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The influence of charge density on the complexation of alkali and alkaline earth metals (#412)

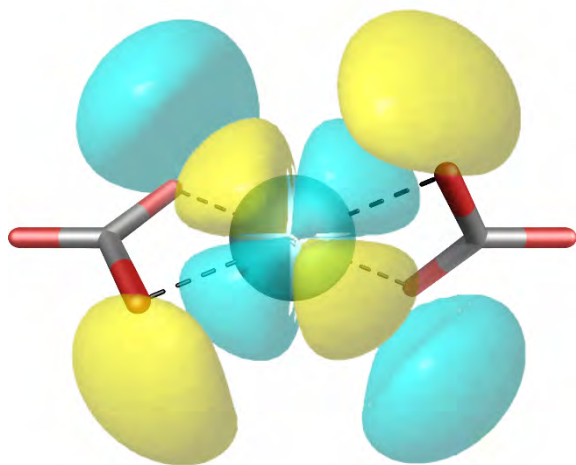
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In contrast to the well-established chemistry of main group and transition metal elements, comprehensive studies of structure and bonding of the elements of the s-block (group I and II) are scarce. This contrasts the high natural abundance of alkali and alkaline earth metal ions and their importance in biological and environmental processes (transmitter ions in neuro-electrical signals, components of hard tissue, mineralization, etc.). One reason is the low atomic ionization energies responsible for the noble gas electronic configuration in which these elements almost exclusively occur. This results in a highly ionic bonding pattern of these ions and, thus, in a low stability of their mononuclear complexes in aqueous solution under ambient conditions.ⁱⁱ Another reason is the unique variation in structure and bonding properties going from the light to the heavy group I and II elements, radically changing with the availability valence d-orbitals. Therefore, the heavier s-block elements are often subsumed under the so-called d⁰-transition metal chemistry.ⁱⁱⁱ

Our interest in alkali and alkaline earth complexes is mainly inspired by their role in the formation of carbonate minerals.^{iv} Contrary to the dynamical aqueous solvation of the individual ions, their incorporation into a crystal network results in a stable mineral form (with high coordination numbers at the metal centers). In our explorative study we show how ionic bonding in s-block complexes is crucially depending on the local charge density of the involved ligands, as well as on covalent contributions supported by empty d-orbitals (if available). In fact, the interplay between covalent and ionic contributions varies drastically along the two groups. The influence of charge alteration on covalent contributions is exemplified by the different bonding modes (mono- and bidentate) of carbonate and carbonic acid in binary calcium complexes.

References

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- ii) X. Wu, G. Frenking et al., "Observation of alkaline earth complexes M(CO)₈ (M = Ca, Sr, or Ba) that mimic transition metals", *Science*, 2018, (361), 912-916.
- iii) M. Kaupp, "Non-VSEPR Structures and Bonding in d⁰ Systems", *Angewandte Chemie International*, 2001, Edition (40), 3534-3565.
- iv) P. Ghosh, *Geochimica et Cosmochimica Acta*, 2006, (70), 1439-1456.



Acceptor rydberg orbital in a calcium carbonate complex
Illustration of the $\text{Ca}(\text{CO}_3)_2$ complex with the Rydberg natural bond orbital which contributes with secondary donor-acceptor interactions. Note that the bidentate carbonate ligands are oriented orthogonally to each other and also the d-type Rydberg orbital is twisted.