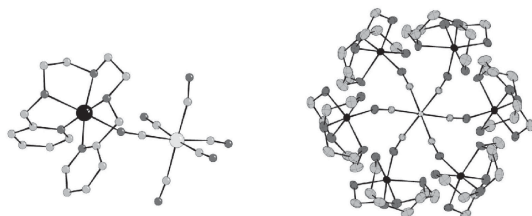


s13.m38.p5 **Hexacyanometalate Molecular Chemistry: Characterisation of Polynuclear Complexes by Single-Crystal X-Ray Diffraction.** C. Guyard-Duhayon^a, V. Marvaud^a, C. Decroix^a, A. Scullier^a, J. Vaissermann^a, J. Marrot^b and M. Verdagner^a, ^aLaboratoire de Chimie Inorganique et Matériaux Moléculaires, CNRS, UMR 7071, Université P. et M. Curie, F-75252 Paris Cedex 05., ^bInstitut Lavoisier, Université de Versailles-Saint-Quentin, 45 Avenue des Etats-Unis, F-78035 Versailles, France. E-mail: duhayon@lcc-toulouse.fr

Keywords: X-Ray diffraction; Polynuclear complexes; High-spin molecules

As part of our research activities devoted to molecular magnetism, we were interested in synthesising in a rational way polynuclear compounds showing both large spin ground state and anisotropy. For this purpose, polycyanometalate precursors have been used successfully, with an effective control of the chemistry, which consist to firstly prepare polydentate ligands and their corresponding mononuclear complexes with varied metallic centres such as Mn(II), Ni(II), Co(II), Cu(II), before synthesising polynuclear compounds with tunable geometry. Thus, bi-, tri-, tetra-, hexa- and heptanuclear species have been obtained in this way with a spin state value ranging from 3/2 to 27/2.



Examples of X-ray structures of polynuclear complexes: CrNi₅ (S=5/2), CrNi₆ (S=15/2),

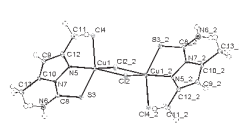
Following this step by step synthetic strategy, a CrNi₃ complex have been synthesised that behave as single molecule magnet. We obtained as well hetero-trimetallic complexes such as CrNi₂Mn₄ (S=13/2). All these compounds were characterised by single crystal X-ray crystallography. The technique is very useful since it permits to confirm the nature of the polynuclear species, to substantiate the eventual existence of magnetic parasitic molecules, and to yield other structural information necessary to a better knowledge of the magnetic properties of these polycyanometalate compounds.

- [1] V. Marvaud, C. Decroix, A. Scullier, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdagner *Chem. Eur. J.* 2003, **9**, N° 8, 1677-1691
- [2] V. Marvaud, C. Decroix, A. Scullier, F. Tuyeras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdagner *Chem. Eur. J.* 2003, **9**, N° 8, 1692-1705

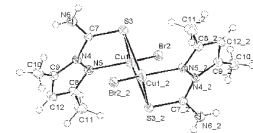
s13.m38.p6 **Synthesis and Characterizations of New Binuclear Cu(I), Cu(II) and Co(II) Complexes with 3,5-Dimethyl-1-thiocarboxamide pyrazole.** Zeljko K. Jacimovic^a, Ivana Radosavljevic Evans^b, Judith A. K. Howard^b, Violeta S. Jevtovic^c and Vukadin M. Leovac^c, ^aFaculty of Metallurgy and Technology, Cetinjski put bb, 81000 Podgorica, Serbia & Montenegro. E-mail: zeljkoj@cg.ac.yu. ^bDepartment of Chemistry, University of Durham, Science Site, South Road, Durham DH1 3LE, E-mail: ivana.radosavljevic@durham.ac.uk, ^cFaculty of Sciences, University of Novi Sad, Trg Dositeja Obradovica 3, 21000 Novi Sad, Serbia & Montenegro. E-mail: vule@ih.ns.ac.yu

Keywords: Cu(I) and Cu(II) complexes; Pyrazole-based ligands

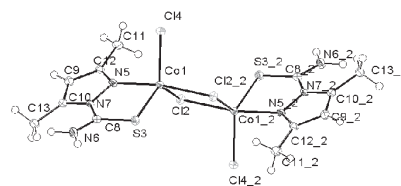
Three new binuclear metal complexes of the formulas [Cu^{II}₂L₂Cl₄] (1), [Cu^I₂L₂Br₂] (2) and [Co^{II}₂L₂Cl₄] (3) (L = 3,5-dimethyl-1-thiocarboxamide pyrazole) have been synthesized and characterized by chemical analysis, FTIR spectroscopy, solution conductivity, solid state magnetic measurements and X-ray single crystal and variable temperature powder diffraction. Complex **1** forms doubly chloro-bridged dimers, with Cu(II) in distorted trigonal bipyramidal coordination with the apical positions occupied by chlorine atoms. Magnetic measurements indicate an antiferromagnetic interaction between the Cu(II) centres in the dimer, with the singlet-triplet exchange parameter of $J = -19.40 \text{ cm}^{-1}$. Complex **2** forms doubly sulphur-bridged dimers, with Cu(I) in distorted tetrahedral coordination with apical positions occupied by bromine atoms. Complex **3** is a cobalt analogue of **1**. It contains dinuclear units formed by five-coordinate high-spin Co(II) in a distorted trigonal bipyramidal environment. The magnetic behaviour of **3** shows no significant departure from Curie-Weiss behaviour between room temperature and 5 K. All crystal structures are stabilized by two-dimensional hydrogen bonding networks between the carboxamide nitrogen donors and the terminal halide acceptors.



Molecular structure of **1**



Molecular structure of **2**



Molecular structure of **3**