Syntheses, Spectral and Thermal Studies, and Crystal Structure of 1,10-Phenanthroline and Picolinamide Complexes of Cobalt(II) Squarate

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Z. Naturforsch. 61b, 1094 – 1100 (2006); received February 7, 2006

Preparations, crystal structures, thermal properties, IR and UV/vis spectroscopic studies and magnetic moments of tris(1,10-phenanthroline)cobalt(II) squarate octahydrate, \([\text{Co(phen)}_3] \text{sq} \cdot 8\text{H}_2\text{O} (1)\) and diaquabis(picolinamide)cobalt(II) squarate, \([\text{Co(H}_2\text{O})_2\text{(pia)}_2] \text{sq} (2)\) are described. 1 crystallizes in the monoclinic system, space group \(P2_1/c\), with \(a = 10.9832(5)\), \(b = 21.4569(12)\), \(c = 17.0649(7)\) \(\text{Å}\), \(\beta = 98.159(3)\)° and \(Z = 8\), while 2 crystallizes in the triclinic system, space group \(P\overline{1}\), with \(a = 6.9624(9)\), \(b = 7.9224(11)\), \(c = 8.0501(11)\) \(\text{Å}\), \(\alpha = 107.404\)°, \(\beta = 93.340(11)\)°, \(\gamma = 93.266\)° and \(Z = 1\). Both 1 and 2 have slightly distorted octahedral coordination geometry, involving six N atoms from bidentately chelating phen ligands and \(\text{trans}–[\text{CoN}_2\text{O}_4]\) coordination geometry, in which the Co atom is located at a center of symmetry. There are significant hydrogen-bonding interactions in the structure of 1. The squarate dianions are linked to the eight solvent water molecules by means of hydrogen-bonding interactions. Moreover, there are links between the complex cation and the squarate dianion \(\text{via} \text{C}–\text{H} \cdots \text{O} \) hydrogen bonds. These interactions hold the crystal structure of 1 in a three-dimensional network, while O–H \cdots O, N–H \cdots O, weak \(\pi \cdots \pi\) and \(\pi \cdots \text{ring}\) interactions lead to a three-dimensional crystal structure for 2. The thermal decomposition pathways of 1 and 2 have been investigated by the help of thermal analyses data (TG and DTA).

Key words: Cobalt(II) Complex, 1,10-Phenanthroline, Picolinamide, Squarate, Thermal Decomposition