

10 Summary

The present paper describes new results in the field of alkali metal azolides. The treatise is subdivided into five parts: *crown ether adducts of alkali metal pyrrolides*, *base-free alkali metal pyrrolides*, *alkylation of alkali metal pyrrolides and their crown ether complexes*, *synthesis and crystal structure of a salt with a „naked“ pyrrolide anion*, and *crown ether adducts of alkali metal pyrazolides, imidazolides, triazolides and indolides*.

In the first part of this paper the synthesis, the properties, and the crystal structures of crown ether adducts of alkali metal pyrrolides are reported. The synthesis of the substances was carried out by reaction of the base-free unsubstituted alkali metal pyrrolides with suitable monocyclic polyether of the crown ether type. Single crystal X-ray analyses of the mononuclear complexes lithium-pyrrolide(12-crown-4) (**6**), sodium-pyrrolide(15-crown-5) (**7**), potassium-pyrrolide(18-crown-6) (**8**) and rubidium-pyrrolide(18-crown-6) (**9**) have been structure determined (e. g. fig. 10.1).

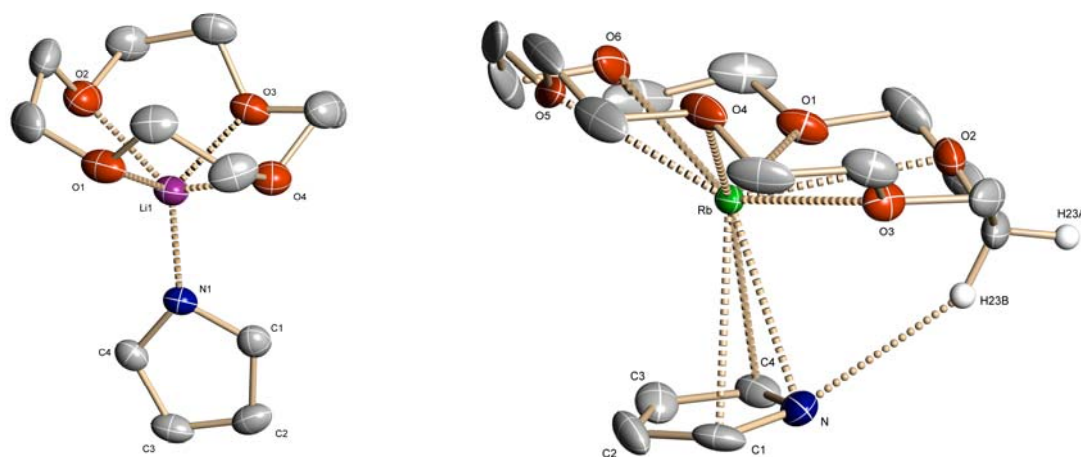


Fig. 10.1: Structure of lithium-pyrrolide(12-crown-4) (**6**) and rubidium-pyrrolide(18-crown-6) (**9**).

The monomeric compounds **6**, **7**, **8** and **9** are built up in a similar fashion showing the alkali metal cations always coordinated above their equatorial plane from the oxygen atoms of the crown ether ligands. The lithium-, sodium- and potassium-complexes exhibit an η^1 -coordination (σ -bonding) between the alkali metal cation and the nitrogen atom of the pyrrolide anion. The M–N-bond length increases from 195.0 pm (**6**) to 271.2 pm (**8**) according to the *Shannon* radii of the cations. The bigger rubidium cation in compound **9** favours an asymmetrical multi haptic π -bonding (η^3 , M–CNC-interaction) between the rubidium cation and the pyrrolide anion, where the rubidium cation is shifted in the direction of the N-atom. The planar pyrrolide ligand of the alkali metal pyrrolides with smaller metal ions (**6**, **7** and **8**)

is nearly vertically located to the mean plane of the crown ether, while the rubidium 18-crown-6 complex is face on coordinated with an angle of 155.6° , possibly caused by the existence of a hydrogen bridge between the nitrogen atom of the pyrrolide anion and a hydrogen atom of the crown ether. Furthermore an unusual binuclear complex $[\text{Cs}(\text{C}_4\text{H}_4\text{N})(18\text{-crown-6})]_2 \cdot \text{H}_2\text{O}$ (**11**) containing a water molecule in combination with a non-protonated pyrrolide anion were synthesized and the solid state structure determined (fig. 10.2). Although water has a smaller pK_A -value than pyrrole (H_2O : $\text{pK}_\text{A} = 15.74$; pyrrole: $\text{pK}_\text{A} = 17.51$) compound **11** crystallizes in the mentioned structure. Obviously the basicity of the pyrrolide anion is reduced by coordination to the cesium cation.

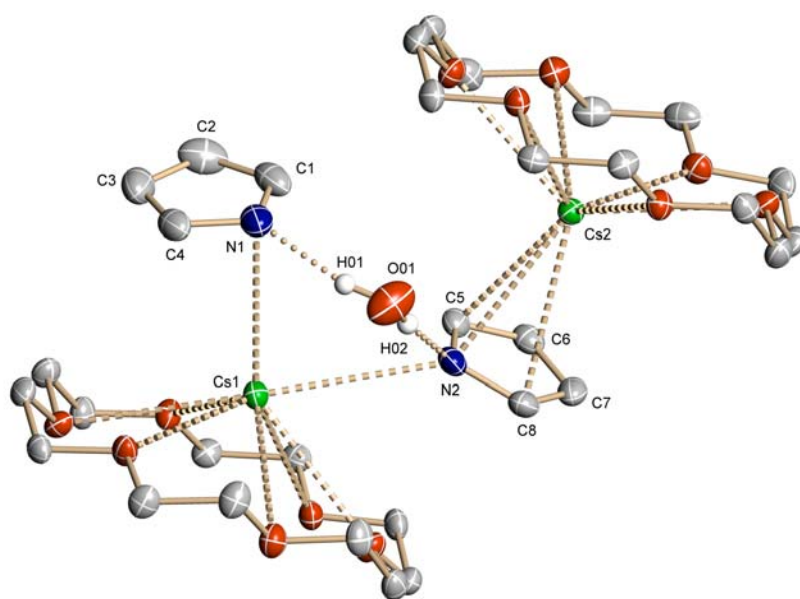


Fig. 10.2: Structure of $[\text{Cs}(\text{C}_4\text{H}_4\text{N})(18\text{-crown-6})]_2 \cdot \text{H}_2\text{O}$ (**11**).

In the second part of this work a structure determination of a base-free alkali metal pyrrolid should be accomplished by X-ray powder diffraction, to ascertain the differences of the coordination mode between a solvent containing and base-free alkali metal pyrrolid. The powder pattern allowed the indexing of all reflections in a orthorhombic crystal system but the resulting data record contains various not observed reflections. The following *Patterson* calculation performed to find the position of the heavy atoms does not result in a structure solution.

The third part of this treatise describes the alkylation of alkali metal pyrrolides and their crown ether complexes. Under same conditions ethylbromide was reacted with lithium-pyrrolide (**1**), rubidium-pyrrolide (**4**), lithium-pyrrolide(12-crown-4) (**6**) and rubidium-pyrrolide(18-crown-6) (**9**). The identification of the products was managed by gas-

chromatographic and mass-spectrometric methods and the combination of different NMR-techniques. The monoalkylation of rubidium-pyrrolide (**4**) and rubidium-pyrrolide(18-crown-6) (**9**) results exclusively in N-alkylation (fig. 10.3). The monoalkylation of lithium-pyrrolide (**1**) and lithium-pyrrolide(12-crown-4) (**6**) results predominantly in C-alkylated products and a small ratio of N-ethylpyrrole (fig. 10.3). The exclusive N-alkylation of the substances **4** and **9** in THF in opposite to the C-alkylation of lithium-pyrrolides (**1** and **6**) could be interesting for synthetic applications and shows an important difference in the reactivity between the alkali metal pyrrolides.

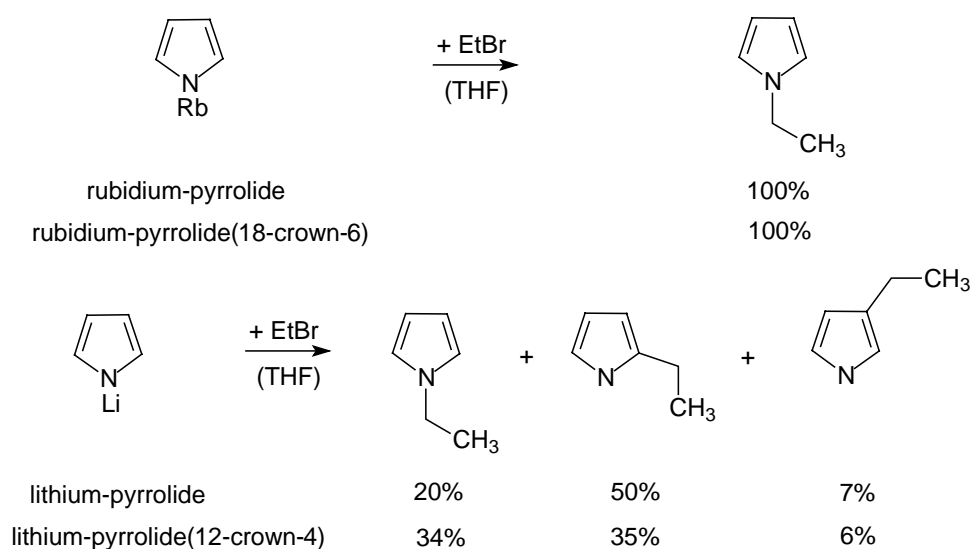


Fig. 10.3: Alkylationproducts of the compounds **1**, **4**, **6** and **9**.

The exclusive N-alkylating rubidium-pyrrolide(18-crown-6) complex (**9**) shows a η^3 coordination sphere in a π -complex. Assuming that a similar bonding mode between the rubidium ion and the pyrrolide anion is found for the compounds **4** and **9** in solution we can understand that the lone electron pair of the pyrrolide's nitrogen atom is available in a π -complex for an alkylation reaction at the nitrogen atom. A possible reaction mechanism is shown in figure 10.4. The formation of C-ethylpyrrol as a main reaction product for the alkylation of compound **1** and **6** in THF indicates the existence of N-associated lithium-pyrrolide complexes, where the lone electron pair of the pyrrolide anion's nitrogen atom is not available for an N-alkylation reaction anymore. Reacting the lithium-pyrrolides with equimolar ratios of alkylating agent results in the formation of di- and triethylpyrroles because of the higher nucleophilicity of the intermediate lithium salts of 2-ethylpyrrole and 3-ethylpyrrole. This demonstrates that polyalkylation is a dominant consecutive reaction. Despite the chelating property of the crown ether the alkylation of lithium-pyrrolide (**1**) and

the base-stabilized lithium-pyrrolide(12-crown-4) complex (**6**) in THF results in the same alkylation products but with different distribution of the C- and N-alkylated products. The loss of selectivity for the C-alkylation of the crown ether adduct of lithium-pyrrolide (**6**) is the main difference in the reactivity compared to base-free lithium-pyrrolide (**1**) ($C/N_{\text{lithiumpyrrrolide}} = 2.8$, $C/N_{\text{lithiumpyrrrolide(12-crown-4)}} = 1.2$). It can be explained as a result of a more favourable N-alkylation on one hand and a reduced C-alkylation reactivity of the base-stabilized complex on the other hand.

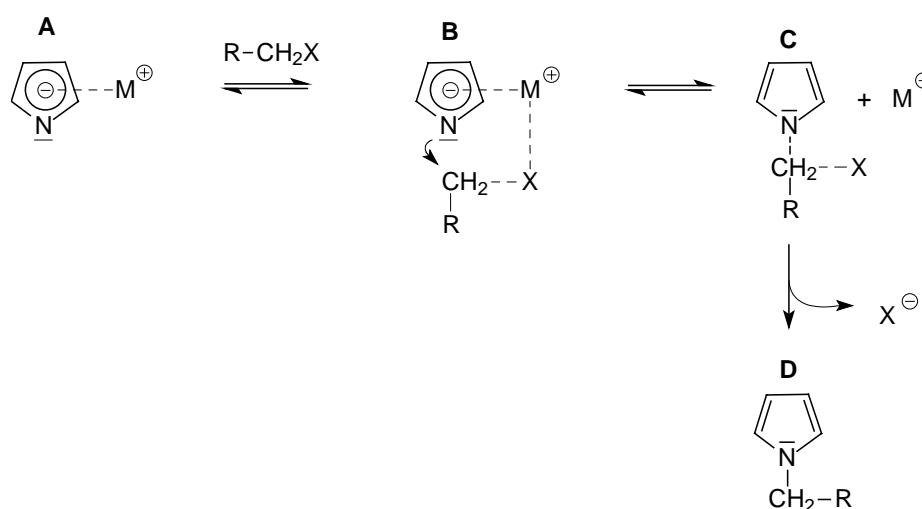


Fig. 10.4: Possible reaction mechanism of the N-alkylation (X: halogen, R: residue).

The fourth part of this work describes the synthesis and structure of a salt with a naked pyrrolide anion. By means of sterically highly demanding solvent molecules it was tried to separate the cation - namely the rubidium ion - from the anion. The synthesis was carried out by reacting rubidium-pyrrolide with 15-crown-5 in a molar ratio of 1:2. A crystalline product with the stoichiometric composition of $[Rb(15\text{-crown-5})_2](C_4H_4N)$ (**12**) could be isolated (fig. 10.5). The single crystal X-ray analysis determined a naked pyrrolide anion, with a statistical CH/N-distribution. To avoid the described disorder it was tried to fix the anion by means of a hydrogen bridge bond between a pyrrolide anion and a neutral pyrrole molecule. This was obtained by reacting $RbN(SiMe_3)_2$ and pyrrole in a stoichiometric ratio 1:2 and a twofold excess of 15-crown-5 (related to $RbN(SiMe_3)_2$) for the following reaction step. In the $[Rb(15\text{-crown-5})_2][H(C_4H_4N)_2]$ (**13**) complex obtained the rubidium ion is enclosed by two parallel 15-crown-5 ligands while the pyrrolide anion and a pyrrole molecule occur as a non-coordinating unit (fig. 10.5). The two planar five-membered rings of complex **13** are connected to each other via hydrogen bridge bonds. The complex **13** is the first literature known example with a non-coordinating pyrrolide unit, which does not possess a disorder of

the pyrrolide anion. Calculations on the DFT level and MP2 calculations for the pyrrole molecule and the pyrrolide anion result in a good match between the calculated and the measured bond lengths and bond angles of the two heterocycles of compound **13**.

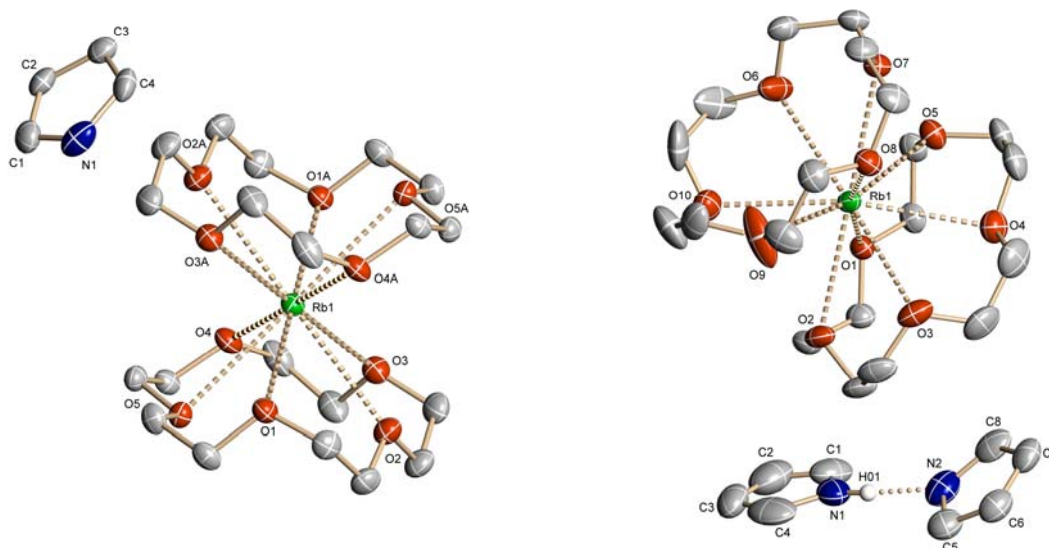


Fig. 10.5: Structure of $[\text{Rb}(\text{15-crown-5})_2](\text{C}_4\text{H}_4\text{N})$ (**12**) (left) and $[\text{Rb}(\text{15-crown-5})_2][\text{H}(\text{C}_4\text{H}_4\text{N})_2]$ (**13**) (right).

In the fifth part of this thesis a closer look on the crown ether adducts of the alkali metal pyrazolides, imidazolides, triazolides and indolides have been taken to enlarge the knowledge of the alkali metal azolides chemistry. It was aimed to synthesize the crown ether adducts by reacting the base-free non-substituted alkali metal azolides (alkali metal: Li, Na, K, Rb, Cs; azolides: pyrazolide, imidazolidine, triazolide and indolide) with the corresponding crown ether. The products have been characterized and recrystallized from various solvents to obtain single crystals. Due to the limited solubility of some alkali metal azolides and their crown ether adducts in certain solvents only a few complexes could be isolated as single crystals for the determination of their crystal structure. The monomeric alkali metal pyrazolides sodium-pyrazolide(15-crown-5) (**14**), potassium-pyrazolide(18-crown-6) (**15**) and rubidium-pyrazolide(18-crown-6) (**17**) with their heterocyclic ligand containing two neighbouring nitrogen atoms within the five-ring exhibit all η^2 coordination via the lone electron pairs of the two nitrogen atoms to the metal ion (e. g.: fig. 10.6).

The complexes potassium-imidazolidine(18-crown-6) (**18**) where the potassium ion is η^1 -coordinated via one of the nitrogen atoms of the imidazolidine anion and rubidium-imidazolidine(18-crown-6) (**19**) where the nitrogen ligand is coordinated in a η^3 fashion (fig. 10.6) reveal both monomeric structures, that only differ in the coordination mode of the imidazolidine anion.

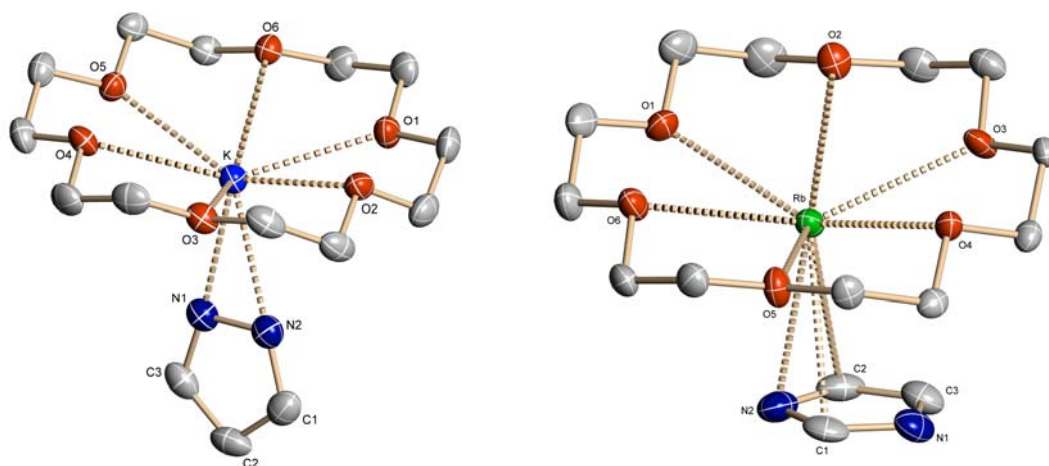


Fig. 10.6: Structure of potassium-pyrazolide(18-crown-6) (**15**) (left) and rubidium-imidazolidine(18-crown-6) (**19**) (right).

Surprisingly compound **19** does not show a η^3 coordination between the rubidium cation and the imidazolidine anion via the C1 atom and the two electron-rich nitrogen atoms, but a η^3 M–CNC interaction. The higher electron density of the N1 atom is partially compensated by inter- and intramolecular hydrogen bridge bonds between the crown ether's hydrogen atoms and the N1 atom of the imidazolidine anion.

From the compound potassium-triazolide(18-crown-6) (**20**) no suitable single crystals for a X-ray structure determination could be obtained. But an analogous synthesis with a twofold excess of the triazole yielded the determined structure of potassium-triazolide(18-crown-6)-(triazole) (**21**). The potassium complex **21** exhibits a distorted hexagonal bipyramide. The potassium ion which is more or less located in the mean plane of the O6-ring builds the base. The two apexes of the bipyramid are build by the η^1 -coordinated neutral triazole and the triazolide anion ligands (fig. 10.7). A vivid example for the difficult prediction of crystal structures offers the complex rubidium-triazolide(18-crown-6) (**22**) (fig. 10.7).

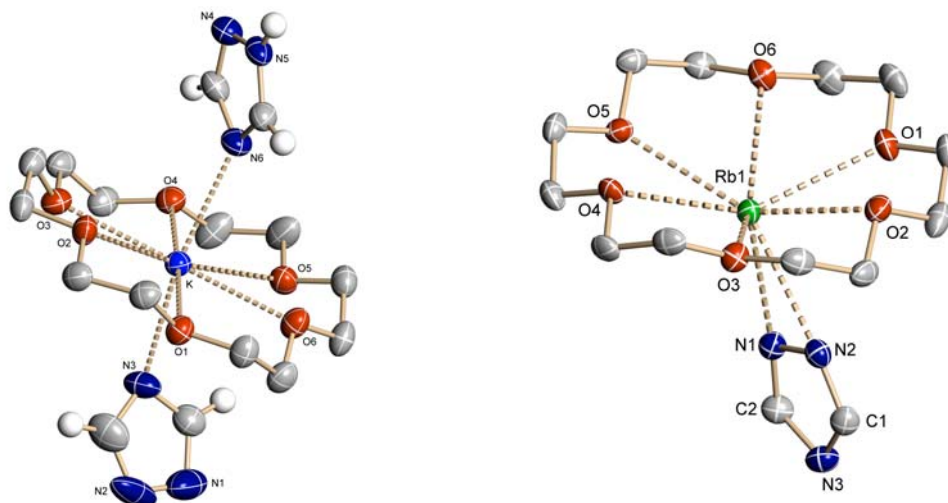


Fig 10.7: Structure of potassium-triazolide(18-crown-6)-(triazole) (**21**) (left) and rubidium-triazolide(18-crown-6) (**22**) (right).

The central rubidium ion does not show the expected face-on coordination to the triazolidine anion, but a η^2 -coordination via the lone electron pairs of the two adjacent nitrogen atoms. The five-ring of the triazolidine ligand stands almost coplanar to the Rb-N-N-area. The crown ether possesses a similar conformation in all investigated complexes, showing the six oxygen atoms located alternately 20 pm above and below their mean plane. The cavity formed inside the crown ether (2.6 Å) is too small to enclose the rubidium cation (2.94 Å) at its equatorial plane. Therefore the five Rb(18-crown-6) compounds investigated within this work exhibited shifts of the cation from the mean plane of the six oxygen atoms of the 18-crown-6 ligand ranging from 85 to 104 pm. In other complexes with Rb(18-crown-6) fragments much higher shifts of the rubidium cation (81-122 pm) have been found.

The alkali metal cations in the complexes sodium-indolide(15-crown-5) (**24**) and rubidium-indolide(18-crown-6) (**26**) are η^1 -coordinated to the lone electron pair of the nitrogen atom of the indolide ligand (e. g.: fig. 10.8). While on the other hand for the dimeric $[\text{Cs}(\text{C}_8\text{H}_6\text{N})(18\text{-crown-6})]_2 \cdot \text{THF}$ (**27**) a central M_2N_2 -four-membered ring was found with a typical geometry for solvated alkali metal amides (fig. 10.8). Going from the neutral indole to the indolide anion results in small changes within the bonding parameters of the molecule, a fact that can easily be confirmed by MO calculations.

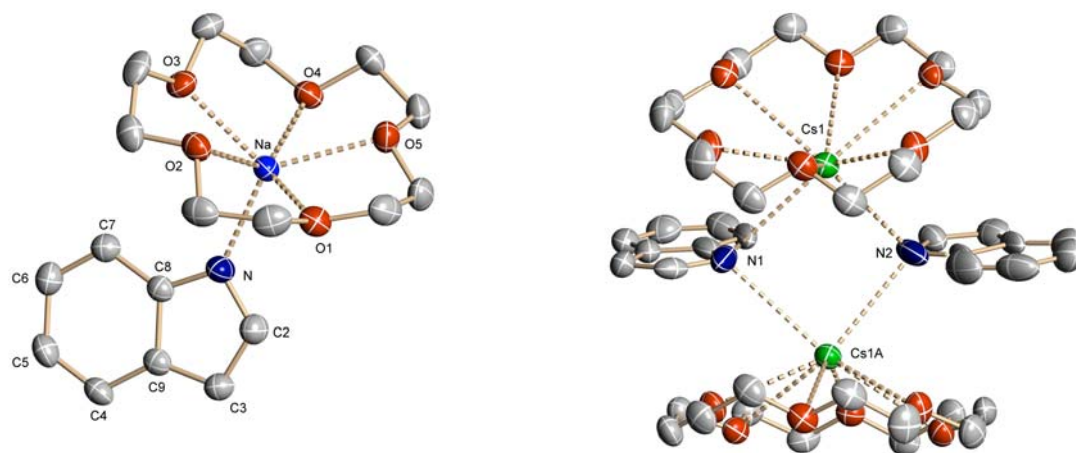


Fig. 10.8: Structure of sodium-indolide(15-crown-5) (**24**) (left) and [Cs(C₈H₆N)(18-crown-6)]₂·THF (**27**) (right).

For the first time this paper offers a complete and systematic investigation of the crystal structures and reactivity of the alkali metal azolides. Hopefully in the field of the so far seldomly investigated complexes of the alkali metal azolides the detailed knowledge will raise in the future to make the factors that determine the bonding modes in such complexes more understandable.