MS15-P16 Crystal structure and spectroscopic characterization of the 1D coordination polymer. Anissa Mansour[a], Mohamed Salah Belkhiria[a], Bujacz Anna[b], Vincent Guérineau[c] and Habib Nasri[a] *[a]Département de Chimie, Faculté des Sciences de Monastir, Université de Monastir, Avenue de l'environnement, 5019 Monastir, Tunisia. [b]Institute of Technical Biochemistry, Technical University of Lodz, Stefanowskiego 4/10, 90-924 Lodz, Poland.[c] Équipe de Spectrométrie de Masse, Institut de Chimie des Substances Naturelles, CNRS UPR2301, 91198 Gif-sur-Yvette, France*
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A new cobalt(II) porphyrin coordination polymer $\{[CoII(TPP)(\mu-4,4'-bpy)2]\}n$ (TPP = tetraphenylporphyrin) has been prepared by the reaction of an excess of 4,4'-bipyridine to the starting material [CoII(TPP)]. The new species was characterized by UV-vis, IR, 1H NMR, MALDI and photoluminescence spectroscopy. The X-ray structural analysis shows that the polymer crystallizes in the monoclinic space group C2/c. Crystal data for this complex: a=30.5438(15) Å, b=11.7573(3) Å, c=18.1888(8) Å, β=120.032(6)° , Z=4, R1=3.96%, WR2= 8,76% and S=1.036. The average cobalt-pyrrole nitrogen atoms is Co-Np =1.993(1) Å. The coordination geometry around the Co(II) in $\{[CoII(TPP)(\mu-4,4'-bpy)2]\}n$ is octahedral; four N-donor atoms from the four pyrrole moieties of the TPP porphyrin occupy the equatorial position along the porphyrin core. N-donor atoms of the 4,4'-bipyridine species occupy the axial positions (see Figure 1).
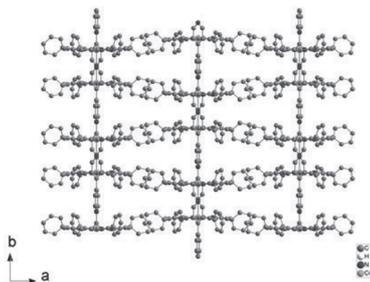

Figure 1. Packing diagram of $\{[Co^{II}(TPP)(\mu-4,4'-bpy)_2]\}$, with view normal [001] showing 1D linear chains parallel to the b axis.

Keywords: cobalt(II) porphyrin ; single-crystal X-ray.

MS15-P17 Systematic investigation of the structure and the electronic requirements of the $Na_{36}Cd_{24}Ga_{56}$ type.
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Only five different compounds $A_{36}M_{80}$ forming the $Na_{36}Cd_{24}Ga_{56}$ type ($Fd3m$, a = 2128.6(1) pm, Z = 4) exist in the literature. In the formula A is an alkaline metal, usually sodium, and M is a distinct ratio of a triel and a late transition metal for electron compensation. The elemental composition of only three of these phases ($Na_{36}Cd_{24}Ga_{56}$ [1], $Na_{36}Zn_{13}In_{67}$ [2], $Na_{36}Ag_7Ga_{73}$ [3]) is certainly identified. The M atom arrangement is characteristic for a whole family of intermetallic phases [4]. The atoms form icosahedra [Ico] and truncated tetrahedra [TT] with isolated M dumbbells [ID] arranged above the hexagonal faces. Every icosahedron has six exo bonds to further icosahedra and to six truncated tetrahedra and vice versa. The truncated tetrahedra and the dumbbells form a 16 atom polyhedron, a so called icosioctahedron. The coordination spheres around the A atoms are truncated tetrahedra (CN= 12), allowing only sodium or smaller cations like lithium [1] or magnesium [2] to be incorporated. Twenty of the truncated tetrahedra surround the icosahedron by building a Samson polyhedron. $Na_{36}Zn_{13}In_{67}$ was reinvestigated and assigned the new formula $Na_{36}Zn_{20}In_{60}$. In addition, a new compound with Li, Cd, Ga was obtained from stoichiometric melts of the elements. The total density of states (DOS) of the virtual compound $Na_{36}In_{80}$ was determined by FP-LAPW-methods and revealed two distinct minima around the Fermi level (EF) which result in 248 and 260 valence electrons (v.e.) per formula unit respectively. The electronic requirements of the structure type are in agreement with the new single crystal data and accurate elemental composition of $Na_{36}Zn_{20}In_{60}$. The icosahedra can be explained using Wades rules for closo clusters n+2 (26 v.e./Ico). The icosioctahedra have been interpreted in the literature as distinct clusters, despite the fact that they contain an A cation and some M-M bonds are significantly increased with respect to the sum of the covalent radii. Extendend Hückel calculation indicated 36 v.e. [3] for this polyhedron, which does not fit Wades electron count for closo clusters. A new interpretation results in 32 v.e. for the truncated tetrahedron, considering 3c-2e bonds at the triangular faces. The dumbbell requires 10 to 12 v.e. compared with binary reference compounds like Ca_3Cd_2 and $Ca_5M_3^{III/IV}$. The total formula is therefore $[M_{12}(Ico)]_4[M1_2(TT)]_2[M_2(ID)]_4$ and thus 256/260 electrons. This new interpretation is hence consistent with the calculated electron requirement.

[1]   A. Chahine, M. Tillard-Charbonnel, C. Belin, *Z. Kristallogr.*, 80, 1994.
[2]   Q. Lin, J. D. Corbett, *Inorg. Chem.*, 512-518, 2005.
[3]   M. Tillard-Charbonnel, C. Belin, *Mat. Res. Bull.*, 1277-1286, 1992.
[4]   V. Mihajlov, C. Röhr, *Z. Kristallogr. Suppl.*, 90, 2011.

Keywords: intermetallic phases, cluster compound, gallium compound