

Temperature Dependence of the Crystal Lattice Organization of Coordination Compounds Involving Nitronyl Nitroxide Radicals: A Magnetic and Structural Investigation.

Fettouhi, Mohammed; El Ali, Bassam; El-Ghanam, Abdel Moneim; Golhen, Stephane; Ouahab, Lahcene; Daro, Nathalie; Sutter, Jean-Pascal. Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Inorganic Chemistry (2002), 41(14), 3705-3712.

Abstract

Four new mononuclear complexes Cd(PN)₄(NCS)₂ (A), Cd(PNN)₄(N₃)₂ (B), Zn(PNN)₄(N₃)₂ (C), and Zn(PNN)₂(NCS)₂ (D), where PNN stands for 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and PN for 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, were synthesized and structurally and magnetically characterized. The x-ray structures of compds. B and C were also detd. at 90 K. Compds. A-C crystallize in the triclinic space group P $\bar{1}$, and D crystallizes in the monoclinic space group P2₁/m. A-C adopt a centrosym. distorted octahedral geometry in which the metal ions are bonded to four radical ligands through the nitrogen atom of the pyridyl rings and the azido or thiocyanato ligands occupy the apical positions. Compd. D adopts a distorted tetrahedral geometry in which the zinc ion is bonded to two radicals and two thiocyanato ligands. As suggested by their magnetic behavior, the low-temp. x-ray structures of B and C show that these compds. undergo a clear structural change with respect to the room-temp. structures. The exptl. magnetic behaviors were perfectly reproduced by a dimer model for A-C and an alternating chain model for D while the sudden breaks obsd. in the χ_{MT} vs. T curves for B and C were well accounted for by the high- and low-temp. x-ray structures. For all these complexes the crystal structures favor significant overlap between mol. magnetic orbitals leading to rather strong intermol. antiferromagnetic interactions.