P22

SYNTHESIS, STRUCTURE, ERP AND MAGNETIC PROPERTIES OF SOME NEW CHROMIUM(III) HETEROMETALLIC NITRILOTRIACETATES

V. Ciornea,[1] A. Borta,[2] R. Galeev,[3] L. Mingalieva,[3] V. Voronkova,[3] J.-P. Costes,[4] I. Filippova,[2] Gh. Novitchi,[5] A. Gulea[1]

[1]Moldova State University, Chisinau
[2]Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau
[3]Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan, Russian Federation,
[4]LCC CNRS, Toulouse Cedex, France
[5]Institute of Chemistry, Academy of Sciences of Moldova, Chisinau

Four heterometallic compounds with general formula $M^{II}(2,2'\text{-}bpy)_2Cr_2(OH)_2(nta)_2 \cdot nH2O$ (M^{II} = Mn (n=8) (**1**); Co (**2**), Ni(**3**) and Zn (**4**) (n=9); *bpy* = 2,2′-bipyridine, *nta* = nitrilotriacetate ion) have been prepared by reaction of $Ba[Cr_2(OH)_2(nta)_2]5H_2O$ and corresponding M^{II}-sulphates in presence of 2 mol of 2,2′-bipyridine. Substances **1-4** have been characterised by magnetic susceptibility measurements and X-ray crystal structure analysis.

Compounds **2-4** are isostructural and consist of non-centrosymmetric dimeric anion $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$, complex cation $[M^{II}(bpy)_2(H_2O)_2]^{2+}$ and solvate water molecules. The octahedral coordination of chromium atoms implies four donor atoms of the nta^{3-} ligands and two bridging OH groups. Adjacent anions are connected to each other by strong $OH...O_{carb}$ hydrogen bonds and form chains along *a* axis. Multiple hydrogen bonds of coordinated and solvate water molecules link the anions with the cations in a 3-D network. A similar $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ unit is found in **1**. One carboxylate oxygen atom of *nta* ligand performs the bridging function that leads to formation of a trinuclear complex $[Mn(bpy)(H_2O)_2Cr_2(\mu\text{-}OH)_2(nta)_2]$. The Cr-dimers are joined together by $OH...O_{carb}$ hydrogen bonds.

The experimental and calculated frequency and temperature dependences of EPR spectra of the new compounds are presented. The program for the simulation of EPR spectra for polycrystalline samples of the compound consisting of Cr-dimers taking into account the isotropic and anisotropic exchange, dipole-dipole interaction and zero-field splitting tensor of chromium was compiled. The temperature dependence of the fine structure of EPR spectra of compound **4** is analyzed in details. It is established that the main part of EPR signals is due to the transitions in the spin states of a spin multiplet with S=2. The analysis of temperature dependences of experimental and calculated spectra of compounds **1-4** showed the absence of the interaction between ions of metals (M^{II}) and Cr-dimers in **2-3** and the presence of the weak interaction Mn –Cr in **1**.

The temperature dependence of magnetic susceptibilities for **1-4** was fitted on the basis of the expression derived from isotropic *Hamiltonian* including a bi-quadratic exchange term. The values of the coupling interaction between chromium ions (*J)* ranges from -14.02(2) cm^{-1} to -5.80(2) cm^{-1} and the bi-quadratic terms (*j*) from +0.71(2) to 2.35(2) cm^{-1}. The experimental and theoretical (calculated, with the *Glerup-Hodgson-Pedersen* model) values of *J* have been discussed.

Acknowledgements. This work is supported by the Russian Foundation for Basic Research grants №04-02-17163 and Scientific School 6213.2006.2.