

Article

The First Chelate-Free Crystal Structure of a Silicide Transition Metal Complex $[\text{K}_{0.28}\text{Rb}_{7.72}\text{Si}_9\text{Ni}(\text{CO})_2]_2 \cdot 16\text{NH}_3$

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Abstract: Single-crystals X-ray structure analysis of very thermally labile and moisture sensitive ammoniate crystals of $[\text{K}_{0.28}\text{Rb}_{7.72}\text{Si}_9\text{Ni}(\text{CO})_2]_2 \cdot 16\text{NH}_3$ show the presence of the very rarely observed nickel-silicide complex $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$, which was up to now only known in the 18-crown-6 involving solid $[\text{Rb}@18\text{-crown-6}]_2[\text{K}@18\text{-crown-6}]_2\text{Rb}_4[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2] \cdot 22\text{NH}_3$. This shows that, like already known for the heavier homologues, the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) is no precondition for the stabilization of the silicide cluster anion in solid state and the absence of the alkali metal ligand even allows for the crystallization in the higher symmetric monoclinic space group $C2/c$ compared to the triclinic space group $P-1$ when 18-crown-6 is present.

Keywords: silicides; ammonia; crystal structure; cluster compounds; Zintl ions

1. Introduction

Homoatomic polyanions of group 14 elements represent naked, anionic elemental building blocks and are an intriguing field of main group chemistry due to their versatile reaction possibilities. They can be used as promising starting materials for the synthesis of new compounds, and especially the monocapped square antiprismatic shaped nine atom cluster anions E_9^{4-} show a wide synthetic potential [1–4]. For the heavier homologues of this group, germanium, tin and lead, an abundance of

beautiful examples can be found in literature, reaching from coupled clusters [5] over alkylated derivatives [6,7] ending at the involvement of transition metals, where the cluster is acting as a ligand (sometimes under rearrangement of the atoms yielding new cluster shapes) [8] and even endohedral metalloids are formed [9,10] (for a recent overview see [1]). The case is different for the lighter homologue silicon, of which a solution chemistry has only been known since 2004 [11–14] and very few examples of reactions are known up to now. Therefore, only a diminutive number of products, a total of three, have been characterized. In addition to $[\text{Si}_9\text{ZnPh}]^{3-}$ [15] (Ph = phenyl = C_6H_5) and $[(\text{MesCu})_2\text{Si}_4]^{4-}$ [16] (Mes = mesitylene = $\text{C}_6\text{H}_2(\text{CH}_3)_3$) (Figure 1a,b), where organometallic precursors have been used during synthesis, we previously could show that the Si_9^{4-} cluster anions act as ligands in a simple ligand-exchange reaction of triphenylphosphine in the transition metal complex $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ (PPh_3 = triphenylphosphine = $\text{P}(\text{C}_6\text{H}_5)_3$) yielding the new complex $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ [17] (Figure 1c). All hitherto known crystal structures have the involvement of chelating additives in common, which are used during synthesis for the enhancement of the solubility of the Zintl educt material $\text{A}_{12}\text{Si}_{17}$ [18,19]. The question arose whether 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) or [2.2.2]-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) are imperatively necessary for the stabilization of the complex anion in the crystal structures. We here present the fourth crystal structure at all of a silicide complex anion in the crystal structure of $[\text{K}_{0.28}\text{Rb}_{7.72}\text{Si}_9\text{Ni}(\text{CO})_2]_2 \cdot 16\text{NH}_3$, which proves the stability of the transition metal complex in a rigid cation-anion-ammonia network without any further chelating additives.

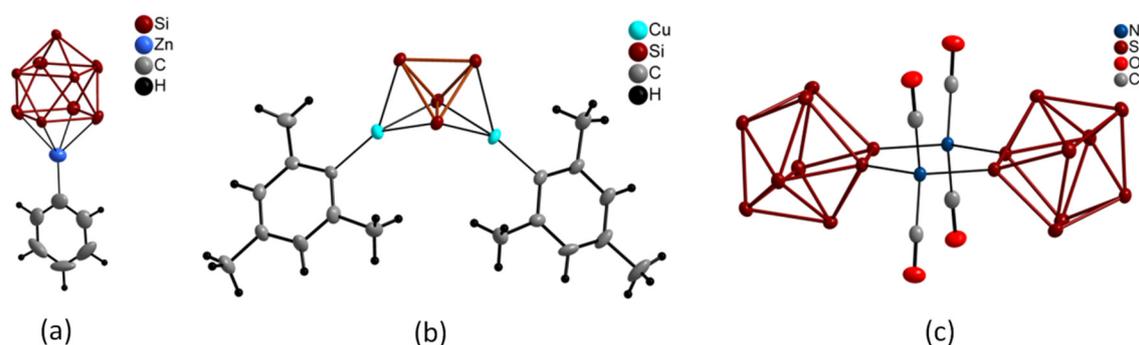


Figure 1. Silicon cage anions in transition metal complexes: (a) $[\text{Si}_9\text{ZnPh}]^{3-}$ [15]; (b) $[(\text{MesCu})_2\text{Si}_4]^{4-}$ [16]; (c) $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ [17].

2. Results and Discussion

The reaction of the ternary Zintl material $\text{K}_6\text{Rb}_6\text{Si}_{17}$ and $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ in the presence of 18-crown-6 resulted in the first chelate free crystal structure of the silicide transition metal complex $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ and proves the stability of the complex in the solid state, independently from 18-crown-6. Although 18-crown-6 is absent in the crystal structure of the here discussed compound, an even larger excess was used during the synthesis, compared to the synthesis of the 18-crown-6 involving material. This might indicate the basic necessity of the chelating additive for a better solubility of the precursor material but disproves its stabilizing effects in solid state. In the following, the new compound $[\text{K}_{0.28}\text{Rb}_{7.72}\text{Si}_9\text{Ni}(\text{CO})_2]_2 \cdot 16\text{NH}_3$ (**1**) is compared to the known crystal structure of $[\text{Rb}@18\text{-crown-6}]_2[\text{K}@18\text{-crown-6}]_2\text{Rb}_4[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2] \cdot 22\text{NH}_3$ (**2**) in order to analyze similarities

and discrepancies in the crystal structures of both compounds. As the mixed-cationic compound $K_6Rb_6Si_{17}$ was used during synthesis, the positions of all cations were carefully investigated for mixed occupancy during the refinement using the derived electron density maps. A mixed cationic site could only be resolved for one cation site (Rb_4/K_4 0.725(7):0.275(7)), the remaining four crystallographically independent cation positions turned out to be exclusively occupied by rubidium. One cationic site (Rb_5) is located beside an inversion center within the glide plane (site coordinates 0.25, 0.75, 0.5, Wyckoff position 4c) and therefore the s.o.f. (site occupancy factor) was fixed at 0.5. The crystal data and details of the structure refinement are given in Table 1.

Table 1. Crystal data and structure refinement details for $[K_{0.28}Rb_{7.72}Si_9Ni(CO)_2]_2 \cdot 16NH_3$ (**1**).

Item	Numerical Value
CCDC No.	1043014
Chemical formula	$[K_{0.28}Rb_{7.72}Si_9Ni(CO)_2]_2 \cdot 16NH_3$
M_r ($g \cdot mol^{-1}$)	1678.63
Temperature (K)	123(2)
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	30.669(6)
b (Å)	9.919(2)
c (Å)	19.894(4)
α (°)	90
β (°)	110.18(3)
γ (°)	90
V (Å ³)	5680(2)
Z	4
ρ_{calc} (g/cm^3)	1.963
μ (mm^{-1})	7.676
$F(000)$ (e)	3260.0
Crystal size (mm^3)	$0.18 \times 0.12 \times 0.1$
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection (°)	4.636 to 55.28
Index ranges	$-39 \leq h \leq 39, -12 \leq k \leq 12, -25 \leq l \leq 25$
Reflections collected	46,537
Independent reflections	6534 [$R_{int} = 0.0729, R_{sigma} = 0.0523$]
Data/restraints/parameters	6534/6/253
Goodness-of-fit on F^2	0.954
R_1, wR_2 ($I \geq 2\sigma(I)$)	$R_1 = 0.0349, wR_2 = 0.0667$
R_1, wR_2 (all data)	$R_1 = 0.0568, wR_2 = 0.0711$
$\Delta\rho_{max}, \Delta\rho_{min}$ ($e \text{ \AA}^{-3}$)	0.90/−0.46

In both compounds, the complex anion $[\{Ni(CO)_2\}_2(\mu-Si_9)_2]^{8-}$ is located on an inversion center of space group $C2/c$ (**1**), respectively $P-1$ (**2**), and this results in very similar dimensions of the latter in both crystal structures (Figure 2, Table 2). This proves that the geometry of the anion is not affected by packing effects or cation-anion interaction.

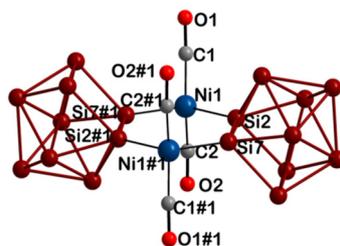


Figure 2. $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ complex anion in **1** and **2**; distances are given in Table 2.

Table 2. Distances within the complex anion $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ in the two known crystal structures **1** and **2**; atom assignment is given in Figure 2.

1			2		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Ni1	Si2	2.3052(12)	Ni1	Si2	2.3033(17)
Ni1	Si7	2.3044(13)	Ni1	Si7	2.3001(18)
Ni1	C1	1.738(4)	Ni1	C1	1.743(8)
Ni1	C2	1.746(4)	Ni1	C2	1.729(6)
C1	O1	1.167(5)	C1	O1	1.169(8)
C2	O2	1.159(5)	C2	O2	1.183(8)

In **2**, the complex anion shows direct contacts to six rubidium cations, two of which are symmetrically independent. A very similar arrangement is found for **1**, but the absence of cation chelating crown ether molecules allows for more direct cation contacts (Figure 3). The anionic moiety in **2** exclusively shows contacts to rubidium, and the potassium cations are only coordinated by 18-crown-6 molecules and ammonia molecules, agreeing with the HSAB (hard and soft acids and bases) principle.

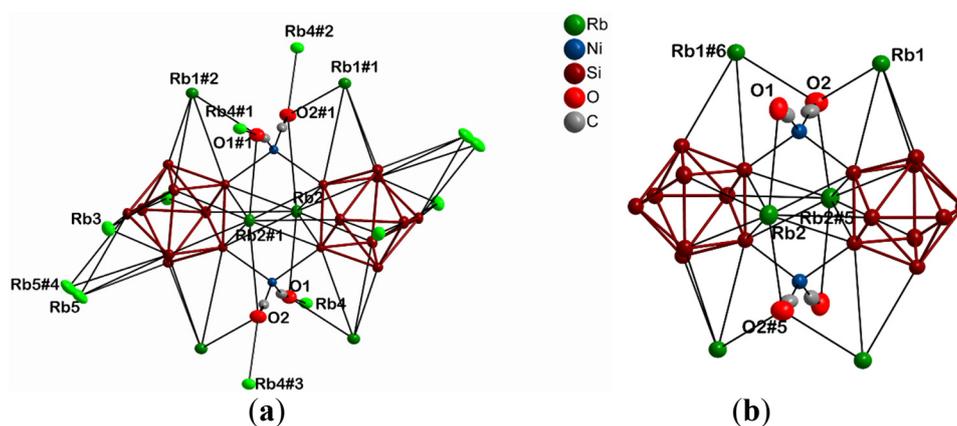


Figure 3. The comparison of the cation coordination of the complex anion $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ in **1** (**a**) shows the presence of additional contacts (given in bright green) compared to the cation coordination of the complex anion $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$ in **2** (**b**). The position of Rb4 is mixedly occupied by rubidium and potassium (see text and Figure 3). Displacement ellipsoids are drawn at the 50% probability level. (Symmetry codes: #1: $1 - x, 2 - y, 1 - z$; #2: $x, 1 + y, z$; #3: $1 - x, 1 - y, 1 - z$; #4: $0.5 - x, 1.5 - y, 1 - z$; #5: $2 - x, 1 - y, -z$; #6: $1 - x, 1 - y, z$).

The shortest Rb-O distances to the oxygen atoms of the carbonyl group of the complex anion in **2** are found at 3.275(5) Å (Rb2-O2#2), whereas the lack of 18-crown-6 in **1** results in short Rb-O distance of the carbonyl oxygen atoms O1 and O2 to the additional cationic site K4/Rb4 (see Table 3). Interestingly, the mixed occupancy perfectly agrees with the HSAB principle, as the smaller and therefore harder potassium prefers to coordinate to the small and hard oxygen atoms of the carbonyl ligand and short K/Rb-O distances can only be realized for this cationic site. The coordination of the cations is completed by contacts to the silicon atoms of the complex anion and ammonia molecules (Figure 4, Table 3). Altogether, a dense network of cations, anions and ammonia molecules is observed, which is also reflected by the calculated density of 1.963 g·cm⁻³ for **1** compared to the value 1.517 g·cm⁻³ for **2**.

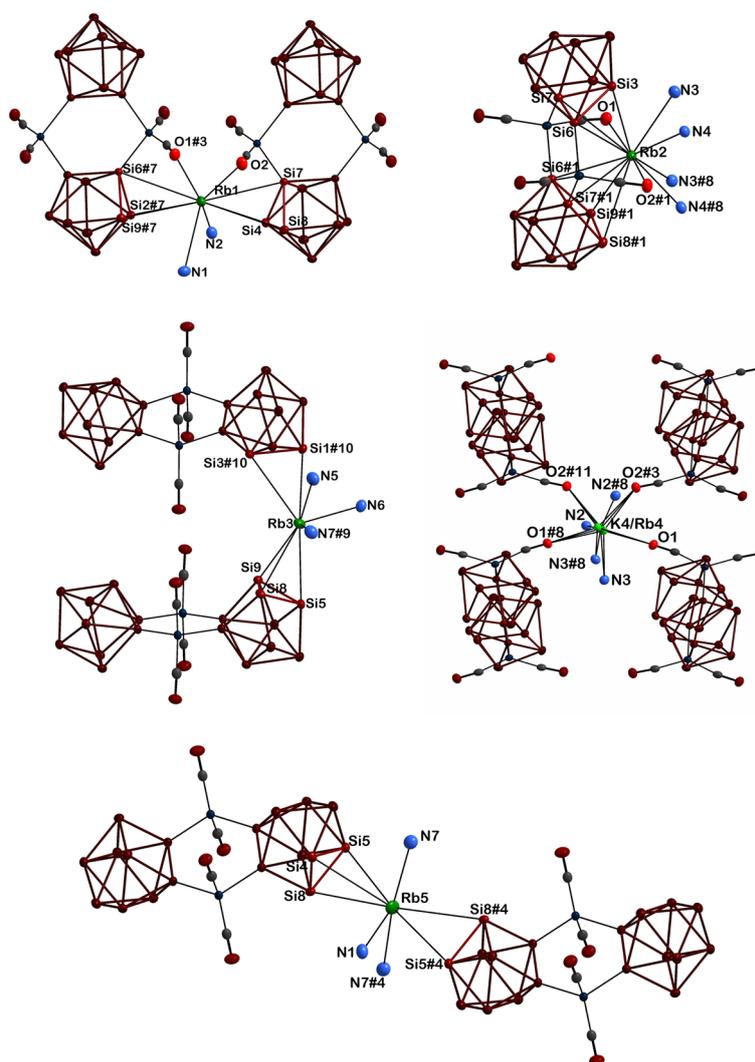


Figure 4. Coordination spheres of all five crystallographically independent cationic sites. The mixedly occupied cationic site K4/Rb4 shows only contacts to oxygen atoms of the carbonyl group and ammonia molecules, which agrees with the HSAB principle. The according distances are given in Table 2. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity (Symmetry codes: #1: 1 - x, 2 - y, 1 - z; #3: 1 - x, 1 - y, 1 - z; #4: 0.5 - x, 1.5 - y, 1 - z; #7: x, -1 + y, z; #8: 1 - x, y, 0.5 - z; #9: 0.5 - x, 0.5 + y, 0.5 - z; #10: x, 3 - y, -0.5 + z; #11: x, 1 - y, -0.5 + z).

Table 3. Distances for the coordination of the cations according to Figure 3.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Rb1	Si7	3.9366(14)	Rb4	N2	3.300(4)
	Si9#7	3.7493(15)		N3	3.007(4)
	Si2#7	3.8338(14)		O1	2.832(3)
	Si4	3.6312(14)		O2#3	2.855(4)
	Si7	3.9366(14)	K4	O1	2.70(3)
	Si8	4.0366(15)		O1#8	2.99(3)
	N2	3.116(4)		O2#3	2.79(2)
	N1	3.322(4)		O2#11	2.98(2)
	O2	3.853(4)		N2	3.04(3)
	O1#3	3.241(4)		N2#8	3.58(2)
		N3		2.776(17)	
		N3#8		3.246(19)	
Rb2	Si7#1	3.5962(15)	Rb5 *	Si5	3.619(4)
	Si6#1	3.5971(15)		Si5#4	3.639(4)
	Si6	3.8961(13)		Si4	4.049(3)
	Si3	3.4674(13)		Si8#4	3.744(4)
	Si9#1	3.5273(17)		Si8	3.988(3)
	Si8#1	3.8988(17)		N7	3.234(6)
	Si7#1	3.5961(15)		N7#4	3.222(6)
	N3	3.406(4)		N1	3.258(5)
	N3#8	3.367(4)			
	N4#8	3.157(4)			
	N4	3.090(4)			
	O1	3.263(4)			
O2#1	3.702(4)				
Rb3	Si5	3.7988(13)			
	Si1#10	3.7609(14)			
	Si8	3.6490(13)			
	Si3#10	4.0429(18)			
	Si9	3.7252(14)			
	N5	2.935(5)			
	N7#9	3.227(5)			
	N6	3.000(4)			

Note: * Rb5 is located beside a twofold axis; the distances for the Rb5 generated by symmetry are given in the cif file (Supplementary materials).

3. Experimental Section

All manipulations were performed under inert atmosphere in an argon filled MBraun Labmaster 130 G glove box. Schlenk tubes were used as reaction vessels. Ni(CO)₂(PPh₃)₂ (ABCR) was used without further purification. 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane; Sigma-Aldrich Chemie GmbH, Munich, Germany) was sublimated and then stored under argon. The solvent liquid ammonia was stored over potassium to remove traces of water before it was condensed on the reactands. For the synthesis of the precursor material K₆Rb₆Si₁₇ 0.294 g (7.5 mmol) K, 0.644 g (7.5 mmol) Rb and 0.5 g (17.8 mmol) Si were placed in a duran glass ampoule, which had been dried *in vacuo* before, and sealed under argon. The ampoule was placed in a second quartz glass ampoule for safety and heated to

460 °C using a heating rate of 25 °C/h. The temperature was kept for 72 h, afterwards the product was cooled down using a cooling rate of 20 °C/h. 0.12 g (0.098 mmol) of the blue black precursor phase, 0.063 g (0.098 mmol) of Ni(CO)₂(PPh₃)₂ and 0.08 g (0.30 mmol) 18-crown-6 were weighed in a Schlenk tube. Approximately 15 mL of dry ammonia were condensed on the reactands at −78 °C. The solution immediately changed color from yellow to red after shaking. The reaction vessel was kept at −40 °C, where an increase in color could be observed. After four weeks red, rod shaped crystals suitable for X-ray structure analysis could be obtained

4. Conclusions

The here presented crystal structure of [K_{0.28}Rb_{7.72}Si₉Ni(CO)₂]₂·16NH₃ proves the stability of the silicide complex anion [₂{Ni(CO)₂}(μ-Si₉)₂]⁸⁻ without any chelating additives in solid state, but the presence of 18-crown-6 for solubility enhancement might be a necessity.

Author Contributions

Markus Hamberger and Stefanie Gärtner carried out experimental work (synthesis, crystallization and X-ray structure determination), Stefanie Gärtner prepared the manuscript, Nikolaus Korber designed and conceived the study.

Supplementary Information

Supplementary materials can be accessed at: <http://www.mdpi.com/2073-4352/5/3/0275/s1>.

Conflicts of Interest

The authors declare no conflict of interest.

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