

Supramolecular dimer formation through hydrogen bond extensions of carboxylate ligands : path for magnetic exchange.

Autorzy

Z. Vasková
Jan Moncol
Maria Korabik
Dušan Valigura
Jozef Švorec
Tadeusz Lis
M. Valko
Milan Melnik
Rok wydania

2010

Czasopismo

Polyhedron

Numer woluminu

29

Strony

154-163

DOI

10.1016/j.poly.2009.06.056

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A new complex of unusual composition $[\text{Cu}(\text{3-O}_2\text{Nbz})_2(\text{nia})(\text{H}_2\text{O})_2]$ (**1**) (nia = nicotinamide, 3-O₂Nbz = 3-nitrobenzoate) has been prepared and studied together with two other complexes of composition $[\text{Cu}(\text{4-O}_2\text{Nbz})_2(\text{nia})_2(\text{H}_2\text{O})_2]$ (**2**) and $[\text{Cu}(\text{4-O}_2\text{Nbz})_2(\text{nia})_2] \cdot (\text{4-O}_2\text{NbzH})_2$ (**3**) (4-O₂Nbz = 4-nitrobenzoate). The composition of all complexes has been determined by elemental analysis, the complexes have been studied by electronic, infrared and EPR spectroscopy, as well as by magnetization measurements over the temperature range 1.8–300 K, and their structures have been solved. The structure of complex (**1**) consists of molecules, where Cu(II) atom is monodentately coordinated by the pair of 3-nitrobenzoato anions in *trans*-positions together with water and nicotinamide molecules, forming nearly tetragonal basal plane, and by another water molecule in axial position of tetragonal-pyramidal coordination polyhedron. The neighboring molecule coordination polyhedron basal planes are coplanar and allow formation of supramolecular dimers with strong H-bonds between hydrogen atoms from equatorially coordinated water molecules and uncoordinated carboxylate oxygen atoms thus giving the nearest CuCu distance of 4.886(2) Å. Magnetization measurements showed that complex (**1**) exhibits maximum of magnetic susceptibility at 6.5 K and a fit to Bleaney-Bowers equation gave singlet–triplet energy gap $2J = -6.25 \text{ cm}^{-1}$, and $zJ' = -0.03 \text{ cm}^{-1}$. This might be an experimental proof that the carboxylate bridges extended with hydrogen bonds are the pathway of the spin–spin interactions. The temperature dependence of changes in EPR spectra of (**1**) and the spectrum at 4.2 K have confirmed its hydrogen bonded dimeric structure. The calculated CuCu distance 4.8 Å is in very good agreement with the value obtained from crystal structure. The complexes (**2**) and (**3**) at 300 K exhibit magnetic moment $\mu_{\text{eff}} = 1.98 \text{ B.M.}$ and $\mu_{\text{eff}} = 1.84 \text{ B.M.}$, respectively. These values

practically do not change with lowering the temperature up to 5 K and only small drops to $\mu_{\text{eff}} = 1.87$ B.M. (for **(2)**) and $\mu_{\text{eff}} = 1.79$ B.M. (for **(3)**) at 1.8 K have been observed. The EPR spectra of complex **(2)** at room temperature as well as at 77 K are of axial type with $g_{\perp} = 2.062$ and $g_{\parallel} = 2.285$ and exhibit resolved parallel hyperfine splitting with $A_{\parallel} = 160$ Gauss. The EPR spectra of complex **(3)** at room temperature as well as at 77 K are of axial type with $g_{\perp} = 2.065$ and $g_{\parallel} = 2.235$ and exhibit unresolved parallel hyperfine splitting. EPR spectra of **(2)** and **(3)** are consistent with the X-ray structure.

Słowa kluczowe

Copper complexes, crystal structure, hydrogen bonds, supramolecular structure, magnetic properties

Adres publiczny

<https://doi.org/10.1016/j.poly.2009.06.056>

Strona internetowa wydawcy

<http://www.elsevier.com>