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Exploring {2}-Metallacryptands and {2}-Metallacryptates with Quantum Chemical Methods – When (not only) Computer Chemists' Dreams Come True

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Abstract Semiempirical PM3 computations are reported for the {2}-gallium cryptand and {2}-gallium cryptates with three 2,6-bis(acetylaceto)pyridine ligands. Optimized "sparkles" are employed for the description of metal ion guests for which no PM3 parameters are available. Calculated structures agree well with available X-ray structures of the corresponding {2}-iron cryptates. The trend in the computed complexation energies of the guest metal ions, compared to solvent complexes, agrees with experimental findings: for experimentally known complexes, exothermic exchange is computed, while endothermic exchange is calculated for cryptates that could not be synthesized. In the case of lead, the predicted favorable cryptate formation subsequently was verified experimentally.

Keywords Supramolecular chemistry, Metallacryptates, Semiempirical calculations, Sparkles

Introduction

Selective complexation of guest molecules is an essential prerequisite for the functionality of enzymes and receptors. In order to mimic the structural and electronic requirements for such complexation, model systems with varying cavity sizes and electronic structures have been synthesized. For example, bicyclic iron cryptands and cryptates can be considered models for siderophores, Figure 1.[1]

In the last decade, quantum chemical computations have become an established method for the prediction of novel structures and properties and are now being used widely to support experimental work. As such, they could provide a powerful tool for rational design of supramolecular systems. However, in the quest for novel structures and properties, researchers still rely almost exclusively on experiment. Only a few computational publications, mainly dealing with purely organic species, have appeared to date.[2] The reason is obvious: the large size of supramolecular system is likely to make quantum chemical calculations prohibitively expensive.

Computations using semiempirical methods like AM1 [3] and PM3 [4] are fast enough to make studies of supramolecular systems feasible. However, the availability of parameters for the elements of interest is a severe limit-

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday ing factor. While these methods are known to perform well for the ”organic” elements and halogens, this is much less the case for compounds containing main group metals. The situation is even worse for the transition metals: to date, parameters are available for PM3(tm),[5] a proprietary modification of PM3, but parameterization details and validation data have not yet been published. Thus, it may seem impossible to investigate transition metal containing supramolecular complexes semiempirically. However, we will demonstrate in this contribution that PM3 calculations can be used effectively to reproduce experimental supramolecular structures, to interpret observed preferences, and to predict whether the formation of particular host-guest complexes can be expected.

As the prototype system for this study, we chose the {2}-gallium cryptand **1**, Figure 2, containing 2,6-bis(acetylaceto)pyridine ligands, analogous to the {2}-iron cryptand **2** and {2}-iron cryptates investigated previously.[6] Replacing iron (which has not yet been parameterized in PM3) by gallium (for which good semiempirical parameters are available) was motivated by the work of Raymond *et al.*,[7] who synthesized and characterized complexes of similar ligand systems, both with iron and with gallium. For those systems, they could demonstrate that the structures and, in particular, the properties relevant for this study, *e.g.*, cavity size, are essentially the same for the Fe^{3+} and Ga^{3+} host complexes. Therefore, even though a direct comparison between computed and experimental structures is not possible, – the {2}-gallium cryptand **1** and all {2}-gallium cryptates $[M\subset\mathbf{1}]^{n+}$ studied so far experimentally are insoluble, which prohibited NMR and X-ray crystallographic studies – we are confident that the conclusions from our computations on gallium complexes are also valid for the corresponding iron(III) complexes.

Two requirements must be met for a guest molecule or ion to be incorporated successfully into a host system: the guest must ”fit” into the cavity of the host molecule and a favorable, stabilizing interaction between host and guest must be possible.[8] We evaluate the first, structural criterion by comparing the computed geometries of the {2}-gallium cryptate $[M\subset\mathbf{1}]^{n+}$ with that of the ”empty” {2}-cryptand **1** and with a complex $[ML_n]^{n+}$ of the guest ion with, *e.g.*, solvent molecules like water or pyridine. For this purpose, the ion ligand interactions in the reference complex should be

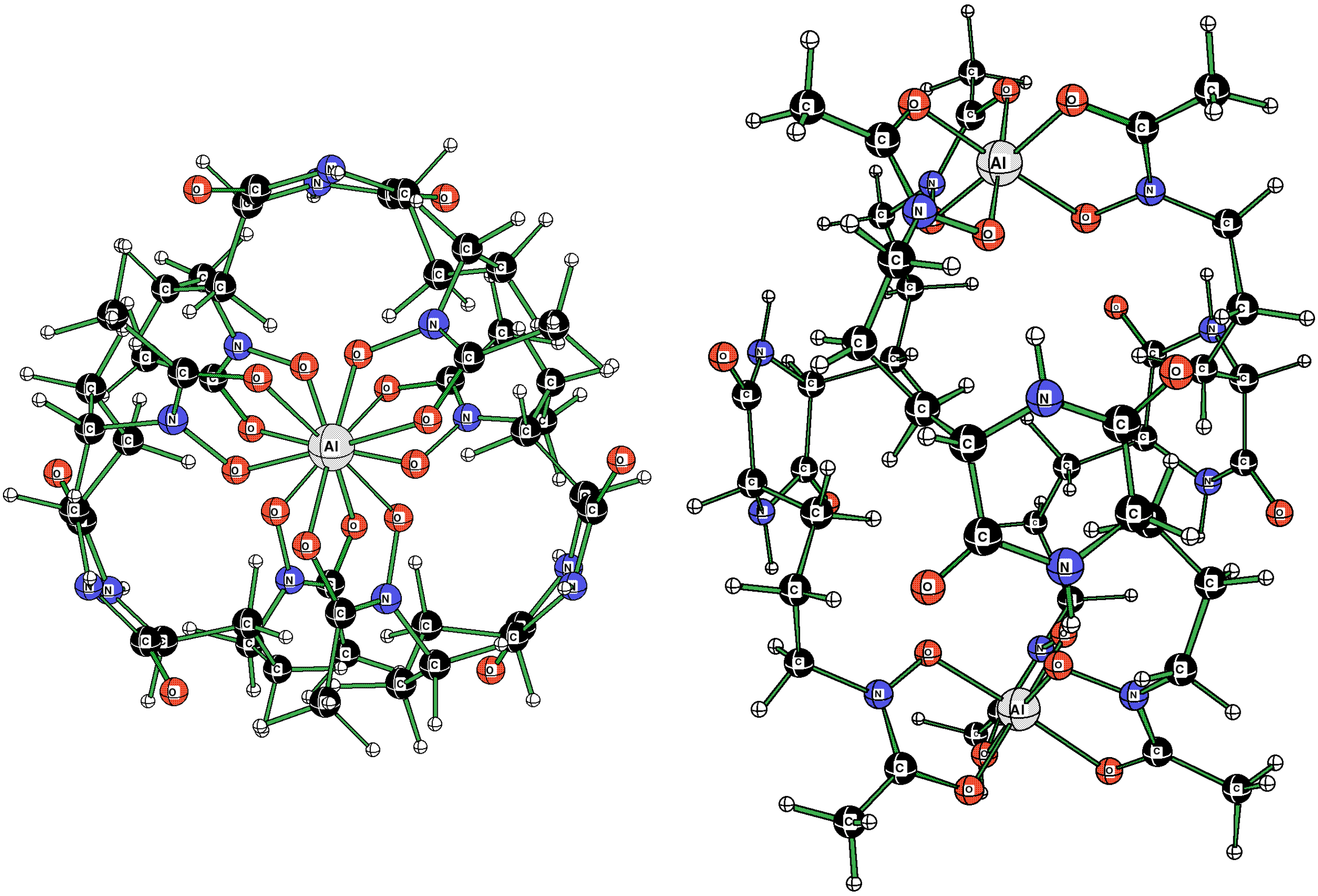


Figure 1 *PM3 calculated structure of Aluminumrhodontulate, a typical siderophore*

similar to those inside the cryptate. In addition, computed structures of experimentally known complexes were used for comparison. The degree of correspondence between computed and X-ray structures allows an assessment of the accuracy of the calculations.

Evaluation of the interaction energy by combining a metal ion M^{n+} and the {2}-gallium cryptand **1** to give the {2}-cryptate $[M\subset\mathbf{1}]^{n+}$ is not possible, since electrostatic interactions will always make this reaction strongly exothermic. Therefore, we employ the model reaction shown in Scheme 1, exchange of the guest ion between the cryptand and a suitable ligand system.

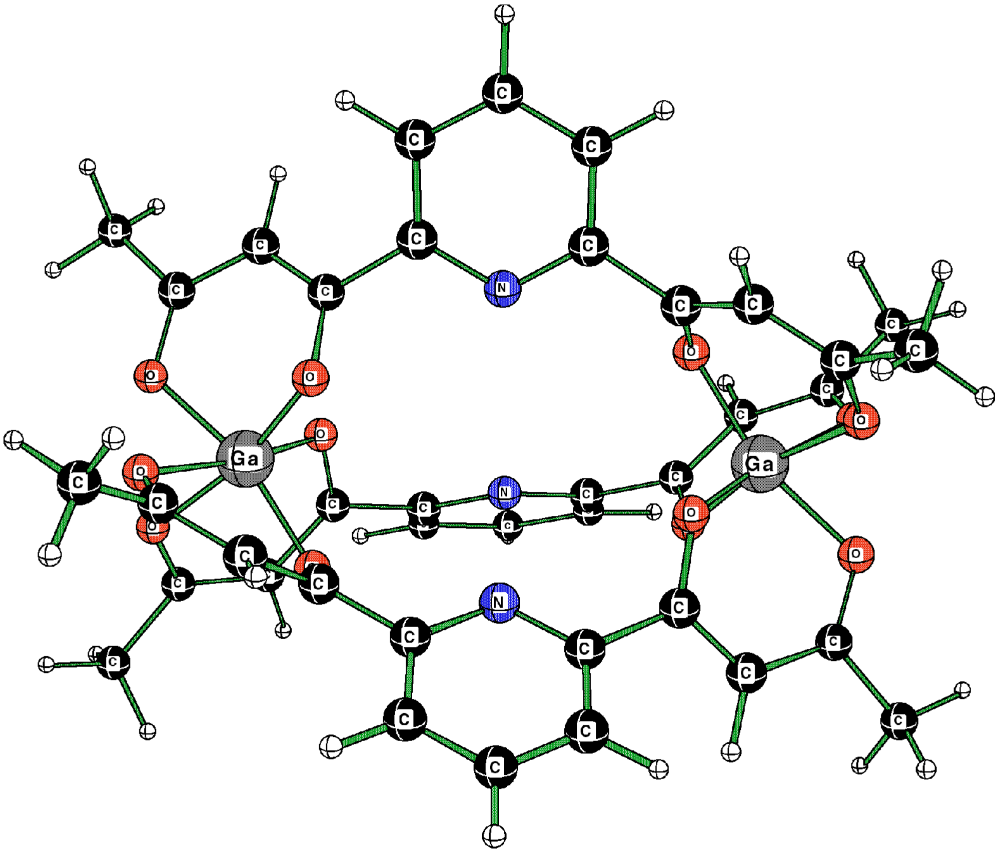
Throughout this study, we use octahedral complexes of the metal ion with six pyridine ligands [9] as reference systems. In addition, comparisons are made with experimentally known complexes of Europium and Lead.

It should be kept in mind, however, that the model reaction shown in Scheme 1, while useful to gain an impression of the relative stabilities, is unsuitable for a precise evaluation. The octahedral coordination environment in the reference complex $[M(\text{pyridine})_6]^{n+}$ might not be optimal, possible complex-solvent interactions are neglected and entropy effects (the model reaction has a significant positive entropy contribution) should be considered. Inclusion of these points is beyond the scope of the present work.

Computational details

Calculations on the {2}-gallium cryptates $[M\subset\mathbf{1}]^{n+}$ obviously require PM3 parameters for the guest metals. When we started this study, host guest complexes containing sodium, potassium, calcium, strontium, barium, cerium, and lanthanum were known experimentally. Of these, only calcium has been parameterized for PM3, while for potassium, the MNDO parameters due to Havlas [10] are available. Otherwise, PM3 parameters are available only for lithium, beryllium, and magnesium. In order to be able to model further guest ions, *e.g.*, europium, strontium or rubidium, we decided to employ ”sparkles”, charged pseudo atoms optimized for these elements following the procedure outlined by de Andrade *et al.*.[11, 12] These sparkles describe the electrostatic properties of the metal ions satisfactorily, but are unsuitable for describing covalent contributions to bonding. Comparison of the results calculated for $[M(NH_3)_6]^{n+}$ and $[M(H_2O)_6]^{n+}$ complexes, (M = alkali metal, alkaline earth metal, or lanthanide) with experimental structures and with structures computed using density functional theory (using the B3LYP [13] functional and the 6-311G* [14] and LANL2DZ,[15] augmented with polarization functions on non-hydrogen atoms,[16] basis sets) shows that the sparkle model works well.[17] In our case, the metal ions complexed inside the

Figure 2 *PM3 calculated structure of our prototype {2}gallium cryptand*



cavity interact electrostatically with the nitrogen and oxygen lone pairs, so that sparkles will adequately describe the guest ion.

Semiempirical calculations that employed sparkles were performed using the MOPAC [17] program package, version 6. For other semiempirical calculations, both the programs MOPAC-6 and VAMP [18] were used. Density functional calculations were performed with the Gaussian–98 program package.[19]

The {2}-gallium Cryptand

According to Raymond *et al.*,[5] gallium is a suitable model for iron in our complexes. How well do the calculations on {2}-gallium cryptands and cryptates agree with the corresponding iron species? Of particular importance for the present work is the size of the cavity. Unfortunately, a comparison between computed and experimental structures for the free cryptands is not possible. The {2}-iron cryptand **2** can only be synthesized in fully protonated form, *i.e.* with an H^+ on each pyridine nitrogen. The strong Coulomb interactions caused by the threefold positive charge make this species unsuitable for a detailed theory *vs.* experiment comparison.

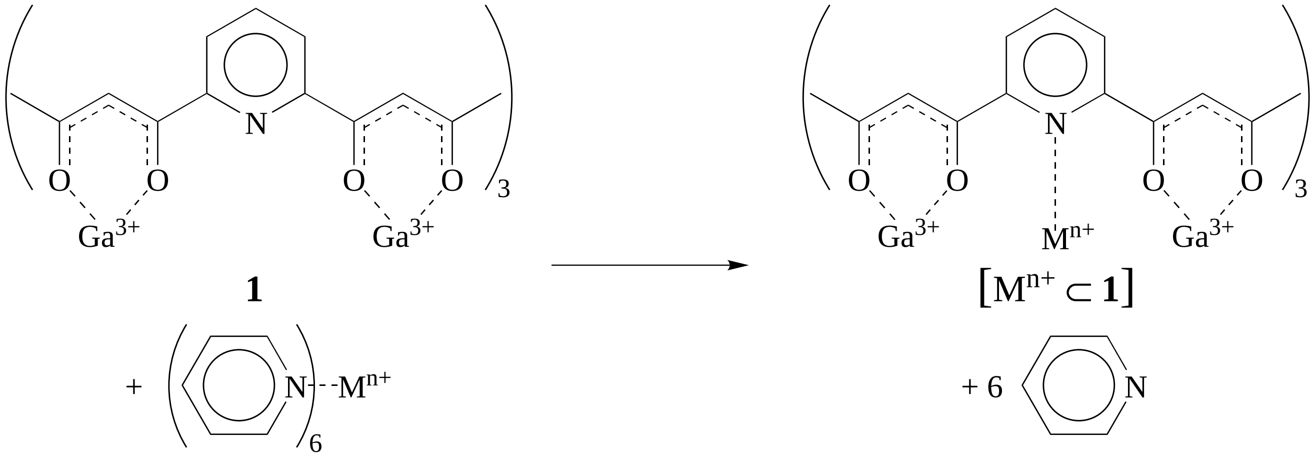
The performance of PM3 in describing organic systems is well documented.[2] What remains to be checked is the difference between calculated Ga–O and experimental Fe–O distances, since this immediately influences the cavity size. Tris(acetylacetonate) salts provide a suitable reference here. Experimental (X-ray) distances are 1.956 Å for Ga–O [20] and 1.993 Å for Fe–O.[21] DFT (B3LYP/6-311G*) calculations give values of 1.986 Å and 2.014 Å, respectively. The PM3 value for the Ga–O distance is 1.817 Å. Similar differences are seen when comparing the X-ray structures of the potassium [4] and strontium [1] {2}-iron cryptates with the computed {2}-gallium cryptates. This means that the cavity in our model {2}-gallium cryptand **1** will be somewhat too small compared to the iron species **2**.

Potassium

As the first {2}-gallium cryptate, we consider the potassium complex $[K\subset\mathbf{1}]^+$. An X-ray structure of the corresponding {2}-iron cryptate $[K\subset\mathbf{2}]^+$ is available and shows an achiral, ”paddle-wheel” form, in which the *meso*-{2}-iron cryptand has a (Δ,Λ)-*fac* coordination around iron. This contrasts with the helical, chiral X-ray structures of the free, albeit N-protonated {2}-iron cryptand and of other {2}-iron cryptates, which have (Δ,Δ)-*fac* or (Λ,Λ)-*fac* coordination around iron.[4] Our semiempirical PM3 computations on the {2}-gallium cryptate $[K\subset\mathbf{1}]^+$ reproduce the structural features of the {2}-iron cryptate $[K\subset\mathbf{2}]^+$ very well. They even confirm the preference for the *meso*-form of $[K\subset\mathbf{1}]^+$ over the helical form, although we consider the energy difference of less that 1 kcal mol^{-1} too low to allow conclusions to be drawn.

The computed potassium-nitrogen and potassium-oxygen distances compare relatively well with those calculated for the complexes of a potassium cation with six pyridine or water ligands. With 2.84 Å, the K–O distance in $[K\subset\mathbf{1}]^+$ is 0.15 Å longer than in the hexaaquo complex. In line with what is expected on the basis of the cryptand structure (*vide supra*), the K–N distance of 2.67 Å is 0.06 Å shorter than in the potassium hexapyridine complex.

The stability of the potassium {2}-gallium cryptate $[K\subset\mathbf{1}]^+$ can be evaluated by applying the model reaction shown in Scheme 1, in which $[K(pyridine)_6]^+$ and **1** react to give $[K\subset\mathbf{1}]^+$ and 6 molecules of pyridine. With –43 kcal mol^{-1}, this reaction is computed to be clearly exothermic.



Scheme 1 *Model reaction for the evaluation of the guest ion exchange energy*

Ammonium

The ammonium cation is generally considered to exhibit similar chemical behavior to potassium or rubidium cations. Enthalpies of hydration are comparable and the ionic radii are similar (K^+: 1.33 Å, NH_4^+: 1.43 Å, Rb^+: 1.48 Å).[22] Based on these similarities, we had expected that inclusion of the ammonium cation in our {2}-iron cryptand **2** would be possible, but hitherto, the ammonium {2}-iron cryptate $[NH_4\subset\mathbf{2}]^+$ could not be realized experimentally.

Our computational results are completely in line with this experimental failure. Despite the expected energetically favorable electrostatic interaction between the guest ion and the cryptand host, the reaction enthalpy for the formation of $[NH_4\subset\mathbf{1}]^+$ from **1** and an ammonium cation is computed to be endothermic by no less than 72 kcal mol^{-1}. The calculated structure indicates the reason: while the spherical potassium cation experiences nine-fold coordination in $[K\subset\mathbf{1}]^+$, the tetrahedral ammonium cation can be bound only through four hydrogen bonds.[23]

Rubidium

Despite numerous attempts, we were unable to incorporate a rubidium cation in our {2}-iron cryptand **2**. This failure surprised us, since potassium and rubidium cations have very similar coordination properties and several examples of supramolecular complexes, *e.g.*, in bicyclic cryptands, are known for both metals.[24]

However, the results of our PM3 computations (employing a sparkle to model Rb^+) indicate that the rubidium cation does not fit into our host complex **1**. Comparison of the Rb–O and Rb–N distances computed for the bicyclic rubidium cryptate complex published in 1988 by Haushalter *et al.* [25] with those in $[Rb\subset\mathbf{1}]^+$ clearly shows that the cavity in **1** is too small. In $[Rb\subset\mathbf{1}]^+$, the Rb–O and Rb–N distances are 0.09 Å and 0.30 Å shorter, respectively. Even more impressive are the differences with the solvent complexes: the Rb–O distance in $[Rb(H_2O)_6]^+$ is 0.31 Å longer, the Rb–N distance in $[Rb(pyridine)_6]^+$ is no less than 0.52 Å longer than in $[Rb\subset\mathbf{1}]^+$.

The model reaction of $[Rb(pyridine)_6]^+$ with **1** to give $[Rb\subset\mathbf{1}]^+$ and 6 pyridine underlines the conclusion based on structural arguments: we compute the reaction to be endothermic by 56 kcal mol^{-1}, *i.e.*, almost 100 kcal mol^{-1} less favorable than in the case of potassium.

Calcium and strontium

Compared to the alkali metals, the alkaline earth metals have smaller ionic radii. Thus, while potassium appears to constitute the upper size limit for inclusion of an alkali metal into the host complex **1**, incorporating the smaller alkaline earth metals should be no problem. Indeed, mass spectrometry and elementary analysis proved the formation of the calcium {2}-iron cryptate complex $[Ca\subset\mathbf{2}]^{2+}$. For the corresponding strontium {2}-iron cryptate $[Sr\subset\mathbf{2}]^{2+}$, an X-ray structure is available.

For $[Ca\subset\mathbf{1}]^{2+}$, we compute a structure with Ca–O distances of 2.52 Å and Ca–N distances of 2.60 Å. For comparison, the corresponding distances in the solvent complexes are 2.42 Å in the calcium hexaaquo complex and 2.55 Å in $[Ca(pyridine)_6]^{2+}$. These values, as well as the computed reaction enthalpy of –44 kcal mol^{-1} for the formation of $[Ca\subset\mathbf{1}]^{2+}$ and 6 pyridine from $[Ca(pyridine)_6]^{2+}$ and **1**, are in nice agreement with the experimental results: the calcium dication is a very suitable guest for our host complex.

The same picture is seen for the strontium {2}-gallium cryptate $[Sr\subset\mathbf{1}]^{2+}$, in which the strontium dication again is modeled by a sparkle. The computed Sr–O distances of 2.62 Å are 0.06 Å longer than in the hexaaquo complex, $[Sr(H_2O)_6]^{2+}$, while the Sr–N distance, 2.55 Å, is only 0.02 Å shorter than in the hexapyridine complex, $[Sr(pyridine)_6]^{2+}$. The model reaction for the formation of $[Sr\subset\mathbf{1}]^{2+}$ is exothermic by –37 kcal mol^{-1}. Again, our PM3 computations on the model {2}-gallium cryptates are completely in line with the experimental findings.

Europium

After potassium and strontium could be successfully incorporated in our {2}-iron cryptand **2**, the question arose whether it would be possible to prepare {2}-iron cryptates containing lanthanide ions. So far, this has only been possible for cryptates containing lanthanum and cerium.

Semiempirical treatment of lanthanides is presently limited to the europium trication, which is described by the sparkle developed by de Andrade *et al.* Comparison of the computed structure for $[Eu\subset\mathbf{1}]^{3+}$ with those for the solvent complexes $[Eu(H_2O)_6]^{3+}$ and $[Eu(pyridine)_6]^{3+}$ shows that behavior of europium differs from that of the main group metal cations discussed above. In the latter, the metal nitrogen distance is generally shorter and stronger than the metal oxygen distance. In the europium cryptate, we see the opposite. The Eu–O distance in the {2}-gallium cryptate complex, 2.41 Å, is essentially the same as in the hexaaquo complex, but the Eu–N distance in $[Eu\subset\mathbf{1}]^{3+}$, 2.51 Å, is significantly longer than the values of 2.25 Å computed for the hexapyridine complex and 2.30 Å calculated for $[Eu(NH_3)_6]^{3+}$.

The consequences of the apparently non ideal coordination of Eu^{3+} for the stability of $[Eu\subset\mathbf{1}]^{3+}$ are seen when evaluating the model reaction for exchange of Eu^{3+} between $[Eu\subset\mathbf{1}]^{3+}$ and $[Eu(pyridine)_6]^{3+}$: formation of $[Eu\subset\mathbf{1}]^{3+}$ is computed to be 18 kcal mol^{-1} endothermic. Alternatively, one might compare $[Eu\subset\mathbf{1}]^{3+}$ with the complex [Eu⊂6,6’,6”,6’”,6””,6’”””-bis(nitrilotri(methylene))tris(2,2’-bipyridine)$]^{3+}$ described in 1988 by Rodriguez-Urbis *et al.*:[26] in this case, the Eu^{3+} exchange to give $[Eu\subset\mathbf{1}]^{3+}$ is computed to be 34 kcal mol^{-1} endothermic. In the light of these values, we are not surprised that attempts to prepare $[Eu\subset\mathbf{2}]^{3+}$ were not successful.

Lead

In all cases described so far, PM3 calculations agreed with experimental findings: reasonable structures and exothermic ion exchange were computed when the corresponding {2}-iron cryptates were known experimentally, whereas poor structures and endothermic exchange resulted in the ”unknown” cases. In order to test the potential of our approach, we now consider two new cases, which had not yet been explored experimentally.

The first example involves the lead dication. On the basis of the ionic radius and coordination chemistry, which is similar to that of the alkali and alkaline earth metals, Pb^{2+} appeared to be a suitable candidate. The calculated structure of $[Pb\subset\mathbf{1}]^{2+}$ is in agreement with this expectation, although (*vide supra*) the cavity appears to be somewhat small: the Pb–N distance of 2.64 Å is 0.11 Å shorter than the distance in $[Pb(pyridine)_6]^{2+}$ and 0.04 Å shorter than in $[Pb(NH_3)_6]^{2+}$; the Pb-O distance, 2.85 Å, is 0.09 Å longer than in the hexaaquo complex.

The energy computed for the model reaction of **1** with $[Pb(pyridine)_6]^{2+}$ to give $[Pb\subset\mathbf{1}]^{2+}$ and 6 pyridine is mildly endothermic, 4 kcal mol^{-1}. On the other hand, in the comparison between $[Pb\subset\mathbf{1}]^{2+}$ and the known complex $[Pb\subset N(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)_3N]^{2+}$,[27] our lead {2}-gallium cryptate is computed to be favored by 14 kcal mol^{-1}. Hence, the conclusion seemed justified that Pb^{2+} might be a suitable guest ion for the {2}-iron cryptand, albeit less favored than the calcium and strontium. Subsequent experiments indeed verify this: the incorporation of the lead dication into the {2}-iron cryptand **2** was confirmed by elementary analysis, infrared and mass spectrometry.[28]

Bismuth

The bismuth trication comprises our second ”test case”. The ionic radius of Bi^{3+} is similar to that of Ca^{2+}, so that the bismuth trication can be expected to fit into our host system. Suitable reference systems, like $[Bi(H_2O)_9]^{3+}$, are known experimentally. [29]

However, the PM3 parameters for bismuth [2] were derived using a very small set of only three reference compounds, none of which contained oxygen. We therefore checked the performance of these parameters in describing metal ligand interactions by comparing the results for complexes with ammonia and water with values from DFT calculations (B3LYP/LANL2DZ with polarization functions on non-hydrogen atoms). The Bi–N interaction appears to be described reasonably well, whereas the Bi–O interaction is treated poorly. Two of the reference systems used in this study illustrate this. The PM3 value of 2.60 Å for the Bi–N distance in $[Bi(NH_3)_6]^{3+}$ agrees very well with the DFT value of 2.59 Å. For $[Bi(H_2O)_6]^{3+}$, however, PM3 gives a very irregular structure with Bi–O distances ranging from 2.11 to 3.02 Å. The DFT value is 2.40 Å, while the experimental distance range, 2.45 to 2.58 Å, determined for $[Bi(H_2O)_9]^{3+}$,[27] is in line with the DFT value.

Nevertheless, the structure computed for $[Bi\subset\mathbf{1}]^{3+}$ appears quite reasonable: the computed Bi–N distance of 2.39 Å compares well with the value of 2.30 Å found for four of the Bi–N bonds in $[Bi(pyridine)_6]^{3+}$ (two pyridines appear to be hardly bound, Bi–N distances are 2.78 Å for those ligands). The Bi–O distances of 2.93 Å appear relatively long. Energetic evaluation, using the Bi^{3+} exchange with $[Bi(pyridine)_6]^{3+}$ model reaction, favors $[Bi\subset\mathbf{1}]^{3+}$ by 19 kcal mol^{-1}. Therefore, even though the quality of the bismuth PM3 parameters appears to be far from optimal, we are inclined to conclude from our computations that Bi^{3+}, too, might be a reasonable guest ion for our {2}-iron cryptand host system. Experiments to prepare the bismuth {2}-iron cryptate $[Bi\subset\mathbf{2}]^{3+}$ are underway.

Conclusions

This work demonstrates that semiempirical PM3 calculations are suitable for the investigation of metal-containing supramolecular systems. For the compounds considered here, our PM3 results are in agreement with experimental experience: known cryptates are indicated to be favorable, while poor structures and unfavorable energetics are computed in cases where attempts to prepare the cryptates have failed. More important, our computations predicted the lead cryptate to be a viable compound; it could subsequently be synthesized.

We are extending this work to other, related metallacryptand and metallacryptate systems. Development of sparkles for further ions is in progress.

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Supplementary material 3D representation of all computed species are available in VRML format.

References

1. Saalfrank, R. W.; Seitz, V.; Caulder, D. L.; Raymond, K. N.; Teichert, M.; Stalke, D. *Eur. J. Inorg. Chem.* **1998**, *1*, 1313 and literature cited therein.
2. *Cf., e.g.,* a) Castro, R.; Berardi, M. J.; Córdova, E.; de Olza, M. O.; Kaifer, A. E.; Evanseck, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 10257. b) Rauwolf, C.; Straßner, T. *J. Mol. Model.* **1997**, *3*, 1.

3. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
4. (a) Stewart, J. J. P. *J. Comput. Chem.*, **1989**, *10*, 209. b) Stewart, J. J. P. *J. Comput. Chem.*, **1991**, *12*, 320.
5. (a) Spartan, version 4.1: Wavefunction, inc., 18401 Von Karman Ave., #370, Irvine, CA 92715, U.S.A. (b) For an evaluation of the PM3(tm) method, see: Børve, K. J.; Jensen, V. R.; Karlsen, T.; Stovneng, J. A.; Swang, O. *J. Mol. Model.* **1997**, *3*, 193.
6. Saalfrank, R. W.; Dresel, A.; Seitz, V.; Trummer, S.; Hampel, F.; Teichert, M.; Stalke, D.; Stadler, Ch.; Daub, J.; Schünemann, V.; Trautwein, A. X. *Chem. Eur. J.* **1997**, *3*, 2058.
7. *Cf., e.g.*, Caulder, D. L.; Raymond, K. N. *Angew. Chem.* **1997**, *109*, 1508.
8. (a) Vögtle, F. *Supramolecular Chemistry: An introduction*; Wiley & Sons: New York, 1993. (b) Schneider, H.-J.; Dürr, H.; eds. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Verlag Chemie: Weinheim, 1991. (c) Lehn, J.-M. *Supramolecular Chemistry*; Verlag Chemie: Weinheim, 1995. (d) Atwood, J. L.; Davies, J. E. D.; Macnical, D. D.; Vögtle, F.; Lehn, J.-M. eds. *Comprehensive Supramolecular Chemistry*, 1st ed; Pergamon Press: Oxford, 1996, especially Volume 1: Gokel, G. W., Ed. *Molecular Recognition: receptors for Cationic Guests* and Volume 9: Sauvage, J.-P.; Hosseini, M. W., eds. *Templating, Self-Assembly and Self-Organization*.
9. For $[Na(Pyridine)_6]^+$, crystal structures are available: Xie, X.; McCarley, R. E.; *Inorg.Chem.* **1996**, *35*, 2713. Xie, X.; McCarley, R. E.; *Inorg.Chem.* **1997**, *36*, 4665.
10. Havlas, Z.; Nick, S.; Bock, H. *Int. J. Quantum Chem.* **1992**, *44*, 449.
11. de Andrade, A. V. M.; da Costa, N. B. , Jr.; Simas, A. M.; de Sa, G. F. *Chem. Phys. Lett.* **1994**, *227*, 349.
12. Puchta, R.; van Eikema Hommes, N. J. R., in preparation.
13. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch M. J. *J. Phys. Chem.* **1994**, *98*, 11623 and references cited therein.
14. (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (c) Wachters, A. J. H. *J. Chem. Phys.*, **1970**, *52*, 1033. (d) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377. (e) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062. (f) Binning, R. C. , Jr.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206. (g) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104. (h) McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, *94*, 511.
15. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284, 299.
16. Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.
17. MOPAC 6.0; Stewart, J. J. P. *QCPE 455*.
18. VAMP, Version 7; Clark, T.; Alex, A.; Beck, B.; Chandrasekhar, J.; Gedeck, P.; Horn, A.; Hutter, M.; Rauhut, G.; Sauer, W.; Steinke, T., Erlangen, **1999**.
19. Gaussian 98, Revision A.5: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. , Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, **1998**.
20. Dymock, K.; Palenik, G. J. *Acta Crystallog. B.* **1974**, *30*, 1364.
21. Iball, J.; Morgan, C. H. *Acta Crystallog.* **1967**, *23*, 239.
22. Hollemann, A. F.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*; Walter de Gruyter: Berlin, 1985, p. 949.
23. Chin, J.; Walsdorff, Ch.; Stranix, B.; Oh, J.; Chung, H. J.; Park, S.-M.; Kim, K. *Angew. Chem.* **1999**, *111*, 2923.
24. Lehn, J.-M. *Angew. Chem.* **1988**, *100*, 92.
25. Haushalter, R. C. *J. Chem. Soc., Chem. Comm.* **1988**, 1027.
26. Rodriguez-Urbis, J. -C.; Alpha, B.; Plancherel, D.; Lehn., J.-M. *Helv. Chem. Acta.* **1994**, *67*, 2264.
27. Martin, N.; McKee, V.; Nelson, J. *Inorg. Chim. Acta* **1994**, *218*, 5.
28. Seitz, V.; Saalfrank, R. W. in preparation.
29. Frank, W.; Reiß, G. J.; Schneider, J. *Angew. Chem.* **1995**, *107*, 2573.