

Sodium Cyclopentadienide

Strong Intermolecular Interactions Shaping a Small Piano-Stool Complex**

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Dedicated to Professor Bernt Krebs on the occasion of his 75th birthday

Sodium cyclopentadienide is a very important precursor for metallocene synthesis of s and related sandwich- and half sandwich-complexes of d-block elements by transmetalation or salt elimination routes.^[1] Parent sodium cyclopentadienide (NaCp), which is easily prepared from dicyclopentadiene and sodium metal in laboratory scale,^[2] is virtually insoluble in common organic solvents except tetrahydrofuran (THF), and its solid-state structure of infinite coordination polymer chains of the formula $[\eta^5\text{-CpNa}]_\infty$ was determined^[3] only a century after the initial discovery of the substance class.^[4]

There have been numerous reports of solid-state structures containing CpNa moieties. These smaller aggregates ultimately are nothing else than ligand-terminated fragments derived from the polymeric parent coordination polymer. However, few structural reports contain monomeric sodocene^[6] $[\text{NaCp}_2]^-$, inverse sandwich complexes^[7] $[\text{L}_n\text{NaCpNaL}_n]^+$, or heterobimetallic sandwich complexes^[8] (with n donating solvent molecules L), and only two different structures of piano stool-like complexes of the type $[\text{L}_n\text{NaCp}]$ have been published.^[9] The latter have been restricted to bulky multidentate ligands L with resulting solid-state structures quite contrary to the small archetypical cyclopentadienyl carbonyl d-block metal complexes.

The Cp-metal interaction in organo alkali metal species is dominated by the Coulomb attraction between anion and cation when compared to transition-metal complexes, where covalent contributions are more significant.^[10] The donor ligand properties, including dipole moments, hapticity, and steric demand, play the most important role for the formation of the molecular assembly.^[11] In the course of our work on the synthesis of reactive intermediates with organo alkali metal species,^[12] it turned out that ammonia as coordinating solvent facilitates the synthesis of the missing link between the solvent-separated ion pair $[\text{L}_n\text{Na}]^+[\text{Cp}]^-$ and sandwich- or

inverse sandwich complexes. The three-legged piano stool contact ion-pair complex $[\text{CpNa}(\text{NH}_3)_3]$ (**1**), reported herein, was only feasible by crystallization from a saturated solution of ammonia in THF at -40°C .

We were able to obtain a high-resolution X-ray diffraction data set of a single crystal of **1** and conducted a XD2006 multipole refinement (Figure 1). A topological analysis according to the framework of Bader's quantum theory of

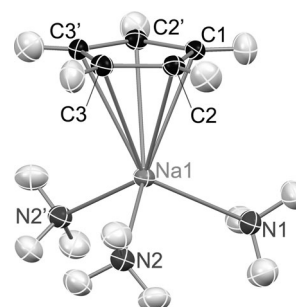


Figure 1. Representation of the molecular solid-state structure of **1**.^[5] It crystallizes in the orthorhombic space group $Pnma$, and the asymmetric unit consists of half the molecule. Ellipsoids are set at 50% probability; disordered hydrogen atoms are omitted for clarity.

atoms in molecules (QTAIM) on the charge density map from an XD2006 multipolar refinement was carried out.^[13] As the general structure of **1** is clear and not tainted by secondary (packing) effect of bulky donor bases (see Figure 1), it is a paradigmatic case to study intra- and intermolecular forces in the solid state.

Most obviously, the sodium atom is shifted away from the geometric center of the Cp ring by 0.172 \AA . A search in the Cambridge Structural Database (CSD) reveals that the observed shift of the sodium atom in **1** is unusual. The median value of metal-Cp ring center shift distribution in the database is 0.035 \AA .^[14] We have reported different structural motifs in the ammine complexes of alkali metal cyclopentadienide compounds^[12b,c] ranging from sigma-like η^1 to half sandwich η^5 coordination and solvent separated ion pairs. Judging from its structural parameters, the geometry of **1** could well be interpreted as an intermediate between η^3 and η^5 coordination.

Secondly, the hydrogen atoms in **1** are not directed away from the sodium atom but rather to the opposite direction. While the displacement parameters of the hydrogen atoms were kept at fixed values during refinement, their positional

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parameters were refined without restraints. It is important to note in this context that great care should indeed be taken in the refinement and discussion of the hydrogen atom positions derived from X-ray diffraction data. However, at least a qualitative discussion should be considered appropriate,^[15] given that low-temperature data up to high resolution were used, and non-spherical atom refinement was carried out in which bonding electron density cannot create a bias as in conventional independent atom models.

The out-of-plane bending of hydrogen atoms in lithium cyclopentadienide has been a topic in computational chemistry since the mid-70s.^[16] However, our experimentally derived structure is in disagreement with what had been predicted for the isolated complex, namely an inverse out-of-plane bending towards the metal ion is observed. To gain insight on the origin of this observation, we have performed theoretical calculations with local correlation methods. Starting from the X-ray diffraction coordinates, the structure of **1** was optimized at the DF-LMP2/VTZ (cc-pCVTZ for Na and cc-pVTZ for the remaining atoms) level of theory in the gas phase.^[17] The structure obtained is shown in Figure 2 along with relevant distances and angles. While our theoretical results essentially

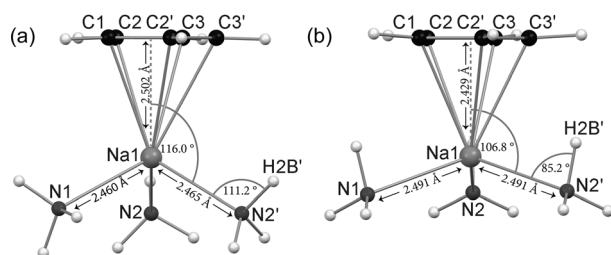


Figure 2. Comparison between a) the experimentally derived and b) the DF-LMP2/VTZ optimized structure of **1**. Both plots are on the same scale.

reproduce the findings that were reported by Streitwieser et al. for lithium cyclopentadienide, the geometrical parameters are clearly still in contrast to the mentioned features of the experimental structure. The hydrogen atoms are bent away from the sodium atom by about 5.0°, and the sodium atom is located over the geometric center of the Cp ring at a distance of 2.429 Å, and is thus 0.07 Å closer to the center than in the experiment. Another difference between the experimental and calculated structure is the tilt of the ammonia molecules towards the Cp ring. The much wider Na(NH₃)₃ umbrella enables much closer N–H... π interactions in the calculated structure.

The out-of-plane bending of the C–H bonds in [LiCp] was explained by Streitwieser et al. by attractive Coulombic interactions that are maximized by shifting electron density to the side of the Cp ring that faces the cation.^[16b] This rationale neglects covalent bonding between the alkali metal ion and the Cp ring atoms, which would lead to an out-of-plane bending towards the metal ion.

Our results from the QTAIM analysis indeed support the picture of a purely ionic interaction between [Na⁺] and [Cp[−]]. An integration of the charge density in the boundaries of each

atomic basin yields the atomic Bader charges. Group charges^[18] of chemically sensible groups of atoms were calculated as a sum of the atomic charges. The C₅H₅ ring is strongly negatively charged (−1.30 e), while the ammine ligands are close to neutral (average: 0.11 e) and the sodium atom is positively charged (0.92 e). The charge density map was analyzed for critical points and bond paths in the charge density $\rho(\mathbf{r})$. Only one of the expected bond critical points (BCPs) between the sodium atom and the Cp ring was located. As a consequence, the respective bond paths could not be traced either, and ring critical points (RCPs) as well as a cage critical point (CCP) between the sodium atom and the Cp ring could not be found. Such a situation has been similarly reported in the case of slipping indenyl ligands,^[19] but the bonding situation could clearly be described as intermediate between η^1 and η^2 . It is well-known that the localization of critical points in the very shallow charge density between metal ions and π ligands is difficult.^[20] The closed-shell nature of the present interaction between cyclopentadienide and sodium ions makes the absence of bond paths perhaps more understandable, and it has to be kept in mind that the presence or absence of bond paths is no indicator for an increase or decrease in binding energies.^[21]

Present or missing intermolecular interactions as indicated by a Hirshfeld surface analysis^[22] (Figure 3) are the most likely reason for the observed large discrepancy between the experimental and theoretical structure. As shown in Figure 3, very short distances between hydrogen and carbon

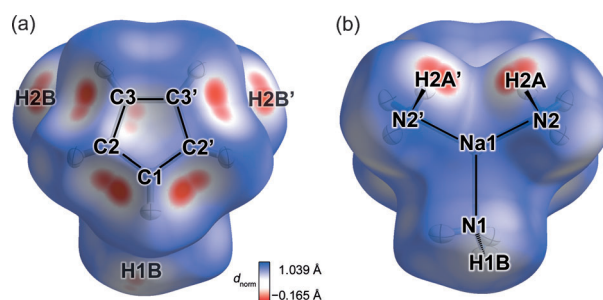


Figure 3. The normalized contact distance^[23] d_{norm} mapped on the Hirshfeld surface. The red and blue color indicates contact distances that are shorter or longer, respectively, than the sum of van der Waals radii of those two atoms inside and outside the surface that are closest to the corresponding pixel. a) View on top of the piano chair "seat cushion" approximately along the Cp_{center}–Na vector. b) View from the "bottom" of the piano chair (NH₃)₃-stand approximately along the Na–Cp_{center} vector. Graphics were created using the Software CrystalExplorer 3.0.^[24]

atoms strongly indicate N–H... π interactions. Three ammonia hydrogen atoms participate in the shortest intermolecular contacts (H1B, H2A, H2B'; see Figure 4). Those hydrogen atoms point towards the Cp ring centroid rather than towards atoms as it has been predicted theoretically,^[25] but only H1B is located directly above the ring plane. The observed N–H-centroid angles are 153° (H1B), 170° (H2A), and 173° (H2B). No intermolecular bond paths were found between hydrogen and carbon atoms, although the short contacts and the distortion of the experimental structure with respect to the

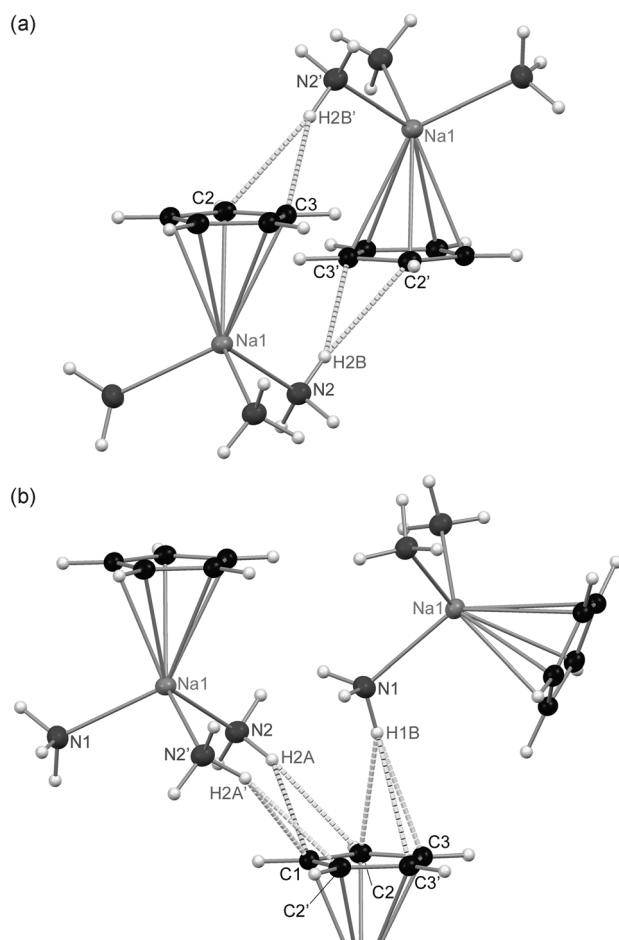


Figure 4. Detail from the packing plot of the solid-state structure of **1**. Short intermolecular contacts are indicated with dashed connection lines. Only the atoms H2A, H2B, and H1B participate in N–H... π contacts. Distances [Å]: H2A–C1 2.56(2), H2A–C2 2.62(2), H2B–C2 2.66(2), H2B–C3 2.57(2), H1B–C1 2.91(2), H1B–C2 2.75(2), H1B–C3 2.72(2).

isolated gas-phase optimized structure of **1** suggest intermolecular interactions to be the structure-determining factors. Maps of the deformation density^[26] and of the Laplacian illustrate the polarizing influence of intermolecular contacts on the density of the Cp ring (Supporting Information, Figures S5–S12). This is especially obvious at C1, which has the shortest distance to two N–H... π bond donors from at the top of the Cp ring. A pronounced shift of density away from the sodium atom causes the C–H bonds to bend towards the metal, also detectable in the topology of the Laplacian around C1.

To obtain another measure for the relative importance of the N–H... π interactions, we used the source function (SF), which facilitates the representation of the charge density $\rho(\mathbf{r})$ at any point \mathbf{r} as a sum of contributions of the atomic basins in the crystal.^[27] A description of $\rho(\mathbf{r})$ with the SF can thus serve as a measure of the relative importance of contributions from each atomic basin to the density at defined reference points (RPs), such as BCPs. The SF contributions from those hydrogen atoms that take part in N–H... π contacts are significant for reference points on ring critical points in the

addressed Cp rings (H1B –2.9%, H2A –2.8%, H2B –2.4%). Compared to the relative contributions of distant carbon atoms to C–C BCPs in the Cp ring they are in the same order of magnitude (see the Supporting Information), which is remarkable given the fact that the Cp ring is a delocalized system.

In this context we have taken into account these close interactions by simulating the solid state as a lattice of point charges. Thus, the optimizations were performed again relaxing only the hydrogen atoms in the cyclopentadienide anion taking different sizes of the lattice, namely, 13, 57, 153, 345, and 587 units of the complex (Supporting Information, Figure S14). The structures obtained in this way show a bending out-of-plane angle toward the sodium atom, in good agreement with the experimental observation. The value of this angle depends on the dimension of the lattice considered converging at around 1.5° beyond a lattice size of 300 units (Supporting Information, Figure S15). This value is remarkably close to the experimentally observed values and indicates that the inversed bending is the result of electrostatic interactions with neighboring units.

To explain the differences between the gas phase and the crystal structures, the electronic density was computed at DF-LMP2/VTZ level of theory, complemented with natural population analysis (NPA).^[28] For this calculation we have built up a model geometry of the piano-stool complex where the cyclopentadienide anion moiety is replaced by one previously optimized with D_{5h} symmetry. The density of the already established complex is then subtracted from the sum of each constituting fragment. For comparison, we have performed this kind of calculation for two systems, the unit alone and the unit with all the molecules placed at 3 Å from the ring, effectively simulating the nearest environment. The results are displayed in Figure 5.

For the complex in the gas phase, charge accumulation above the ring can be observed and, at the same time, charge depletion below the ring. Clearly, this situation would lead to a hydrogen atom out-of-plane bending away from the sodium atom to strengthen the favorable electrostatic effects. On the other hand, when the surrounding ammonia molecules are present, the charge accumulation is still above the ring but the charge depletion is not directly below it, as in the former case. Instead, the hydrogen atoms of the ammonia molecules interacting with the ring are donating the density. Thereby, they effectively repel the ring hydrogen atoms, as the interaction is not shielded (as with the sodium) and the distances are relatively small. Nevertheless, the full effect is only reproduced by including several units up to a distance of 25 Å. Only then the optimized Cp–Na distance is 2.511 Å, which is in excellent agreement with the experimentally observed distance of 2.502 Å.

To conclude, the experimental charge density distribution in [CpNa(NH₃)₃] (**1**) can be considered a spectacular illustration of the structure-determining strength of intermolecular interactions; the N–H... π interactions are strong enough to compete with the polarizing effect of the sodium cation towards the density of the cyclopentadienide ring. This is confirmed by extensive theoretical calculations, which even were able to reproduce the experimentally found inverse out-

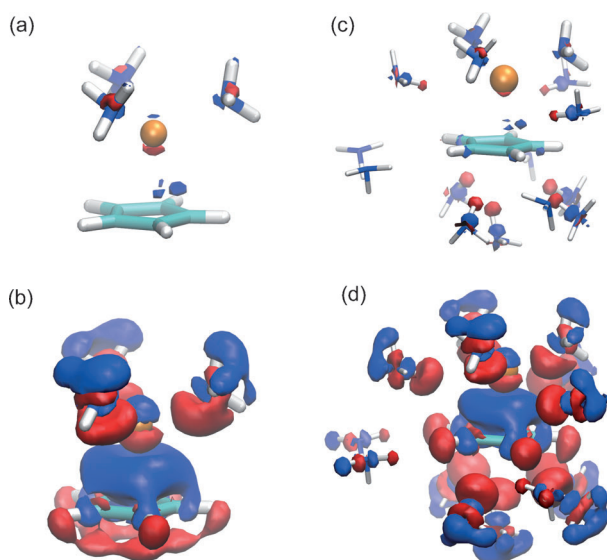


Figure 5. Density difference pictures. Isosurface plots of the DF-LMP2/VTZ density differences between the complete complex $[\text{CpNa}(\text{NH}_3)_3]$ (1) and the sum of the density of each fragment, that is, $\text{Na}(\text{NH}_3)_3$ and Cp. a), b) Isocontours of the complex without explicit surrounding ammonia molecules; c), d) isocontours of the complex with nine explicit surrounding ammonia molecules. The isovalues are 0.0038 a.u. (a,c) and 0.001 a.u. (b,d). Blue/red isosurfaces embrace positive/negative difference density, respectively.

of-plane bending of the hydrogen atoms. The structure can perhaps be considered as a crystallized metastable phase bound for the transition state between being a contact ion pair and becoming a solvent separated ion pair. The geometry indicating a slippage of the Cp^- ring away from the $[(\text{H}_3\text{N})_3\text{Na}]^+$ moiety and the lack of four out of five bond paths between sodium cation and cyclopentadienyl ring may serve as an assertion of the metastability of the structure.

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