Sodium tri(pyrazol-1-yl)-germanate and -stannate: New Tridentate Claw-ligands' containing group 14 metals

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[(thf)\textsubscript{3}Na{(pz)}\textsubscript{3}Ge] \textsuperscript{1} and [(thf)\textsubscript{2}(pzH)Na{(pz)}\textsubscript{3}Sn] \textsuperscript{2} (pz = pyrazol-1-yl) are obtained by the reaction of pzNa with GeCl\textsubscript{2}·dioxane and SnCl\textsubscript{2}, respectively, in a 3:1 molar ratio in thf (thf = tetrahydrofuran); the X-ray structure determination shows that the {(pz)}\textsubscript{3}Ge unit in \textsuperscript{1} is a tridentate ligand to the sodium, while the {(pz)}\textsubscript{3}Sn unit in \textsuperscript{2} is only bidentate resulting in dimerisation to produce overall a twelve-membered ring system.

Germanium(n) and tin(n) compounds are well known as acid-base systems and undergo a wide spectrum of reactions. The metal centre can either interact with electrophiles because of the free electron pair\textsuperscript{1,2} or with nucleophilic reagents to saturate its coordination sphere.\textsuperscript{3,4} Mixed-metal complexes containing germanium, tin or lead are known e.g. alkoxides of the composition M(OBu\textsubscript{3})\textsubscript{2}E (E = Ge, Sn and Pb; M = alkali metals, earth alkali metals, In, Tl and Pb).\textsuperscript{5} Heteroaromatic functions such as pyridyl or pyrazolyl should also be promising substituents for the formation of mixed-metal complexes. Recently we reported the synthesis and structure of dimethylaluminiumdi(2-pyridyl)phosphide, in which the pyridyl rings
separate the two main group elements. Poly(pyrazol-yl)-alkanes, borates and gallates are well known as nitrogen donor ligands for metal complexes.\(^6\)\(^9\) We aimed to replace the central atom of these ligands with group 14 metals like germanium, tin or lead. The reaction of \(E\) halides with, for example, alkali metal or alkali earth metal pyrazol derivatives in excess, should lead to complexes in which the resulting (pz)\(^2\)E unit interacts with an excess (pz)\(^2\)M\(^0\) unit as an acid-base adduct. The donor ability of the 2-nitrogen atoms in the pyrazol substituents bridge the alkali metal and the germanium or tin atom, respectively. The reaction of pyrazolysodium, prepared from NaH and pyrazol in toluene, with GeCl\(_2\)-dioxan and SnCl\(_2\), respectively, in a 3:1 molar ratio in tetrahydrofuran at \(-78\) °C yielded pale yellow gels. The resulting NaCl could be separated by treating the mixtures with \(n\)-hexane.

Suitable crystals of \(1\) could be obtained after storage of the filtered solutions at \(-18\) °C for 3 d. The colourless crystals of both compounds decompose instantaneously at room temperature, because they rapidly lose solvent. The crystals were selected and transferred to the diffractometer at \(-30\) °C.\(^10\)

\(1\) is monomeric in the solid state (Fig. 1).\(^\dagger\) The molecule adopts a threefold symmetry. The germanium and the sodium atoms are located on the threefold axis and are connected via three pyrazol rings, demonstrating that the sodium cation as a hard Lewis-acid prefers the hard 2-nitrogen atoms rather than the softer germanium base. In the substituent separated contact ion pair the ([pz]2Ge)\(^-\) unit forms a tridentate claw gripping around the sodium atom, which is furthermore coordinated by three thf molecules. The Ge(1)-N(1) distance is 196.5(6) pm and the N-Ge-N angle 96.2(3)°. Similar structure patterns are found in the tri(pyrrozol-yl)borates, which are often used as tridentate monoanionic ligands.\(^7\)\(^8\) In contrast to the structure of [Li(12-crown-4)][Ge(SiMe\(_3\)>3] where the alkali metal is solvent separated from the germanium atom,\(^11\) in \(1\) the sodium atom is separated from the germanium atom through the pyrazol substituents, forming a contact ion pair. The crystal structure of \(1\) also contains an uncoordinated thf molecule, which is disordered on the three-fold axis.

\(2\) Crystallizes as a dimer (Fig. 2).\(^\dagger\) The structure can be interpreted as a twelve-membered ring system where two tin and two sodium atoms are connected via four pyrazolyl functions. Two of the three pyrazol rings of each unit are bridging to a sodium atom while one is terminal. Furthermore the sodium atoms are coordinated by two thf molecules and one neutral pyrazol molecule. All Sn-N distances are in the same range [Sn(1)-N(1) 217.0(3), Sn(1)-N(3) 216.0(3) and Sn(1)-N(5) 217.6(4) pm]. Because the pyrazolyl rings are planar, the nitrogen donor electron pairs

[Diagram Image]
ligand. Transmetallation reactions of these complexes with metal halides should give mixed metal compounds of defined composition, by sodium halide elimination. This feature should give access to a vast number of mixed metal complexes containing central group 14 metal substituents separated from a variety of metals (i.e. alkaline, alkaline earth, lanthanides, etc.). It may also be interesting to see what coordination properties the mixed sodium-germanium complex \(1\) has towards soft acid centres such as platinum or mercury. This might prevent a route to hard-soft bimetallic reagents due to coordination site selective behaviour.

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References


![Fig. 2 X-Ray structure of 2. Selected distances (pm) and angles (°): Sn(1)-N(1) 217.0(3), Sn(1)-N(3) 216.0(3), Sn(1)-N(5) 217.6(4), Na(1)-N(2) 243.9(4), Na(1)-N(4a) 239.0(4), Na(1)-N(7) 245.1(4); N(1)-Sn(1)-N(3) 86.4(1), N(1)-Sn(1)-N(5) 86.8(1), N(3)-Sn(1)-N(5) 88.9(1), N(2)-Na(1)-N(4a) 103.3(1).](image)