On the Formation of the Intermetalloid Cluster $[AgSn_{18}]^{7-}$ - The Reactivity of Coinage Metal NHC Compounds towards $[Sn_9]^{4-}$

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Experimental Section

All manipulations were carried out under a purified argon atmosphere using standard Schlenk and glove box techniques. K_4Sn_9 was prepared by fusion of stoichiometric amounts of the elements in sealed steel autoclaves and stored under argon atmosphere. 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride and $NHC^{Dipp}MCl$ (M: Cu, Ag, Au) were prepared according to modified literature procedures.[1-4] [2.2.2-Crypt] was dried in vacuo overnight. Liquid ammonia was dried and stored over sodium metal.

Syntheses:

1: K_4Sn_9 (62 mg, 0.050 mmol, 1 eq.), $NHC^{Dipp}CuCl$ (24.5 mg, 0.05 mmol, 1 eq.) and [2.2.2-crypt] (35 mg, 0.090 mmol, 1.86 eq.) were weighted into a Schlenk tube. Addition of ammonia (approximately 2 mL) led to the formation of a deep red suspension. The reaction mixture was homogenized by shaking the Schlenk tube several times and subsequently stored in a freezer at -70 °C. Compound **1** crystallizes as black block-shaped crystals. Since the crystals cannot be isolated from the reaction solution (decomposition due to loss of ammonia), the yield of approximately 30 % can only be estimated from the amount of crystalline material found in the reaction mixture.

2 and **4**: K_4Sn_9 (44 mg, 0.036 mmol, 1 eq.), $NHC^{Dipp}AgCl$ (19 mg, 0.036 mmol, 1 eq.) and [2.2.2-crypt] (54 mg, 0.144 mmol, 4 eq.) were weighted into a Schlenk tube. Addition of ammonia (approximately 1 mL) led to the formation of a deep red suspension. The reaction mixture was homogenized by shaking the Schlenk tube several times and subsequently stored in a freezer at -70 °C. After several months black block-shaped crystals had formed. Single crystal X-ray diffraction examination revealed a ratio of crystals of compound **4** to those of compound **2** of 9:1. Since the crystals cannot be isolated from the reaction solution (decomposition due to loss of ammonia), the yield of approximately 25 % (with respect to amount of Zintl phases used) can only be estimated from the amount of crystalline material found in the reaction mixture.

3: K_4Sn_9 (44 mg, 0.036 mmol, 1 eq.), $NHC^{Dipp}AuCl$ (22 mg, 0.036 mmol, 1 eq.) and [2.2.2-crypt] (25 mg, 0.067 mmol, 1.86 eq.) were weighted into a Schlenk tube. Addition of ammonia (approximately 1 mL) led to the formation of a deep red suspension. The reaction mixture was homogenized by shaking the Schlenk tube several times and subsequently stored in a freezer at -70 °C. Compound **3** crystallizes as black block-shaped crystals. Since the crystals cannot be isolated from the reaction solution (decomposition due to loss of ammonia), the yield of approximately 30 % can only be estimated from the amount of crystalline material found in the reaction mixture.

NMR experiments:

NMR spectra were measured on a Bruker Avance Ultrashield 400 MHz spectrometer. After evaporation of NH_3 (l) the residue was dissolved in MeCN to give a deep red solution. An aliquot sample of this solution was transferred to an NMR inner tube which was sealed with a plastic cap and positioned in a $CDCl_3$ filled standard NMR tube. The NMR spectrum was calibrated on the residual proton signal of $CDCl_3$.

Crystal Structure Determinations

The thermally very unstable, air and moisture sensitive crystals of **1**-**4** were transferred from the mother liquor into cooled perfluoroalkylether oil under a cold N_2 gas stream. For single crystal data collection, the single crystals were fixed on a glass capillary and positioned in a 100 K (**1**) or 120 K (**2**-**4**) cold N_2 gas stream using the crystal cap system. Single crystal data collection was either performed at an Oxford-Diffraction Xcalibur3 diffractometer ($Mo_{K\alpha}$ radiation) (**2-4**) or a Bruker AXS D8 diffractometer (**1**). Structures were solved by Direct Methods (SHELXS-2014) and refined by full-matrix least-squares calculations against F^2 (SHELXL-2014).[5] The positions of the hydrogen atoms were calculated and refined using a riding model. Unless otherwise stated, all non-hydrogen atoms were treated with anisotropic displacement parameters. The supplementary crystallographic data for this paper have been deposited with the Cambridge Structural database and are available free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure determination discussion:

The crystallographic data for compounds **1**-**4** are summarized in Table SI 1 and Table SI 2. In compounds **1**-**3** one of the ammonia molecules reveals only 50 % occupancy. In compound **2** some N atoms of ammonia molecules could not be refined anisotropically. For several different crystals of compound **4**, after structure refinement large residual electron density remained in the vicinity of atoms Sn11, Sn14, and Sn18, which have been included as additional Sn atoms (Sn19, Sn20, Sn21) and were refined as split atoms with a common occupancy factor. The two resulting individuals of the Sn_9 cluster are shown in Fig. SI 2. Furthermore, one of the $[K(2.2.2\text{-crypt})]^+$ units in **4** is disordered and was refined on split positions.

Table SI 1: Crystallographic data for compounds **1**-**3**.

Compound	**1**	**2**	**3**
formula	$Sn_9CuC_{81}H_{216}N_{32}O_{18}K_3{}^*$	$Sn_9AgC_{81}H_{216}N_{32}O_{18}K_3{}^*$	$Sn_9AuC_{81}H_{216}N_{32}O_{18}K_3{}^*$
fw (g·mol^{-1})	3175.90	3220.23	3309.32
space group (no)	*C*2/*c*	*C*2/*c*	*C*2/*c*
a **(Å)**	58.988(13)	57.925(2)	58.0663(14)
b **(Å)**	16.921(4)	16.7406(3)	16.7942(3)
c **(Å)**	31.528(7)	31.1204(8)	31.1263(7)
α **(deg)**	90	90	90
β (deg)	116.24(10)	115.003(3)	115.319(3)
γ **(deg)**	90	90	90
V **(Å^3)**	28225(11)	27349.6(1.3)	27437.9(1.2)
Z	8	8	8
T **(K)**	100(2)	120(2)	120(2)
λ **(Å)**	Mo *Kα*	Mo *Kα*	Mo *Kα*
ρ_{calcd} (g·cm^{-3})	1.495	1.564	1.602
μ **(mm^{-1})**	1.859	1.907	2.826
collected reflections	73013	147792	375392
independent reflections	24209	26868	26937
R_{int} / R_δ	0.0404/0.0463	0.0830/0.1113	0.1486/0.0708
parameters / restraints	1310/12	1290/30	1290/42
R_1 [$I > 2\ \sigma(I)$ / all data]	0.0300/0.0428	0.0363/0.0811	0.0361/0.0613
wR_2 [$I > 2\ \sigma(I)$ / all data]	0.0658/0.0716	0.0698/0.0759	0.0805/0.0848
goodness of fit	1.008	0.826	0.952
max./min. diff. el. density (e / Å^{-3})	0.93/-0.66	1.45/-0.64	1.34/-0.76
CCDC	1530025	1530026	1530027

[*]: 23.5 NH_3 cocrystallized molecules per formula unit are included in the sum formulae.

Table SI 2: Crystallographic data for compound **4**.

Compound	**4**
formula	$Sn_{18}Ag_1C_{72}H_{213}N_{31}O_{24}K_7$*
fw (g·mol⁻¹)	4415.71
space group (no)	$P\bar{1}$
a **(Å)**	17.3360(2)
b **(Å)**	17.5287(2)
c **(Å)**	27.4117(3)
α **(deg)**	78.650(1)
β **(deg)**	85.741(1)
γ **(deg)**	71.589(1)
V **(Å³)**	7748.2(2)
Z	2
T **(K)**	120(2)
λ **(Å)**	Mo *Kα*
ρ_{calcd} **(g·cm⁻³)**	1.893
μ **(mm⁻¹)**	3.212
collected reflections	289154
independent reflections	29513
R_{int} / R_{δ}	0.0878/0.0455
parameters / restraints	1547/176
R_1 **[*I* > 2 *σ*(*I*) / all data]**	0.0462/0.0667
wR_2 **[*I* > 2 *σ*(*I*) / all data]**	0.1242/0.1325
goodness of fit	1.077
max./min. diff. el. density (e / Å⁻³)	2.67/-1.63
CCDC	1530028

[*]: 23 NH_3 cocrystallized molecules per formula unit are included in sum formula.

Molecular Structures

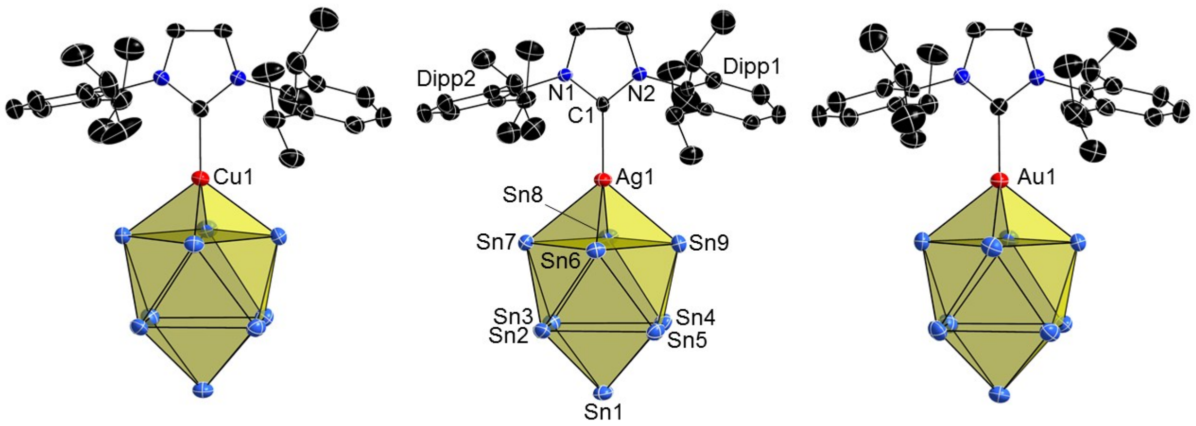

Figure SI 1: Molecular structures of **1a** (left) **2a** (middle) **3a** (right). Displacement ellipsoids are shown at a 50% probability level. For clarity hydrogen atoms, counterions and cocrystallized NH_3 molecules are omitted. Diisopropylphenyl-wingtips of NHC ligand are abbreviated as Dipp1 and Dipp2. **1a** and **3a** are labelled analogously to **2a**.

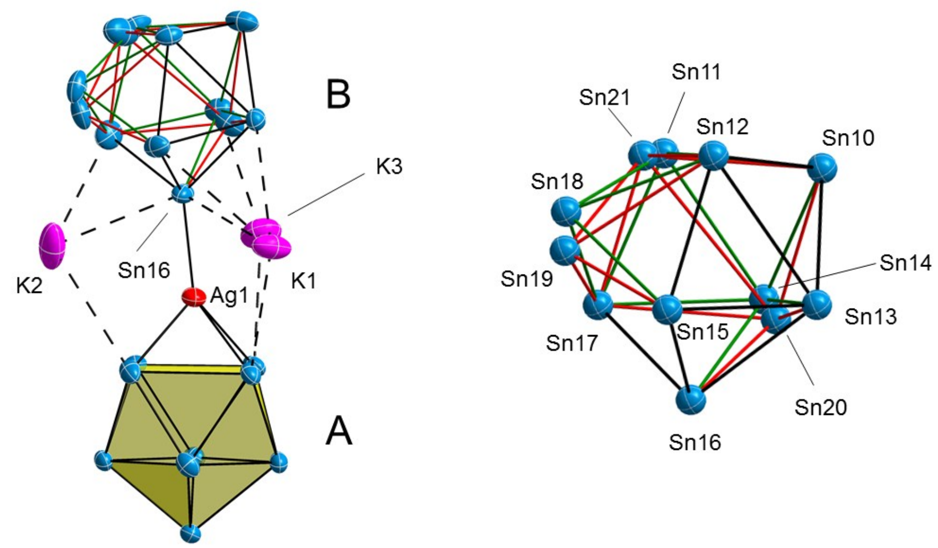

Figure SI 2: The dimeric cluster anion in compound **4**, exhibiting the two orientations of the disordered cluster B, with occupancies of 80.1 % (green) and 19.9 % (red). Also shown is the arrangement of "naked" potassium cations around the Sn-Ag-Sn bonding axis, which coordinate to both Sn_9^{4-} clusters with K-Sn distances below 4 Å (left). Displacement ellipsoids are shown at a 50% probability level. Moreover, a detailed view on the two orientations of disordered cluster B is given (right). For clarity atoms are here shown in ball and stick style.

Selected Distances and Angles

Table SI 3: Selected bond lengths [Å] and angles [°] in polyanions **1a**-**4a**.

	$[NHC^{Dipp}M(\eta^4\text{-}Sn_9)]^{3-}$			$[(\eta^1\text{-}Sn_9)M(\eta^4\text{-}Sn_9)]^{7-}$	
	1a	**2a**	**3a**	**4a (A)**	**4a (B)**
d(M-Sn6)	2.7216(7)	2.8527(6)	2.8149(4)	2.9111(8)	-
d(M-Sn7)	2.7376(8)	2.8698(6)	2.8310(4)	2.8785(8)	-
d(M-Sn8)	2.7491(7)	2.8670(6)	2.8206(4)	2.8749(9)	-
d(M-Sn9)	2.7391(6)	2.8419(5)	2.8055(4)	2.8884(8)	-
d(M-L)[a]	1.979(3)	2.181(5)	2.092(4)	2.7126(8)	-
d_{min}(Sn-Sn)	2.9458(6) (Sn1-Sn5)	2.9210(6) (Sn2-Sn6)	2.9307(5) (Sn1-Sn5)	2.9165(8) (Sn4-Sn9)	2.913(3) (Sn10-Sn14)
d_{max}(Sn-Sn)	3.3104(7) (Sn2-Sn5)	3.2737(5) (Sn2-Sn5)	3.2648(5) (Sn2-Sn5)	3.2572(7) (Sn3-Sn4)	3.2499(7) (Sn12-Sn13)
D2/D1[b]	1.01	1.00	1.01	1.00	1.08
∡(csp-M-L)[a][c]	179.83(2)	178.48(3)	179.18(2)	172.86(2)	-
torsion angle α[d]	178.90(2)	178.87(2)	178.88(1)	179.41(1)	177.24(2)

[a] L: NHC^{Dipp} for **1a**-**3a** and η^1-Sn_9 for **4a (A)**.

[b] D2/D1: diameter ratio of the square open plane with D2 (Sn7-Sn9) and D1 (Sn6-Sn8) for **1a**-**4a (A)** and D2 (Sn15-Sn17) and D1 (Sn16-Sn18) for **4a (B)**.

[c] csp: center of gravity of the atoms of the open square of the Sn_9^{4-} cluster.

[d] α: torsion angle of the open square (Sn6-Sn7-Sn8-Sn9).

Table SI 4: M-Sn and Sn-Sn distances [Å] in compounds **1** (left), **2** (middle), and **3** (right).

bond	distance [M = Cu]	distance [M = Ag]	distance [M = Au]
M-Sn6	2.7216(7)	2.8527(6)	2.8149(4)
M-Sn7	2.7376(8)	2.8698(6)	2.8310(4)
M-Sn8	2.7491(7)	2.8670(6)	2.8206(4)
M-Sn9	2.7391(6)	2.8419(5)	2.8055(4)
M-C1	1.979(3)	2.181(5)	2.092(4)
Sn1-Sn2	2.9939(7)	2.9428(5)	2.9471(5)
Sn1-Sn3	2.9773(7)	2.9540(6)	2.9612(5)
Sn1-Sn4	2.9868(7)	2.9564(6)	2.9643(5)
Sn1-Sn5	2.9458(6)	2.9261(6)	2.9307(5)
Sn2-Sn3	3.1938(6)	3.1681(6)	3.1539(5)
Sn3-Sn4	3.2284(7)	3.1923(6)	3.1864(5)
Sn4-Sn5	3.1959(7)	3.1792(6)	3.1646(5)
Sn5-Sn2	3.3104(7)	3.2737(5)	3.2648(5)
Sn2-Sn6	2.9529(7)	2.9210(6)	2.9319(4)
Sn2-Sn7	2.9771(6)	2.9500(5)	2.9573(5)
Sn3-Sn7	3.0122(8)	2.9664(5)	2.9730(5)
Sn3-Sn8	2.9965(8)	2.9672(6)	2.9761(5)
Sn4-Sn8	3.0039(6)	2.9592(5)	2.9707(5)
Sn4-Sn9	2.9965(7)	2.9637(6)	2.9708(5)
Sn5-Sn9	2.9614(6)	2.9294(6)	2.9396(5)
Sn5-Sn6	3.0199(7)	2.9700(5)	2.9762(5)
Sn6-Sn7	3.0868(7)	3.1005(5)	3.1231(5)
Sn7-Sn8	3.1049(6)	3.0849(5)	3.1033(5)
Sn8-Sn9	3.0938(7)	3.1189(6)	3.1414(5)
Sn9-Sn6	3.1151(6)	3.1029(5)	3.1219(5)
Sn6-Sn8	4.3647(8)	4.3734(5)	4.3977(5)
Sn7-Sn9	4.4037(8)	4.3996(5)	4.4336(5)

Table SI 5: Ag-Sn and Sn-Sn distances in **4**.

bond	distance in [Å]	bond	distance in [Å]
Ag-Sn6	2.9118(9)	Sn11-Sn12	3.186(2)
Ag-Sn7	2.8785(8)	Sn11-Sn14	3.184(4)
Ag-Sn8	2.8749(9)	Sn11-Sn17	2.933(3)
Ag-Sn9	2.8884(8)	Sn11-Sn18	2.946(4)
Sn1-Sn2	2.9523(7)	Sn12-Sn13	3.2499(7)
Sn1-Sn3	2.9280(7)	Sn12-Sn15	2.9439(8)
Sn1-Sn4	2.9458(7)	Sn12-Sn18	2.924(3)
Sn1-Sn5	2.9541(7)	Sn13-Sn15	2.9767(8)
Sn2-Sn3	3.2366(7)	Sn13-Sn16	2.9702(7)
Sn3-Sn4	3.2572(7)	Sn14-Sn16	3.005(3)
Sn4-Sn5	3.1633(7)	Sn14-Sn17	2.945(3)
Sn5-Sn2	3.1870(7)	Sn15-Sn16	2.9276(8)
Sn2-Sn6	2.9499(7)	Sn16-Sn17	2.9321(8)
Sn2-Sn7	2.9683(7)	Sn17-Sn18	3.034(2)
Sn3-Sn7	2.9252(8)	Sn15-Sn18	3.013(3)
Sn3-Sn8	2.9237(7)	Sn15-Sn17	4.3645(8)
Sn4-Sn8	2.9607(7)	Sn16-Sn18	4.046(1)
Sn4-Sn9	2.9165(8)	Sn10-Sn20	3.03(1)
Sn5-Sn9	2.9773(7)	Sn10-Sn21	3.23(2)
Sn5-Sn6	2.9527(7)	Sn12-Sn19	3.220(8)
Sn6-Sn7	3.0902(8)	Sn12-Sn21	3.16(1)
Sn6-Sn8	4.3896(8)	Sn13-Sn20	2.95(1)
Sn7-Sn9	4.3833(7)	Sn15-Sn19	2.65(1)
Sn8-Sn9	3.0892(8)	Sn16-Sn19	3.53(2)
Ag-Sn16	2.7126(8)	Sn17-Sn19	2.79(1)
Sn10-Sn11	2.922(4)	Sn17-Sn20	3.15(2)
Sn10-Sn12	2.9514(9)	Sn17-Sn21	2.79(1)
Sn10-Sn13	2.9203(8)	Sn19-Sn21	3.01(2)
Sn10-Sn14	2.913(3)		

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