

Cobalt(II) complexes with N-thioacylamidophosphates and 2,2'-bipyridyl and 1,10-phenanthroline. Crystal structures, solution ¹H NMR spectral and magnetic properties

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Abstract

Structure and magnetic properties of N-diisopropoxyphosphorylthiobenzamide PhC(S)-N(H)-P(O)(OiPr)₂ (HL I) and N-diisopropoxyphosphoryl-N'-phenylthiocarbamide PhN(H)-C(S)-N(-)-P(O)(OiPr)₂ (HL II) complexes with the Co II cation of formulas [Co{PhC(S)-N-P(O)(OiPr)₂}₂] (1), [Co(PhN(H)-C(S)-N-P(O)(OiPr)₂)₂] (2), [Co{PhC(S)-N(H)-P(O)(OiPr)₂}₂{PhC(S)-P(O)(OiPr)₂}₂] (1a) and [Co{PhC(S)-N-P(O)(OiPr)₂}₂](2,2'-bipy)] (3), [Co{PhC(S)-N-P(O)(OiPr)₂}₂](1,10-phen)] (4), [Co{PhN(H)-C(S)-N-P(O)(OiPr)₂}₂](2,2'-bipy)] (5), [Co(PhN(H)-C(S)-N-P(O)(OiPr)₂)₂](1,10-phen)] (6) were investigated. Paramagnetic shifts in the ¹H NMR spectrum were observed for high-spin Co II complexes with HL I,II, incorporating the S-C-N-P-O chelate moiety and two aromatic chelate ligands. Investigation of the thermal dependence of the magnetic susceptibility has shown that the extended materials 1-2 and 6 show ferromagnetic exchange between distorted tetrahedral (1, 2) or octahedral (1a, 6) metal atoms whereas 3 and 5 show antiferromagnetic properties. Compound 4 behaves as a spin-canted ferromagnet, an antiferromagnetic ordering taking place below a critical temperature, T_c = 115 K. Complexes 1 and 1a were investigated by single crystal X-ray diffraction. The cobalt(II) atom in complex 1 resides a distorted tetrahedral O₂S₂ environment formed by the C=S sulfur atoms and the P=O oxygen atoms of two deprotonated ligands. Complex 1a has a tetragonal-bipyramidal structure, Co(O_{ax})₂(O_{eq})₂(S_{eq})₂, and two neutral ligand molecules are coordinated in the axial positions through the oxygen atoms of the P=O groups. The base of the bipyramid is formed by two anionic ligands in the typical 1,5-O,S coordination mode. The ligands are in a trans configuration. © 2007 WILEY-VCH Verlag GmbH & Co. KGaA.

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Keywords

Amidophosphates, Chelate, Cobalt, Magnetic properties, NMR spectroscopy