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

Autorzy

Damir A. Safin

Piotr Młynarz

F. E. Hahn

Maria G. Babashkina

F. D. Sokolov

N. G. Zabirov

Joanna Gałęzowska

Henryk Kozłowski

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Streszczenie

Structure and magnetic properties of *N*-diisopropoxyphosphorylthiobenzamide PhC(S)-N(H)-P(O)(O*i*Pr)$_2$ (**HL^{I}**) and *N*-diisopropoxyphosphoryl-*N′*-phenylthiocarbamide PhN(H)-C(S)-N(H)-P(O)(O*i*Pr)$_2$ (**HL^{II}**) complexes with the Co^{II} cation of formulas [Co{PhC(S)-N-P(O)(O*i*Pr)$_2$}$_2$] (**1**), [Co{PhN(H)-C(S)-N-P(O)(O*i*Pr)$_2$}$_2$] (**2**), [Co{PhC(S)-N(H)-P(O)(O*i*Pr)$_2$}$_2${PhC(S)-N-P(O)(O*i*Pr)$_2$}$_2$] (**1a**) and [Co{PhC(S)-N-P(O)(O*i*Pr)$_2$}$_2$](2,2′-bipy)] (**3**), [Co{PhC(S)-N-P(O)(O*i*Pr)$_2$}$_2$(1,10-phen)] (**4**), [Co{PhN(H)-C(S)-N-P(O)(O*i*Pr)$_2$}$_2$(2,2′-bipy)] (**5**), [Co{PhN(H)-C(S)-N-P(O)(O*i*Pr)$_2$}$_2$(1,10-phen)] (**6**) were investigated. Paramagnetic shifts in the ^{1}H 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 O_2S_2 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.

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