

PS07.02.02 LOW TEMPERATURE NEUTRON AND X-RAY DIFFRACTION STUDIES OF $Mn(cth)Cu(oxpn)(CF_3SO_3)_2$ (cth)=(±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclohexadecane; ($oxpn$)= N,N' -Bis(3aminopropyl)oxamide. V. Baron^a, H. Rundlöf^b, R. Tellgren^b, B. Gillon^c, O. Kahn^d, ^aNFL Studsvik, S-611 82 Nyköping, Sweden, ^bInst. of Chem., Uppsala Univ., Box 531, S-751 21 Uppsala, Sweden, ^cLLB, CEA- CNRS, CEN Saclay, 91191 Gif-sur-yvette cedex, France, ^dICMCB, Chateau de Brivazac, 33600 Pessac, France

The present investigation illustrates the complementarity of neutron and x-ray diffraction for studies of disordered and hydrogen-bonded heterodinuclear compounds. This has been performed to provide nuclear structure factors and to form the basis for a spin distribution study of $Mn(cth)Cu(oxpn)(CF_3SO_3)_2$ (1,2).

A neutron diffraction study at 40 K was first attempted; however, it was not possible to refine all parameters. The number of atoms was 100 atoms/unit cell including 48 hydrogen atoms and the triflate anions were found to be disordered. We therefore believe that a combination of x-ray and neutron diffraction data was the best way to solve this problem.

The unconventional space group $P2_1/a$ was used to be consistent with the room temperature study (3). The lattice parameters at low temperature are $a=17.525(3)$, $b=17.955(4)$, $c=12.804(2)$ Å, and $\beta=104.97(2)^\circ$ with $Z=4$. The structure consists of an oxamido-bridged $Mn^{II}Cu^{II}$ part and two uncoordinated triflate anions. The Mn(II) ion is in an elongated octahedral surrounding, and the Cu(II) ion in a square-planar surrounding. The intramolecular Mn—Cu separation is 5.440(1) Å whereas the shortest intermolecular metal-metal (Mn—Cu) is equal to 7.825(1) Å.

- (1) O.Kahn, B.Gillon, R.Tellgren, H. Rundlöf, V. Baron. (In press).
 (2) V.Baron these de l'universite de Paris XI -Orsay (19 Decembre 1994).
 (3) C.Mathoniere, O. Kahn, J.-C. Daran, H. Hilbig, F.H. Köhler, Inorg.Chem., 32, 4057, 1993.

PS07.02.03 STRUCTURES OF THREE NOVEL DINUCLEAR COMPLEXES OF $Eu(III)$, $Pr(III)$ and $Nd(III)$ WITH BRIDGING ALANINEHYDROXAMIC ACID. By Zdzislaw Galdecki, Institute of General and Ecological Chemistry, Technical University of Łódź, ul. Zwirki 36, 90-924 Łódź, Poland

The structures of bis(*m*-D,L- α -alaninehydroxamic acid-1:2*kO*,1*kO'*) bis(hexaquaeuropium)(6+) tetraoxochlorate(1-), $[Eu(D,L-\alpha Alaha)(H_2O)_6]_2(ClO_4)_6$ (1), and the isostructural complexes of neodymium (2), and praseodymium (3) have been determined. The compounds were synthesized by J. Legendziewicz and P. Gawryszewska at the Institute of Chemistry of the Wrocław University and this study is a part of a broader investigation of novel complexes of lanthanides as model substances in biological systems.

The investigated complexes are binuclear; the lanthanide atoms coordinate 9 oxygen atoms: 6 water molecules, one oxygen atom of carboxyl group and two bridging oxygen atoms of hydroxamic groups. Unexpectedly the bridging oxygen atom in the complexes is not the carboxyl-oxygen atom, but the hydroxamic-oxygen atom. X-ray data were collected on a KM-4 diffractometer with Mo $K\alpha$ radiation at 293 K. The structures were solved by direct methods and refined by full-matrix least squares using SHELXTL-PC programs, on F values, with anisotropic temperature factors for non-hydrogen atoms. Positions of hydrogen atoms were taken from ΔF syntheses and refined with isotropic temperature factors. The space group of the isostructural complexes is $P2_1/n$ ($Z=4$) and the crystal data and R factors are given below:

Compound	a [Å]	b [Å]	c [Å]	β [°]	Final R
1	10.345(2)	11.312(2)	16.957(3)	95.39(3)	0.041
2	10.317(3)	11.332(4)	16.876(4)	95.90(3)	0.046
3	10.464(2)	11.329(1)	16.963(3)	95.90(3)	0.035

On the basis of the author's results and of the Cambridge Structural Database, the crystal chemistry of the investigated compounds in comparison with known lanthanides complexes will be discussed in detail.

PS07.02.04 CRYSTAL STRUCTURES OF ORGANOMETALLIC ALUMINUM AMINO-ALKOXIDES T. Gelbrich^{a)}, J. Sieler^{a)}, E. Hecht^{b)}, U. Dümichen^{b)} a) Institut für Anorganische Chemie der Universität, D-04103 Leipzig, Linnéstr. 3, b) Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, D-06217 Merseburg, Geusaer Straße, Germany.

Aluminum compounds can be stabilized by donor ligands. This stabilization is especially pronounced when chelating ligands are present [1].

Compounds of general formula Me_2AlOR^* [$OR^* = (+);(-)$ -dimethylamino-2-propoxide 1, (S);(+)-amino-2-propoxide 2, (+);(-)-2-piperidylmethoxide 3] have been characterized by single crystal X-ray structure analysis at 200 K. In the solid state, compounds 1-3 are dimeric. The central four-membered Al_2O_2 rings are planar and each aluminum is coordinated in a distorted trigonal bipyramidal fashion by two methyl groups (axial), two alkoxide substituents (axial and equatorial) and the N atom of the aminoalkoxide (equatorial). In 1-3 the axial Al-O bond length is significant shorter than the equatorial one. In 1, the center of the Al_2O_2 ring coincides with a crystallographic inversion center (space group $P2_1/c$). The absolute of structure of 2 (space group $P2_12_12_1$) was found to be (S) (Flack parameter = 0.04). Compound 3 crystallizes with two non-interacting molecules of toluole per formula unit.

[1] Dümichen, U., Thiele, K.-H., Gelbrich T., Sieler, J., J. Organomet. Chem., 495 (1995) 71-75.

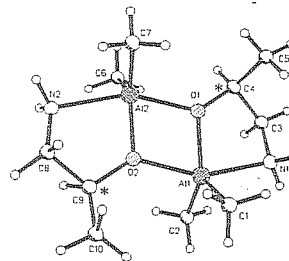


Figure 1: Molecular structure of (S);(+)-amino-2-propoxide 2

PS07.02.05 TWO BINUCLEAR MANGANESE(III) COMPLEXES CONTAINING BRIDGING KETONIC OXYGEN ATOM. Shi-Xiong Liu^{*} and Yun-Long Feng, Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, China

Two binuclear manganese(III) complexes containing bridging ketonic oxygen atom have been characterized by X-ray crystallography. They are $[Mn_2(bzacen)_2(MeOH)_2](ClO_4)_2$ (1) and $[Mn_2(bzacen)_2(MeOH)_2] (ClO_4)_2 \cdot 2H_2O$ (2), where $bzacen^{2-}$ is N,N' -ethylenebis(1-phenyl-3-imino-1-butanonato). These Schiff base compounds crystallize in Space group $P 2_1/n$ for (1) and $P bca$ for (2). Coordination geometry around Mn atoms in these two complexes is a distorted octahedron with an equatorial plane N_2O_2 from the $bzacen^{2-}$, while the axial sites are occupied by two oxygen atoms of methanol molecules. The very strong axial elongation has unusually found in a few complexes, for example, Mn-O(axial) bond being 2.493 Å in (1) and 2.448(8) Å in (2). The $[Mn_2(bzacen)_2(MeOH)_2]^{2+}$ cation in these complexes is a centrosymmetric dimer in which two Mn(III) atoms are joined by two ketonic oxygen atoms (Mn-O: 1.908 and 2.448 Å for (1); 1.910 and 2.493 Å for (2)). Therefore, Mn_2O_2 cores in the dimers being a parallelogram with Mn..Mn separation (3.387 Å for (1) and 3.355 Å for (2)) and Mn-O-Mn angles (99.7° for (1) and 100.0° for (2)). It was reported in Mn Schiff base complexes that the bridging oxygen atoms were from the μ_2-O^{2-} anion, μ_2 -phenoxy, and μ_2 -alkoxo. To our knowledge, the two structures are the first structure containing bridging ketonic oxygen atom in Mn Schiff base complexes.