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Small and Large Rings: Compounds with Geminal Donor and Acceptor Centres

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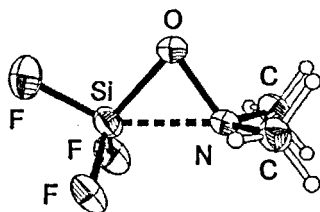
Selected examples of compounds which have units consisting of acceptor and donor centres in geminal position to one another are discussed with respect to their different types of aggregation, and the different nature of the interactions between these centres.

Keywords: Donor-acceptor interactions; hypercoordination; silicon; aluminium; gallium; hydroxylamines

Introduction: Main group compounds with geminal donor and acceptor centres have many possibilities for intra- and intermolecular aggregation. We shall demonstrate this versatility with two compounds with SiON units and one with AlCN units.

F₃SiONMe₂ We have demonstrated the occurrence of attractive interactions between Si, Ge and Sn atoms with nitrogen centres in

β -position for compounds containing SiON-,¹ GeON- and SnON units.² The strongest interaction leading to a three-membered SiON ring with hypercoordinate silicon has now been found in $F_3SiONMe_2$.³ This compound was prepared from SiF_4 and LiONMe. The molecular geometry turned out to be markedly dependent on the polarity of the surrounding medium and is favourably monitored by the SiON angle which is $77.1(1)^\circ$ (Fig.



1) in the crystal (m.p. -64°C), 87.1° in benzene solution (NMR/ab-initio/IGLO method) and $94.3(9)^\circ$ in the gas phase (electron diffraction).

Figure 1: Crystal structure of $F_3SiONMe_2$

$[-Cl_2SiO(Me)NCH_2N(Me)O-]_2$ The twelve-membered ring compound $(-Cl_2SiOMeNCH_2NMeO-)_2$ was prepared from $SiCl_4$ and the bifunctional LiOMeNCH₂NMeOLi.

According to a crystal structure determination (Fig. 2) the ring system contains four SiON linkages, of which two show attractive Si...N interactions (SiON angles 96.1 and 101.9°) and two do not (SiON angles 112.5 and 117.8°).

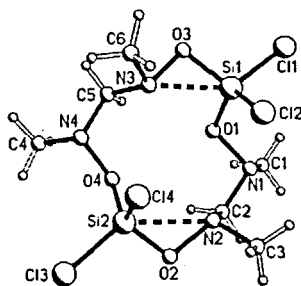
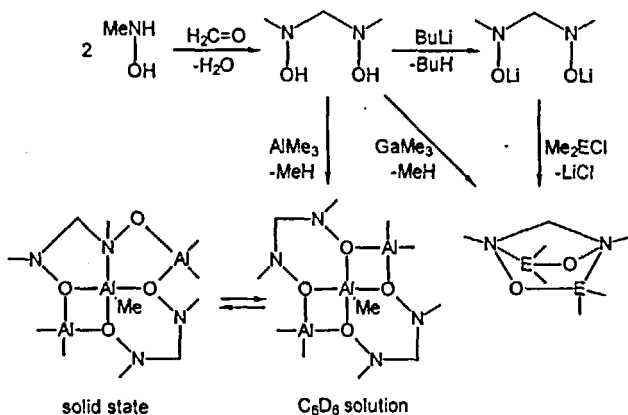


Figure 2: Crystal structure of $[-Cl_2SiO(Me)NCH_2N(Me)O-]_2$

[HO(Me)N]₂CH₂ as flexible ligand [HO(Me)N]₂CH₂ has been introduced as ligand in boron chemistry by Kliegel.⁴ We could show the parent bishydroxylamine to react in different ways with trimethylaluminium and -gallium (see Scheme 1). The reaction with AlMe₃ yields a tetracyclic product with two four- and two six-membered rings connecting two tetracoordinate Me₂Al groups and a pentacoordinate MeAl group (¹H, ¹³C and ²⁷Al NMR). Upon crystallisation this structure rearranges to a product with one four-, two five- and one six-membered ring (single crystal XRD).



Scheme 1

[(Me₂AlCH₂N(Me))₂CH₂] Compounds with electropositive metals and electronegative donor atoms in geminal positions do often show unusual reactivity such as the carbenoids.⁵ We have prepared compounds with AlCN units and shall present a novel alumina-aza-norbornane, which is generated from Karsch's

dilithiated aminale $[\text{LiCH}_2\text{N}(\text{Me})]_2\text{CH}_2^6$ and Me_2AlCl by simultaneous formation of two Al-C and two Al-N bonds.

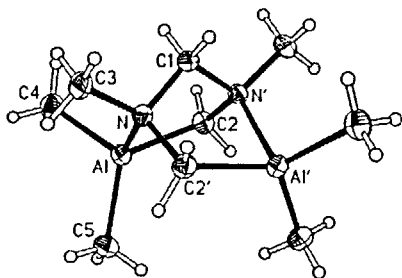


Figure 3: Crystal structure of $[(\text{Me}_2\text{AlCH}_2\text{N}(\text{Me}))_2\text{CH}_2]$

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