

Short communication

Interaction Between the Rubidium Cation and [2.2.2]Paracyclophane: Experimental and Theoretical Study

Emanuel Makrlík,^{1,*} Stanislav Böhm,² David Sýkora,²
Magdalena Kvičalová¹ and Petr Vaňura²

¹ Faculty of Environmental Sciences, Czech University of Life Sciences, Kamýčká 129, 165 21 Prague 6 - Suchbát, Czech Republic

² University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

* Corresponding author: E-mail: makrlik@centrum.cz

Phone: +420 376 594 672

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Abstract

By means of electrospray ionization mass spectrometry (ESI-MS), it was evidenced experimentally that the rubidium cation (Rb^+) reacts with the electroneutral [2.2.2]paracyclophane ligand ($\text{C}_{24}\text{H}_{24}$) to form the cationic complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$. Moreover, applying quantum chemical calculations, the most probable conformation of the proven $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ complex was solved. In the complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ having a symmetry very close to C_3 , the “central” cation Rb^+ , fully located in the cavity of the parent [2.2.2]paracyclophane ligand, is coordinated to all three benzene rings of [2.2.2]paracyclophane via cation- π interaction. Finally, the binding energy, $E(\text{int})$, of the considered cation- π complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ was evaluated as -99.3 kJ/mol, confirming the formation of this fascinating complex species as well. This means that the [2.2.2]paracyclophane ligand can be considered as a receptor for the rubidium cation in the gas phase.

Keywords: [2.2.2]Paracyclophane; Rubidium cation; Cation- π interaction; DFT calculations; Structures.

1. Introduction

It is well-known that π -prismoids and certain hydrocarbon cyclophanes are capable of forming π -complexes with some small metal cations, where benzene rings act as π -donors for the respective complexes.¹ This fascinating complexation behavior is especially effective for [2.2.2]paracyclophane and related structures.^{2,3} Pierre et al.³ have reported the preparation of the silver triflate complex of [2.2.2]paracyclophane and claimed that it was the first member of a new class of compounds; owing to the complexation properties, they proposed the name π -prismoid for such hydrocarbon cyclophanes. Furthermore, Vögtle et al.⁴ have shown that concave hydrocarbon cyclophanes can extract certain metal ions from an aqueous phase into a nonpolar phase. They have tested these hydrocarbons as ionophores and have shown that PVC-[2.2.2]paracyclophane membranes demonstrated remarkable sensitivity toward the univalent silver cation.⁴ Recently, the first-principles model of Fermi resonance in the alkyl CH stretch

region has been applied to 1,2-diphenylethane and [2.2.2]paracyclophane.⁵ Finally, the role of the metal formal charge in the cation- π interactions has been evaluated with relativistic DFT methods involving a versatile π -cryptating structure, namely [2.2.2]paracyclophane.⁶

Cation- π interaction refers to the noncovalent attraction between a cation and a π -system.^{7,8} Its strength is often comparable with the interaction between a cation and traditional ligands, including water, alcohols, and amines. As a result of this cation- π interaction, there are extraordinarily important driving forces in molecular recognition processes in many biological and artificial systems.^{9–12} The considered cation- π interaction is a well-established phenomenon in the gas phase, as well as in the solid state,^{13–19} and is known to play very important role in the stabilization of tertiary structures of various proteins.²⁰

We must emphasize that the cation- π interactions of [2.2.2]paracyclophane ($\text{C}_{24}\text{H}_{24}$; see Figure 1) with the

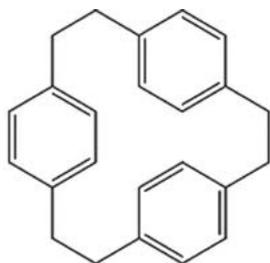


Figure 1. Structural formula of [2.2.2]paracyclophane ($C_{24}H_{24}$).

“soft” cations Ag^+ ,^{3,21,22} and Tl^+ ²³ have been investigated and proven quite unambiguously.

However, up to now, interaction of the mentioned electroneutral [2.2.2]paracyclophane ligand with a very bulky cation has not been studied and [2.2.2]paracyclophane was considered to be a receptor for the transition metal cations.⁶ On the other hand, in our previous work we show, that paracyclophane [2.2.2] could also encapsulate light alkali metal cation Na^+ .²⁴

Therefore, in the present work, electrospray ionization mass spectrometry (ESI-MS) was applied as an experimental technique for characterization of the cation- π interaction between the very voluminous heavy univalent rubidium cation (Rb^+) and this [2.2.2]paracyclophane ligand in the gas phase. In this context we must state that the cation Rb^+ was chosen for the present study especially for the sake of an expected fascinating structure of the resulting cationic complex involving the [2.2.2]paracyclophane ligand. Furthermore, by means of quantum chemical DFT calculations, the most probable conformation of the experimentally evidenced cationic complex $[Rb(C_{24}H_{24})]^+$ in the gas phase was suggested.

2. Experimental

[2.2.2]Paracyclophane (puriss., $\geq 99\%$) was purchased from Aldrich, while rubidium chloride (puriss., $\geq 99\%$), $RbCl$, was supplied by Fluka. Other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. In this context it should be stated that rubidium has two stable isotopes, i.e., ^{85}Rb (natural abundance: 72.168%) and ^{87}Rb (natural abundance: 27.832%).

The mass spectra were measured on the 3200 Q TRAP (AB Sciex, Canada) mass spectrometer. This instrument was equipped with an electrospray ion source. The experiments were carried out in a positive-ion mode. Nitrogen was used as a nebulizer gas. The operating conditions for the mass spectrometer were set as follows: ion-spray voltage 5.5 kV; curtain gas 10 arbitrary units, ion source gas(1) 18 arbitrary units and ion source gas(2) 0 arbitrary units; ion source temperature ambient; declustering potential 35 V and entrance potential 10 V. Mass spectra were recorded from m/z 100 to 800. A mixture of

[2.2.2]paracyclophane (8×10^5 mol/L) and $RbCl$ (2×10^{-3} mol/L) dissolved in methanol/chloroform (1:1) was introduced into the ESI source via a PEEK capillary at a flow rate of 10 $\mu L/min$.

3. Results and Discussion

3.1. Electrospray Ionization Mass Spectrometry

Figure 2 depicts an ESI mass spectrum measured in a positive-ion mode for a mixture of [2.2.2]paracyclophane ($C_{24}H_{24}$) with $RbCl$ in a methanol/chloroform (1:1) solution. The intense peaks in the mass spectrum at m/z 397 and 399 evidently belong to the cationic complex $[Rb(C_{24}H_{24})]^+$. Besides, two insets in Figure 2 represent the real and calculated isotope patterns of the cationic cluster $[Rb(C_{24}H_{24})]^+$ related to the presence of two stable isotopes of rubidium, i.e., ^{85}Rb and ^{87}Rb , in natural abundances 72.168 and 27.832%, respectively. It is necessary to emphasize that under the present experimental conditions, the cationic complex species $[Rb(C_{24}H_{24})]^+$ was proven in the gas phase. No other [2.2.2]paracyclophane complexes with Rb^+ were found by using this experimental method.

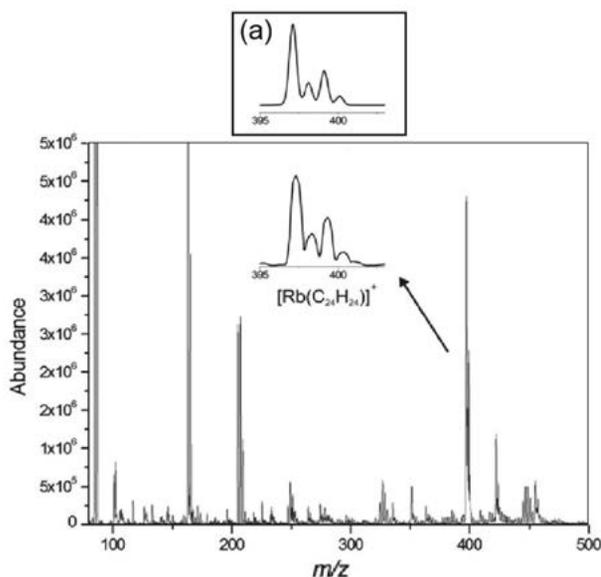


Figure 2. Positive-ion mode ESI mass spectrum of a mixture of [2.2.2]paracyclophane (8×10^5 mol/L) with $RbCl$ (2×10^{-3} mol/L) in methanol/chloroform (1:1). The inset shows the real isotope pattern of the $[Rb(C_{24}H_{24})]^+$ complex on an expanded mass scale. The inset (a) provides the calculated isotope pattern of the considered $[Rb(C_{24}H_{24})]^+$ complex.

Furthermore, Figure 3a shows a collision induced dissociation (CID) mass spectrum of the ions $[^{85}Rb(C_{24}H_{24})]^+$ (m/z 397), where the only one significant fragment ion signal was found at m/z 85. Analogously, in a

CID mass spectrum of $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ given in Figure 3b, the sole fragment ions at m/z 87 were observed. These facts clearly indicate that the only significant fragmentation channel in the investigated complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ is the loss of one electroneutral [2.2.2]paracyclophane ligand, similarly as in our recent paper.²³

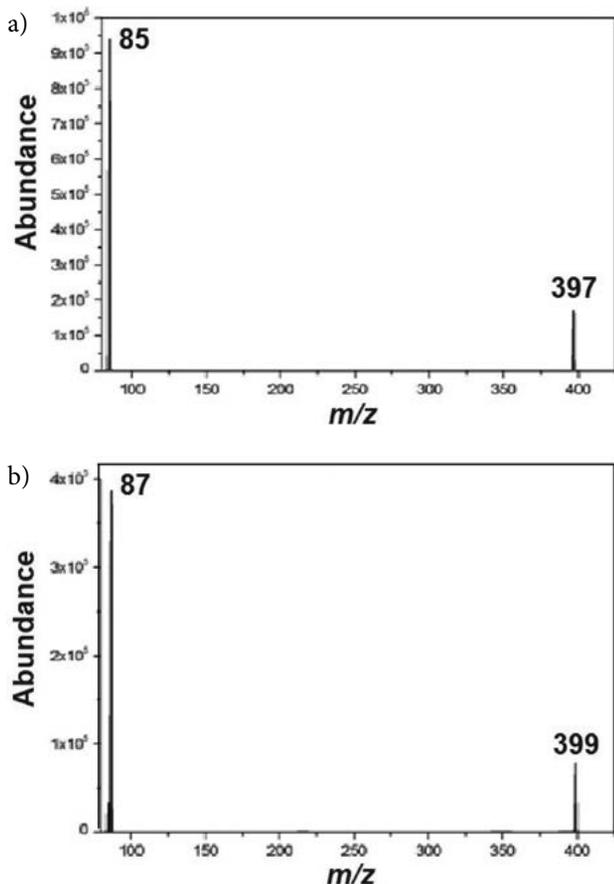


Figure 3. CID mass spectra of (a) $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ and (b) $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ ions obtained with nitrogen (1×10^{-2} mbar) at collision energy of 15 eV (laboratory frame).

In summary, we have evidenced experimentally that the cationic complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ must be present in the gas phase, and when the mentioned complex is collisionally activated, it decomposes almost exclusively via elimination of the electroneutral [2.2.2]paracyclophane molecule (i.e., $\text{C}_{24}\text{H}_{24}$), while the charge is retained on the rubidium atom in the form of Rb^+ .

3. 2. Quantum Chemical DFT Calculations

The theoretical calculations were performed at the density functional level of theory by using modern hybrid ω -B97XD functional including long range and dispersion corrections,²⁵ employing the Gaussian 09 suite of programs.²⁶ Modern balanced def2-TZVP basis set²⁷ was used, and the optimizations were unconstrained. In order

to increase the numerical accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell. This was ensured by means of the Gaussian 09 keyword “integral(ultrafinegrid)”.

The most probable conformation of the $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ cationic complex was predicted on the basis of the thorough conformational analyses (i. e., eight very different initial mutual positions of the [2.2.2]paracyclophane ligand and the Rb^+ cation were considered during the geometry optimization) and the respective vibrational frequency analyses, analogously as in our articles.^{28–32}

During the model calculations, the molecular geometries of the free [2.2.2]paracyclophane ligand and its cation- π complex with Rb^+ were optimized, similarly as in our previous papers.^{28–32} The optimized conformation of this free [2.2.2]paracyclophane, having a symmetry very close to C_3 , is given in Figure 4.

Furthermore, we must emphasize that the only conformation was obtained by the full DFT optimization of the [2.2.2]paracyclophane – Rb^+ complex (i.e., $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$), which is shown in Figure 5. It should be

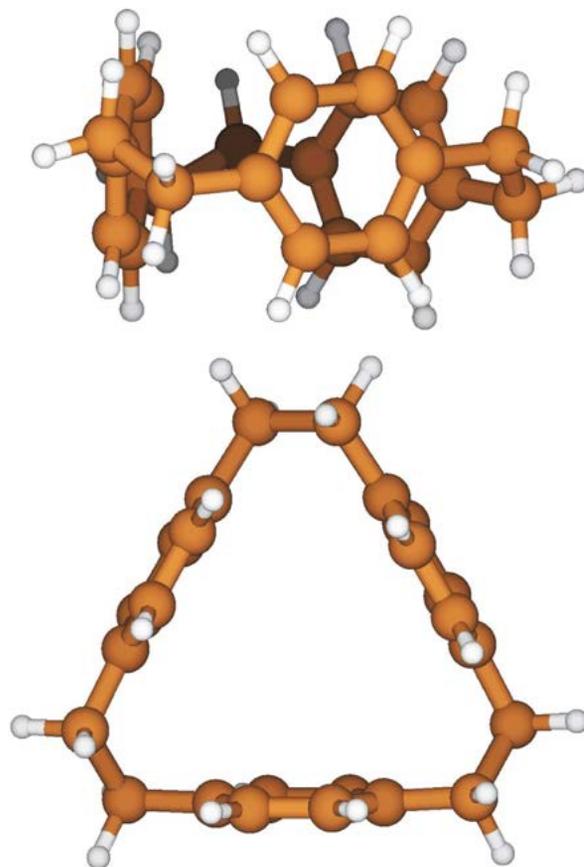


Figure 4. Two projections of the DFT optimized structure of free [2.2.2]paracyclophane (ω -B97XD / def2-TZVP).

stated that the respective vibrational calculations found no imaginary frequencies. In the cationic complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ with a symmetry very close to C_3 as well, the “central” cation Rb^+ , fully located in the cavity of the parent [2.2.2]paracyclophane ligand, is coordinated to all three benzene rings of [2.2.2]paracyclophane via cation- π interaction (the distances between the “central” cation Rb^+ and the centroids of the three benzene rings are 2.88, 2.88, and 2.88 Å), as also presented in detail in Figure 5. Further conformation of the $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ complex was not found by using the above-mentioned theoretical procedure. Besides, from comparison of Figure 4 with Figure 5, it is obvious that the inclusion of the rubidium cation causes a slight deformation of the ligand molecule in the considered $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ complex. It must be pointed out that encapsulation of light alkali metal cation Na^+ do not cause any deformation of the mentioned [2.2.2]paracyclophane ligand (see Figure 6).²⁴

Finally, the binding energy, $E(\text{int})$, of the $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ complex, involving the 7point correction for the basis set superposition error (BSSE),^{33,34} was calculated as -99.3 kJ/mol. Recently, the binding energy of the

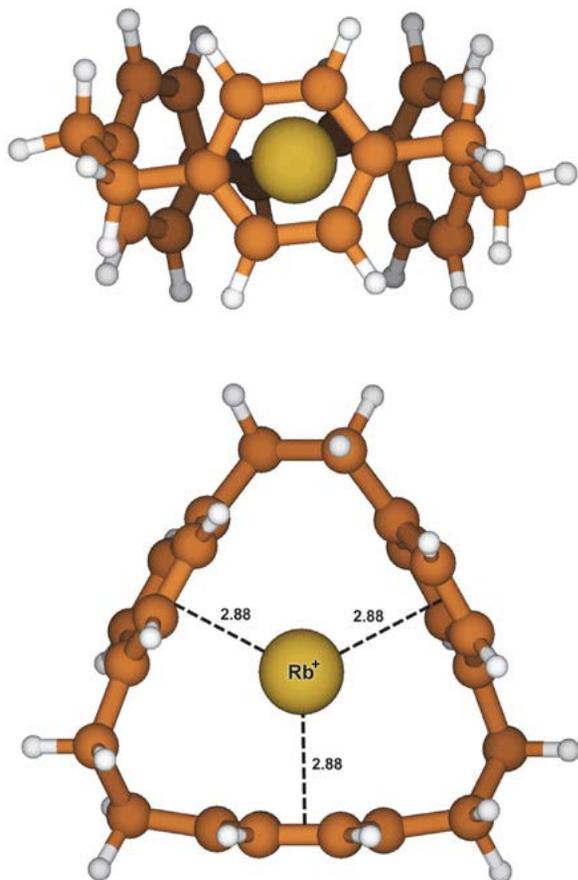


Figure 5. Two projections of the DFT optimized structure of the $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ complex (ω -B97XD / def2-TZVP); the distances between the “central” cation Rb^+ and the centroids of the three benzene rings are 2.88, 2.88, and 2.88 Å.

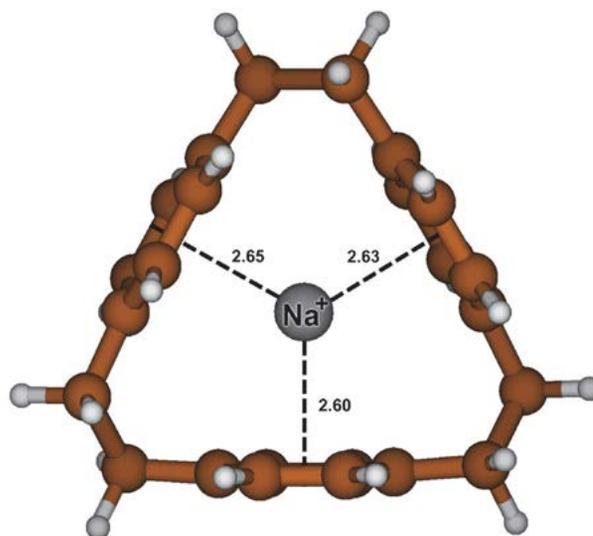


Figure 6. DFT optimized structure of the $[\text{Na}(\text{C}_{24}\text{H}_{24})]^+$ complex (ω -B97XD / def2-TZVP); the distances between the “central” cation Na^+ and the centroids of the three benzene rings are 2.65, 2.63, and 2.60 Å (Ref. ²⁴).

complex [2.2.2]paracyclophane – Tl^+ (i.e., $[\text{Tl}(\text{C}_{24}\text{H}_{24})]^+$) in the gas phase has been determined as -198.1 kJ/mol.²³ It means that the stability of the investigated complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ in the gas phase is substantially lower than that of the mentioned $[\text{Tl}(\text{C}_{24}\text{H}_{24})]^+$ complex species, although the deformation of the ligand, caused by an inclusion of the Tl^+ cation is even higher, than in the case of the Rb^+ cation.²³ This is evidently caused by the higher “softness” of Tl^+ in comparison with Rb^+ .

4. Conclusions

In this work, we have shown that an experimental (ESI-MS) and theoretical (DFT calculations) approach can provide important information concerning the noncovalent binding interaction between the electroneutral [2.2.2]paracyclophane ligand and the univalent rubidium cation (Rb^+) in the gas phase. On the basis of the mentioned experimental method, the cationic complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ was evidenced quite unambiguously. In addition, employing DFT calculations, the most probable conformation of this fascinating rubidium(I) complex was suggested. In the resulting complex $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$ with a symmetry very close to C_3 , the “central” cation Rb^+ , fully located in the cavity of the parent [2.2.2]paracyclophane ligand, is coordinated to all three benzene rings of [2.2.2]paracyclophane via cation- π interaction. It means that [2.2.2]paracyclophane can be considered as a receptor for the rubidium cation in the gas phase. As follows from the previous facts, the present work may be a significant contribution especially to both experimental and theoretical study of [2.2.2]paracyclophane, as well as to structural chemistry in general.

5. Acknowledgements

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Povzetek

Z uporabo elektrosprej ionizacijske masne spektrometrije (ESI-MS) smo dokazali, da rubidijev kation (Rb^+) z elektronevtralnimi [2.2.2] paraciklofanskimi ligandi ($\text{C}_{24}\text{H}_{24}$) tvori kationski kompleks $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$. S pomočjo kvantno-kemijskih izračunov smo določili tudi najbolj verjetno konformacijo tega kompleksa. Ugotovili smo, da ima simetrijo zelo blizu C_3 , da je „osrednji“ kation Rb^+ v celoti umeščen v prostor matičnega [2.2.2]paraciklofanskega liganda, in koordiniran z vsemi tremi benzenskimi obroči [2.2.2]paraciklofana preko kation- π interakcije. Ocenili smo energijo vezave, $E(\text{int})$, obravnavanega kation- π kompleksa $[\text{Rb}(\text{C}_{24}\text{H}_{24})]^+$. Vrednost $-99,3$ kJ/mol potrjuje verjetnost nastanka tega zanimivega kompleksa, kar pomeni, da [2.2.2]paraciklofanski ligand lahko obravnavamo kot receptor Rb^+ v plinski fazi.