

X-ray analyses, spectroscopic and magnetic properties of $[\text{Cu}_4(\text{succinato})(\text{tpmc})_2](\text{ClO}_4)_6 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})\text{tpmc}](\text{ClO}_4)_3 \cdot 0.5\text{CH}_3\text{OH} \cdot 0.5\text{H}_2\text{O}$ complexes.

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Streszczenie

$[\text{Cu}_4(\text{succinato})(\text{tpmc})_2](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (tpmc=N,N',N'',N'''-tetrakis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, succinato=dianion of succinic acid) has been prepared and characterized by elemental analysis, UV/vis, IR, EPR (X-band) spectra, conductivity and magnetization measurements (SQUID). Based on a low-temperature measurements (100(2) K), X-ray analyses of the first tetranuclear Cu(II)-tpmc complex, single crystal of which corresponded to the $[\text{Cu}_4(\text{succinato})(\text{tpmc})_2](\text{ClO}_4)_6 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 4\text{H}_2\text{O}$ (1) and of the previously described $[\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})\text{tpmc}](\text{ClO}_4)_3 \cdot 0.5\text{CH}_3\text{OH} \cdot 0.5\text{H}_2\text{O}$ (2) were also done. The complexes crystallize in triclinic $P1^-$ (1) and monoclinic $P2_1/c$ (2) space groups. The geometry around the first Cu(II) coordination sphere in the tetranuclear complex (1) is almost regular square-based pyramidal, while significant distortion around the other metallic center was observed. The angular structural parameter (τ), which is applicable to five coordinate structures as an index of degree of trigonality, was found to be 0.05 and 0.40, respectively. In the binuclear complex (2) the geometry around the first Cu(II) coordination sphere is regular square-based pyramidal ($\tau=0.09$), while around the other is distorted trigonal bipyramidal ($\tau=0.79$). In complexes (1) and (2) the bridging carboxylate groups are coordinated to metallic centres in a syn-anti mode. Weak ferromagnetic interactions are observed between copper(II) ions, connected through syn-anti monocarboxylate bridges ($2J=+1.26$ and $+1.84\text{cm}^{-1}$ in complexes (1) and (2), respectively). Additional antiferromagnetic interaction through succinato anion ($zJ'=-1.57\text{cm}^{-1}$) gives finally rise to antiferromagnetic interactions, observed in magnetic measurements in tetrameric complex (1).

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