

MAGNETIC STUDIES OF [ClCNSSS-][AsF₆] BY MULTIFREQUENCY ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

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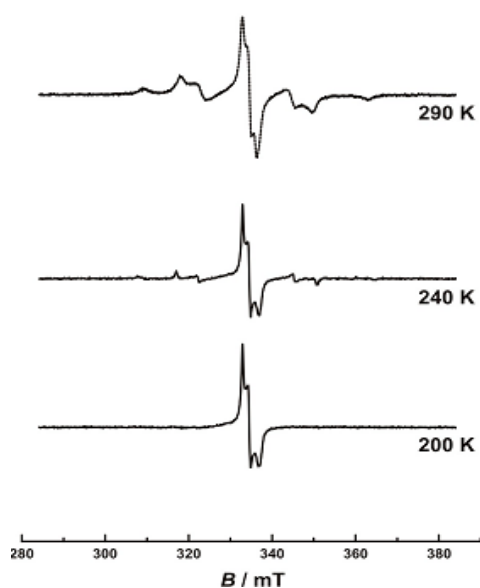


Fig. 1. Evolution of the EPR spectra as a function of temperature.

[ClCNSSS-][AsF₆] comprises an ordered network of radical cations with shortest intermolecular S...S distances of about 3.2 Å suggesting a possible strong exchange interaction. The complicated multifrequency (4-25 GHz) c.w. EPR powder spectra come from a superposition of a rhombic electron spin doublet signal arising from monomeric radical cations and a contribution of six resonance lines as expected for a randomly oriented rhombic electronic spin triplet state.

(Fig. 1) The triplet signal is attributed to a pair of exchange coupled radicals formed by a pairwise association of the cations. A single set of spin-Hamiltonian parameters for each spin state gives good

spectrum simulations for solutions, glasses and powders at all frequencies, and most importantly for a single-crystal study. The antiferromagnetic character of the exchange interaction between the coupled spins was confirmed from the temperature dependence of intensities of the resonance lines in the thermally populated triplet, and this also gave an estimation of the singlet-triplet energy gap.

Analysis of the Zero Field Splitting parameter $|D|$ as a function of temperature is consistent with shortening the S...S distance on cooling and consequent increase in dipolar character of the interaction between spins. The temperature hysteresis of the intensities of the triplet resonance lines and values of $|D|$ indicate a dynamic character to the changes in structure of the lattice (Fig. 2).

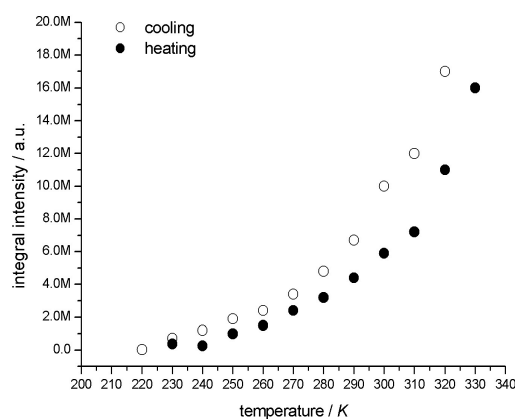


Fig. 2. Temperature dependence of triplet integral intensities.