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ORIGINAL PAPER

Magnetic chains formed from tetra-coordinate Co(II) complexes[‡]

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Two tetra-coordinate Co(II) complexes, $[CoCl_2(bzfupy)_2]$ and $[CoCl_2(p\text{-}tol)_2]$ with N-donor ligands, are apparently mononuclear systems. The magnetic susceptibility at low temperature attains a maximum which is a fingerprint of the exchange interaction. The exchange coupling constant fitted to a model of 1D-magnetic chain yields $J/hc = -0.50$ cm^{-1} and -0.57 cm^{-1}, respectively. The magnetic interaction is mediated by the π–π stacking in the first complex, and the short Cl$\cdots$Cl contacts in the second.
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Introduction

Cobalt(II) complexes are very variable from the perspective of magnetochemistry (Lloret et al., 2008; Papánková et al., 2010). They adopt either a quasi-octahedral hexa-coordinate configuration, or a quasi-tetrahedral tetra-coordinate configuration, although penta-coordination is also frequent.

In the compressed tetragonal bipyramid, the ground electronic term is $^4A_{1g}$ and this is subjected to zero-field splitting. As a consequence, the effective magnetic moment on cooling from the laboratory temperature remains constant and it decreases at low temperature. The zero-field splitting is a gap between the two lowest crystal-field multiplets (Kramers doublets) $\Delta = 2D = E(\Gamma_7) - E(\Gamma_6) > 0$. The reported D-values are high: $D \sim 10^2$ cm^{-1} (Boča, 2004; Titiš & Boča, 2011). By contrast, for the elongated tetragonal bipyramid, the ground electronic term is orbitally degenerate – ^4E_g and it produces four Kramers doublets; this situation needs modelling beyond the spin-Hamiltonian formalism (Boča, 2006). The effective magnetic moment, on cooling, then passes through a round maximum.

In tetra-coordinate complexes, the ground term is $^4A_2$ and the situation can be described by the spin Hamiltonian that accounts for the zero-field splitting. Moderate D-values, both negative and positive, were reported (Krzystek et al., 2004); in the regular tetrahedron $D = 0$ holds true.

A lot of dinuclear and trinuclear complexes are known where the D-parameter has been determined by fitting the magnetic data (Hudák et al., 2011).

In this article we report on two mononuclear Co(II) complexes of the general formula $[CoCl_2L_2]$ where L stands for an N-donor heterocyclic ligand: bzfupy = benzofuro[3,2-c]pyridine and p-tol = p-toluidine.

Experimental

$CoCl_2 \cdot 6H_2O$, toluidine, and ethanol were purchased from commercial sources and used as received. The target complexes $[CoCl_2(bzfupy)_2]$ and $[CoCl_2(p\text{-}tol)_2]$, subsequently I and II, were prepared by the methods already described elsewhere (Vrábel et al., 2007; Malinovskii, 1957).

Electronic spectra (in Nujol mull) were measured using a Specord 200 instrument (Analytik Jena AG,

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