

s13.m42.p11 **Early Transition Metal Calixarene and Tripod Ligand Complexes for Ethylene Polymerisation.** Mark R.J. Elsegood^a, Carl Redshaw^b, Sophie H. Dale^a, Abdessamad Arbaoui^b, Michael Rowan^b, Lee Warford^b, Carol Peréz Casas^c and Takehiko Yamato^c, ^aChemistry Department, Loughborough University., UK, ^bSchool of Chemical and Pharmaceutical Sciences, UEA, UK, and ^cDepartment of Applied Chemistry, Saga University., Japan. E-mail: m.r.j.elsegood@lboro.ac.uk

Keywords: Calixarene; Synchrotron; Tripod ligands

The field of calixarene chemistry has grown substantially in the past decade. There are now many reported applications including sensors, medical diagnostics and phase transfer agents. [1] Use in polymerisation catalysis for a variety of chemical systems has, however, only recently gained attention with mixed success. [2-6]

This paper focuses on our discoveries with early transition metal (primarily vanadium) oxo or organoimido fragments supported on the hexahomotrioxacalix[3]arene ligand (see figure for an example) or by one of a range of new tripod ligands. Oxacalix[3] ligands have gained very little attention in the literature thus far, in contrast to the rich literature for the well-known calix[4]arenes.

Here we report the structures and high ethylene polymerisation catalytic activity of the new compounds. The structural work has been undertaken using both laboratory-based conventional X-ray sources and synchrotron radiation at Daresbury Laboratory, all at low temperature.

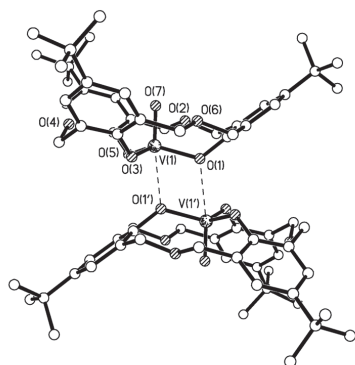


Figure: Weakly associated pairs of [V(O)(*p*-^tBu-hexahomotrioxacalix[3]arene)] molecules.

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- [6] L. Gianni, *et al*, *J. Am. Chem. Soc.*, **1997**, 119, 9198.

s13.m42.p12 **Polymorphism and Phase Transitions in Maleic Hydrazide.** Andrzej Katrusiak¹ and Anna Katrusiak², ¹Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan; ²Department of Organic Chemistry, Karol Marcinkowski University of Medical Sciences, Grunwaldzka 6, 60-780 Poznan, Poland. E-mail: katran@amu.edu.pl

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Maleic hydrazide (MH) was reported to crystallize in three polymorphic forms, one triclinic (MH1) [1], and two monoclinic ones (MH2 and MH3) [2,3]. The crystal structures of these polymorphs are built of OH--O and NH--O bonded aggregates. It was found, that despite the similar pattern of hydrogen bonds in their structures, the polymorphs have different chemical properties - their reaction of chlorination with POCl₃ gave either a mixture of 3,6-dichloropyridazine and 6-chloro-3-pyridazinone, or exclusively the dichloro derivative [4]. The origin of this different reactivity has been connected with different orientation of the hydrogen-bonded ribbons of MH molecules relative to the crystal faces. The temperature study of the polymorphs has shown, that two of them are stable between 90 and 300K, while the most reactive one undergoes two phase transitions, which significantly affect the geometry of the NH--O hydrogen bonds, responsible for the formation of the ribbon aggregates. The differences in the structures will be related to the chemical properties of the polymorphs.

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