Investigations on Undisturbed Metal Carbonylates and Zintl Clusters in Liquid Ammonia

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semimetals, so called Zintl anions, have been a topic of interest since their discovery.^[1] These polyanions can be synthesized and isolated through the solid-state synthesis of alkali metal phases, followed by dissolution in liquid ammonia.^[2] To improve the solubility of the solid-state precursors in liquid ammonia, sequestering agents like [2.2.2]crypt and 18-crown-6 are often used. Since the discovery of the Tt_0^{4-} clusters, only one Tt_0^{4-} Zintl anion with fully sequestered cations has been isolated, in the form of $[Na@[2.2.2]crypt]_{4}Sn_{9}$.^[3] Due to the encapsulation of the metal cations,

comparsion of gas phase calculations against crystal structure data. The Homo- or heteroatomic polyanionic clusters of main group metals and increased size of the cationic structural elements also makes it possible to easily describe complex structures with simple crystal packing considerations by atom-to-aggregate replacement, which leads to similarities to element structure types like α-Uranium or to binary structure types like Caln₂. On our poster, we present an overview of our latest findings regarding fully sequestered cation structures of group 14 Zintl clusters and group 6 carbonylate complexes and a comparison with similar reported structures. The emphasis herein will be on the undisturbed interactions with the anions are minimized which allows for a good structure of the anions and the crystal packing.

Caln₂

 $(K@crypt)_{2}Sn_{5}^{[5]}$





 $(Rb@crypt)_2Cr(CO)_5$

| | 2.940 3.055 3.07 | 3 |
|--|------------------------|---|
|--|------------------------|---|

| | Na@crypt | Rb@crypt | calc. |
|------------|------------|------------|---------|
| capping | 2.937(4) - | 2.953(1) - | 3.040 - |
| / Å | 2.971(4) | 2.968(1) | 3.062 |
| capped | 3.193(3) - | 2.992(1) - | 3.390 - |
| square / Å | 3.308(5) | 3.637(1) | 3.421 |
| connecting | 2.928(6) - | 2.933(1) - | 3.062 - |
| / Å | 3.022(4) | 3.092(1) | 3.092 |
| bottom | 2.943(5) - | 2.940(1) - | 3.055 - |
| square / Å | 2.973(4) | 2.985(1) | 3.080 |
| diagonal | 4.163(4) | 3.462(1) | 4.327 |
| / Å | 4.205(5) | 4.699(1) | 4.351 |
| h/e | 1.171 | 1.171 | 1.170 |



B3LYP def2-TZVP

| | | C1 | 1.172 |
|--------------------------------|--|--|-----------------------|
| | K@crypt | Rb@crypt | calc. |
| Cr - C | 1.8148(1) - | 1.820(2) - | 1.833 - |
| / Å | 1.8233(1) | 1.869(2) | 1.867 |
| C - O | 1.0619(1) - | 1.174(2) - | 1.171 - |
| / Å | 1.1554(1) | 1.185(2) | 1.181 |
| α/° | 171.789(1) | 170.02(7) | 178.84 |
| β / ° | 143.040(1) | 120.42(6) | 119.9 |
| δ/° | 28.75 | 50.10 | 58.94 |
| / Å α / ° β / ° δ / ° | 1.1554(1) 171.789(1) 143.040(1) 28.75 | 1.185(2) 170.02(7) 120.42(6) 50.10 | 1.181178.84119.958.94 |



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[2]

[3]

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