

Metallacycles

Supramolecular Metallacycles and Their Binding of Fullerenes

Christian R. Göb,^[a] Andreas Ehnbom,^[b] Lisa Sturm,^[a] Yoshito Tobe,^[c] and Iris M. Oppel*^[a]

Abstract: The synthesis of a new triaminoguanidinium-based ligand with three *tris*-chelating [NNO]-binding pockets and C_3 symmetry is described. The reaction of *tris*-(2-pyridinylene-*N*-oxide)triaminoguanidinium salts with zinc(II) formate leads to the formation of cyclic supramolecular coordination

compounds which in solution bind fullerenes in their spherical cavities. The rapid encapsulation of C_{60} can be observed by NMR spectroscopy and single-crystal X-ray diffraction and is verified using computation.

Introduction

The development of supramolecular coordination compounds and their corresponding cages has attracted wide interest in recent years.^[1] They have the potential to transport chemicals from one location to another in a specific manner, for example, being used in drug delivery or as contrast agents.^[2] The structural design of these containers requires precise and complementary building blocks but they are not limited to the incorporation of small organic molecules.^[3] There are only a few examples of toroid coordination compounds and larger aggregates in the literature (Figure 1 A).^[4] Those compounds can be used as single molecular magnets or in the separation of fullerenes.^[5] Stang introduced the concept of using building blocks to form cage compounds,^[6] whereas the groups of Saalfrank, Fujita, and Nitschke used cages to stabilize reactive species like white phosphorous P_4 and organometallic complexes.^[6b,7]

Toroids can be useful in binding guest molecules. Covalently bonded systems are quite common, for example, cyclodextrins, cucurbiturils and cryptands which bind cations,^[8] anions,^[9] or hydrophobic molecules^[10] by variation of their peripheral deco-

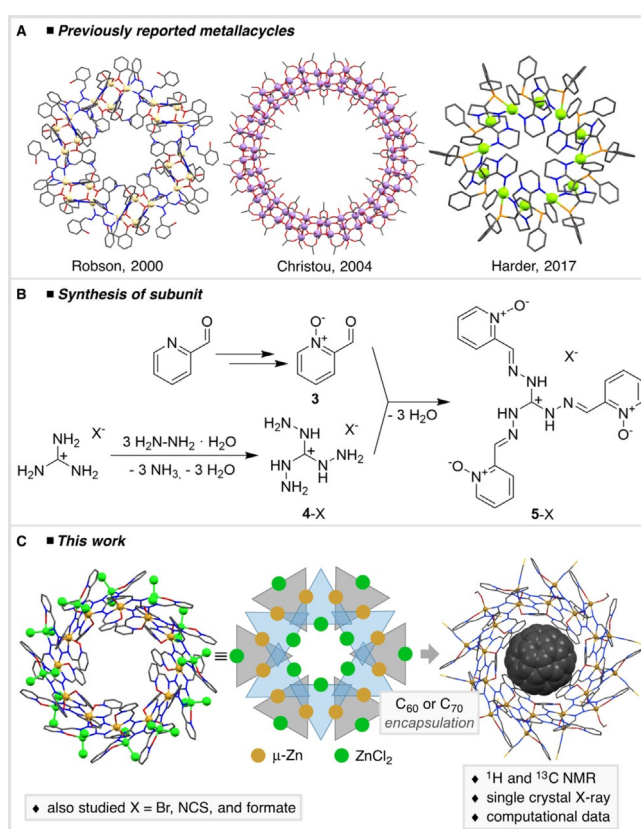


Figure 1. (a) Previously reported supramolecular metallacycles. Hydrogen atoms and solvent molecules were omitted for clarity. Different scales were applied and metal ions highlighted as spheres. (b) Synthesis of the ligands $[\text{H}_3(\text{pyO})_3\text{L}]\text{X}$ (5-X), (X = Cl^- , NCS^- , BF_4^-). (c) Supramolecular metallacycle $[\text{Zn}_{24}\text{Cl}_{24}\{\text{(pyO)}_3\text{L}\}_{12}]$ (ZnCl₂ in green), schematic drawing and inclusion complex $\text{C}_{60}\text{C}9$.

ration. Toroidal coordination cages are also able to bind guest molecules and separate fullerenes.^[11]

These systems are challenging to model using density functional theory (DFT) due to their large size. Herein we demonstrate not only that a geometry-optimized structure of a large empty metallacycle can be obtained, but also the C_{60} and C_{70}

[a] Dr. C. R. Göb, L. Sturm, Prof. Dr. I. M. Oppel
Institute of Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: iris.oppel@ac.rwth-aachen.de

[b] A. Ehnbom
Department of Chemistry, Texas A&M University
P.O. Box 30012, College Station, TX 77843-3012 (USA)

[c] Prof. Dr. Y. Tobe
Division of Frontier Materials Science
Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka 560-8531 (Japan)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/chem.201905390>.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

encapsulated supramolecular entity. We were able to compute spectroscopic properties and assign the C_{60} signals in both the free state and bound inside of the metallacycle (Figure 1C). There are a large number of studies reporting the computations of C_{60} itself. However, publications focusing on the interaction of C_{60} with other macrocycles are limited. Most studies including these interactions involve smaller, and often purely organic macrocyclic systems.^[12] To the best of our knowledge, this is the first study to computationally investigate such large interacting systems (>4000 electrons) using non-truncated models.

Results and Discussion

Our group demonstrated the synthesis of supramolecular structures by self-assembly of C_3 -symmetric building blocks with three *tris*-chelating binding pockets and suitable co-ligands (analogous to Figure 1B).^[13] Counter ions or solvent molecules typically serve as templates in the synthesis, so that discrete coordination cages like $M_{12}L_4$ (Figure 2, left), $M_{18}L_6$, or $M_{24}L_8$ are accessible.^[13d] We did not observe any activation of small molecules with these assemblies, even though a high number of potential catalytically active metal centers are located proximal to each other.

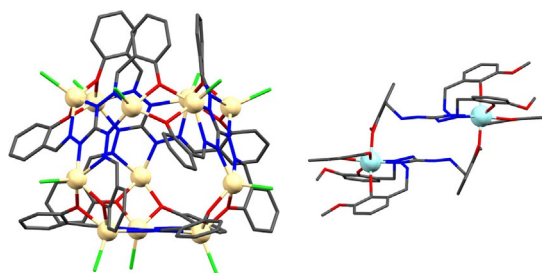


Figure 2. $M_{12}L_4$ tetrahedron and M_2L_2 dimer ($M = \text{Cd}, \text{Sn}$, respectively). Hydrogen atoms and solvent molecules were omitted for clarity.^[14,13a]

The overall negative charge of these complexes might be the reason why substrates like lactide are not satisfyingly activated. It was thus necessary to increase the amount of positive charges of the resulting coordination compounds by using stronger Lewis acids, such as Sn^{IV} or Zr^{IV} , instead of Cd^{II} or Pd^{II} .^[14] The resulting complexes typically form dimers or trimers and are able to oligomerize acetone in up to 15 repeating units (Figure 2, right).^[13d,15]

In this work we address the charge issue by increasing the number of positive charges in the ligand itself, while maintaining the isoelectronic structure of the previously reported ligands. The ligand is prepared from a condensation reaction between 2-formylpyridine-*N*-oxide and the corresponding triaminoguanidinium salts TAG-Cl (**4-Cl**), TAG-NCS (**4-NCS**), or TAG- BF_4 (**4-BF₄**), respectively (Figure 1B).

The synthesis of *N*-oxide (**3**) requires standard protection and deprotection procedures for the aldehyde moiety. The oxidation of the pyridine nitrogen can be realized under mild conditions by using urea hydrogen peroxide with phthalic an-

hydride in acetonitrile.^[16] Triaminoguanidinium salts (**4-X**) are obtained by the amination of guanidinium salts with hydrazine hydrate.^[17] The resulting compounds (**5-X**) serve as an excellent ligands for Zn^{II} . The reaction of $[\text{H}_3(\text{pyO})_3\text{L}]\text{Cl}$ (**5-Cl**) with $\text{Zn}(\text{O}_2\text{CH})_2$ in *N,N*-dimethylformamide results in the formation of a supramolecular coordination compound $[\text{Zn}_{24}\text{Cl}_{24}\{(\text{pyO})_3\text{L}\}_{12}]$ (**6**, Figure 1C) next to a coordination polymer of unknown composition. This torus-shaped metallacycle exhibits an outer diameter of 31.7 Å and Zn^{II} ions are octahedrally coordinated between two alternately oriented ligands holding together the assembly (Figure 3 and Figure 4, left). The ZnCl_2 moieties occupy the remaining [NNO] binding pockets. A spherical cavity of 10.7 Å can be found inside the complex with a pore opening of 8.2 Å. Each value is corrected by the covalent radii of hydrogen or carbon atoms.

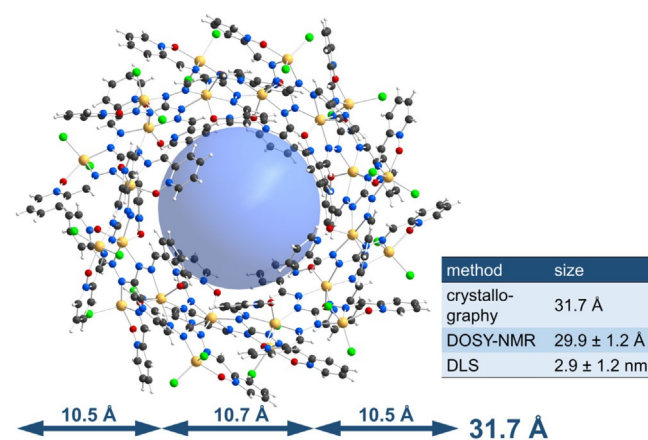


Figure 3. Molecular dimensions of metallacycles by X-ray diffraction compared to spectroscopic data of **7**. The void space is indicated by the blue sphere.

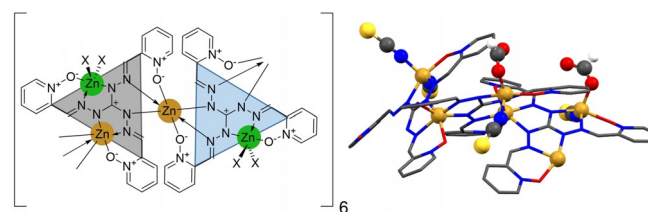


Figure 4. Schematic representation of metallacycles ($X = \text{Cl}, \text{Br}, \text{NCS}, \text{O}_2\text{CH}$) and asymmetric unit of $[\text{Zn}_{24}(\text{NCS})_{16}(\text{O}_2\text{CH})_6\{(\text{pyO})_3\text{L}\}_{12}]_6$ **8**. Disordered solvent molecules were removed by the Squeeze routine (Platon) and hydrogen atoms were omitted for clarity.^[18]

An isostructural cyclic coordination oligomer $[\text{Zn}_{24}\text{Br}_{24}\{(\text{pyO})_3\text{L}\}_{12}]$ (**7**) can be crystallized from the reaction mixture containing $[\text{H}_3(\text{pyO})_3\text{L}]\text{BF}_4$, ZnBr_2 and NaO_2CH . DOSY-NMR spectroscopy ($[\text{D}_6]\text{DMSO}$) of **7** shows neither decomposition nor aggregation of the coordination complex in solution. Only one species is detected in addition to solvents and water. The diffusion coefficient of **7** is found to be $D = (7.36 \pm 0.08) \times 10^7 \text{ cm}^2 \text{ s}^{-1}$. The hydrodynamic diameter of **7** can be determined to be $29.9 \pm 1.2 \text{ Å}$ using the Stokes–Einstein equation,

which corresponds well with the observed diameter of the crystal structure (Supporting Information Figure S5 and S6).

Introduction of isothiocyanate leads to the formation of the analogous NCS-metallacycle $[\text{Zn}_{24}(\text{NCS})_{16}(\text{O}_2\text{CH})_8\{\text{(pyO)}_3\text{L}\}_{12}]$ (**8**) with a 59% yield. The zinc(II) ions, which were formally occupied by the halides Cl^- or Br^- , share those sites with isothiocyanate and formate co-ligands (Figure 4, right). The presence of this coordination compound, and the absence of smaller or larger aggregates in the DMSO solution, was confirmed by dynamic light scattering (Supporting Information). Since the co-ligands point outwards and exhibit a slightly increased steric demand, the system crystallizes in the tetragonal space group $P4_21c$ with solvent filled channels along the crystallographic c -axis (Figure 5 a). Host-guest chemistry seems feasible since the cavities of the coordination oligomers should be accessible in the solid state. To our surprise, it was not possible to soak crystals of $[\text{Zn}_{24}(\text{NCS})_{16}(\text{O}_2\text{CH})_8\{\text{(pyO)}_3\text{L}\}_{12}]$ (**8**) with a toluene solution of C_{60} , as there was no observed color change.^[19]

From these experimental results we decided to encapsulate the fullerenes into the metallacycles in solution. A solution of empty metallacycle (**8**) was added to a toluene solution of C_{60} or C_{70} . Single crystals of the respective inclusion compounds were collected after a few days (Figure 5 b–d). The C_{60} and C_{70} are fully incorporated into the cavity of the metallacycle

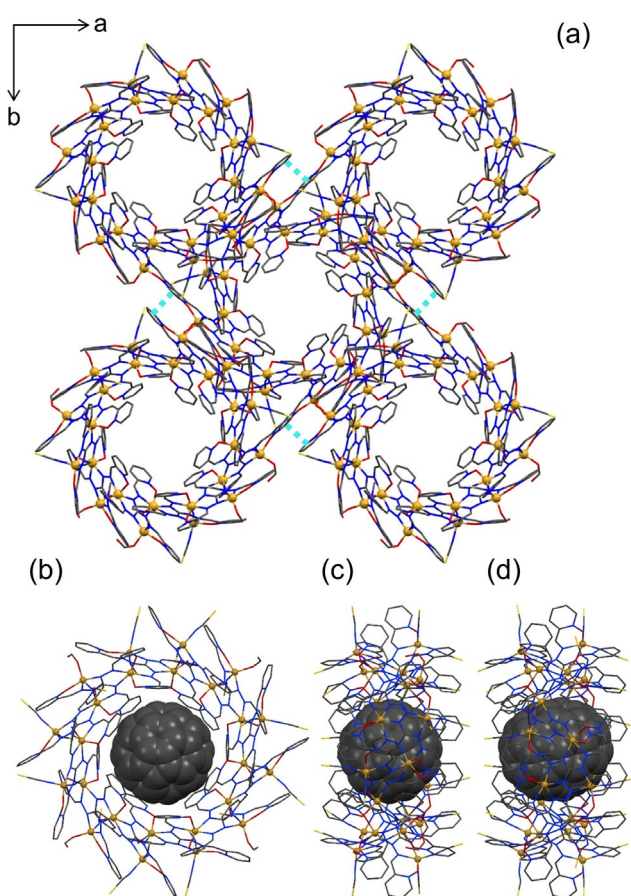


Figure 5. (a) Crystal packing of **8**, π - π -interactions are highlighted in turquoise. (b,c) C_{60}C_9 , (d) C_{70}C_9 . Disordered solvent molecules were removed by the Squeeze routine and hydrogen atoms were omitted for clarity.

$[\text{Zn}_{24}(\text{NCS})_{20}(\text{O}_2\text{CH})_4\{\text{(pyO)}_3\text{L}\}_{12}]$ (**9**). The lattice parameters underwent a slight change compared to **8**, whereas the space group was maintained. The periphery of the metallacycle was slightly perturbed, presumably due to the change in polarity of the solvent mixture.

The incorporation of C_{60} in solution is validated by NMR spectroscopy (Figure 6). Crystals of **8** and C_{60}C_9 were removed from the crystallization solution, washed with THF and dissolved in $[\text{D}_6]\text{DMSO}$. The ^1H NMR spectrum shows a shift and broadening of the signals due to the molecular tumbling of C_{60} . The ^{13}C NMR of C_{60}C_9 shows only one signal for C_{60} which is in agreement with all carbon atoms being chemically and magnetically equivalent. The encapsulated C_{60} can only be detected next to free C_{60} in a highly diluted solvent mixture, and therefore ^{13}C -enriched C_{60} was used. The 2 ppm signal shift from 142.18 ppm (free C_{60}) to 140.40 ppm (C_{60}C_9) clearly indicates the incorporation of C_{60} in the cavity of the metallacycle.

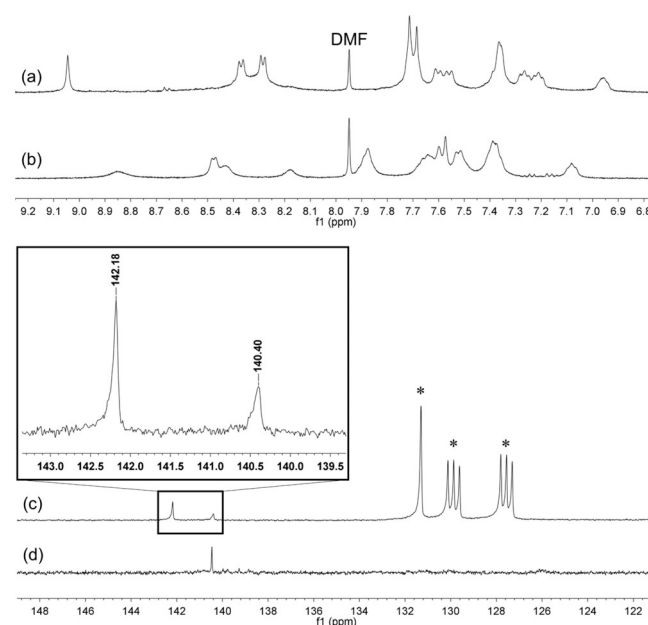


Figure 6. (a,b) ^1H NMR spectra in $[\text{D}_6]\text{DMSO}$ of **8** and C_{60}C_9 respectively. (c) ^{13}C NMR spectrum of **8** (1 equiv) and C_{60} (2 equiv) in $[\text{D}_6]\text{DMSO}/1,2$ -dichlorobenzene- d_4 1:1 (v/v). (d) ^{13}C NMR spectrum of C_{60}C_9 in $[\text{D}_6]\text{DMSO}$.

Calculations predicted the encapsulation of C_{60} by the metallacycle (**6**) to be favorable (Figure 7cA). However, there is an additional local minimum (**C**) where the C_{60} interacts with the periphery of the metallacycle. This has also been observed crystallographically. An analogous binding plot is observed for the C_{70} case (see Supporting Information for details). The use of dispersion corrections in these calculations is critical in order to correctly model the attractive interaction. In addition to the entropy loss, there is an electronic energy barrier (**B**) that C_{60} (and C_{70}) must overcome caused by steric interactions between the $\text{C}_{60/70}$ and pyridinyl groups located at the entrance of the metallacycle. Due to the nature of these calculations, stepwise single-point calculations from the fully optimized state (**A**) were applied. The binding energetics are only

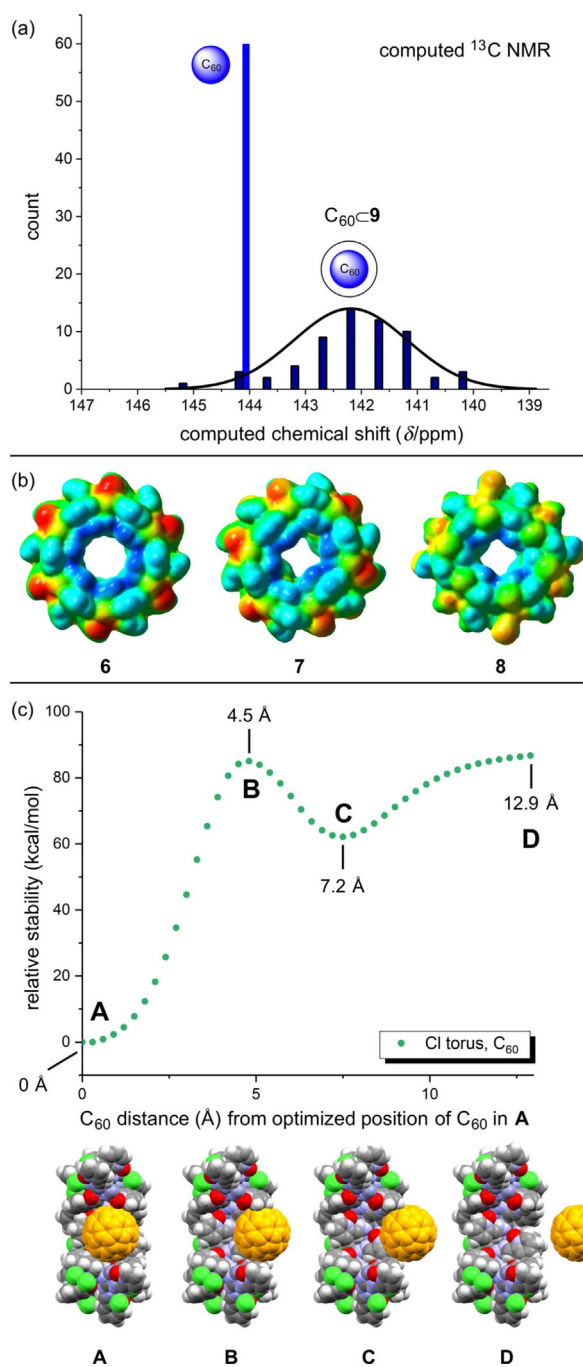


Figure 7. (a) Computed ^{13}C NMR of **8** and C_{60}C_9 , (b) electrostatic potential maps (ESP) of **6**, **7**, and **8**. (c) An electronic energy diagram showing the relative stability (kcal mol^{-1}) as a function of the C_{60} distance from its position in the fully optimized state (A) in C_{60}C_9 . The C_{60} is stepwise extruded.

qualitative. The differences in electrostatic potentials for **6–8** are shown in Figure 7b. The chloride metallacycle has the largest positive inner core while the outside ZnCl_2 moieties carry the negative potential. This is gradually attenuated in the series of **6** > **7** > **8** with **8** having the least positive inner core. These potentials might be useful in tuning the affinity and specificity for guest molecules.

In agreement with experimental data, spectroscopic assignments using computations (DFT, see Supporting Information

for details) predict an approximately 2.0 ppm upfield shift for the encapsulated C_{60}C_9 species versus the free C_{60} (144.3 ppm vs. 142.2 ppm) (Figure 7a). The IR signatures of an empty chloride metallacycle (**6**) also match the computed IR spectrum and the fingerprint region contains several characteristic absorptions (Figure S25 in the Supporting Information).

Summary

We report the synthesis of a new type of *tris*-chelating pyridine-*N*-oxide based ligands $[\text{H}_3(\text{pyO})_3\text{L}]\text{X}$. Coordination of zinc(II) ions leads to structurally interesting cyclic coordination oligomers which serve as hosts for fullerenes C_{60} and C_{70} . The inclusion of fullerenes was observed by single-crystal X-ray diffractometry and NMR spectroscopy, and was validated using computations. These metallacycles are robust and show no sign of decomposition. Although computations on such large systems are challenging, we were able to model the $\text{C}_{60}/\text{C}_{70}$ encapsulated metallacycles and even predict spectroscopic data, which are in strong agreement with the experimental results. Electrostatic potential maps reveal that the positive charges of the cavity cores can be tuned by the peripheral halide co-ligands. These computations help to provide a deeper understanding of host-guest interaction in these metallacycles. Similar computations will no doubt be useful for the rational design of host molecules with other cargo. In the future, these complexes could serve as container molecules transporting important cargo.^[2f,20]

Experimental Section

Experimental methods, synthesis, computational details and results can all be found in the Supporting Information.

CCDC 1830922, 1830936, 1830997, 1851696, 1831512, 1831515, 1831516 (**3**, **5-Cl**, **6**, **7**, **8**, C_{60}C_9 , C_{70}C_9 , respectively), contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Acknowledgements

We gratefully acknowledge the International Research Training Group 1628 *SeleCa* "Selectivity in Chemo- and Bio-catalysis" <http://www.seleca.rwth-aachen.de> (Deutsche Forschungsgemeinschaft) for funding this work. Furthermore, we like to thank Dr. Khai Nghi Truong from the group of Prof. Dr. Ulli Englert (RWTH Aachen University) and Manuela Winter from the group of Prof. Dr. Roland A. Fischer (Ruhr-Universität Bochum) for collection single-crystal X-ray diffraction data, Rachida Bomahrat and Dr. Gerhard Fink for NMR spectroscopic measurements. We are grateful to the Alexander von Humboldt Foundation for support of A.E. We thank Prof. Dr. John A. Gladysz (Texas A&M University) and the U.S. National Science Foundation (CHE-1566601, 1664866, 1900549) for financial support. We thank Prof. Dr. Michael B. Hall and Dr. Lisa M. Pérez (Texas A&M University) for fruitful discussions and the Laboratory for

Molecular Simulation. We thank the Texas A&M High Performance Research Computing Facility for computational resources. We thank Prof. Dr. Steven E. Wheeler (University of Georgia) for providing scripts to generate ESP plots.

Conflict of interest

The authors declare no conflict of interest.

Keywords: cage compounds · density functional calculations · fullerenes · host–guest systems · self-assembly

- [1] T. R. Cook, P. J. Stang, *Chem. Rev.* **2015**, *115*, 7001–7045.
- [2] a) Y. Cai, H. Shen, J. Zhan, M. Lin, L. Dai, C. Ren, Y. Shi, J. Liu, J. Gao, Z. Yang, *J. Am. Chem. Soc.* **2017**, *139*, 2876–2879; b) I. V. Grishagin, J. B. Pollock, S. Kushal, T. R. Cook, P. J. Stang, B. Z. Olenyuk, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 18448–18453; c) X. Li, J. Tsibouklis, T. Weng, B. Zhang, G. Yin, G. Feng, Y. Cui, I. N. Savina, L. I. Mikhailovska, S. R. Sandeman, C. A. Howel, S. V. Mikhailovsky, *J. Drug Targeting* **2017**, *25*, 17–28; d) L. O. Liepold, J. Abedin, E. D. Buckhouse, J. A. Frank, M. J. Young, T. Douglas, *Nano Lett.* **2009**, *9*, 4520–4526; e) S. van Dun, C. Ottmann, L. G. Milroy, L. Brunsveld, *J. Am. Chem. Soc.* **2017**, *139*, 13960–13968; f) M. J. Webber, R. Langer, *Chem. Soc. Rev.* **2017**, *46*, 6600–6620; g) X. Yan, T. R. Cook, P. Wang, F. Huang, P. J. Stang, *Nat. Chem.* **2015**, *7*, 342–348.
- [3] a) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; b) M. Zhang, H. Xu, M. Wang, M. L. Saha, Z. Zhou, X. Yan, H. Wang, X. Li, F. Huang, N. She, P. J. Stang, *Inorg. Chem.* **2017**, *56*, 12498–12504.
- [4] a) J. Langer, B. Maitland, S. Grams, A. Ciucka, J. Pahl, H. Elsen, S. Harder, *Angew. Chem. Int. Ed.* **2017**, *56*, 5021–5025; *Angew. Chem.* **2017**, *129*, 5103–5107; b) I. M. Müller, D. Möller, K. Föcker, *Chem. Eur. J.* **2005**, *11*, 3318–3324; c) I. M. Müller, R. Robson, *Angew. Chem. Int. Ed.* **2000**, *39*, 4357–4359; *Angew. Chem.* **2000**, *112*, 4527–4530; d) N. Sahiner, S. B. Sengel, M. Yildiz, *J. Coord. Chem.* **2017**, *70*, 3619–3632; e) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 2117–2121; *Angew. Chem.* **2004**, *116*, 2169–2173.
- [5] a) A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C. E. Anson, J. Richter, M. Afrontero, J. Schnack, A. K. Powell, *NPJ Quantum Mater.* **2018**, *3*, 1–6; b) W. Brenner, T. K. Ronson, J. R. Nitschke, *J. Am. Chem. Soc.* **2017**, *139*, 75–78; c) E. Huerta, E. Cequier, J. de Mendoza, *Chem. Commun.* **2007**, 5016–5018; d) G. F. Whitehead, F. Moro, G. A. Timco, W. Wernsdorfer, S. J. Teat, R. E. Winpenny, *Angew. Chem. Int. Ed.* **2013**, *52*, 9932–9935; *Angew. Chem.* **2013**, *125*, 10116–10119.
- [6] a) T. B. Karpishin, T. D. P. Stack, K. N. Raymond, *J. Am. Chem. Soc.* **1993**, *115*, 182–192; b) R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851–853; *Angew. Chem.* **1988**, *100*, 878–880; c) P. J. Stang, B. Olenyuk, D. C. Muddiman, R. D. Smith, *Organometallics* **1997**, *16*, 3094–3096.
- [7] a) R. A. Bilbeisi, T. K. Ronson, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2013**, *52*, 9027–9030; *Angew. Chem.* **2013**, *125*, 9197–9200; b) J. L. Bolliger, A. M. Belenguer, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2013**, *52*, 7958–7962; *Angew. Chem.* **2013**, *125*, 8116–8120; c) M. Kawano, Y. Kobayashi, T. Ozeki, M. Fujita, *J. Am. Chem. Soc.* **2006**, *128*, 6558–6559; d) T. Kusukawa, M. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 13576–13582; e) P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* **2009**, *324*, 1697–1699; f) W. J. Ramsay, T. K. Ronson, J. K. Clegg, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2013**, *52*, 13439–13443; *Angew. Chem.* **2013**, *125*, 13681–13685.
- [8] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89–112; *Angew. Chem.* **1988**, *100*, 91–116.
- [9] M. J. Langton, C. J. Serpell, P. D. Beer, *Angew. Chem. Int. Ed.* **2016**, *55*, 1974–1987; *Angew. Chem.* **2016**, *128*, 2012–2026.
- [10] T. Auletta, M. R. de Jong, A. Mulder, F. C. van Veggel, J. Huskens, D. N. Reinhoudt, S. Zou, S. Zapotoczny, H. Schonherr, G. J. Vancso, L. Kuipers, *J. Am. Chem. Soc.* **2004**, *126*, 1577–1584.
- [11] S. I. Kawano, T. Fukushima, K. Tanaka, *Angew. Chem. Int. Ed.* **2018**, *57*, 14827–14831; *Angew. Chem.* **2018**, *130*, 15043–15047.
- [12] a) M. Miklitz, L. Turcani, R. L. Greenaway, K. Jelfs, *Commun. Chem.* **2020**, *3*, 10; b) Y. Xu, M. von Delius, *Angew. Chem. Int. Ed.* **2020**, *59*, 559–573; *Angew. Chem.* **2020**, *132*, 567–582.
- [13] a) I. M. Müller, R. Robson, F. Separovic, *Angew. Chem. Int. Ed.* **2001**, *40*, 4385–4386; *Angew. Chem.* **2001**, *113*, 4519–4520; b) I. M. Müller, S. Spillmann, H. Franck, R. Pietschnig, *Chem. Eur. J.* **2004**, *10*, 2207–2213; c) I. M. Müller, D. Möller, *Angew. Chem. Int. Ed.* **2005**, *44*, 2969–2973; *Angew. Chem.* **2005**, *117*, 3029–3033; d) C. von Eßen, C. R. Göb, I. M. Oppel in *Guanidines as Reagents and Catalysts II* (Ed.: P. Selig), Springer, **2015**, pp. 75–94.
- [14] C. von Eßen, I. M. Oppel, *Int. J. Org. Chem.* **2017**, *07*, 325–335.
- [15] C. von Eßen, *Koordinationsverbindungen von C3-symmetrischen Liganden mit vierwertigen Metallen*, Dissertation, RWTH Aachen University, **2016**.
- [16] L. Kaczmarek, R. Balicki, P. Nantka-Namirski, *Chem. Ber.* **1992**, *125*, 1965–1966.
- [17] S. Weiss, H. Krommer, *Process for the Preparation of Triaminoguanidine Salts*, Patent DE3341645A1, **1985**.
- [18] A. L. Spek, *Acta Crystallogr. Sect. C* **2015**, *71*, 9–18.
- [19] Y. Inokuma, T. Arai, M. Fujita, *Nat. Chem.* **2010**, *2*, 780–783.
- [20] A. Galan, P. Ballester, *Chem. Soc. Rev.* **2016**, *45*, 1720–1737.

Manuscript received: November 28, 2019

Accepted manuscript online: December 12, 2019

Version of record online: March 5, 2020