Polyanions

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Chemistry with Bare Silicon Clusters in Solution: A Transition-Metal Complex of a Polysilicide Anion

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Dedicated to Professor Martin Jansen on the occasion of his 65th birthday

Since the first discovery of Group 14 polyanions in solutions in liquid ammonia by Joannis[1] and their structural characterization much later using cryptands,[2] synthetic chemistry using these homoatomic building blocks has come a long way.[3] Especially intriguing have been two developments. On the one hand, the oxidative coupling of the monocapped square antiprismatic Ge_9^{4-} ions leads first to dimers $[Ge_9{-}Ge_9]^{6-}$,[4] trimers $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$,[5] and tetramers $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$,[6] then to one-dimensionally extended $^1_\infty[-Ge_9-]^{2-}$ chains,[7] and finally to a new crystalline germanium elemental modification with the clathrate II structure.[8] On the other hand, a variety of polytetrelide transition-metal compounds have been prepared using the E_9^{4-} ions (E = Ge, Sn, Pb) as starting materials. These include molecular coordination compounds such as $[Sn_9M(CO)_3]^{4-}$ (M = Cr, Mo, and W), in which organometallic fragments cap one face of the cluster anions,[9] and the exciting endohedral clusters in which one or more transition-metal atoms are inserted into the tetrelide cage; examples include $[Ni@Pb_{10}]^{2-}$,[10] $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[11] $[Cu@Sn_9]^{3-}$,[12] $[M@Ge_{10}]^{3-}$ (M = Fe, Co),[13] $[Pt_2@Sn_{17}]^{4-}$,[14] and $[Pd_2@Ge_{18}]^{4-}$.[15] It is evident that a future combination of both preparative trends, that is, the oxidative coupling of endohedral clusters, would offer a totally new route to cluster-assembled nanomaterials based on Group 14 elements.

Given the pivotal technological role of silicon materials, the lack of a corresponding polysilicide solution chemistry is especially noteworthy. While Si_9^{4-} ions are known to be present in binary solids of the composition $M^I_{12}Si_{17}$ ($M^I_{12}[Si_9][Si_4]_2$, M^I = Na–Cs),[16] the first report that these compounds could be dissolved in liquid ammonia to yield Si_9^{3-}, Si_9^{2-}, and Si_5^{2-} ions did not appear until 2004.[17] Evidence that the prototypic Si_9^{4-} ion is also stable in solution and may be crystallized as ammoniate compounds was published only very recently.[18] The only chemical reaction with a polysilicide reported to date is the preparation of $[Si_9ZnPh]^{3-}$ with diphenylzinc.[19] In an interesting convergence, in recent years the synthesis of ligand-stabilized tetrel clusters has increasingly yielded compounds which contain "naked" tetrel atoms,[20] including an example with a naked Si vertex atom.[21]

One of the main obstacles for the development of the solution chemistry of silicon cluster ions is the poor solubility of the $M^I_{12}Si_{17}$ phases. Until now, the only suitable solvent is liquid ammonia,[17–19] and even then, only very low concentrations can be achieved with the crystalline binary phases. Consequently, we now employ a mixed-alkali-metal starting material of the nominal composition $K_6Rb_6Si_{17}$, which is prepared at the comparatively low temperature of 460 °C. This starting material is of rather poor crystallinity, but Raman spectra show bands at 282, 354, and 478 cm^{-1}, which indicate the presence of Si_4^{4-}, and a band at 391 cm^{-1}, which corresponds to the breathing vibration of Si_9^{4-}.[16b,22]

The reaction of $K_6Rb_6Si_{17}$ with $[Ni(CO)_2(PPh_3)_2]$ in liquid ammonia and in the presence of [18]crown-6 yielded the complex $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$, which is the first transition-metal complex of a silicide cluster ion, in the compound $[Rb([18]c\text{-}6)]_2[K([18]c\text{-}6)]_2Rb_4[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]\cdot 22\,NH_3$ (**1**). The central structural unit consists of two dicarbonyl nickel fragments coordinated by two bridging Si_9 cages, resulting in a cyclic binuclear complex anion with a crystallographically imposed center of symmetry (Figure 1). Taking the eightfold negative charge indicated by the number of alkali metal counterions into account, the reaction with $[Ni(CO)_2(PPh_3)_2]$ is essentially a simple ligand exchange in which Si_9^{4-} replaces PPh_3. It is interesting to note that the corresponding reaction with Ge_9^{4-} and Sn_9^{4-} in ethylenediamine yields completely different products. The reaction of

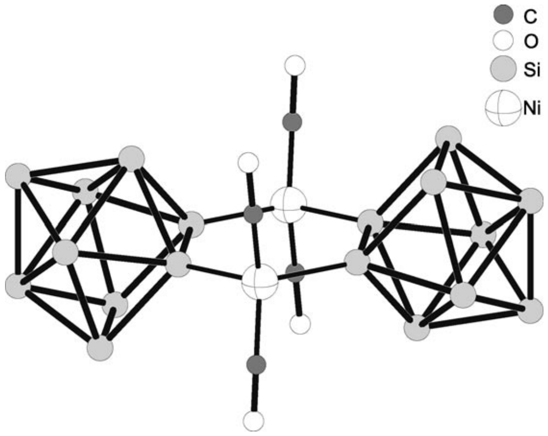

Figure 1. $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$ complex anion in **1**.

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$[Ni(CO)_2(PPh_3)_2]$ with Ge_9^{4-} resulted in the first endohedral cluster $[Ni@(Ge_9NiPPh_3)]^{2-}$ with one nickel atom inside the germanium cage and the other capping one of the faces, in which the charge of the Ge_9 cages has been reduced to minus two.[23] A similar redox reaction, presumably with the protons of the solvent, takes place in the case of Sn_9^{4-}, which is oxidized to Sn_9^{3-} in the endohedral cluster $[Ni@(Sn_9NiCO)]^{3-}$.[24] In contrast to these reactions, no redox reaction takes place during the preparation of **1**, likely owing to the lower temperature regime in liquid ammonia.

In the crystal structure of **1**, two of the crystallographically independent rubidium cations have direct contacts to the $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$ complex, while the third rubidium cation and the potassium cation are sequestered by crown ether molecules (Figure 2a). The Rb2 cation caps the approximately quadratic side of the Si_9 ligands, the shape of which is clearly derived from the monocapped square antiprismatic structure well-known from all E_9^{4-} cages (E = Si, Ge, Sn, Pb).[2] Additionally, Rb2 caps one of the triangular faces of the other Si_9 cage of the same complex, bringing the number of Rb2–Si contacts up to seven, with distances ranging between 3.406 and 3.986 Å. The coordination sphere of Rb2 is completed by two contacts to the oxygen atoms of the CO ligands of the complex (3.541 and 3.393 Å) and one short separation to an oxygen atom of the crown ether molecule harboring the Rb3 cation (3.213 Å); thus, the total coordination number of Rb2 is ten. The Rb1 cation bridges adjacent $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$ complexes generated by translational symmetry, thus leading to one-dimensionally extended strands in the crystallographic [100] direction (Figure 2b). Rb1 caps a triangular side of a Si_9 cage and an edge of another Si_9 cage of a neighboring complex (Rb1–Si between 3.567 and 4.013 Å). Again, contacts to two carbonyl oxygen atoms of the thus joined complexes complete the coordination sphere of Rb1 (3.387 and 4.597 Å), together with one ammonia molecule of crystallization (Rb1–N4 3.431 Å). The crown ether sequestered cations Rb3 and K1 are situated between the strands. Rb3 is positioned 1.080 Å above the mean plane of the crown ether and is also coordinated by four ammonia molecules of crystallization. It is rather unusual that this situation is repeated in the case of K1, as K^+ is usually a perfect fit for [18]crown-6. Instead of sitting in the exact center of the ligand, K1 is also situated above the plane of the molecule and is coordinated by two additional ammonia molecules. The remaining four of the eleven crystallographically independent ammonia molecules of crystallization are not attached to any cation.

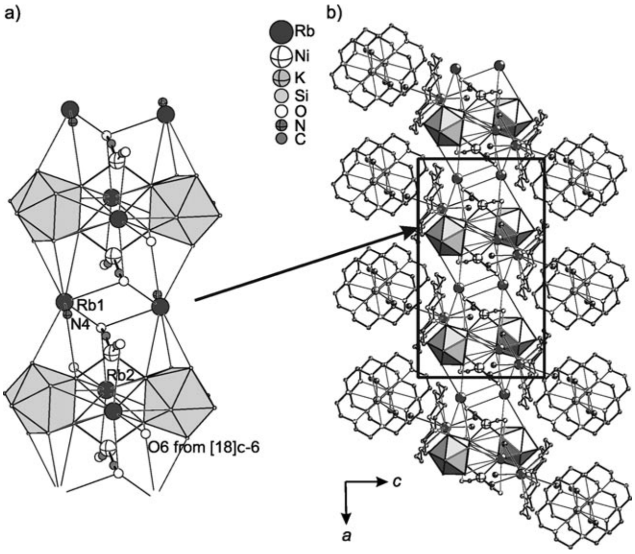

Figure 2. a) Small section of the crystal structure showing the coordination spheres of Rb1 and Rb2 in the crystal structure of **1**. b) Larger section of the crystal structure of **1** showing the strands in the [100] direction and the surrounding crown ether complexes. Unattached ammonia molecules of crystallization are omitted for clarity.

The Si_9^{4-} cluster remains more or less unperturbed by the two η^1-like coordination contacts to the $Ni(CO)_2$ fragments. The bond between the two Ni-coordinating silicon atoms (2.413 Å) is a small amount shorter while the Si–Si bond on the opposite side of the quadrangular face (2.547 Å) is significantly longer than the other two Si–Si bonds of this face (2.473 and 2.436 Å) and than the mean value for the corresponding bonds in other Si_9^{4-}-containing compounds characterized by X-ray structure analysis (2.46 Å).[16,18]

The Ni–Si bonds in **1** measure 2.285 and 2.304 Å. We are not aware of any comparable Ni^0 complex with ligands containing silicon donor atoms, but the observed bond lengths agree well with those observed for silyl or silylene complexes of Ni^{II}, Ni^{III}, or even Ni^{IV}: $[\{o\text{-}(SiMe_2)_2C_2B_{10}H_{10}\}Ni(PEt_3)_2]$ 2.242 Å,[25] $[\{1,2\text{-}C_6H_4(SiH)(SiH_2)\}_2Ni_2(Me_2PCH_2CH_2PMe_2)_2]$ 2.210–2.304 Å,[26] $[\{1,2\text{-}C_6H_4(SiH_2)\}_2Ni(Me_2PCH_2CH_2PMe_2)]$ 2.252 and 2.290 Å.[27]

Preliminary quantum chemical calculations of the central $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$ complex on Hartree–Fock level[28] indicate that the Ni–Si bonding situation is very similar to any other Ni coordination with a third-row donor atom; there is very little π back-bonding. Electron localization function (ELF)[29,30] calculations show that the disynaptic valence basin between Ni and Si has a population of 2.04, which corresponds to a single bond. The Ni–CO disynaptic valence basin, on the other hand, displays a higher population of 2.54, which agrees well with the synergistic bonding model for the carbonyl ligand.[31] The disynaptic valence basin between the Si atoms that coordinate to Ni at the quadrangular base of the cage has a population of 1.80, while the basin between the Si atoms on the opposite side of this face is populated by only 1.27 electrons, which corresponds well to the observed difference in bond lengths. As in our previous calculations on Si_9^{4-}, there is no indication of trisynaptic or tetrasynaptic basins.[18]

The solution of **1** in liquid ammonia is extremely sensitive to air and moisture, and any exposition causes immediate loss of color. As in the vast majority of ammoniates, **1** is thermally labile and decomposes rapidly at temperatures above −20 °C under loss of the ammonia of solvation. The dark red decomposition product was investigated by vibrational spectroscopy under inert conditions. The IR spectrum shows CO bands at 1937 and 1999 cm^{-1}, which are virtually unchanged compared to the starting material $[Ni(CO)_2(PPh_3)_2]$. The Raman spectrum has the band at 394 cm^{-1}, which is characteristic of the Si_9^{4-} cage.[16b,22] The latter observation indicates that, while the solid-state structure of the ammoniate **1** has broken down, the $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$ complex might still be intact. There is no indication of the presence of Si_4^{4-}; as in all polysilicide solution reactions reported to date, it remains unclear what happens to this component of the $M^{I}_{12}Si_{17}$ starting materials.

The preparation of **1** shows that, despite synthetic and methodic obstacles, transition-metal coordination chemistry with silicon cluster anions in solution is possible. A chemistry as rich and diverse as that of the heavier homologues, which in turn was probably as difficult to envision only ten years ago, now seems within reach.

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