

Na₂CO₃ and oxydiacetic acid or thiodiacetic acid, respectively. Complex **1** is a one-dimensional polymer with a planar bridging oxydiacetate ligand in a meridional disposition; whereas **2** is a monomer containing the typical tridentate thiodiacetate ligand with a facial configuration. Both are, as far as we know, the first structural determinations of Mg-oda and Mg-tda complexes [1].

[1] Gorrane A., Pastor A., Álvarez E., Galindo A., *Inorg. Chemm. Commun.*, accepted.

Keywords: oxydiacetate, thiodiacetate, crystal structures

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Structural Variation of 1:1 Adducts of Lead(II) Chloride and Bromide with *N,N'*-Dimethylethylenediamine from 123K to 303K
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It has been reported that *N*-methyl substituted ethylenediamines form 1:1 adducts with lead(II) halides [1]. Among them *N,N'*-dimethylethylenediamine with PbX₂ (X=Cl, Br or I) crystallizes in the tetragonal system forming 4₁ spirals with two bridging halides. We examined which part contributes mostly to volume contraction upon cooling, comparing the different halides [2].

All cells undergo contraction predominantly along the *c* axis, which is connected to lower order bonds of the halogen bridge, while the bonds within the chelate do not contribute to the cell contraction.

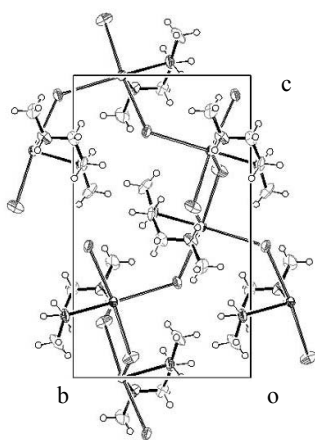


Fig. 1. Crystal packing viewed along a.

[1] Miyamae H., Hatanaka Y., Iijima Y., Hihara G., Nagata M., *AsCA Program Abstracts*, 1992, **16S**, 44. [2] Miyamae H., Enomoto K., Maruyama Y., Hihara G., *AsCA'03/Crystal*, 2003, **23**, 154.

Keywords: lead halide, temperature dependence, adduct

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Structural Studies of Boracalixarenes

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Boracalixarenes have significant potential as fluorescent sensors [1]. Davidson [2] and Mair [3] have recently reported the ease and difficulties associated with organoboron derivatisation at the lower rim of calix[4]arenes. We have developed new synthetic routes to such species avoiding the use of thermally unstable [(Ar^f)₂BF·Et₂O] reagents. Structures have been determined, in part, at Daresbury Laboratory stations 9.8 and the recently commissioned 16.2 SMX; both now equipped with Bruker AXS APEX II CCD detectors. The structures presented include those with bulky, electron-withdrawing perfluoroaryl ligands, halides (including those where halide exchange has occurred), and an example where calix[4]arenes have been coupled via B–O–B bridges. Rare examples of organometallic intramolecular π–π interactions are presented. Calixarene conformations are discussed as a consequence of the degree of substitution with arylboron groups versus halide.

[1] Gutsche C.D., *Calixarenes Revisited*, Royal Society of Chemistry, London, 1998. [2] Arimori S., Davidson M.G., Fyles T.M., Hibbert T.G., James T.D.,

Kociok-Köhn G.I., *Chem. Commun.*, 2004, 1640. [3] Cross W.I., Lightfoot M.P., Mair F.S., Pritchard R.G., *Inorg. Chem.*, 2000, **39**, 2690.

Keywords: calixarenes, synchrotron diffraction, π–π interactions

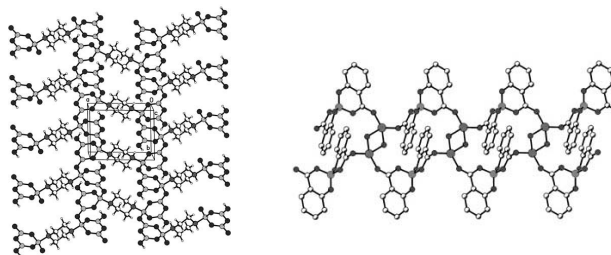
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Flux Synthesis of New Organo-borate Hybrids

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Molten boric acid 'flux' synthesis has been used for the preparation of borate-rich clusters[1] and porous frameworks[2]. We recently found that use of boric acid flux conditions can lead to direct coupling of organic bases with inorganic borate fragments. A new family of organo-borates containing direct B–N covalent bondings was formed. Piperazine affords the 2D network solid [(C₄H₁₀N₂)(B₆O₁₀H₂)] (left) and imidazole the molecular anion [(C₃H₄N₂)(B₅O₁₀H₄)]⁻. New bis(borosalicylate) structures (right) can also be prepared by this HT method and some novel salts of these will also be discussed.



[1] Williams I.D., Wu M., Sung H.H-Y., Zhang X.X., Yu J., *Chem. Commun.*, 1998, 2463. [2] Rowsell J.L., Taylor N.J., Nazar L.F., *J. Amer. Chem. Soc.*, 2002, **124**, 6522.

Keywords: inorganic organic structures, framework structures, flux synthesis

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The Role of Inter- and Intramolecular H...H Contacts in the Crystals of Carboranes

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On the basis of the high-resolution X-ray diffraction study of the electron density distribution function as well as quantum-chemical calculations of the crystal structures the attractive intramolecular contacts in the crystals of both aryl-substituted carboranes and metallacarboranes have been investigated. Their energy values have allowed creating the scheme, for the estimation of the lattice energy using only the X-ray diffraction data for the carborane derivatives.

Using R. Bader's theory "Atoms in Molecules" for both X-ray data and relaxed quantum-chemical scans of the potential energy surfaces of aryl-substituted carboranes along the coordinate defining the conformation of the substituent, it was found that despite the presence of close intramolecular H...H contacts between the hydrogen atoms of an aryl ring and those of the carborane moiety, all studied mono-substituted aryl-carboranes are characterized by the absence of a barrier to the rotation of the ring, due to the presence of the attractive interaction between the corresponding pairs of hydrogen atoms. Upon such barrierless rotation of the aryl rings the changes of the C–C and C–B bonds lengths of the carborane icosahedrons occur due to the transfer of the π-density of an aromatic ring to the corresponding antibonding orbital of one of these bonds. Close examination of the C–C bond properties in *o*-carboranes has allowed to suppose, that this bond can be described as a "single π-bond".

Keywords: inter- and intramolecular interactions, electron density distribution in bonds, topological properties of charge distribution