

Rich magnetic chemistry of cobalt(II) complexes with N-phosphorylthioureas. Crystal structure and solution ^1H NMR spectral properties

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Abstract

Structure and magnetic properties of Co(II) complexes with N-phosphorylthiourea derivatives $[\text{RC}(\text{S})\text{NHP}(\text{O})(\text{O}i\text{Pr})_2]$ (HL) $[\text{Co}\{\text{Et}_2\text{NC}(\text{S})\text{NP}(\text{O})(\text{O}z\text{Pr})_2\}_2]$ (1), $[\text{Co}\{(\text{PrNHC}(\text{S})\text{NP}(\text{O})-(\text{O}i\text{Pr})_2)_2\}_2]$ (2), $[\text{Co}\{[i\text{-BuNHC}(\text{S})\text{NP}(\text{O})(\text{O}i\text{Pr})_2\}_2]$ (3), $[\text{Co}\{p\text{-MeOC}_6\text{H}_4\text{NHC}(\text{S})\text{NP}(\text{O})(\text{O}(\text{Pr})_2)_2\}_2]$ (4), $[\text{Co}\{P\text{-BrC}_6\text{H}_4\text{NHC}(\text{S})\text{NP}(\text{O})(\text{O}(\text{Pr})_2)_2\}_2]$ (5) were investigated. Paramagnetic shifts in the ^1H NMR spectrum were observed for high-spin Co(II) complexes with HL, incorporating amidophosphate moiety $\text{C}(\text{S})\text{NP}(\text{O})$. The thermal dependence of the magnetic susceptibility has shown that the extended materials 2, 3 and 5 show ferromagnetic exchange between distorted tetrahedral metal atoms, while in complex 4 antiferromagnetic behavior takes place. Compound 1 behaves as a spin-canted ferromagnet, an antiferromagnetic ordering taking place below a critical temperature, $T_c = 175$ K. Complex 2 was investigated by single crystal X-ray diffraction. The cobalt(II) atom in complex 2 is in distorted tetrahedral CoO_2S_2 environment formed by the $\text{C}=\text{S}$ sulfur atoms and the $\text{P}=\text{O}$ oxygen atoms of two deprotonated ligands. © 2007 WILEY-VCH Verlag GmbH & Co. KGaA.

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Keywords

Amidophosphate, Chelate, Magnetic susceptibility, Nmr-spectroscopy, Thioureas