der Waals forces of $2.1 \text{ kcal.mole}^{-1}$ is found for the stacking pictured in Figure 2-d.

The final model proposed, corresponding to the theoretical RDF (Figure 1, dotted line) consists of three stacked molecules in conformation 3 and one in conformation 2.

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