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A mononuclear complex and a cubane cluster from the initial use of 2-(hydroxymethyl)pyridine in nickel(II)carboxylate chemistry.

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Streszczenie

The reactions of 2-(hydromethyl)pyridine, hmpH, with $Ni(O_2CMe)_2{\cdot}4H_2O$ in H_2O, in the absence of counterions, have been investigated. The synthetic study has led to the two new complexes $[Ni(O_2CMe)_2(hmpH)_2]$ (**1**) and $[Ni_4(O_2CMe)_4(hmp)_4(H_2O)_2]$ (**2**). Complex **1** can also be transformed into **2** by reacting with an excess of NaOH in H_2O. The structures of **1** and **2**·2.25H_2O·0.5(1,4-dioxane) have been solved by single-crystal, X-ray crystallography. The octahedral Ni^{II} center in centrosymmetric **1** is coordinated by two 1.10 (Harris notation) $MeCO_2^-$ groups and two *N*,*O*-chelating (1.11) hpmH ligands. The tetranuclear cluster molecule of **2**·2.25H_2O·0.5(1,4-dioxane) possesses a distorted cubane $\{Ni_4(\mu_3\text{-}OR')_4\}^{4+}$ core [R′ = (2-pyridyl)CH_2–] with the Ni^{II} ions and the oxygen atoms from the 3.31 hmp^- ligands occupying alternate vertices of the cube. Two 2.11 $MeCO_2^-$ groups cap two opposite faces of the cube, while two 1.10 $MeCO_2^-$ ions and two aqua ligands complete the octahedral coordination sphere of the metal centers. Characteristic IR bands for the two complexes are discussed in terms of the nature of bonding and the structures of the two complexes. The variable-temperature magnetic properties of **2** have been modeled with two *J* values, and reveal antiferromagnetic exchange interactions between the four Ni^{II} ions to give a diamagnetic ground state.

Słowa kluczowe

Acetate ligands, Crystal structures, 2-(Hydroxymethyl)pyridine metal complexes, Magnetic properties, Nickel(II) cubane clusters

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