A systematic exploration of nickel(II)/acetate/Di-2-pyridyl ketone chemistry: neutral and cationic tetranuclear clusters, and a novel mononuclear complex.

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Abstract

The further use of di-2-pyridyl ketone [$(2\text{-py})_2$CO] innickel(II) acetate chemistry has been investigated. Various synthetic procedures have led to the synthesis ofcomplexes $[Ni_4(O_2CMe)_2\{(2\text{-py})_2C(OH)O\}_4(H_2O)_2](ClO_4)_2$ (**1**), $[Ni(O_2CMe)\{(2\text{-py})_2C(OH)_2\}\{(2\text{-py})_2CO\}](ClO_4)\cdot H_2O$ (**2**·H_2O), $[Ni_4(O_2CMe)_3\{(2\text{-py})_2C(OH)O\}_4](ClO_4)\cdot 2H_2O\cdot 2EtOH$ (**3**·$2H_2O$·2EtOH), $[Ni_4(O_2CMe)_4\{(2\text{-py})_2C(OH)O\}_4]$·2MeCN (**4**·2MeCN), and $[Ni_4(O_2CMe)_3\{(2\text{-py})_2C(OH)O\}_4](O_2CMe)\cdot 6H_2O$·MeCN (**5**·$6H_2O$·MeCN). The Ni^{II}-mediated hydrolysis of $(2\text{-py})_2$CO to give the coordinated molecule $(2\text{-py})_2C(OH)_2$ or the monoanion $(2\text{-py})_2C(OH)O^-$ involves nucleophilic attack by H_2O on the carbonyl group. The NI^{I} ion in **2**·H_2O is coordinated by one monodentate acetate, one *N*,*N*′,*O*-tridentate chelating $(2\text{-py})_2C(OH)_2$ molecule, and one *N*,*N*′-bidentate chelating $(2\text{-py})_2$CO ligand. The tetranuclear cluster cation of **1** has a cubane $\{Ni_4(\mu_3\text{-}OR)_4\}^{4+}$ core with Ni^{II} ions and deprotonated oxygen atoms occupying alternate vertices. The $[Ni_4(O_2CMe)_3\{(2\text{-py})_2C(OH)O\}_4]^+$ cations present in the complexes **3**·$2H_2O$·2EtOH and **5**·$6H_2O$·MeCN have almost identical cubane structures that are different from the structure of the cation of **1**. The four metal ions in the centrosymmetric molecules of **4**·2MeCN are located at four vertices of a defect dicubane (with two missing vertices) and are bridged by six oxygen atoms. Characteristic IR bands are discussed in terms of the known structures of **1**–**5**. The magnetic data for the Ni^{II} cubane **1** has been modeled with two *J*values, and shows that the coupling consists of two ferromagnetically coupled pairs that are antiferromagnetically coupled to give a diamagnetic ground state. The magneticproperties of **4** have been modeled with three*J* values, andreveal competing antiferromagnetic and ferromagneticcoupling between the four Ni^{II} ions.

Słowa kluczowe

Acetate ligands, Di-2-pyridyl ketone, Magnetic properties, Nickel (II) cubanes, Nickel (II) defect dicubanes, X-ray diffractions