

[s9'.m1.p17] Low-Temperature Structure, Molecular Dynamics and Phase Transition of Phenothiazine.

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Phenothiazine is a molecular crystal which undergoes a ferroelastic phase transition at and atmospheric pressure, a very interesting fact given that the number of neutral molecular crystals which display ferroelasticity is small.

The high-temperature phase has been reported to be orthorhombic at room temperature¹, space group *Pbnm*, with four molecules in the unit cell located in special positions at mirror planes. It has been claimed² that this structure is disordered with respect to the mirror plane in view of the large values of the crystallographic thermal parameters in the direction perpendicular to the mirror plane. The low-temperature phase (LTP) cannot be solved with single-crystal work because of the existence of ferroelastic twin domains.

We have carried out a structural analysis of the LTP using X-ray powder diffraction and Rietveld refinements. The results show that it is monoclinic *P2₁/n* with small structural changes with respect to the orthorhombic high-temperature phase. Besides *e*₁₃ the shear strain corresponding to the transition from the orthorhombic to the monoclinic unit cells, the main structural change is a molecular tilt.

Molecular dynamics simulations of the HTP with atom-atom potential functions used in previous studies of this compound³⁻⁵ yield *Pbnm* a orthorhombic structure in good agreement with the experimental one which shows large molecular movements with respect to the mirror plane, contradicting the static disorder hypothesis.

At low temperatures the MD simulation finds a *P2₁/n* monoclinic structure which agrees with the experimental one although the calculated transition temperature is lower than the experimental one. The MD calculation of the *C*₅₅ elastic constant as a function of temperature shows a softening at the transition point in agreement with the experimental data and the ferroelastic character of the transition. A possible mechanism for the LTP? HTP transition is proposed where the increasing rotational motion of the molecules with temperature in the LTP induces the softening of the *C*₅₅ elastic constant and hence the transition.

[s9'.m1.p18] Synthesis, Crystal Structure and Magnetic Properties of Linear Trinuclear Nickel(II) Complexes.

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[Ni₃ (C₂ H₃ O₂)₂ (CH₃O)₂ L₂] [L = 1,3 - Bis (5 - chlorosalicylideneamino)propan-2-ol (C₂H₃O₂) =acetate, (CH₃O) = methanol] (**1**) and [Ni₃(C₂H₃O₂)₂(C₃H₈NO)₂L₂] [(L = N , N' - 1,3 - propyl - disalicylaldimine), (C₂H₃O₂) = acetate (C₃H₈NO) = hydroxymethyl-dimethylamine] (**2**) were synthesized and their crystal structures determined. [C₄₀H₄₀N₄O₁₂Cl₄Ni₃·2H₂O] (**1**), monoclinic, space group *P2₁/n*, a=12.694(2), b=13.281(4), c=15.420(3) Å, β=111.25(2)°, V=2422.9(9) Å³, Z=2. [C₄₄H₅₄N₆O₁₀Ni₃] (**2**), triclinic, space group *P1̄*, a = 9.560(1), b = 10.681(1), c = 12.200(1) Å, α = 112.17(1), β = 101.25(1), γ = 90.32(1)°, V=1127.3 Å³, Z=1. Both compounds are linear trinuclear with nearly octahedral coordination of each nickel ion. Two adjacent nickel(II) ions are bridged by oxygen atoms of ligands and oxygen atoms of acetato ligands, the coordination sphere of terminal nickel(II) ions is completed by an oxygen atom of methanol in compound (**1**) and an oxygen atom of hydroxymethyl-dimethylamine in compound (**2**). In the compound (**1**) the adjacent nickel(II) centers are separated by 3.043(1) Å and weak antiferromagnetically coupled (J₁ = - 3.4 cm⁻¹), the terminal nickel(II) centers are separated by 6.086(1) Å with very weakly antiferromagnetic coupling (J₂ = -0.3 cm⁻¹) which follows from temperature-dependent magnetic susceptibility measurements in the temperature range 4.5 to 318 K. For compound (**2**) magnetic susceptibility measurements in the range 4.2<T<280 K have revealed antiferromagnetic coupling between adjacent Ni atoms (J₁ = -2.2 cm⁻¹) and between the terminal Ni atoms (J₂ = -1.7 cm⁻¹). The nature of the magnetic super-exchange interactions of the compound (**1**) and (**2**) are compared with similar linear trinuclear Ni(II) complex¹ by considering Anderson-Kanamori rules^{2,3}.

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