Unusual Magnetism of an Unsymmetrical Trinickel Chain

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ABSTRACT

An unsymmetrical trinickel extended metal atom chain (EMAC) compound, [Ni₃(dpa)₄(CH₃CN)](PF₆)₂·2CH₂Cl₂, 1·2CH₂Cl₂ (dpa is the anion of 2,2'-dipyridylamine), has the central Ni atom in an essentially square planar configuration while the two terminal metal centers have notable different axial interactions with one having a strongly bound acetonitrile molecule with a Ni(3)–N(3) distance of 2.108(5) Å. In this outer unit, the Ni atom is pulled out of the idealized plane of the four equatorial nitrogen atoms by 0.239 Å. The other terminal Ni unit has a very weak interaction with an axial PF₆ anion (Ni(1)···F(1) separation of 2.690 Å) and this metal atom is pulled from the plane of the equatorial nitrogen atoms by only 0.097 Å. In 1 there are two unpaired electrons and the $S = 1$ state prevails from ca. 25 to 300 K, consistent with the presence of two non-magnetic Ni(II) units in a nearly square planar arrangement and a paramagnetic entity in a pyramidal environment. This magnetic behavior differs considerably from that of symmetrical trinickel EMACs with two pyramidal terminal nickel atoms. A discussion of the effect of various axial ligands on the geometry of the terminal nickel atoms is provided.