

FA4-MS34-P30

Crystal structures of $[\text{Cu}(L)(\text{C}(\text{CN})_3)_2]_n$ isomers and polymorphs ($L = 1,10$ -phenanthroline or $2,2'$ -bipyridine). Ivan Potočný, Katarína Lacková, *Institute of Chemistry, P.J. Šafárik University in Košice, Slovakia*
E-mail: ivan.potocnak@upjs.sk

From the reaction mixtures containing $\text{Cu}(\text{ClO}_4)_2$, bidentate ligands L ($L = 1,10$ -phenanthroline, *phen*, or $2,2'$ -bipyridine, *bpy*) and $\text{KC}(\text{CN})_3$, pairs of $[\text{Cu}(\text{phen})(\text{C}(\text{CN})_3)_2]_n$ (**1** and **2**) and $[\text{Cu}(\text{bpy})(\text{C}(\text{CN})_3)_2]_n$ (**3** and **4**) complexes have been isolated. The composition of **1** and **2** on the one hand as well as **3** and **4** on the other hand is the same, nevertheless the IR spectra in the $\nu(\text{C}\equiv\text{N})$ region of individual pairs of complexes were different and thus indicated different bonding modes of $\text{C}(\text{CN})_3$ anions in individual pairs of complexes. This was definitely confirmed by the X-ray analysis which revealed that the complexes **1** and **2** represent a pair of isomers while **3** and **4** are two polymorphic modifications. The complexes **1** ($P-1$; 7.5679(3), 10.1032(4), 12.7758(4) Å, 106.612(3), 98.268(3), 101.575(3)°) and **2** [1] ($P-1$; 7.7223(3), 10.0670(3), 12.6470(4) Å, 108.016(3), 104.825(3), 101.715(3)°) are isostructural and their crystal structures are formed by zigzag wave-like chains parallel with the (110) crystallographic plane. The Cu(II) atoms, which are six-coordinated in the form of an elongated tetragonal bipyramid (tetragonality factor $T = 0.731$ and 0.774 , respectively), are bridged by two *cis* disposed $\mu_{1,5}$ - $\text{C}(\text{CN})_3$ ligands. The chains pack in such a fashion that the L ligands, which are in the crests of the waves, associate and each chain interacts with the two adjacent ones through weak π - π interactions between the *phen* and *bpy* ligands, respectively, leading to layered structures. Crystal structure of **2** ($P2_1/n$; 7.5252(2), 14.1862(4), 17.7653(6) Å, 101.002(3)°) is formed by zigzag chains, too, parallel with the a axis. Cu(II) atoms, which are five-coordinated in the form of a deformed tetragonal pyramid (trigonal parameter $\tau = 15.3$), are bridged by only one $\mu_{1,5}$ - $\text{C}(\text{CN})_3$ ligand. The coordination sphere is completed by chelating *phen* and monodentate μ_1 - $\text{C}(\text{CN})_3$ ligand. Contrary to the structure of **1** there are no π - π interactions between the *phen* ligands. On the other hand both $\text{C}(\text{CN})_3$ ligands are involved in π - π interactions with the *phen* ligands. Crystal structure of **3** ($Pbcn$; 6.3443(6), 21.1969(19), 12.5946(16) Å) is similar with the structure of **4** – it is formed by zigzag wave-like chains parallel with the c axis and the six-coordinated Cu(II) atoms in the form of an elongated tetragonal bipyramid (tetragonality factor $T = 0.815$) are bridged by two *cis* coordinated $\mu_{1,5}$ - $\text{C}(\text{CN})_3$ ligands, too. On the other hand, the chains differ in some details and they pack in an interdigitated fashion, such that the chelating *bpy* ligands in the crests of one chain are directed into valleys of the neighboring chain and thus different π - π interactions between the *bpy* ligands occur. This work was supported by the grant of the Slovak Grant Agency VEGA No. 1/0079/08 and by Slovak Research and Development Agency under the contracts Nos. APVV-VVCE-0058-07 and APVV-0006-07.

[1] Yuste C., Armentano D., Marino N., Canadillas-Delgado L., Delgado F.S., Ruiz-Perez C., Rillema D.P., Lloret F., Julve M., *Dalton Trans.*, 2008, 1509.

Keywords: copper-tricyanomethanide complexes, isomers, polymorphs

FA4-MS34-P31

Structural relationships between $\{\text{ZR}_6\}\text{X}_{12}\text{R}$ and $\{\text{ZR}_6\}\text{X}_{10}$ type cluster complexes. Christian Rustige, Gerd Meyer *Department für Chemie, Universität zu Köln, Germany*
E-mail: christian.rustige@uni-koeln.de

New compounds in the systems Tb/X/Z and Er/X/Z have been obtained by reduction of the respective trihalides, TbX_3 and ErX_3 , with their corresponding metals R (= Tb, Er). Transition metals were used as the third component Z and added to the reaction mixture as pure elements. The reactions were carried out in tantalum containers within the temperature range 1100-1350 K for 10-14 days.

All products are air and moisture sensitive and were, hence, handled in a glove-box under a dry nitrogen atmosphere. The compounds were obtained as single crystals and data sets were collected at ambient temperature on STOE IPDS I/II diffractometers.

The recently synthesized compounds $\{\text{ZTb}_6\}\text{I}_{12}\text{Tb}$ ($Z = \text{Mn, Fe, Co, Ni, Ru, Pt}$), $\{\text{FeTb}_6\}\text{Br}_{12}\text{Tb}$ and $\{\text{IrEr}_6\}\text{I}_{12}\text{Er}$ are isostructural with $\{\text{NSc}_6\}\text{Cl}_{12}\text{Sc}^{[1]}$ whereas $\{\text{ZTb}_6\}\text{I}_{10}$ ($Z = \text{Os, Ir}$), $\{\text{ZTb}_6\}\text{Br}_{10}$ ($Z = \text{Co, Ni, Ru, Ir}$) and $\{\text{ZEr}_6\}\text{I}_{10}$ ($Z = \text{Ni, Ir}$) are similar to the $\{\text{RuY}_6\}\text{I}_{10}$ -type^[2] of structure. The structural relationship between the $\{\text{ZR}_6\}\text{X}_{12}\text{R}$ and $\{\text{ZR}_6\}\text{X}_{10}$ phases is based on the common packing of the halogen atoms X and the endohedral transition metal atoms Z. The packing atoms are arranged in layers which are stacked in an ABC manner and are therefore the motif of a cubic closest packing. In $\{\text{ZR}_6\}\text{X}_{12}\text{R}$ there are seven out of thirteen octahedral voids occupied by rare-earth metal atoms while in $\{\text{ZR}_6\}\text{X}_{10}$ six out of eleven octahedral voids are filled accordingly. It can be shown that these two structures may be interconverted through a shear plane under the formal loss of a rare-earth dihalide in accordance to the sum formulae $\text{R}_7\text{X}_{12}\text{Z}$ resp. $\text{R}_6\text{X}_{10}\text{Z}$.

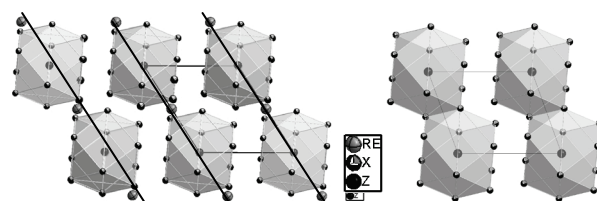


Fig. 1 Interconversion between the structures of $\{\text{ZR}_6\}\text{X}_{12}\text{R}$ (left) and $\{\text{ZR}_6\}\text{X}_{10}$ (right) under the formal loss of “ RX_2 ” through a shear plane. All metal atoms which build up octahedral clusters are omitted.

[1] Hwu, S.J., Corbett, J.D., *J. Solid State Chem.*, 1986, 64, 331. [2] Hughbanks, T., Corbett, J.D., *Inorg. Chem.*, 1989, 28, 631.

Keywords: Reduced rare-earth halides, endohedral transition metals, cluster

FA4-MS34-P32

Crystalline odorants – syntheses and structures of adducts and clathrates of volatile molecules. Silvia Schnitzler, Carina Merckens, Ruimin Wang, Yutian Wang, Irmgard Kalf, Ulli Englert, *Institute of Inorganic Chemistry, RWTH Aachen University, Germany*