A new Cu(II) [12]metallocrown-4 pentanuclear complexe based on a Cu(II)-malonomonohydroxamic acid unit.

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Streszczenie

The first example of a Cu(II) [12]-MC-4 hydroxamic metallacrown compound containing a carboxyl group as a supporting donor function is described. The solution equilibria of malonomonohydroxamic acid (MACZ, H_2L) with Cu(II) are investigated in aqueous solution using a combination of potentiometry, UV-vis absorption spectrophotometry, EPR spectroscopy and ESI mass spectrometry. Among the four complexes fitting the best speciation model ([CuL], $[Cu_5L_4H_{-4}]^{2-}$, $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$), a pentameric metallacrown molecule of composition Cu : L = 5 : 4 predominates in solution over the pH 4 to 11 range, and the corresponding complex was isolated in the solid state. The crystallization of the complex $[Cu_5L_4H_{-4}]^{2-}$ in the presence of $[Cu(en)_2(H_2O)_2]^{2+}$ cations resulted in the isolation of $[Cu(en)_2(H_2O)_2]_n[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n \cdot 20nH_2O$ (**1**), whose crystal structure has been determined by X-ray analysis. The structure of **1** consists of centrosymmetric complex cations $[Cu(en)_2(H_2O)_2]^{2+}$, infinite complex anionic chains $[Cu(en)_2(H_2O)(\mu\text{-}H_2O)\{Cu_5(L_4H_{-4})(H_2O)_3\}_2]_n^{2n-}$ and solvate water molecules. Within the complex anionic chains, the decanuclear double-decked bis([12]-MC-4) complex anions $\{Cu_5(L_4H_{-4})(H_2O)_3\}_2^{4-}$ are united by the $[Cu(en)_2(H_2O)_2]^{2+}$ complex cations due to the bridging function of the axial water molecule O(5). The magnetic behaviour of **1**, studied in the temperature range 1.8–300 K, suggests the presence of both antiferromagnetic and ferromagnetic contributions to the observed magnetic susceptibility, resulting in a ground state of $S = 2$ per formula unit.

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