

Dibenzylgallium(indium) Chalcogenolates

Dibenzylgallium- and Indiumchalcogenolates have been prepared in methathesis reactions (1) at room temperature in various solvents:



Ph = Phenyl

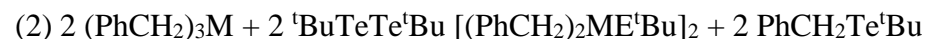
^tBu = tert.-Butyl

M = Ga; E = O, S, Se, Te

M = In; E = Te.

The reaction, employing the analogous Seleno-Grignard reagent ^tBuSeMgBr, led to the gallate $[\text{Mg}(\text{THF})_6][(\text{PhCH}_2)_2\text{GaBr}_2]_2$ as the main product.

In reaction (2) higher yields are observed for compounds containing the heavy chalcogene tellurium:



M = Ga, In; E = Te

Due to the Lewis acidic character of the metal centers the chalcogenolates form dimers in the solid state and in solution, as shown by cryoscopic measurements in benzene. The resulting four membered M_2E_2 -rings with m^2 -bridging chalcogene atoms essentially determine the properties of the chalcogenolates.

X-ray-diffraction reveals the ring of the alcoholate to be planar and centrosymmetric. The other compounds build up folded rings. An example is shown in figure 1.

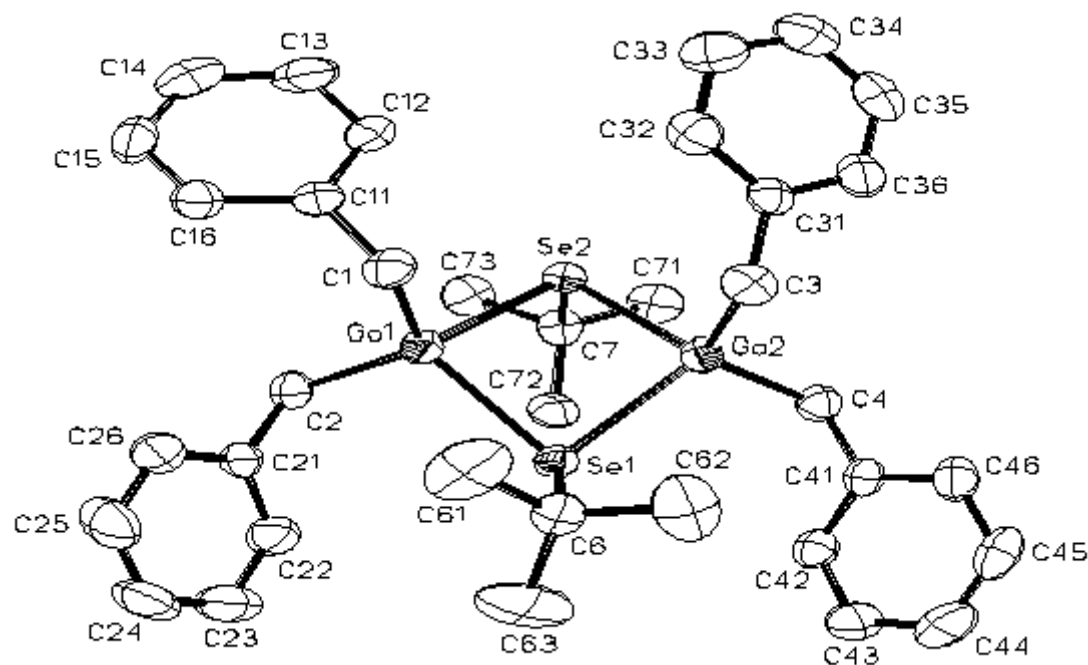


figure 1

The two tert.-Butylligands in the compounds with folded rings occupy transoid endo/exo-positions. Since the endo-ligand is "trapped" between two methylene groups (see figure 2) and the exo-ligand is directed off the folding of the ring, for the methylene protons results a diastereotopic environment.

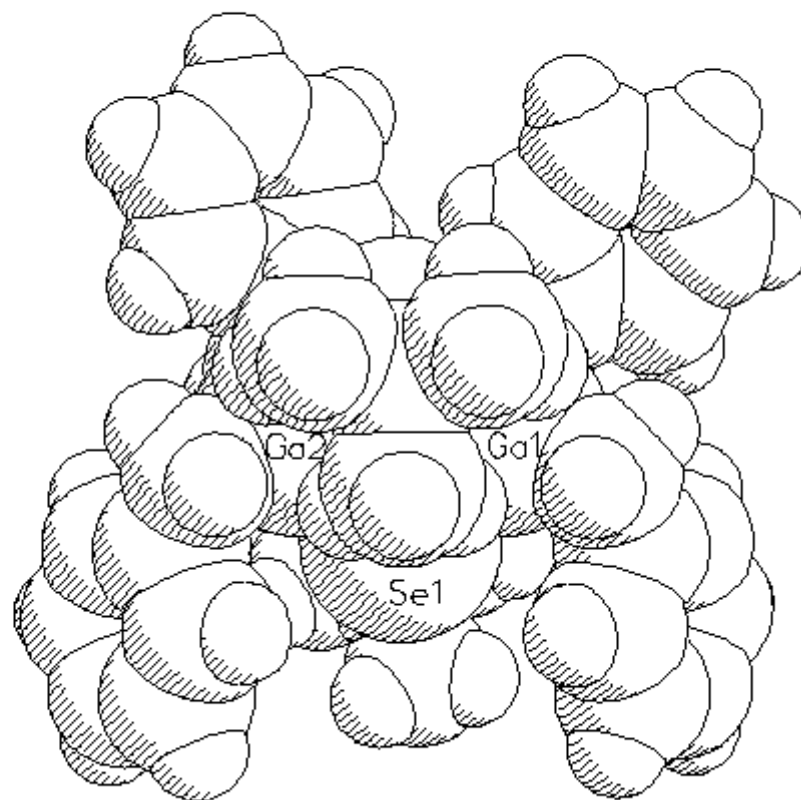


figure 2

NMR-experiments at room temperature only show one signal for the methylene groups because of the inversion of the ring being fast relative to NMR timescale. Low-temperature measurements at 198 K reveal the protons to be diastereotopic by two sharp doublets.

Literature:

Mike R. Kopp, B. Neumüller: *Z. anorg. allg. Chem.* **1997**, 623, 796.