FA4-MS34-P30

Crystal structures of $[Cu(L)(C(CN)_3)_2]_n$ isomers and polymorphs (L = 1,10-phenanthroline or 2,2'-bipyridine).

Ivan Potočňák, Katarína Lacková, *Institute of Chemistry, P.J. Šafárik University in Košice, Slovakia*
E-mail: ivan.potocnak@upjs.sk

From the reaction mixtures containing $Cu(ClO_4)_2$, bidentate ligands L (L = 1,10-phenanthroline, *phen*, or 2,2'-bipyridine, *bpy*) and $KC(CN)_3$, pairs of $[Cu(phen)(C(CN)_3)_2]_n$ (**1** and **2**) and $[Cu(bpy)(C(CN)_3)_2]_n$ (**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 ν(C≡N) region of individual pairs of complexes were different and thus indicated different bonding modes of $C(CN)_3$ 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 **4** [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 $\mu_{1,5}$-$C(CN)_3$ 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 (trigonality parameter τ = 15.3), are bridged by only one $\mu_{1,5}$-$C(CN)_3$ ligand. The coordination sphere is completed by chelating *phen* and monodentate μ_1-$C(CN)_3$ ligand. Contrary to the structure of **1** there are no π-π interactions between the *phen* ligands. On the other hand both $C(CN)_3$ 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 $\mu_{1,5}$-$C(CN)_3$ 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.

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Keywords: copper-tricyanomethanide complexes, isomers, polymorphs

FA4-MS34-P31

Structural relationships between $\{ZR_6\}X_{12}R$ and $\{ZR_6\}X_{10}$ 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 $\{ZTb_6\}I_{12}Tb$ (Z = Mn, Fe, Co, Ni, Ru, Pt}, $\{FeTb_6\}Br_{12}Tb$ and $\{IrEr_6\}I_{12}Er$ are isostructural with $\{NSc_6\}Cl_{12}Sc$[1] whereas $\{ZTb_6\}I_{10}$ (Z = Os, Ir), $\{ZTb_6\}Br_{10}$ (Z = Co, Ni, Ru, Ir) and $\{ZEr_6\}I_{10}$ (Z = Ni, Ir) are similar to the $\{RuY_6\}I_{10}$-type[2] of structure. The structural relation-ship between the $\{ZR_6\}X_{12}R$ and $\{ZR_6\}X_{10}$ 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 $\{ZR_6\}X_{12}R$ there are seven out of thirteen octahedral voids occupied by rare-earth metal atoms while in $\{ZR_6\}X_{10}$ 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 $R_7X_{12}Z$ resp. $R_6X_{10}Z$.

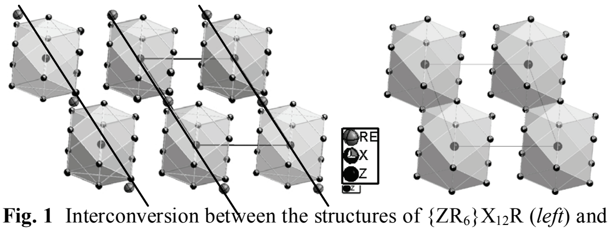

Fig. 1 Interconversion between the structures of $\{ZR_6\}X_{12}R$ (*left*) and $\{ZR_6\}X_{10}$ (*right*) under the formal loss of "RX_2" through a shear plane. All metal atoms which build up octahedral clusters are omitted.

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

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Crystalline odorants – syntheses and structures of adducts and clathrates of volatile molecules.

Silvia Schnitzler, Carina Merkens, Ruimin Wang, Yutian Wang, Irmgard Kalf, Ulli Englert, *Institute of Inorganic Chemistry, RWTH Aachen University, Germany*

E-mail: Silvia.Schnitzler@gmx.de

Odorants are low-boiling compounds such as esters, ketones or ethers [1]. Their structures in the gas phase may be studied by microwave spectroscopy [2]. Odorants are active in condensed phase, and hence their solid-state structures are of interest, too. In addition to *in situ* crystallization [3], one can imagine two alternative strategies to achieve the determination of their crystal structures despite their volatility.

a) The synthesis of clathrates. In this process the odorants are enclosed in the cavities of a host crystal. We have cocrystallized several ethers and ketones with cholesteric acid [4] and obtained mixed crystals of remarkably high quality: Single crystals of the inclusion compound allylacetate in cholesteric acid gave a well-resolved data set ($\sin \theta/\lambda = 1.15$ Å^{-1}) sufficient for multipole refinement [5].

b) Coordination of the odorant to a Lewis acid. In order to identify suitable cations as coordination partners and appropriate synthetic procedures, we searched the CSD [6] for simple coordinated solvent Lewis bases such as acetone or diethylether. Dinuclear Ag carboxylates [7] or Cu(II) complexes in which the equatorial coordination sites are occupied by preferably small ligands such as dimethyl-ethylendiamine [8] represent promising candidates for binding the target molecules in axial positions. We will attempt to coordinate more complex odorants to the same chemical systems and study the resulting Lewis acid-base adducts.

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Keywords: inclusion compounds, organic and inorganic coordination compounds, conformation, charge density

FA4-MS34-P33

Synthesis, Structures and Characterization of Diorganotin complexes.

See Mun, Lee[a], Mohd. Ali, H., Kong Mun, Lo[b], [a]*Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia*
E-mail: smlee@um.edu.my

Metal complexes are widely prepared and have been successfully used in the treatment of numerous human diseases including cancer. Among the many metal complexes, organotin complexes have been widely studied for their biological activities such as anticancer, antihistamine, antifungal, biocides and anti-fouling. Schiff base derived from substituted 2-hydroxyacetophenone has been widely used as polydentate ligands in the preparation of metal complexes. In the present studies, a series of Schiff base ligands were prepared by reacting 3-hydroxy-2-naphthoic hydrazide with substituted 2-hydroxyacetophenone. The diorganotin complexes were subsequently prepared by adding the ligands with diorganotin dichloride or oxide in 1:1 molar ratio and were characterized by various spectroscopic methods including IR, NMR spectroscopies. The x-ray structures of some of the diorganotin complexes namely{[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV) and{[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV). All the complexes were found to be isostructures and the tin atom in each of the complexes is in a distorted *cis*-C_2NO_2Sn trigonal-bypyrimidal coordination. The deprotonated ligand is coordinated as tridentate via the azomethine nitrogen and two phenoxo oxygens. The tridentate 5-bromo-7-methyl-salicylideneaminato(3-hydroxy-2-naphthohydrazidate) and 5-chloro-7-methylsalicylideneaminato(3-hydroxy-2-naphthohydrazidate) dianion of each of the complexes are stabilized by an intramolecular hydrogen bonding O-H—N. The distortion from the trigonal-bypyrimidal coordination is influenced by the presence of the R groups.

Keywords: crystal structure, isostructure, organotin

FA4-MS34-P34

Complexation Properties of Completely Reduced meso-Octamethylporphyrinogens (Calix[4]pyrroles).

Helen Stoeckli-Evans,[a] Guillaume Journot[b], Frédéric Bruyneel[b], Reinhard Neier[b], [a] *Insitut de Physique, Université de Neuchâtel, Switzerland,* [b]*Insitut de Chimie, Université de Neuchâtel, Switzerland*
E-mail: helen.stoeckli-evans@unine.ch

Calixpyrroles bind anions efficiently and can be transformed into transition-metal complexes only under forcing conditions. Reducing the macrocycle creates a ligand that easily forms classical Werner complexes with copper, nickel, palladium, and iron ions. The metal complexes present an array of four directed hydrogen bonds, which specifically bind the counterions [1,2].

The reaction of the reduced macrocycle with iron triflate has produced some surprises. One complex exhibits a phase change at 173 K, transforming from a monoclinic system (Z' = 1) to a triclinic system (Z' = 2). The triclinic phase appears to be a twinned crystal, which on heating reverts cleanly to the monoclinic non-twinned crystal. The question is posed, at 173 K is the crystal really twinned or simply split? Can image plates lie?

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Keywords: macrocyclic complexes, phase transformation, twinning

FA4-MS34-P35

Synthesis, Crystal Structure and Magnetic Properties of a Novel di-μ_2-Alkoxo Bridged Binuclear Manganese(III) Schiff Base Complex.

Yasemin Yahsi[a,b], Hulya Kara[a], Lorenzo Sorace[b]