

Poster Presentations

[MS33-P02] Variable Pressure Single Crystal Diffraction Study of $[\text{GeX}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]$, $\text{X}=\text{Cl, Br, I}$.

Claire Wilson^a, D. A. Allan^a, S. J. Coles^b, K. George, W. Levason, G. Reid & W. Zhang.

^aDiamond Light Source, UK.

^bChemistry, University of Southampton, Southampton, UK.

Email: claire.wilson@diamond.ac.uk

Attention towards the p-block elements has recently been stimulated by the need for new reagents for materials and electronics applications, as well as the intrinsic interest. Our studies of the coordination chemistry of Ge(II) with a range of neutral ligands, few reports of which existed until recently, have revealed many striking features including diverse structural motifs and highly variable coordination numbers (between 3 and 8). [1,2] A series of homologous Ge(II) diphosphine complexes; $[\text{GeX}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]$, $\text{X}=\text{Cl, Br, I}$ exhibit a number of weak, secondary Ge...neutral ligand, Ge...halogen and even Ge...Ge interactions, longer than conventional covalent bonds but well within the sum of the van der Waals radii. [2] The Cl and Br complexes are isomorphous ($C2/c$) with a puckered Ge_2X_2 core, whereas, the iodide analogue ($P21/c$) has a planar Ge_2I_2 core. Through single crystal X-ray diffraction studies, carried out using the DLS beamline I19 at pressures between 1 and ~100 kbar, we investigated the structural consequences of applying pressure to these complexes with the aim of gaining insights into the role of the secondary bonding interactions and a better understanding of the subtleties of the bonding in these very unusual systems. Our studies show that subjecting these complexes to high pressures results in significant structural changes. While the chloride and iodide complexes show a gradual reduction in the size of the unit cell and the length of the secondary bonding interactions with increasing pressure, the bromide complex undergoes a phase transition between 29 and 46 kbar involving a sharp change in β -angle of $\sim 20^\circ$ and changes to the packing arrangement in the

cell. In particular, the interactions between the benzene rings change from an edge-to-face to a parallel offset arrangement, similar to that found in the iodide structure.

[1] F. Cheng, J.M. Dyke, F. Ferrante, A.L. Hector, Levason, G. Reid, M. Webster and W. Zhang (2010), Dalton Trans., 39, 847-856

[2] F. Cheng, A.L. Hector, W. Levason, G. Reid, M. Webster & W.J. Zhang, Inorg. Chem. 2010, 49, 752

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