Electronic Supplementary Material (ESI) for Dalton Transactions.

Structural isomerism in the $[(Ni@Sn_9)In(Ni@Sn_9)]^{5-}$ Zintl ion.

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Supporting Information

1. Experimental details

General Synthetic Methods: All manipulations and reactions were performed in a nitrogen atmosphere using standard Schlenk or glovebox techniques. The intermetallic precursors, $K_5Ni_3Sn_9$ and K_4Sn_9 were synthesized according to previously reported procedures from stoichiometric mixtures of the elements (K: 99.95%, Aldrich; Sn: 99.8%, Strem, Ni: 99.95%) heated to 1000 °C for 72 h in sealed niobium containers. [2.2.2]-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8] hexacosane, purchased from Sigma-Aldrich, 98%) was dried under a vacuum for 1 day prior to use. $In(C_6H_5)_3$ was prepared according to a literature procedure. $Ni(COD)_2$ (COD = cyclooctadiene) (Strem, 98%) is used as received after careful drying under a vacuum. Ethylenediamine (en) (Aldrich, 99%), N, Ndimethylformamide (DMF), and acetonitrile (MeCN) were freshly distilled over CaH_2 prior to use. Toluene (tol) (Aldrich, 99.8%) was distilled from sodium/benzophenone under dinitrogen and stored under dinitrogen.

X-ray Crystal Structure Determination: Suitable crystals were selected for single-crystal X-ray diffraction analyses. Crystallographic data were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT program. Structures were solved using direct methods (SHELXT, Olex2) and then refined using SHELXL-2014 and Olex2 to convergence, in which all of the non-hydrogen atoms were refined anisotropically. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. A summary of the crystallographic data for these two complexes is listed in Table 1. Selected bond distances and angles are given in Tables S1−S5. CCDC 1579015−1579019 contain the supplementary crystallographic data for this paper.

Mass Spectrometry: Electrospray ionization mass spectrometry (ESI-MS) was performed in negative-ion mode on an LTQ linear ion trap spectrometer. The spray voltage was 5.48 kV, and the capillary temperature was kept at 300 °C. The capillary voltage was 30 V. The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an airtight syringe by direct infusion with a Harvard syringe pump at 15 µL/min.

2. Mass spectrometry.

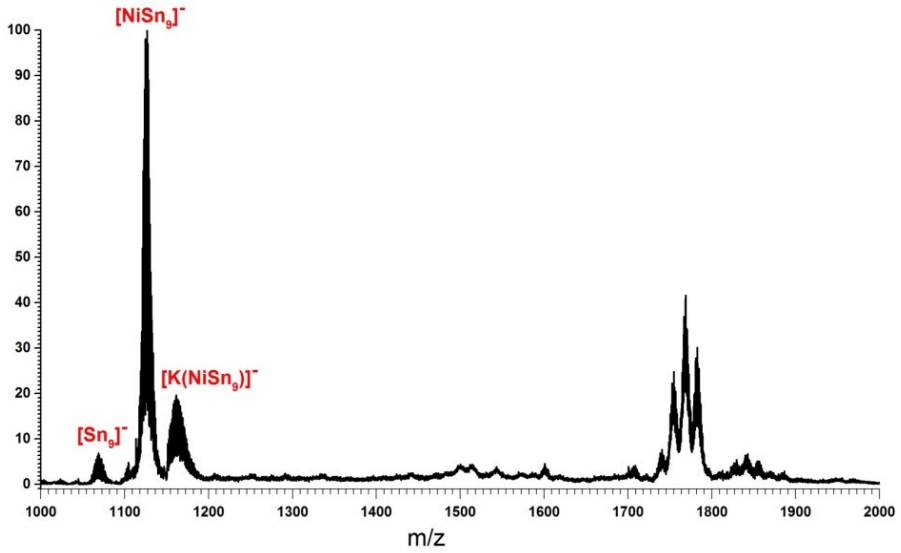


Figure S1. The full electrospray mass spectrum (m/z: 1000-2000) in negative ion mode of the DMF solution of the phase "$K_4Ni_3Sn_9$"

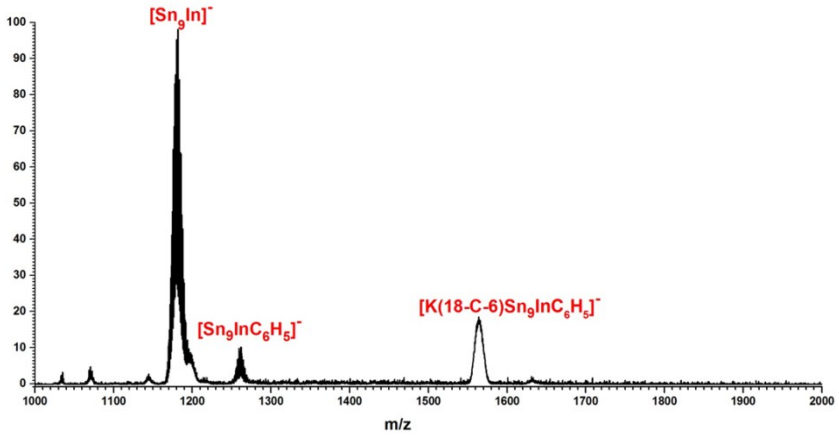


Figure S2. The full electrospray mass spectrum (m/z: 1000-2000) in negative ion mode of the en solution of the mixture of "K_4Sn_9"and $In(C_6H_5)_3$.

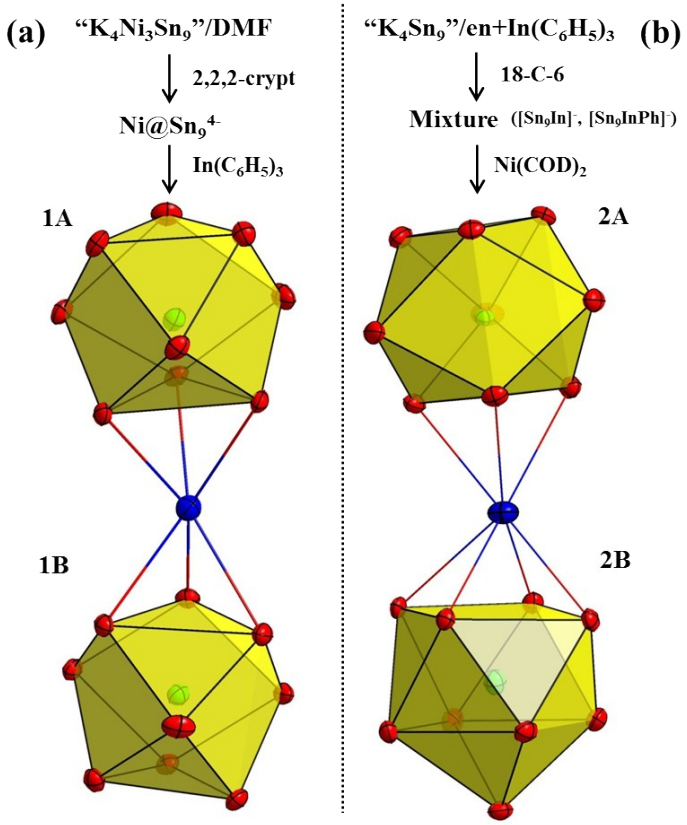


Figure S3. Overview on synthetic details and structures of **{[η³-(Ni@Sn$_9$)]In[η³-(Ni@Sn$_9$)]}$^{5-}$** (**1**) and **{[η³-(Ni@Sn$_9$)]In[η⁴-(Ni@Sn$_9$)]}$^{5-}$** (**2**).

3. Crystallographic Supplementary information

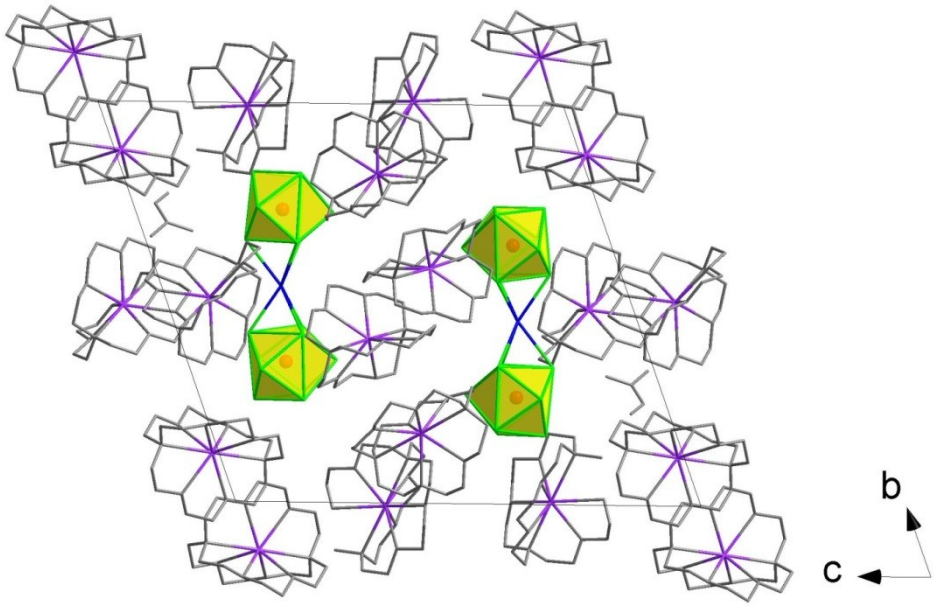


Figure S4. Packing of cations and anions in **[K(2,2,2-crypt)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]** viewed down the *a* axes. Solvent molecules and hydrogen atoms are omitted for clarity.

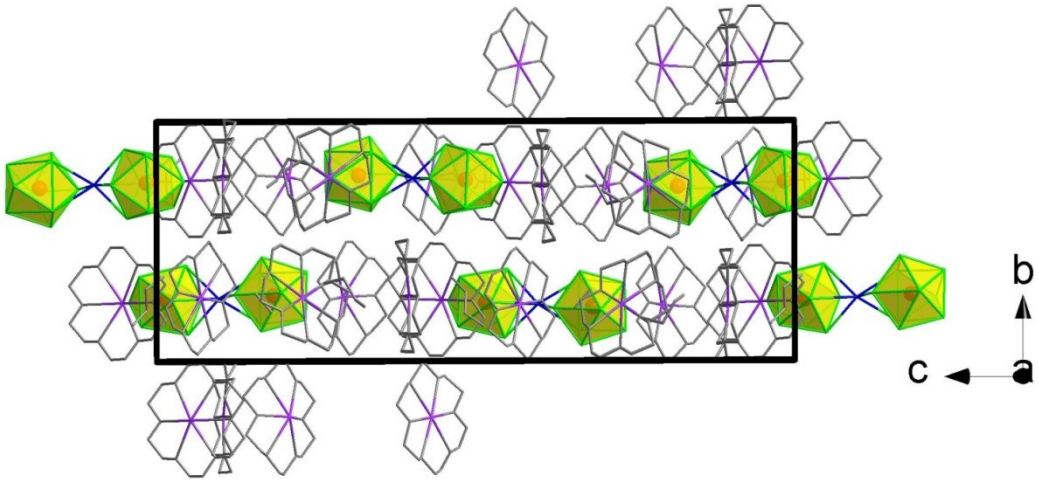


Figure S5. Packing of cations and anions in**[K(18-crown-6)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]** viewed down the *a* axes. Solvent molecules and hydrogen atoms are omitted for clarity.

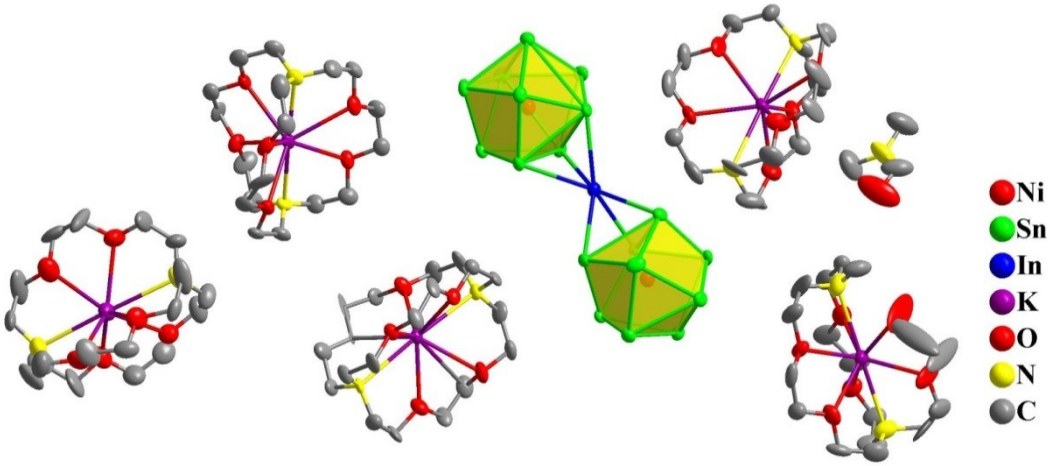


Figure S6. Asymmetric unit of **[K(2,2,2-crypt)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]**. Thermal ellipsoids are drawn at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

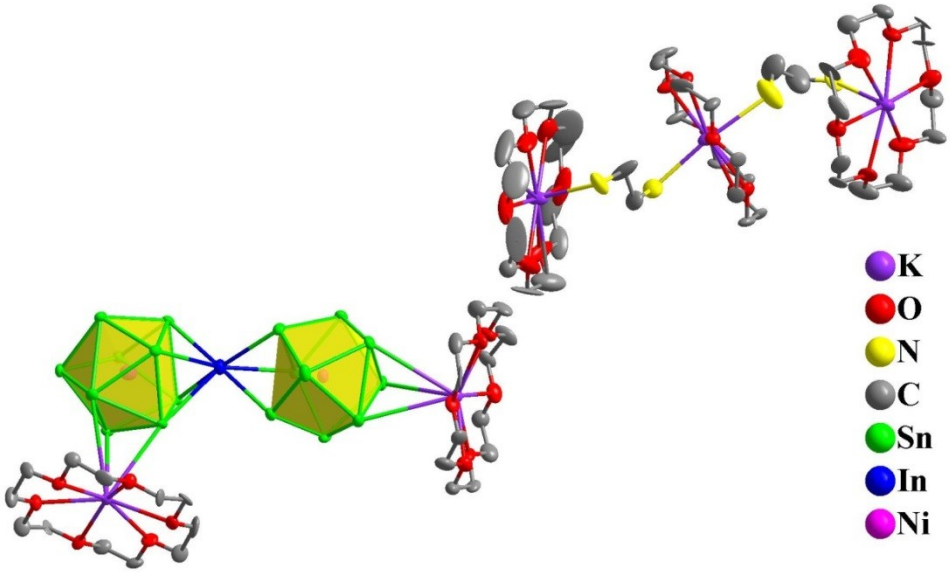
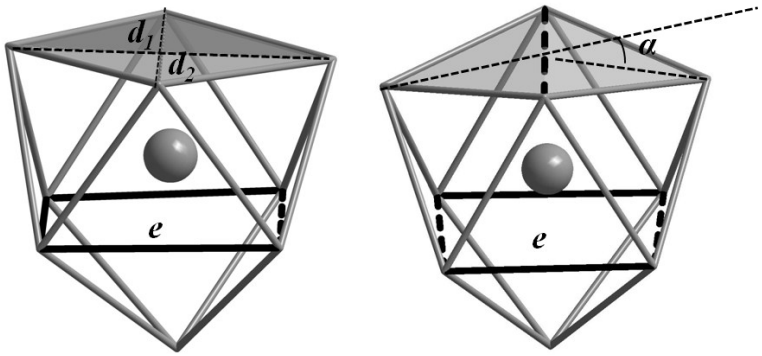


Figure S7. Asymmetric unit of **[K(18-crown-6)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]**. Thermal ellipsoids are drawn at 50% probability. Solvent molecules and hydrogen atoms have been omitted for clarity.

Table S1. Dimensions of the clusters in ***1*** and ***2***.

Cluster	Symmetry	h_1	h_2	h_3[a]	h_m [Å]	h_m/e_m[b]	α_{min} [°][c]	d_1/d_2[d]	hapticity
[K(2,2,2-crypt)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$] (DMF) (1)									
1A	**D_{3h}**	**3.57**	**3.58**	**3.61**	**3.59**	**1.14**	**169.40**	**1.28**	**η_3**
1B	**D_{3h}**	**3.40**	**3.65**	**3.70**	**3.58**	**1.13**	**159.71**	**1.23**	**η_3**
[K(18-crown-6)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$] 3(en) (2)									
2A	**D_{3h}**	**3.56**	**3.52**	**3.67**	**3.58**	**1.12**	**156.31**	**1.26**	**η_3**
2B	**C_{4v}**	**4.39**	**3.64**	**3.18**	**3.73**	**1.21**	**177.34**	**1.01**	**η_4**

a) *h* is defined as prism height.
b) ratio of mean prism height and mean length of basal edges
c) *α*min is defined as the dihedral angle closest to 180° in the cluster.
d) *d*1 and d2 are the diagonals in square face that includes α_{min}.



C_{4v} symmetry D_{3h} symmetry

Table S2. Selected interatomic distances (in angstroms) of the experimental structures of ***1*** and ***2***.

Bonds of **1**	Length/ Å	Bonds of **2**	Length/ Å
Sn(1)-Sn(2)	3.026(2)	Sn(1)-Ni(1)	2.6155(24)
Sn(1)-Sn(3)	3.0311(19)	Sn(1)-Sn(5)	3.0206(19)
Sn(1)-Sn(4)	3.0542(18)	Sn(2)-Ni(1)	2.5935(27)
Sn(1)-Sn(5)	3.0126(18)	Sn(2)-Sn(3)	3.0651(17)
Sn(1)-Ni(1)	2.584(3)	Sn(2)-Sn(4)	3.0489(20)
Sn(2)-Sn(3)	3.0291(18)	Sn(2)-Sn(6)	3.0548(20)
Sn(2)-Sn(5)	3.024(2)	Sn(2)-Sn(1)	3.0548(16)
Sn(2)-Sn(6)	3.037(2)	Sn(3)-Sn(1)	3.0481(18)
Sn(2)-Ni(1)	2.584(3)	Sn(3)-Ni(1)	2.5884(25)
Sn(3)-Sn(4)	3.0145(17)	Sn(3)-Sn(5)	3.0262(20)
Sn(3)-Sn(6)	3.0285(19)	Sn(4)-Sn(8)	2.9368(20)
Sn(3)-Ni(1)	2.589(2)	Sn(4)-Sn(1)	3.0319(17)

Sn(4)-Sn(7)	2.936(2)	Sn(4)-Ni(1)	2.7010(24)
Sn(4)-Sn(8)	2.9415(17)	Sn(5)-Sn(7)	2.9613(17)
Sn(4)-Ni(1)	2.701(2)	Sn(5)-Sn(8)	2.9715(17)
Sn(5)-Sn(8)	2.9393(19)	Sn(5)-Ni(1)	2.7113(22)
Sn(5)-Sn(9)	2.959(2)	Sn(6)-Sn(7)	2.9347(20)
Sn(5)-Ni(1)	2.707(3)	Sn(6)-Sn(3)	3.0275(17)
Sn(6)-Sn(7)	2.9497(17)	Sn(6)-Sn(9)	2.9367(20)
Sn(6)-Sn(9)	2.9509(17)	Sn(6)-Ni(1)	2.7080(24)
Sn(6)-Ni(1)	2.695(3)	Sn(7)-Ni(1)	2.5364(26)
Sn(7)-Sn(8)	3.2797(18)	Sn(7)-In(1)	3.1691(18)
Sn(7)-Sn(9)	3.2704(16)	Sn(8)-In(1)	3.1212(18)
Sn(7)-In(1)	3.0542(16)	Sn(8)-Sn(7)	3.2464(16)
Sn(7)-Ni(1)	2.537(3)	Sn(8)-Ni(1)	2.5283(26)
Sn(8)-Sn(9)	3.2873(18)	Sn(9)-In(1)	3.1194(21)
Sn(8)-In(1)	3.0508(18)	Sn(9)-Sn(4)	2.9554(19)
Sn(8)-Ni(1)	2.527(3)	Sn(9)-Ni(1)	2.5637(22)
Sn(9)-In(1)	3.1143(16)	Sn(10)-Sn(15)	2.9933(18)
Sn(9)-Ni(1)	2.521(3)	Sn(10)-Ni(2)	2.6214(24)
Sn(10)-Sn(14)	2.9320(18)	Sn(10)-Sn(14)	2.9783(18)
Sn(10)-Sn(15)	2.9299(18)	Sn(10)-In(1)	2.9916(20)
Sn(10)-In(1)	3.0981(17)	Sn(11)-Sn(15)	2.9273(20)
Sn(10)-Ni(2)	2.536(2)	Sn(11)-Sn(16)	3.0332(17)
Sn(11)-Sn(12)	3.2194(18)	Sn(11)-Sn(12)	3.0483(15)
Sn(11)-Sn(13)	2.949(2)	Sn(11)-In(1)	3.0712(18)
Sn(11)-In(1)	3.1252(17)	Sn(11)-Sn(10)	3.2132(15)
Sn(11)-Ni(2)	2.535(3)	Sn(11)-Ni(2)	2.6749(27)
Sn(12)-Sn(13)	2.9225(18)	Sn(12)-Sn(17)	3.0009(18)
Sn(12)-Sn(15)	2.9276(19)	Sn(12)-Sn(16)	3.0145(19)
Sn(12)-In(1)	2.9949(17)	Sn(12)-Sn(13)	3.0521(15)
Sn(12)-Ni(2)	2.533(2)	Sn(12)-In(1)	3.2344(16)
Sn(13)-Sn(17)	3.0288(19)	Sn(12)-Ni(2)	2.707(3)
Sn(13)-Sn(18)	3.039(2)	Sn(13)-Sn(17)	3.0341(17)
Sn(13)-Ni(2)	2.640(3)	Sn(13)-Sn(14)	2.9299(20)
Sn(14)-Sn(16)	3.020(2)	Sn(13)-Ni(2)	2.6553(28)
Sn(14)-Sn(17)	2.9960(19)	Sn(13)-In(1)	3.0484(18)
Sn(14)-Ni(2)	2.704(3)	Sn(13)-Sn(10)	3.2324(16)
Sn(15)-Sn(16)	3.0191(17)	Sn(14)-Sn(18)	2.9509(17)
Sn(15)-Sn(18)	3.0113(17)	Sn(14)-Ni(2)	2.5314(28)
Sn(15-Ni(2)	2.699(3)	Sn(15)-Sn(18)	2.9562(17)
Sn(16)-Sn(17)	3.0551(19)	Sn(15)-Ni(2)	2.5412(28)
Sn(16)-Sn(18)	3.0278(16)	Sn(16)-Sn(18)	3.0021(19)
Sn(16)-Ni(1)	2.582(3)	Sn(16)-Ni(2)	2.5646(25)
Sn(17)-Sn(18)	2.9936(18)	Sn(16)-Sn(15)	3.2586(17)
Sn(17)-Ni(2)	2.585(2)	Sn(17)-Sn(16)	3.1817(16)
Sn(18)-Ni(2)	2.609(3)	Sn(17)-Sn(18)	2.9949(19)

4. ESI-MS Analysis

a. Detailed ESI mass spectrum of the DMF reaction mixtures.

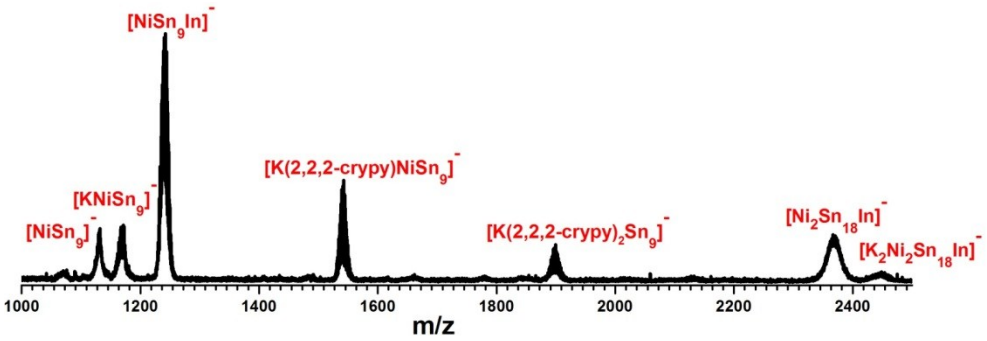


Figure S8. Overview ESI mass spectrum in negative ion mode of a freshly dissolved crystalline sample of **[K(2,2,2- crypt)]$_5$[Ni@Sn$_9$] In[Ni@Sn$_9$]** in DMF.

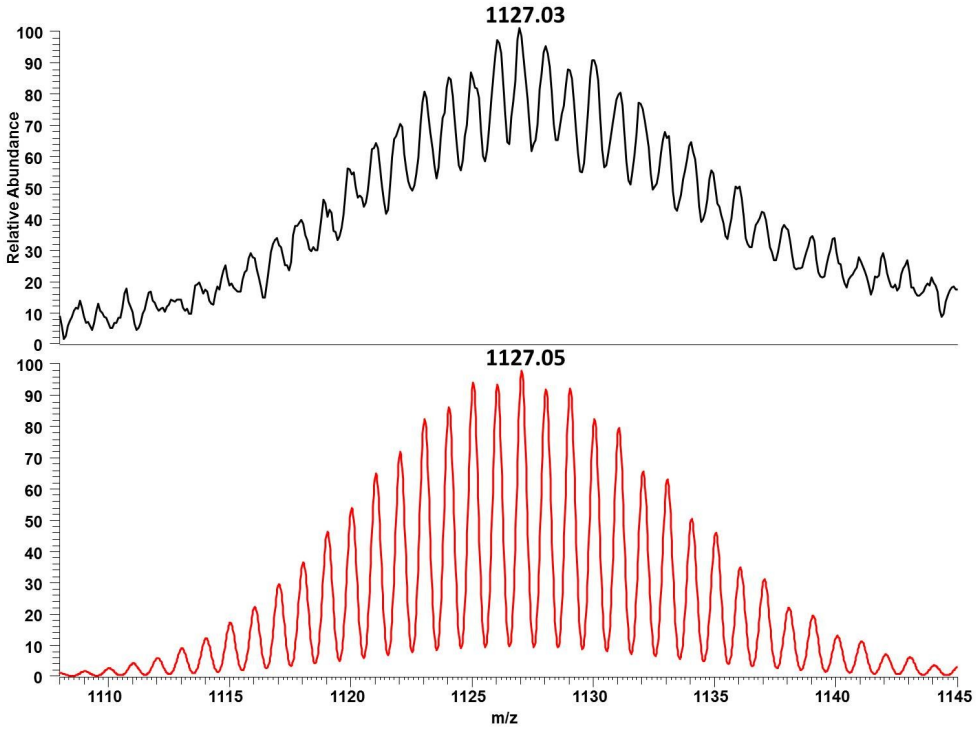


Figure S9. Measured (top) and simulated (bottom) spectrum of the fragment **[NiSn$_9$]$^-$**.

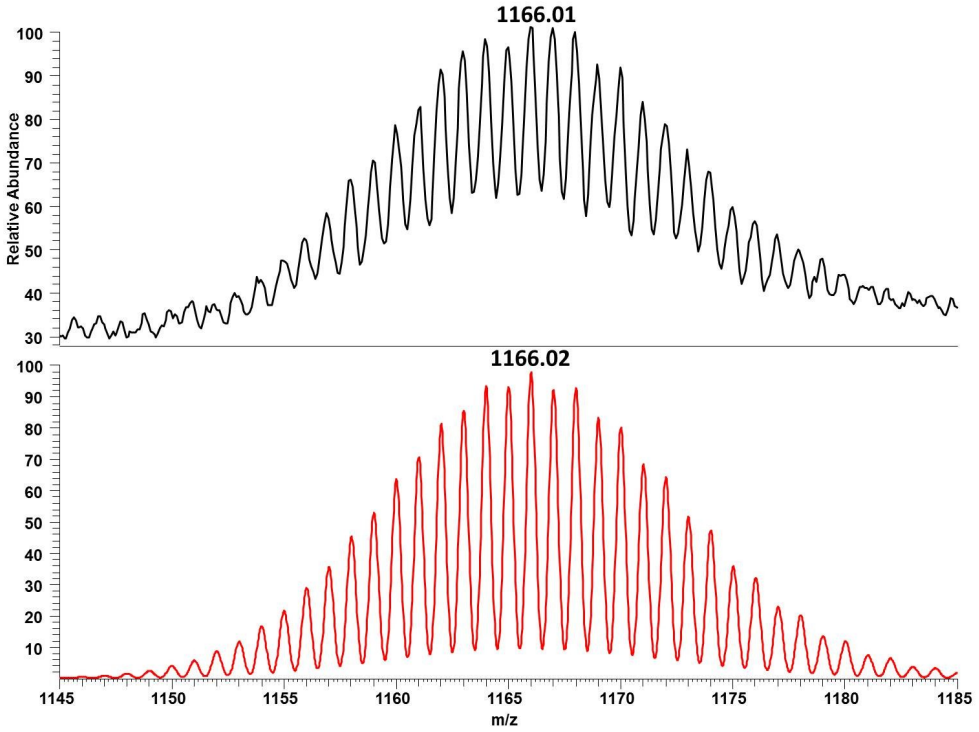


Figure S10. Measured (top) and simulated (bottom) spectrum of the fragment **[KNiSn$_9$]$^-$**.

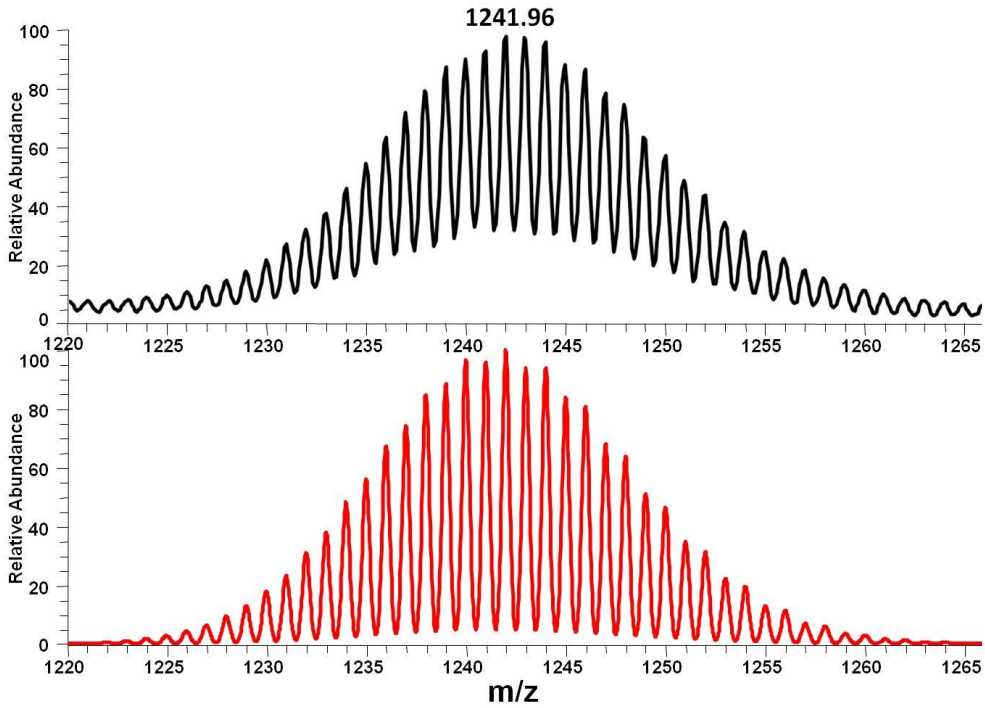


Figure S11. Measured (top) and simulated (bottom) spectrum of the fragment **[NiSn$_9$In]$^-$**.

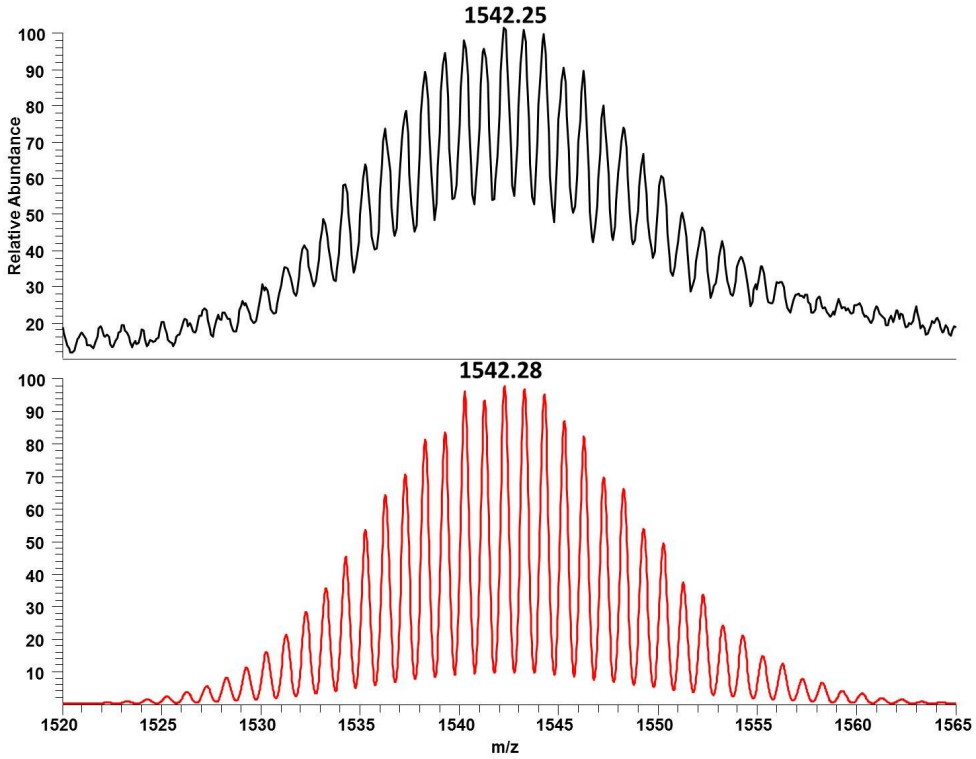


Figure S12. Measured (top) and simulated (bottom) spectrum of the fragment **[K(2,2,2-crypt)NiSn$_9$]$^-$**.

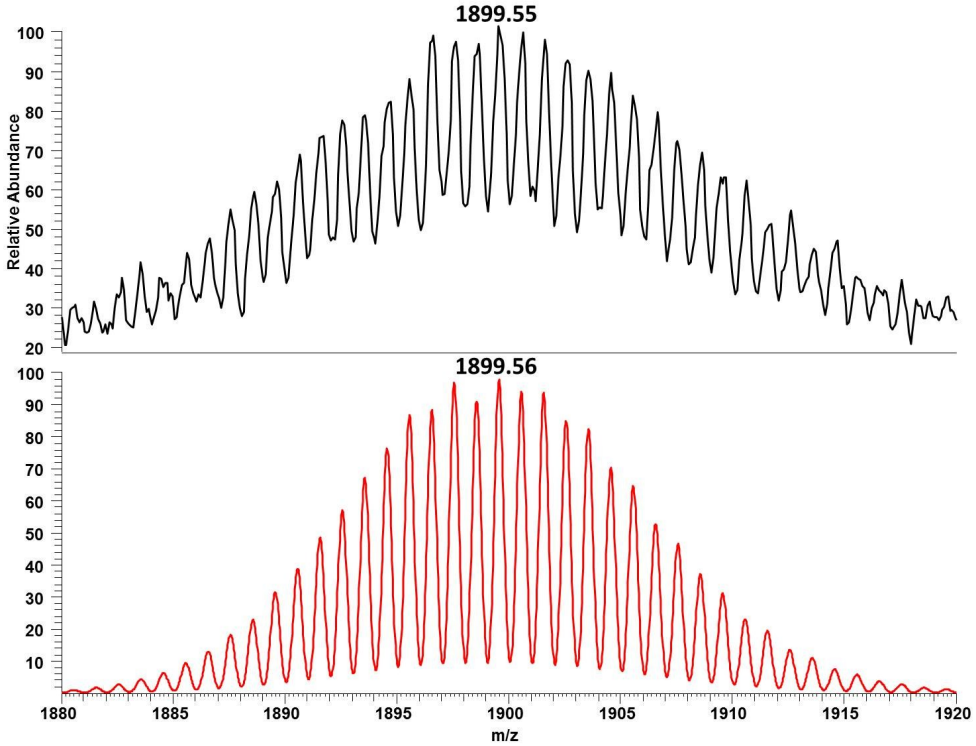


Figure S13. Measured (top) and simulated (bottom) spectrum of the fragment **[K(2,2,2-crypt) Sn$_9$]$^-$**.

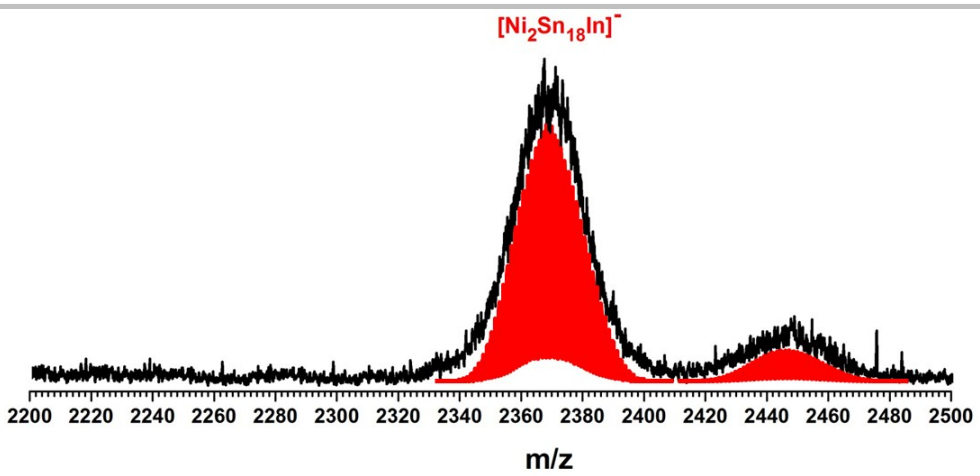


Figure S14. Measured (top) and simulated (bottom) spectrum of the fragment **$[Ni_2Sn_{18}In]^-$** and **$[K_2Ni_2Sn_{18}In]^-$**.

b. Detailed ESI mass spectrum of the en reaction mixtures.

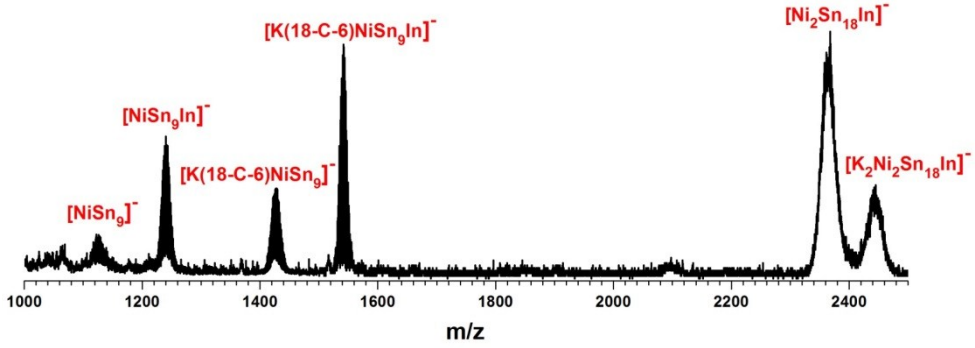


Figure S15. Overview ESI mass spectrum in negative ion mode of a freshly dissolved crystalline sample of **$[K(18\text{-crown-}6)]_5[Ni@Sn_9]In[Ni@Sn_9]$** in en.

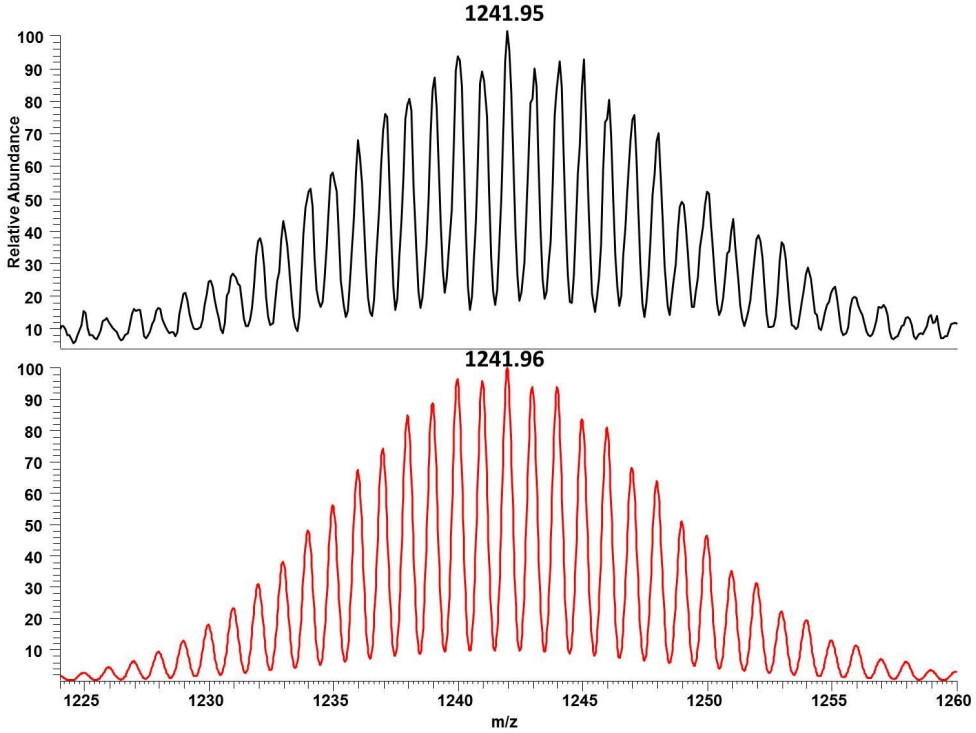


Figure S16. Measured (top) and simulated (bottom) spectrum of the fragment **$[NiSn_9In]^-$**.

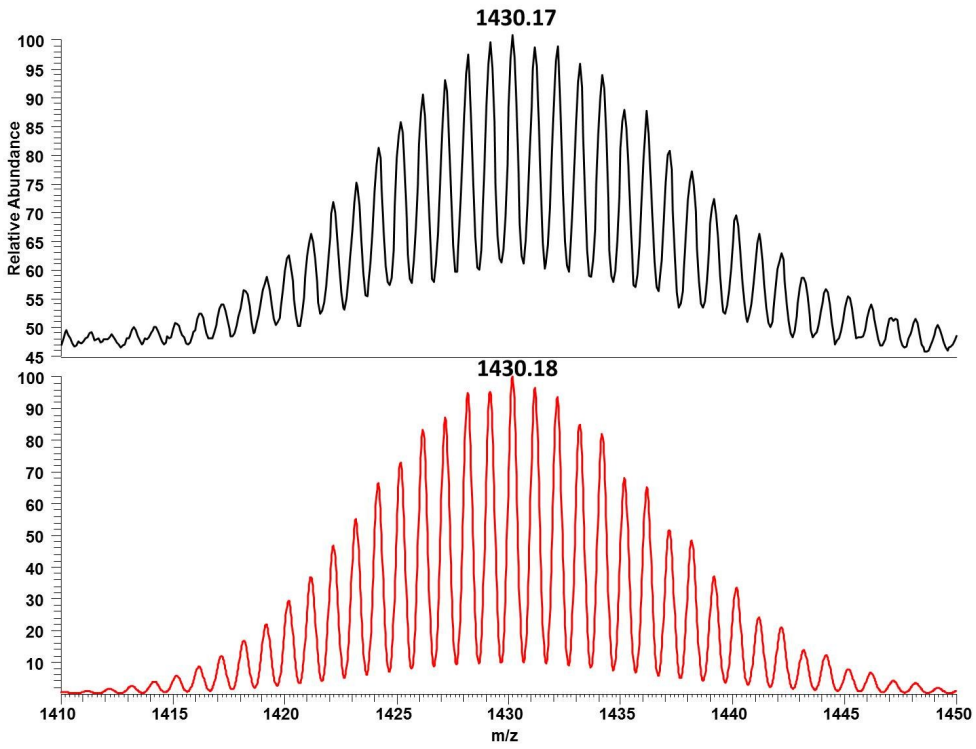


Figure S17. Measured (top) and simulated (bottom) spectrum of the fragment **[K(18-C-6)NiSn$_9$]$^-$**.

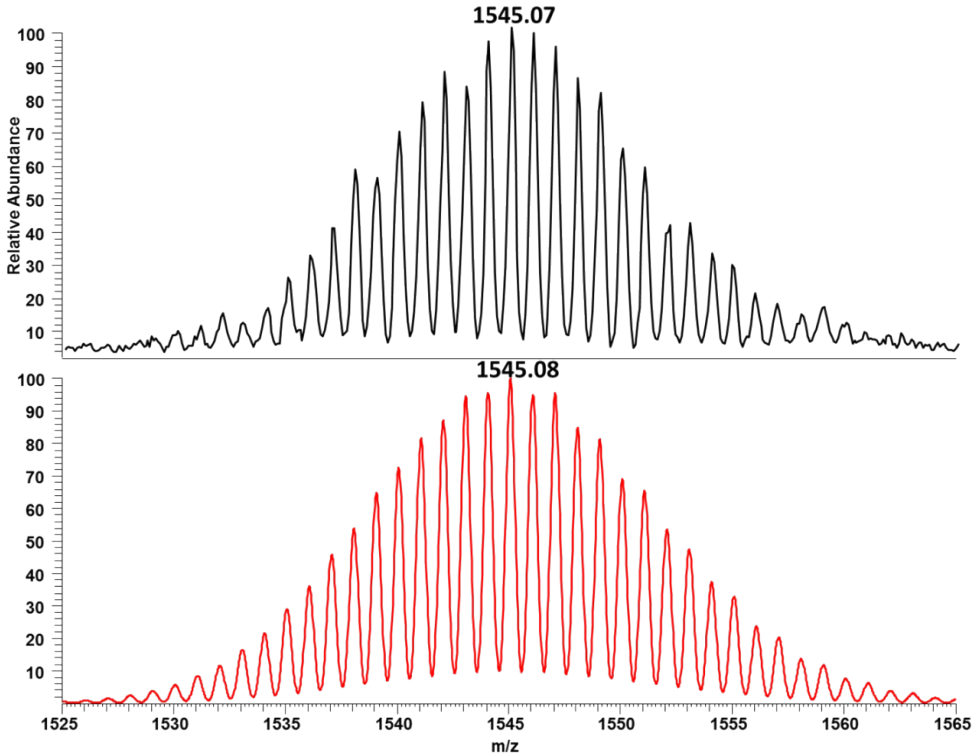


Figure S18. Measured (top) and simulated (bottom) spectrum of the fragment **[K(18-C-6)NiSn$_9$In]$^-$**.

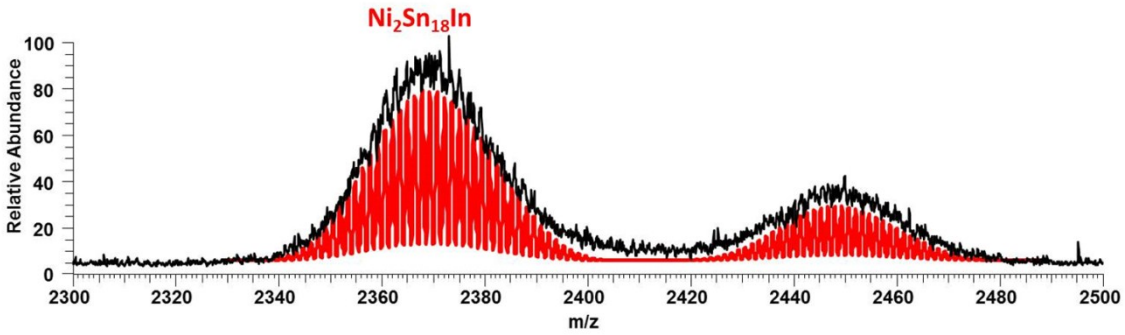
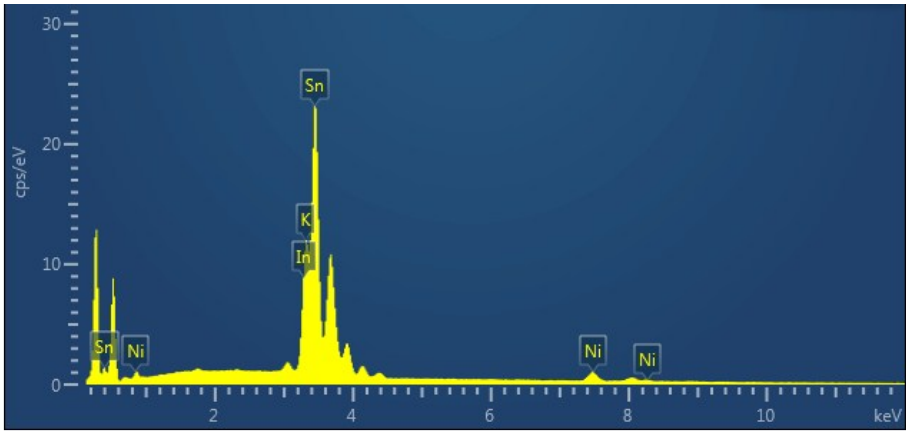


Figure S19. Measured (top) and simulated (bottom) spectrum of the fragment **$[Ni_2Sn_{18}In]^-$** and **$[K_2Ni_2Sn_{18}In]^-$**.

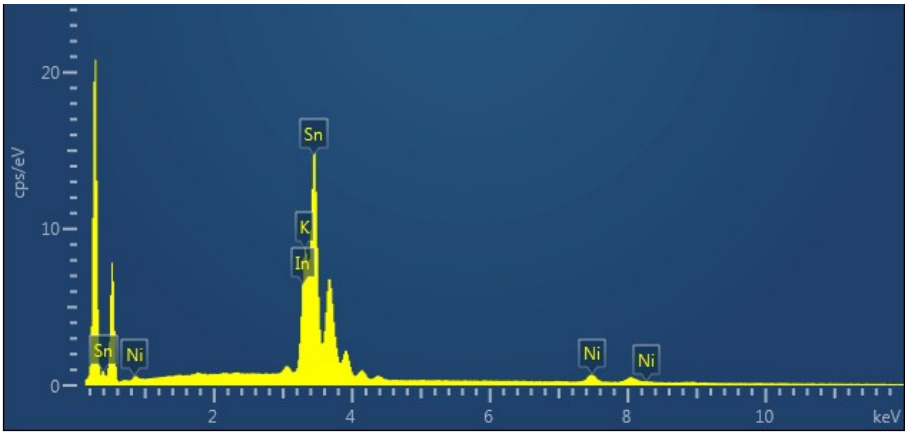
6. Energy Dispersive X-ray (EDX) Spectroscopic Analysis

EDX analysis were performed using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. Data acquisition was performed with an acceleration voltage of 20 kV and an accumulation time of 150 s.



El	Series	wt%	wt% Sigma	Atom. C %
K	K-series	11.71	0.20	27.71
Ni	K-series	4.14	0.14	6.53
In	L-series	4.69	0.39	3.78
Sn	L-series	79.47	0.39	61.98
total :		100.00		100.00

Figure S20. EDX analysis of [**K(2,2,2-crypt)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]**.



El	Series	wt%	wt% Sigma	Atom. C %
K	K-series	14.05	0.23	32.19
Ni	K-series	3.66	0.15	5.59
In	L-series	4.67	0.44	3.64
Sn	L-series	77.62	0.44	58.58
total :		100.00		100.00

Figure S21. EDX analysis of **[K(18-crown-6)]$_5$[Ni@Sn$_9$]In[Ni@Sn$_9$]**.

7. Total Energies and Optimised Coordinates of all DFT-computed Structures.

$[Ni_2InSn_{18}]^{5-}$ - C_s symmetry. Total energy = -7068.908185787090

Sn	6.104541	-1.155464	0.000028
Sn	4.142693	-0.947520	2.397850
Sn	2.462678	-1.689740	-0.000371
Sn	4.143159	-0.946940	-2.398105
Sn	5.819214	1.529632	1.565017
Sn	5.819557	1.530012	-1.564415
Sn	3.722315	3.195891	0.000150
Sn	2.182996	1.242203	-1.713065
Sn	2.182790	1.241961	1.712819
Sn	-2.453998	-0.310897	-2.266616
Sn	-2.231331	-2.535921	0.000073
Sn	-2.453768	-0.310505	2.266561
Sn	-2.686041	1.975277	-0.000297
Sn	-4.786616	-2.252808	1.694989
Sn	-4.786841	-2.253090	-1.694520
Sn	-5.083091	1.175764	1.746683
Sn	-5.083299	1.175364	-1.746895
Sn	-6.762107	-0.662236	0.000286
In	-0.277322	-0.006452	-0.000169
Ni	3.960038	0.432493	-0.000026
Ni	-3.933386	-0.421716	0.000023

$[Ni_2InSn_{18}]^{5-}$ - D_{3h} symmetry. Total energy = -7068.906212441752

Sn	-0.977695	-1.692553	-2.496362
Sn	-0.978555	-1.692269	2.496483
Sn	-0.978358	1.692575	2.496653
In	-0.001211	0.000131	-0.000036
Sn	1.383999	-2.397017	-4.246065
Sn	1.953832	0.000141	-2.495339
Sn	1.953172	0.000038	2.494990
Sn	1.800230	-0.000008	-6.173801
Sn	-0.898341	-1.558132	6.175434
Sn	-0.977835	1.692578	-2.496489
Sn	-0.898231	1.557942	6.175651
Sn	-0.898410	-1.558206	-6.175197
Sn	-2.767967	0.000189	4.248515
Sn	1.383374	-2.397180	4.245608
Sn	-0.898581	1.557930	-6.175317
Sn	1.383773	2.397115	-4.246261
Sn	-2.767585	-0.000147	-4.247624
Sn	1.383578	2.397075	4.245913
Sn	1.800684	-0.000197	6.173219
Ni	0.000215	-0.000014	-4.209118
Ni	-0.000091	0.000011	4.209145

$[Ni_2InSn_{18}]^{5-}$ - D_{3d} symmetry. Total energy = -7068.907795661145

In	-0.000002	-0.000496	0.000002
Ni	-0.002361	-0.000014	4.187071
Ni	0.002361	-0.000014	-4.187071
Sn	1.952223	-0.002737	2.475130
Sn	-1.952224	-0.002735	-2.475132
Sn	0.984658	1.695308	-2.477283
Sn	1.382423	2.400679	4.217372
Sn	-0.984658	1.695310	2.477284
Sn	0.988869	-1.693390	-2.477781
Sn	-0.895913	1.560894	6.150342

Sn	-1.808372	-0.002037	-6.137369
Sn	-0.988870	-1.693389	2.477779
Sn	0.895916	1.560899	-6.150339
Sn	1.808373	-0.002029	6.137368
Sn	-1.382421	2.400679	-4.217374
Sn	-1.376270	-2.404170	-4.218247
Sn	-0.900339	-1.557841	6.150835
Sn	-2.775139	0.003545	4.228314
Sn	1.376269	-2.404169	4.218247
Sn	2.775139	0.003542	-4.228313
Sn	0.900338	-1.557836	-6.150837

$[Ni_2InSn_{18}]^{5-}$ - D_{4d} symmetry. Total energy = -7068.900348703489Eh

In	0.000659	-0.002759	-0.000023
Ni	0.000120	-0.000006	-3.821687
Ni	-0.000100	0.000194	3.821723
Sn	0.884270	-2.068496	-2.325603
Sn	-2.065468	-0.887290	-2.323950
Sn	-0.883433	2.064645	-2.320552
Sn	2.067796	0.881604	-2.323598
Sn	-2.260542	0.904493	-4.821329
Sn	-0.903131	-2.257255	-4.829152
Sn	0.905772	2.260533	-4.820539
Sn	2.257430	-0.905041	-4.827500
Sn	-0.001448	0.007271	-6.650715
Sn	-2.066974	0.882140	2.322686
Sn	-0.883512	-2.068146	2.324960
Sn	2.066264	-0.886798	2.324902
Sn	0.884341	2.064865	2.321196
Sn	0.902830	-2.257134	4.829179
Sn	-2.258176	-0.904906	4.826028
Sn	2.259915	0.904804	4.822950
Sn	-0.906177	2.260626	4.820339
Sn	-0.000436	0.006657	6.650685

$[Ni_2InSn_{18}]^{5-}$ - D_{4h} symmetry. Total energy = -7068.899999304063 Eh

In	-0.000202	-0.000926	-0.000003
Ni	0.002195	0.000034	3.832174
Ni	-0.002193	0.000056	-3.832154
Sn	1.596099	1.587890	2.334134
Sn	-1.584763	1.591410	2.330678
Sn	-1.585499	-1.591714	2.331985
Sn	1.595032	-1.589827	2.335013
Sn	-2.435052	0.000999	4.827700
Sn	0.005930	2.435069	4.833435
Sn	0.004665	-2.434154	4.835451
Sn	2.433138	-0.000604	4.841921
Sn	-0.007282	0.001205	6.658178
Sn	-1.596375	1.587999	-2.334537
Sn	1.584420	1.591535	-2.330369
Sn	1.585207	-1.591695	-2.331629
Sn	-1.595353	-1.589791	-2.335356
Sn	2.435254	0.001052	-4.827157
Sn	-0.005699	2.435060	-4.833527
Sn	-0.004445	-2.434171	-4.835384
Sn	-2.432940	-0.000558	-4.842389
Sn	0.007862	0.001131	-6.658166

$[Ni_3Ge_{18}]^{4-}$ - Total energy = -41913.475089638625 Eh

Ni	0.005452	0.000477	-0.000107
Ni	0.000225	0.000000	2.460708

Ni	0.000956	0.000112	-2.460735
Ge	-0.003916	1.555271	4.451746
Ge	-1.352294	-0.777279	4.448651
Ge	1.343869	-0.778163	4.453665
Ge	-2.152342	1.241446	2.725520
Ge	-0.000507	-2.485399	2.732627
Ge	2.151394	1.242365	2.735032
Ge	0.002994	2.132179	1.396220
Ge	-1.842842	-1.066048	1.391774
Ge	1.847326	-1.067503	1.401290
Ge	-0.004423	-1.555405	-4.451611
Ge	1.343479	0.777898	-4.455254
Ge	-1.352735	0.777878	-4.446992
Ge	2.152164	-1.241143	-2.736518
Ge	-0.000007	2.485216	-2.732637
Ge	-2.151135	-1.243018	-2.724586
Ge	0.004223	-2.131651	-1.395105
Ge	1.850092	1.065844	-1.401583
Ge	-1.841973	1.066924	-1.392105

$[Pd_2Sn_{18}]^{4-}$ - Total energy = -4117.362217266677 Eh

Pd	0.000738	-0.001112	1.770924
Sn	-0.000412	1.779309	4.075218
Sn	-1.538467	-0.890061	4.076724
Sn	1.538485	-0.889061	4.078847
Sn	-2.493652	1.439681	2.226390
Sn	0.001379	-2.880855	2.226552
Sn	2.495495	1.439412	2.228186
Sn	0.001536	2.822731	0.901745
Sn	-2.447272	-1.410367	0.901560
Sn	2.447900	-1.410333	0.901914
Pd	-0.000663	0.001095	-1.770959
Sn	0.000375	-1.779434	-4.075104
Sn	1.538403	0.889980	-4.076908
Sn	-1.538517	0.888908	-4.078921
Sn	2.493730	-1.439542	-2.226570
Sn	-2.495476	-1.439322	-2.227921
Sn	-0.001260	2.880824	-2.226812
Sn	-0.001466	-2.822648	-0.901749
Sn	2.446846	1.410470	-0.900987
Sn	-2.447700	1.410327	-0.902129