

## Other

**PS07.05.01 CRYSTAL STRUCTURE OF A NEW HYDROLYSIS COMPLEX IN THE AQUEOUS ALUMINIUM SYSTEM.** Magnus Karlsson, Dan Bostrom, Lars-Olof Ohman and Torbjorn Gustafsson\* Department of Inorganic Chemistry, Umea University, S-901 87, Sweden, \*Department of Inorganic Chemistry, University of Uppsala, S-751 21, Sweden

The chemistry of aluminium in aqueous solution is of great interest due to its toxic and deleterious environmental effects. The aluminiummonocarboxylic acid (HL) systems have been studied by means of potentiometric measurements<sup>1,2</sup>. Data were mainly explained by the  $Al_2(OH)_2L_3^{3+}$  complex. An attempt to crystallize this complex was made. Aluminium metal and aluminium chloride was dissolved in aqueous solutions of monocarboxylic acids to give solutions containing 0.6 M aluminium, 0.3 M monocarboxylic acid and a pH of around 3.7. After 6 to 12 months of slow evaporation in a refrigerator (6°C), transparent crystals appeared. The structure, solved by applying direct methods, did not contain the anticipated  $Al_2(OH)_2L_3^{3+}$  complex but a new hydrolysis complex with thirteen aluminium ions, that differed from the established Keggin<sup>3</sup> ion  $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ . The preliminary cell parameters were  $a = 13.922 \text{ \AA}$   $b = 23.572 \text{ \AA}$   $c = 22.442 \text{ \AA}$   $\beta = 90.188^\circ$  in the space group  $P2_1/c$ .

<sup>1</sup> E. Marklund, L.-O. Öhman and S. Sjöberg, Acta Chem. Scand., 43 (1989) 641-646

<sup>2</sup> L.-O. Öhman, Acta Chem. Scand., 45 (1991) 258-264

<sup>3</sup> G. Johansson, Ark. Kemi, 20 (1963) 321

**PS07.05.02 SYNTHESSES AND STRUCTURES OF  $[Pb_3Cl_{10}]^{4-}$  AND  $[PbBr_3]^-$ .** H. Miyamae, K. Nagae, G. Hihara, Department of Chemistry, Josai University, Keyakidai 1-1, Sakado-shi, Saitama 350-02, Japan

We found two new types of halogenoplumbate(II) of the formula,  $[Pb_3Cl_{10}]^{4-}$ (a) and  $[PbBr_3]^-$ (b). They are obtained from DMF solution of  $PbX_2$  (X=Cl or Br) with N,N,N',N'-tetramethylethylenediamine (me4pn).

There are two independent Pb atoms in (a). One at the center of symmetry is in regular octahedral coordination of six Cl atoms (Pb-Cl distances are in the range of 2.91~2.99 Å), while the other at general position is in square pyramid (Pb-Cl: 2.68~2.97 Å) with sixth Cl atom at 3.29 Å.

The Pb atom in (b) has 3-bar symmetry as in the case of  $[PbI_3]^-$  of [hmtaH][ $PbI_3$ ] (hmta=hexamethylenetetramine; H. Miyamae, H. Nishikawa, K. Hagimoto, G. Hihara, & M. Nagata, Chem. Lett., 1907-1910 (1988)) with Pb-Br distance of 3.00 Å. These two anions form infinite chain. The infinite chain in (a) is supported by [me4pnH<sub>2</sub>]<sup>2+</sup> ions with two independent N-H...Cl hydrogen bonds.

Crystal data: (a) [me4pnH<sub>2</sub>]<sub>2</sub>[ $Pb_3Cl_{10}$ ], Mr 1240.6, monoclinic, space group  $P2_1/c$  (No. 14),  $a=11.290(3)$ ,  $b=15.164(2)$ ,  $c=11.477(2)$  Å,  $\beta=117.70(1)^\circ$ ,  $V=1739.7(5)$  Å<sup>3</sup>,  $Z=2$ ,  $D_x=2.367$  g cm<sup>-3</sup>,  $m(Mo K\alpha)=15.38$  mm<sup>-1</sup>,  $F(000)=1136$ .

(b) [me4pnH][ $PbBr_3$ ], Mr 578.2, hexagonal, space group  $P6_3$  (No. 173) or  $P6_3/m$  (No. 176),  $a=10.399(2)$ ,  $c=7.945(3)$  Å,  $V=744.0(5)$  Å<sup>3</sup>,  $Z=2$ ,  $D_x=2.780$  g cm<sup>-3</sup>,  $m(Mo K\alpha)=19.38$  mm<sup>-1</sup>,  $F(000)=524$ .

## Hot Structures

**MS07.06.01 CORRELATIONS BETWEEN INDIVIDUAL BOND VALENCE PARAMETERS  $r_0$  AND STEREOCHEMISTRY OF CATIONS WITH LONE-PAIR ELECTRONS.** X. Wang and F. Liebau, Mineralogisches Institut der Universität Kiel, 24098 Kiel, Germany.

Based on correlations found between bond valence parameters,  $r_0$ , and the stereochemistry of lone-pair cations L, it is suggested that valences of the bonds around L consist of two terms: the classic term depending on bond lengths and a correction term taking into account the influence of the lone-pair electrons of L.

Individual  $r_0$  values have been calculated for each coordination polyhedron [ $LX_n$ ] using  $V_i = \Sigma \exp[(r_0 - D_{ij})/0.37]$  (1), where  $V_i$  is the formal valence of  $L_i$  and  $D_{ij}$  are  $L_i-X_j$  bond lengths in Å [1], with  $L=In^I, Tl^I, Sn^{II}, Pb^{II}, Bi^{III}, As^{III}, Sb^{III}, Bi^{III}, S^{IV}, Se^{IV}, Te^{IV}, Cl^{IV}, Br^{IV}$  and  $IV$ , and  $X=F-I, Cl-I, O-II, S-II$  and  $Se-II$ . For each L-X pair, with a few exceptions, such  $r_0$  values are found to be strongly correlated with the lengths of vectors  $\phi_{ij} = -\Sigma \phi_{ij}$  (2), where each vector  $\phi_{ij}$  is directed from  $L_i$  to  $X_j$  and has a length of  $\exp(-D_{ij}/g)$  with  $g$  being constant.  $g$  has been set equal to 0.2 Å, since this led to the best correlation coefficients  $R$  for almost all L-X pairs assuming  $r_0 = P|\phi| + Q$  (3), with  $P$  and  $Q$  being constants. Out of the 36 L-X pairs analyzed, 22 have  $R^2$  values higher than 0.5, of which 9 have  $R^2$  values larger than 0.8. Generally,  $R^2$  is higher for L cations having higher formal valences and/or fewer electron shells, with apparent exceptions of  $Sn^{II}-F-I, -O-II, -S-II$  for which  $R^2$  values are 0.77, 0.90, 0.86, respectively, and  $Se^{IV}-O-II$  for which  $R^2$  is only 0.27. At present, no explanation can be given for such exceptions.

Substituting eqn.(3) into (1) leads to  $V_i = \exp(P|\phi_i|/0.37) \exp[(Q-D_{ij})/0.37]$  (4). Since  $\phi$  can be considered as a measure of the retraction of lone-pair electrons from the nucleus of L, the first term on the right side of eqn.(4) represents a correction of the influence of the lone-pair electrons.

[1] Brown, I.D., Acta Crystallogr. B48 (1992) 553-572.