PS07.00.13 MANGANESE(II) NN'-DIPYRIDOXYLETHYLENE DIAMINE-N,N'-DIACETATE 5,5'-BIS(PHOSPHATE), Mn₃P₂DP₃. B. Fjortoft-Pedersen, L. Ehneborn Tommessen, J. Klawe, University of Oslo, Oslo, Norway.

The hydrate of the disodiummanganese salt of Mn(II)DP₃ is presented. In the hexadentate chelate anion Mn(II) is coordinated to two nitrogens both at a distance of 2.32 Å, two carboxylate oxygen atoms at 2.19 and 2.20 Å and two pyridoxyl oxygen atoms 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 phosphorus and the other two oxygen atoms occupying two possible sites, P(1) distance 1.69 Å and O-O distance 1.51 Å, the other oxygen pointing in opposite direction from the respective phosphoric atoms. The sodium atoms present in the structure are differently six-coordinated, 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 oxygen and two phosphate oxygen 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, a=10.793 Å, b=10.969 Å, c=18.316 Å, α=97.21°, β=96.26°, γ=94.44°.


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: K₂S₂O₃·2H₂O, where R=C₄H₉O₂N₂, 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 hydroboly alkyl groups. In the nearest surrounding of the K⁺ ions there are S and O atoms forming three types of polyhedra: seven- and octahedron. In the first case the polyhedron represents the monohedrad 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 quadrangle prism or antiprism in one of the basis of which there are S atoms of the two xanthate molecules. In the opposite basis there are O and S atoms of the two other xanthate molecules. Monotrope 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 polytoped polyhedra and only in the ethylene xanthate 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. Görts, M. Weidmann, E. Dinius Max-Planck-Gesellschaft Arbeitsgruppe C02-Chemie, Friedrich-Schiller-Universität Jena, Leisingerstraße 12, 07743 Jena, Germany, phone: +49/3641 - 636336, fax: +49/3641 - 636332, e-mail: goerst@x.tlwl.uni.jena.de.

Nickelaoxacyclobutane complexes are postulated as intermediates in the formation of cyclic carbonates from epoxides, carboxyl dioxane and a nickel(II)-species. 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 (trmd, bipy) to stabilize the nickel(II)-center. The reaction of oxiranes 1 with Ni(cod) in the presence of excess trmd leads to the formation of 2 in high yields. If electron rich epoxides (propylene oxide, butylene oxide and ethers of 1,2-epoxypropylines) are used no reactions take place with Ni(cod), under these conditions. The complexes 2 have been characterized spectroscopically and by X-ray diffraction studies.

References:

PS07.00.16 STRUCTURAL INVESTIGATIONS OF NAPHTHALO- AND NAPHTHALOCYANINE PRECURSORS AND THEIR CYCLOMERIZATION PRODUCTS. By Jan Janczak and Ryszard Kubiaik; Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 30-950 Wroclaw, PO.Box 937, Poland.

Recently we determined the structures of 1,2-dicyanobenzene (I) (Acta Chem. Scand. C51 (1995) 2039) and 2,3-dicyanomethaphthalene (II). (II) crystallizes in P1, a=3.878(1), b=49.912(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 triazines derivatives. Scheme shows the products for substrate I.

Several papers on products I(1) and I(2) were published by us (Acta Chem. Scand. C51 (1995) 871). I(3) crystallizes in two forms: P2₁/c, a=4.001(1), b=23.857(5), c=19.574(4) Å, β=94.61(2)° and P1, a=11.276(3), b=12.833(3), c=12.915(3) Å, α=99.09(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(6) 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.