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QUADRATIC ACID AS A STRUCTURAL MOTIVE IN A LEHN-TYPE CRYPTAND - PREDICTION OF ION SELECTIVITY BY QUANTUM CHEMICAL CALCULATIONS. XX😊

Thomas Capponi[1], Ali A. Khairbek[2,3], Dušan Ćoćić[4], Tanja Soldatović[5], Ralph Puchta[1,6,7,8]* and Rudi van Eldik[4,9]

[1] *Berufsfachschule für Medizinisch-Technische Assistenten in der Medizin, Universitätsstraße 42-44, 91054 Erlangen, Germany*
[2] *Department of Chemistry, Faculty of Science, Tishreen University, Lattakia, Syrian Arab Republic*
[3] *Centre of Molecular Medicine and Diagnostics (COMManD), Saveetha Dental College and Hospitals, Saveetha Institute of Medical and Technical Sciences, Saveetha University, Chennai 600 077, India*
[4] *University of Kragujevac, Faculty of Science, Department of Chemistry, Radoja Domanovića 12, 34000 Kragujevac, Republic of Serbia*
[5] *State University of Novi Pazar, Department of Natural-Mathematical Sciences, Vuka Karadžića 9, 36300 Novi Republic of Serbia*
[6] *Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany*
[7] *Computer Chemistry Center, Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, Nägelsbachstr. 25, 91052 Erlangen, Germany*
[8] *Central Institute for Scientific Computing (ZISC), University of Erlangen-Nuremberg, Martensstr. 5a, 91058 Erlangen, Germany.*
[9] *Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Toruń, Poland*
*Corresponding author; E-mail: ralph.puchta@fau.de

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ABSTRACT. The ion selectivity of $[2_{Qua}.2_{Qua}.2_{Qua}]$ was investigated based on descriptors derived from quantum chemical calculations (B3LYP/LANL2DZp), including structural aspects and model reaction energies. The results clearly show that the cryptand $[2_{Qua}.2_{Qua}.2_{Qua}]$ demonstrates the same ion selectivity as the earlier investigated cryptands $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$ and [2.2.2]. There is a clear preference for K^+ (over Rb^+) and Ba^{2+} (over Sr^{2+}). The substitution of the oxalic acid or ethyl moieties by the quadratic acid block, with its sp^2-carbon cycle, makes the cryptates $[M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m+}$ less flexible in comparison to $[M \subset 2_{Oxa}.2_{Oxa}.2_{Oxa}]^{m+}$ and $[M \subset 2.2.2]^{m+}$. To compensate for the quadratic acid-based inflexibility, the cryptand $[2_{Qua}.2_{Qua}.2_{Qua}]$ utilizes twisting the CN···NC angle to improve the coordination of guest cations and nest them in a better way in $[2_{Qua}.2_{Qua}.2_{Qua}]$.

Keywords: selective ion complexation, cryptand, DFT-study.

ORCID:
A. Khairbek - 0000-0002-0477-5896; D. Ćoćić - 0000-0002-8008-7876; T. Soldatović - 0000-0003-3010-6503; R. Puchta - 0000-0003-1370-3875; R. van Eldik - 0000-0003-4271-0118.

INTRODUCTION

One of the reasons why supramolecular chemistry is so appealing to many scientists is that it encompasses a diverse range of chemical sub-disciplines, each of which can make valuable and significant contributions. In addition, the inclusion of a variety of interaction concepts can effectively achieve new binding motifs and new properties in supramolecules.

In the year 1969, 55 years ago, Jean-Marie Lehn and his team presented the first cryptands today known as the [2.2.2] (see Fig. 1). To obtain the intriguing molecule, the researchers employed a conventional, classical organic synthesis approach (DIETRICH *et al.*, 1969a, DIETRICH *et al.*, 1969b).

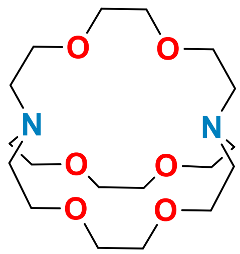
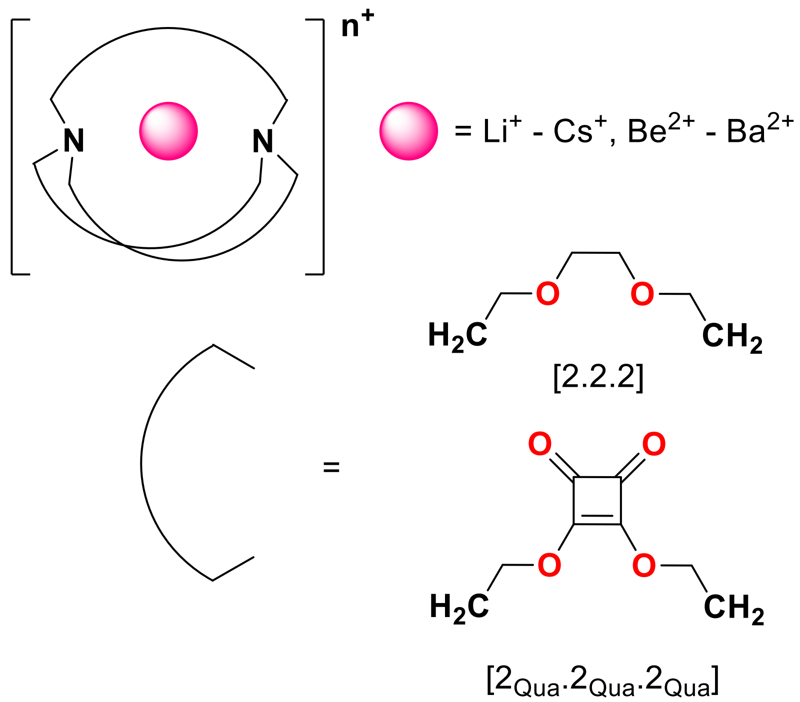


Figure 1. Lehn's original cryptand, best known by Lehn's notation [2.2.2] – system name 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

Three decades later, scientists around the world, including Prof. Rolf W. Saalfrank and his team here in Erlangen, developed the concept of metallo-topomers and established metallo-supramolecular chemistry as a consistent and logical continuation of Lehn's cryptands. While Lehn's cryptands are based on classical organic synthesis, in metallo-supramolecular chemistry the cages are constructed from ligands and metal ions and can then form themselves utilizing the lability of complex bonds for repairing and forming the most stable structure (SAALFRANK *et al.*, 2000, 2008). The field of dynamic chemistry, which is based on the concept of labile covalent bonds, is currently contributing new knowledge, as evidenced e.g. by the work of Max von Delius and his team at Ulm (SHYSHOV *et al.*, 2017 and HOLLSTEIN *et al.*, 2024).

Lehn's classic cryptand [2.2.2] is an unparalleled blueprint for cryptands with new assemblies, and analogous donor properties (two as bridgeheads and six in the bridging groups), and it will continue to inspire new developments in this field. Computational chemistry is the ideal tool for designing and evaluating already before synthesis new cryptands derived from Lehn's classic cryptand [2.2.2]. An incomplete list of systems derived from [2.2.2] is e.g. i) [bpy.bpy.bpy] (PUCHTA *et al.*, 2007) and its mixed [2.2.bpy], [2.bpy.bpy] cryptands, (BEGEL *et al.*, 2013) ii) [phen.phen.phen] and the mixed ryptands [2.2.phen], [2.phen.phen], (PUCHTA *et al.*, 2008) iii) [TriPip222] (BEGEL *et al.*, 2016), iv) [bfu.bfu.bfu] (PALMER and PUCHTA, 2020) or v) the 2.2'-bioxazole-based isomeric bicyclic Lehn-type cryptands (ĆOĆIĆ *et al.*, 2020).

Extending our research on the Lehn-type cryptands derived from [2.2.2], we present in this manuscript a quantum chemical study on the selective alkali and alkaline earth metal ion complexation by a new Lehn-type cryptand, in which the 1,2-diethoxyethane moiety is replaced by a quadratic acid ester group, resulting in [2_{Qua}.2_{Qua}.2_{Qua}]. (See Scheme 1).



Scheme 1. In this study investigated systems with the oxalic acid group and [2.2.2] as a reference.

APPLIED COMPUTATIONAL METHODS

All calculations were performed at the hybrid B3LYP (LEE *et al*., 1988; BECKE, 1993; STEPHENS *et al*., 1994). theory level in combination with the LANL2DZ (DUNNING and HAY, 1977; HAY and WADT, 1985a; HAY and WADT, 1985b; WADT *et al*., 1985;). basis set with effective core potentials, augmented with polarization functions on non-hydrogen atoms, to utilize an uniform and coherent basis set. This combination of the hybrid functional and basis set (further denoted as B3LYP/LANL2DZp), was selected since in earlier studies on selective ion complexation and related topics, we obtained results that were consistent with experimental values. The special challenge in these studies is the missing of experimental complexation energies. Comparison of published experimental values of the complex formation constant logK_S for $[M \subset 2.2.2]^{m+}$ with our gas-phase calculations showed a good correlation and predicted the correct ion selectivity on a relative scale (GALLE *et al*., 2006). The success of calculations at this level has been documented (ILLNER *et al*., 2005; SCHEURER *et al*., 2005; WEBER *et al*., 2005; PUCHTA *et al*., 2006; CAPPONI *et al*., 2024a, CAPPONI *et al*., 2024b) and additionally permits comparison of the results of the current study with our earlier work. By carrying out calculations of vibrational frequencies, all structures were characterized as minima on the potential energy surface with no imaginary frequencies. All calculations were performed without any implicit solvent model. Presented relative energies were corrected for zero-point vibrational energy. The calculations were performed using the GAUSSIAN16 suite of programs (FRISCH *et al*., 2016).

RESULTS AND DISCUSSION

Two descriptors are particularly suitable for determining the ion selectivity of different cryptands:

1. Investigation of the reaction energies of suitable model reactions.

2. Comparison of bond lengths, specifically the distances between the guest cation and the cryptand donor atoms.

This simple and straightforward approach has proven to be very useful and reliable in many of our previous studies (PUCHTA *et al*., 2019) as well as those conducted by other teams (DANKERT *et al*., 2021).

Energetic criteria

To gain insight into the complexation energies of the investigated metal cations in the [$2_{Qua}.2_{Qua}.2_{Qua}$] cryptand, we apply the simple equation 1 (n = 6):

$$[M(H_2O)_n]^{m+} + [2_{Qua}.2_{Qua}.2_{Qua}] \longrightarrow [M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m+} + n\ H_2O \qquad (1)$$

The idea is based on the solvation of the investigated ionic metal centre by a standardised first solvation shell. This reduces the complexation energy compared to pure metal ion complexation in a clear and comprehensible way without the crude approximations of an implicit solvents model. The reliability of this approach has been proven in a couple of investigations. In former studies, we showed that the selected solvent does not affect the predicted ion selectivity, only the absolute energy values change (PUCHTA *et al*., 2019). Our initial study on this topic yielded clear results that the calculated complexation energy for the [2.2.2]-cryptand aligns perfectly with the experimentally determined complexation constants, suggesting identical ion selectiveness (GALLE *et al*., 2006).

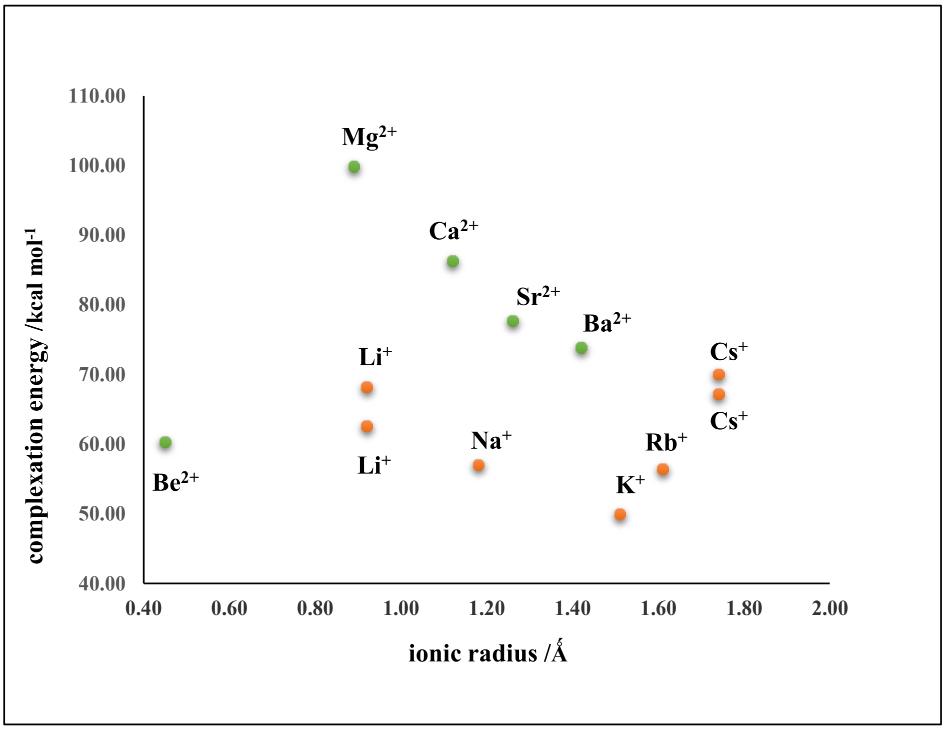
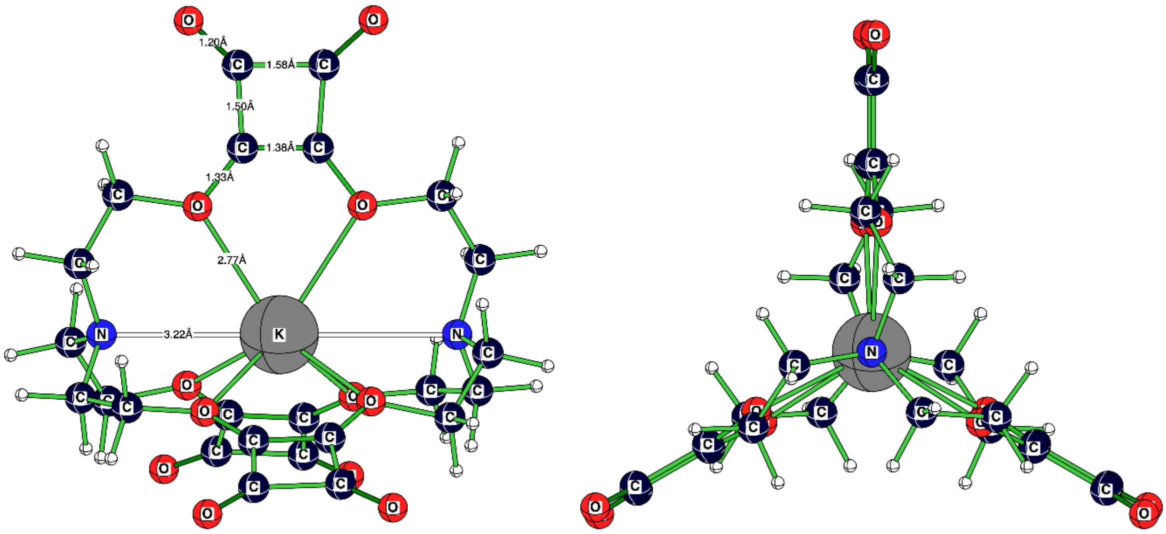


Figure 2. Calculated (RB3LYP/LANL2DZp) complexation energies of [$M \subset 2_{Qua}.2_{Qua}.2_{Qua}$]$^{m+}$ [kcal/mol] according to model reaction equations (1) in correlation with the alkaline (orange) and alkaline earth cations (green) ionic cations.

Figure 2 and Table 1 clearly show that the potassium monocation has the lowest complexation energy of all alkali metal ions (see Scheme 2). The Rb^+ ion is more than 5 kcal/mol less stable. The complexation of the Na^+ ion is only 0.5 kcal/mol less stable than Rb^+ and can therefore be most accurately described as isoenergetic to the Rb^+-cation. The alkaline earth metal ions demonstrate a clear pattern. The barium dictation is the most stable, followed by the Sr^{2+} ion. This same ion selectivity is evident in the classic Lehn cryptand [2.2.2] and in $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$.[Error! Bookmark not defined.,i] A closer look at the three systems immediately reveals that $[2_{Qua}.2_{Qua}.2_{Qua}]$ has even higher energy values than $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$. This can be seen as a first indication that the cryptand presented here could be even less flexible than $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$ due to its cyclic assembly of the square acid and the four sp^2-hybridized carbon atoms in the square of the quadratic acid.



Scheme 2. Calculated (B3LYP/LANL2DZp) structure of cryptate $[K \subset 2_{Qua}.2_{Qua}.2_{Qua}]^+$.

On examination of the structures, it would appear that the six-oxygen donor-atom-metal cation interactions are of central importance. Table 2 and Figure 3 clearly show that the O-cation distances can be interpreted simply. Cations above the bisection line are too small to fit in the cavity. This is because the reference bonds of an undisturbed reference system are shorter, which means the cation cannot stabilize itself in the cage. The ions below are too big for the cavity. The reference bonds are longer, and the cation is compressed in the cavity. Ions on the bisection line have the ideal bond length compared to the reference system $[M(H_2O)_m]^{n+}$, fitting it perfectly. It is evident that the largest cation, Cs^+, is unable to fit within the cavity due to its considerable size, as it lies below the bisection lines. Lithium, the smallest alkaline cation, shows two bond lengths. It stabilizes itself by three M-O-interactions and one M-N-interaction, sitting in one corner of the cage. One bond length is ideal, while the other Li-O distance is too long for a stabilizing interaction. The D_3 structures can be calculated as transition states, despite the local minima of $[Cs \subset 2_{Qua}.2_{Qua}.2_{Qua}]^+$ and $[Li \subset 2_{Qua}.2_{Qua}.2_{Qua}]^+$. However, analysis shows that these structures offer no useful stabilization. Sodium as well as beryllium, magnesium, calcium, and strontium are too small. The beryllium dictation is a special case, as always, it is shifted along the C_3-axis to one side, similar to the lithium cation, and stabilizes itself elegantly by a Be-N interaction and three Be-O interactions. As anticipated, the potassium and barium cations are perfectly positioned on the bisection line, with the Rb^+ cation just a short distance away. It is important to note that the next stable cations, sodium, and strontium, are significantly further away from the bisection line than the Rb-cation.

The same concept was also applicable to the metal ion bridgehead nitrogen atoms interaction (see Fig. 4). The reference complexes are the metal ions, which show a complete first coordination sphere of ammonia ligands ($[M(NH_3)_n]^{m+}$). As already addressed above (*vide supra*) we find two distances between the Be^{2+}- cation and the bridgehead N-atoms, a binding one at 1.71 Å (nearly ideal on the angle bisector) and one not interacting at 5.25 Å.

Consequently, we observe the same situation in the cryptate [Li ⊂ 2Qua.2Qua.2Qua]$^{+}$, as mentioned already while discussing the Li-O interaction. As we discussed before, the ions Li^{+} and Be^{2+} are too small to fit. Similarly, Mg^{2+}, Ca^{2+}, $Sr^{2+,}$ and Na^{+} do not fit and cannot benefit from a proper ion-nitrogen interaction because they are also above the bisection line. Special interest is given to the ions K^{+} and Ba^{2+}. According to the energetic criteria, they fit best in [2Qua.2Qua.2Qua] but do not receive good stabilization from the N-bridge head atoms. The rubidium ion is close to the bisection line and is the second best among alkaline metal ions. The last and largest ion, cesium, is close to the bisection line, whether in D_3- or C_1-symmetry.

Table 1. Calculated complexation energies [kcal mol^{-1}] (B3LYP/LANL2DZp) calculated according to equation (1) for [M ⊂ 2Qua.2Qua.2Qua]$^{m+}$ and related systems.

	Li^{+}	Na^{+}	K^{+}	Rb^{+}	Cs^{+}
Ionic radius [Å]	0.92	1.18	1.51	1.61	1.74
[2Qua.2Qua.2Qua] [kcal/mol]	62.63 (C_3)	57.08 (D_3)	50.01 (D_3)	56.46 (D_3)	67.21 (C_1)
[2Oxa.2Oxa.2Oxa]* [kcal/mol]	61.81	48.11	38.78	43.76	54.69
[2.2.2] [kcal/mol]**	4.86	24.04	-5.00	-1.22	8.26
	Be^{2+}	**Mg^{2+}**	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**
Ionic radius [Å]	0.45	0.89	1.12	1.26	1.42
[2Oxa.2Oxa.2Oxa] [kcal/mol]	60.35 (C_1)	99.92 (C_1)	86.32 (D_3)	77.74 (D_3)	73.93 (D_3)
[2Oxa.2Oxa.2Oxa]* [kcal/mol]	33.14	91.08	69.08	63.70	60.12
[2.2.2] ** [kcal/mol]	3.36	17.14	-11.48	-16.59	-20.18

Ref.** (DANKERT *et al.*, 2021) * Ref.** (CAPPONI *et al.*, 2024a) **values in brackets: Point group of the cryptate complex**

Table 2. Calculated bond length (B3LYP/LANL2DZp) of [M ⊂ 2Qua.2Qua.2Qua]$^{m+}$ and the references [M(H_2O)$_n$]$^{m+}$ and [M(NH_3)$_n$]$^{m+}$.

Ion	Point group	[M(H_2O)$_n$]$^{m+}$ d(M-O) [Å]	[M(NH_3)$_n$]$^{m+}$ d(M-N) [Å]	[M ⊂ 2Qua.2Qua.2Qua]$^{m+}$ d(M-O) [Å]	[M ⊂ 2Qua.2Qua.2Qua]$^{m+}$ d(M-N) [Å]
Li^{+}	C_3	2.11♦	2.13♦	2.03; 3.62	2.10; 4.84
Li^{+} (ts)	D_3			2.28	3.31
Na^{+}	D_3	2.40	2.67	2.63	3.35
K^{+}	D_3	2.76	3.01	2.77	3.22
Rb^{+}	D_3	2.97	3.21	2.85	3.20
Cs^{+}	C_1	3.20	3.45	3.04	3.16; 3.13
Cs^{+} (ts)	D_3			2.94	3.20
Be^{2+}	C_1	1.85♦	1.77♦	1.64; 4.06; 3.70; 4.44	1.71; 5.25
Mg^{2+}	C_1	2.10	2.29	2.22	3.17; 3.12
Ca^{2+}	D_3	2.43	2.63	2.65	2.93
Sr^{2+}	D_3	2.60	2.80	2.74	3.08
Ba^{2+}	D_3	2.80	3.00	2.82	3.12

♦: n =4 all other values n =6

These observations indicate that, for these ions, the metal ion-oxygen interaction is the determining factor. Additionally, we attribute the differences in behaviour to the lower flexibility of [2Qua.2Qua.2Qua] compared to [2.2.2] and even to [2Oxa.2Oxa.2Oxa]. The reason is that N-donors can move more easily towards the guest cation, which, in addition to the importance of the M-O interactions, affects the behaviour.

The cause of the mentioned behaviour can be identified by examination of CN···NC and O-C-C-O angles in the cryptate complexes (see Tab. 3 and Fig. 5).

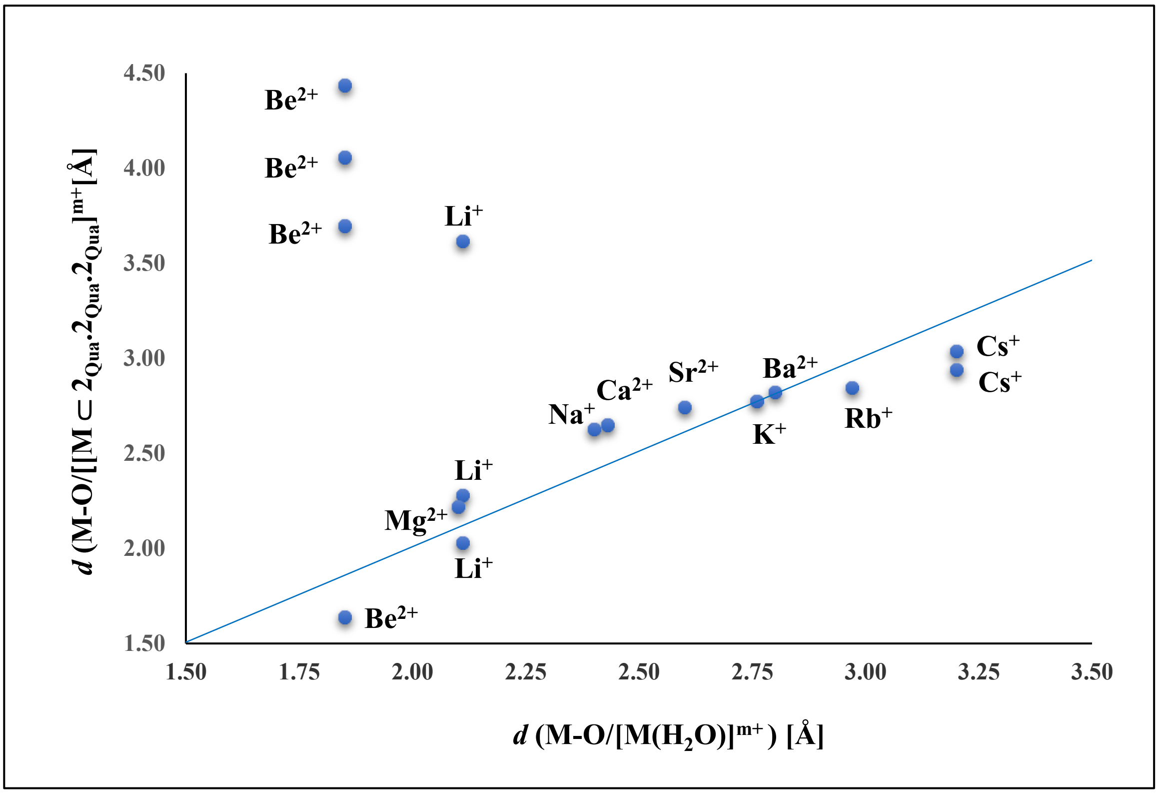


Figure 3. Comparison of the calculated M-O bond lengths [Å] in $[M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m}$ and in $[M(H_2O)_n]^{m+}$ (RB3LYP/LANL2DZp).

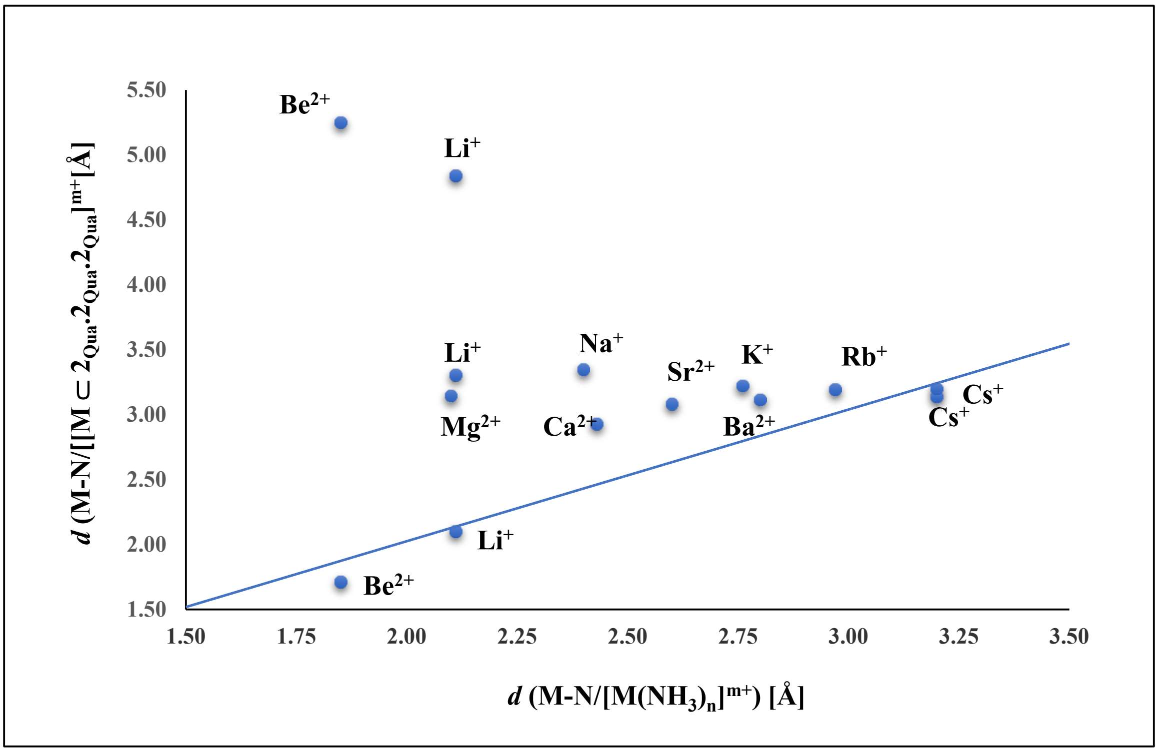


Figure 4. Comparison of the calculated M-N bond lengths [Å] in $[M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m}$ and in $[M(NH_3)_n]^{m+}$ (RB3LYP/LANL2DZp).

Table 3. Calculated dihedral angle (B3LYP/LANL2DZp) O-C-C-O and CN···NC of

[$M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m+}$.

Ion	Point group	O-C-C-O [°]	CN···NC [°]
Li^+	C_3	4.31	-20.17
Li^+ (ts)	D_3	-3.64	35.32
Na^+	D_3	2.99	-15.78
K^+	D_3	4.45	-40.50
Rb^+	D_3	6.25	-40.40
Cs^+	C_1	-0.02	-31.50
Cs^+ (ts)	D_3	9.72	-36.91
Be^{2+}	C_1	2.22; 8.85; -3.86	-20.93; -21.93; -26.40
Mg^{2+}	C_1	3.72	-43.82
Ca^{2+}	D_3	2.47	-87.24
Sr^{2+}	D_3	2.76	-57.85
Ba^{2+}	D_3	3.57	-45.57

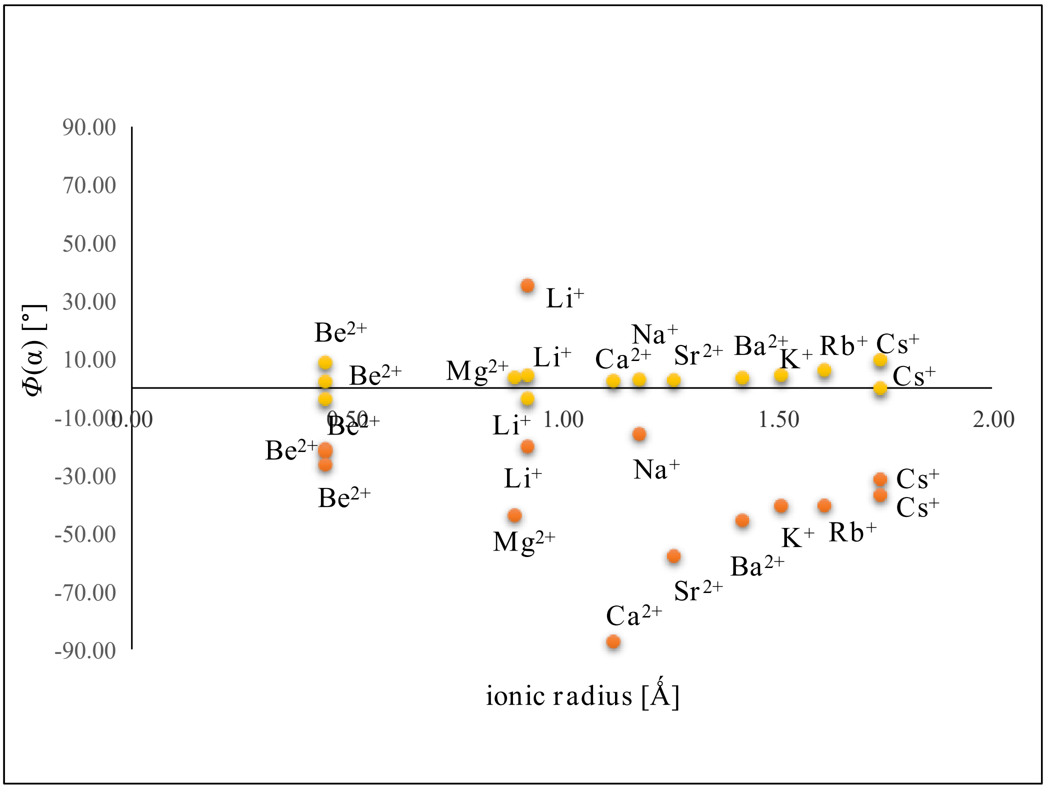


Figure 5. Calculated dihedral angles $\Phi(\alpha)$ O-C-C-O (yellow) and C-N···N-C (orange) of $[M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m+}$ plotted against the ionic radius of M^{m+} (RB3LYP/LANL2DZp).

The CN···NC angles cover a value range of more than 70°, while the OC-CO angles only cover around 10° (15%). A comparison of these values with the CN···NC angles of $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$ (a bit over 100°) and the OC-CO angles (around 70°) clearly shows that $[2_{Qua}.2_{Qua}.2_{Qua}]$ is even more inflexible than $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$. This leads to poorer adaptability to the guests and less stabilization of the guest cations, as expressed in the high energies of our model equation 1 compared to $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$ and much more [2.2.2].
The constant outlier, beryllium, was not considered because the system has already been shown to stabilize itself uniquely and independently. Even if the dihedral angles fall within the expected range, this does not affect the conclusion.

The sevenfold larger range of dihedral angles irrefutably demonstrates the superior flexibility of the CN···NC structural motif compared to the O-C-C-O moiety. This was attributed to the sp^2-hybridization of the moiety and the rectangular cyclic shape of the quadratic acid carbon core, which is inherently more rigid than other structures, dominated by sp^3-hybridization and by non-cyclic cores.

CONCLUSION

Quantum chemical studies have revealed that the cryptand system $[2_{Qua}.2_{Qua}.2_{Qua}]$ exhibits the same ion selectivity as $[2_{Oxa}.2_{Oxa}.2_{Oxa}]$ and [2.2.2], with a marked preference for K^+ (over Rb^+) and Ba^{2+} (over Sr^{2+}). The substitution of the oxalic acid or ethyl-moiety by the quadratic acid-moiety which contains sp^2-carbon cycles makes $[M \subset 2_{Qua}.2_{Qua}.2_{Qua}]^{m+}$ less flexible compared to the two previously investigated systems. This reduced flexibility results in higher relative complexation energies and necessitates the use of the CN···NC angle to enhance the coordination of guest cations in $[2_{Qua}.2_{Qua}.2_{Qua}]$.

Dedicated in memoriam to our friend and colleague **Dr. Jürgen Limmer** (05.01.1943 – 06.08.2024)

☺ for part XIX please see:
Host-guest complexes of two imine based isomeric {2}- Lehn-type cryptands: prediction of ion selectivity by quantum chemical calculations XIX
Alan Adel, Ralph Puchta, Dušan Ćoćić, Majda Kolenović Serezlić, Tanja Soldatović, Rudi van Eldik J. Coord. Chem., 2025, 78, 152 - 164.

Acknowledgments

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