

PS07.00.13 MANGANESE(II)N,N'-DIPYRIDOXYLETHYLENE DIAMINE-N,N'-DIACETATE 5,5'-BIS(PHOSPHATE), MnDPDP. B. Fjartoft-Pedersen, L. Ehnebohm Tonnesen, J. Klaveness, School of Pharmacy, University of Oslo, B. Tirkkonen and T. Aase, Nycomed Imaging AS, Oslo

The hydrate of the disodiummanganese salt of Mn(II)DPDP¹ is presented. In the hexadentate chelate anion Mn(II) is coordinated to two nitrogens both at a distance of 2.32 Å, two carboxylate oxygens at 2.19 and 2.20 Å and two pyridoxyl oxygens at 2.09 and 2.11 Å. The other manganese ion is bonded to one carboxylate oxygen at 2.20 Å, one phosphate oxygen at 2.12 Å and four water molecules at 2.16–2.25 Å, both coordination polyhedra are more or less regular octahedra. One of the phosphate groups is disordered; two of the oxygen atoms being common for the two orientations of the group, with phosphorous and the other two oxygen atoms occupying two possible sites. P–P' distance 1.69 Å and O–O' distance 1.51 Å, the other oxygens pointing in opposite direction from the respective phosphorous atoms. The sodium atoms present in the structure are differently sixcoordinated, one of them to two different complex ions and have one carboxylate and one pyridoxyl oxygen atom from each complex and two water molecules as ligands, the other sodium atom is coordinated to two carboxylate oxygens and two phosphate oxygens from different molecules, ligand no 5 and 6 being one of the disordered phosphate sites. The Na–O distances range from 2.23 Å to 2.65 Å. The crystal contains several water molecules at hydrogen bonding distance in addition to the ones in the coordination sphere. Triclinic P1, Z=2, a=10.793 Å, b=10.969 Å, c=18.316 Å, α=97.21°, β=96.26°, γ=94.44°

¹Rocklage, S.M., Cacheris, W.P., Quay, S.C., Hahn, F.E. & Raymond, K.N. *Inorg. Chem.* (1989) 28 477–485.

PS07.00.14 THE CRYSTAL STRUCTURES OF POTASSIUM XANTHATES. N.A. Frolova, The University of Irkutsk, Irkutsk, Russia.

By X-ray method was determined the structure of potassium xanthates widely used under sulphide ore flotation of the composition: K₂COR, where R–C_nH_{2n+1}, n=2,3,4,5.

The structure have layer character. Inside of the layers there are polyhedra connected with each other. Outside of the layers there are hydrofobe alkyl groups. In the nearest surrounding of the K⁺ ions there are S and O atoms forming three types of polyhedra: seven- and octahill. In the first case the polyhedron represents the monohatted trigonal prism in one of the basis of which there are S atoms. The O atom occupies the seventh summit. In the second case the coordination polyhedron represents the distorted quadriangle prism or antiprism in one of the basis of which there are S atoms of the two xanthates. In the opposite basis there are O and S atoms of the two other xanthate molecules. Monotyped prisms being bonded by the common basis form the infinite columns which are in its turn connected with each other by their S–S edges.

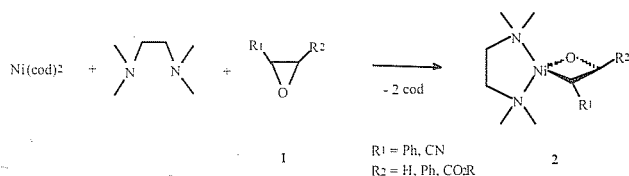
The potassium xanthate structure layers consist of monotyped polyhedra and only in the ethylxanthate it is observed the simultaneous presence of both types of polyhedron. The structure motive explains the good cleavage. The interatomic distances and valent angles in all structures coincide.

PS07.00.15 SYNTHESIS AND CRYSTAL STRUCTURES OF NOVEL NICKELAOXACYCLOBUTANES. H. Görls, M. Weidmann, E. Dinjus Max-Planck-Gesellschaft Arbeitsgruppe CO₂-Chemie, Friedrich-Schiller-Universität Jena, Lessingstraße 12, 07743 Jena, Germany, phone: +49/3641 - 636336, fax: +49/3641 - 636332, e-mail: goerls@xa.nlwl.uni.jena.de

Nickelaoxacyclobutane complexes are postulated as intermediates in the formation of cyclic carbonates from epoxides, carbon dioxide and a nickel(II)-species.[1] The only proof up to now for the existence of nickelaoxacyclobutanes 2 was given by the reaction of atomic nickel and

ethylene oxide in an argon matrix.[2]

For the preparation of complexes of type 2 we present a new and much more convenient method using bidentate nitrogen ligands (tmed, bipy) to stabilize the nickel(II)-center. The reaction of oxiranes 1 with Ni(cod)₂ in the presence of excess tmed leads to the formation of 2 in high yields. If electron rich epoxides (propylene oxide, butylene oxide and ethers of 1,2-epoxypropanes) are used no reactions take place with Ni(cod)₂ under these conditions. The complexes 2 have been characterized spectroscopically and by X-ray diffraction studies.

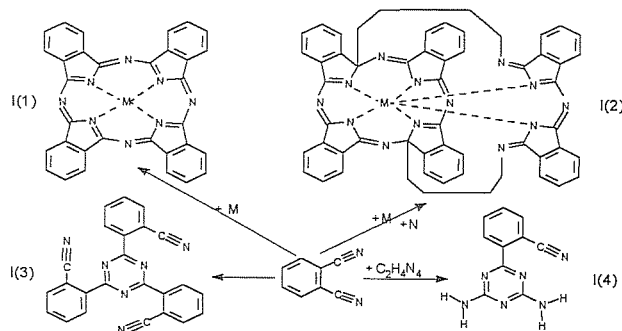


References:

- [1] R.J. De Pasquale, *J. Chem. Soc. Chem. Comm.*, (1973) 157
 [2] E.S. Kline, R.H. Hauge, J.L. Margrave and Z.H. Kafafi, *High Temp. Sci.*, 30 (1990) 69–82

PS07.00.16 STRUCTURAL INVESTIGATIONS OF PHTHALO- AND NAPHTHALOCYANINE PRECURSORS AND THEIR CYCLERIZATION PRODUCTS. By Jan Janczak and Ryszard Kubiak, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, P.O.Box 937, Poland.

Recently we determined the structures of 1,2-dicyanobenzene (I) (*Acta Cryst C* 51 (1995) 2039) and 2,3-dicyanonaphthalene (II). (II) crystallizes in *P1*, a=3.878(1), b=9.491(2), c=12.597(3) Å, α=93.85(3), β=96.20(3), γ=93.07(3)°. We used I, II to synthesis of phthalocyanines or naphthalocyanines and triazine derivatives. Scheme shows the products for substrate I:



Several papers on products I(1) and I(2) were published by us (*Acta Chem. Scand.* 49 (1995) 871). I(3) crystallizes in two forms: *P21/c*, a=4.001(1), b=23.852(5), c=19.574(4) Å, β=94.61(3)° and *P1*, a=11.276(3), b=12.833(3), c=12.915(3) Å, α=99.90(3), β=112.31(3) and γ=115.53(3)°. I(4) crystallizes in *P-1* a=7.332(1), b=7.704(2), c=9.476(2) Å, α=101.42(3), β=103.39(3) and γ=91.44(3)°.

An analogical products scheme is assumed for substrate II. Till now we did not obtained II(1), II(2) and II(3) in crystalline form. II(4) crystallizes in *C2/c*, a=35.757(7), b=7.320(2), c=21.452(4) Å, β=119.98(3)°. Details of these structures will be presented. This work was supported by a grant (No. 2 P303 117 06) from the Polish State Committee for Scientific Research.