DOI: 10.1002/anie.201108197

Metal Stacking

Stacked Platinum Complexes of the Magnus' Salt Type Inside a Coordination Cage**

Guido H. Clever, Wataru Kawamura, Shohei Tashiro, Motoo Shiro, and Mitsuhiko Shionoya**

Dedicated to Professor Bernhard Lippert

Compounds featuring one-dimensional arrays of stacked metal ions such as Magnus' Green salt $\{[Pt(NH_3)_4][PtCl_4]\}_n$[1] and the Krogmann salts $\{M[Pt(CN)_4]X_{\approx 0.3}\}_n$ ($M = Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}, $2\,Na^+$, or $2\,K^+$; $X = Cl^-$ or Br^-)[2] have fascinated researchers ever since their discovery more than 150 years ago.[3] Currently, interest in these compounds is increasing because the precise arrangement of metal ions in a linear fashion is seen as a promising strategy for the generation of molecular wires and information carriers in the emerging field of molecular electronics.[4] The polymeric character, polydispersity, and low solubility of these compounds, however, have rendered the examination and application of most compounds of this class rather difficult. As well as the classical inorganic approaches for their synthesis, bioinspired strategies using DNA[5] or oligopeptide scaffolds[6] have recently been used by us and others for the self-assembly of stacked metal arrays in solution.

However, only a limited number of discrete stacked platinum compounds have been structurally characterized. One species of the family of the "Platinum Blue" compounds with the composition $\{[(Pt^{2.25+})_2(NH_3)_4(\text{acetamidate})_2]^{2.5+}\}_n$, of which a crystal structure with $n = 4$ has been obtained, serves as an example.[7]

Supramolecular compounds featuring an inner cavity, such as cyclodextrins, hydrogen-bonded capsules, and coordination cages,[8] provide a nanosized, confined environment for the stabilization of reactive intermediates[9] and the selective control of chemical reactions in their interior.[10] The limited space can also be used to put a spatial constraint on the self-assembly of supramolecular building blocks, which otherwise would form polymeric products.[11] Fujita and coworkers were the first to apply this principle to the self-assembly of discrete stacks of square-planar coordinated M^{II} complexes (M = Pd, Pt, Cu, or Ni) showing metal–metal *d–d* contacts[12] and spin–spin interaction phenomena[13] inside an organic-pillared coordination box.

Recently, we introduced a new supramolecular coordination cage **1** consisting of four rigid, concave ligands and two square-planar coordinated d^8 metal ions, such as Pd^{II} (**1a**) or Pt^{II} (**1b**), sitting on oppositely arranged poles of a globular structure.[14] The ability of this cage to bind bis(anionic) guest compounds in its interior was studied systematically[15] and led to pH-switchable (pseudo)rotaxanes[16] and a system capable of light-triggered crystallization.[17]

We herein report the first example of the rational preparation of a short stretch of pentanuclear stacked platinum compounds of the Magnus' salt type, in the form of a discrete host–guest compound based on cage **1** in solution and in the solid state Figure 1).

The derivatives of Magnus' salt having the formula $\{[PtY_4][PtX_4]\}_n$ ($X = Cl^-$ or Br^-; Y = neutral N-donor ligands, NH_3, NH_2R, or pyridine) are characterized by an alternate, face-to-face stack of the dicationic and dianionic complexes. Depending on the resulting interatomic Pt–Pt distances, the polymeric compounds have been found to exhibit colors from pink to green as a result of metal-to-metal charge-transfer processes.[1] Our strategy to generate a discrete stretch of stacked platinum complexes by encapsulation is based on the

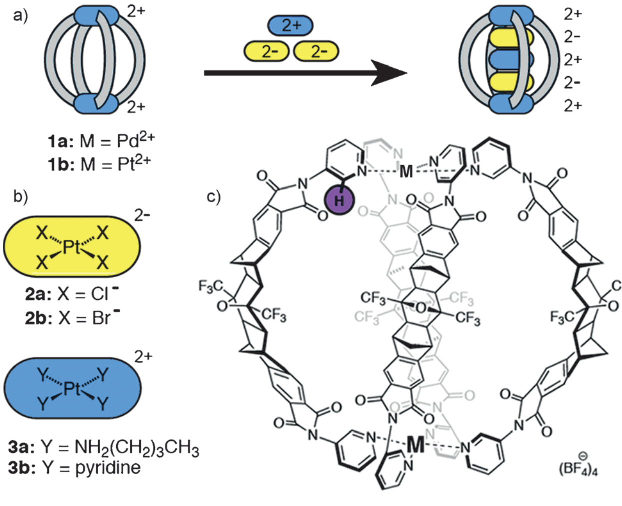

Figure 1. a) Assembly of a discrete stack of alternating $[PtY_4]^{2+}$ and $[PtX_4]^{2-}$ units inside coordination cage **1**, b) and c) structures of the examined guest and host compounds, respectively.

---

[*] W. Kawamura, Dr. S. Tashiro, Prof. Dr. M. Shionoya
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
E-mail: shionoya@chem.s.u-tokyo.ac.jp
Prof. Dr. G. H. Clever
Institute for Inorganic Chemistry, Georg-August University Göttingen, Tammannstr. 4, 37077 Göttingen (Germany)
E-mail: gclever@gwdg.de
Dr. M. Shiro
Rigaku Co. LTD (Japan)

[**] G.C. thanks the JSPS and the Alexander von Humboldt Foundation for a postdoctoral scholarship. This work was supported by Grants-in-Aid from MEXT of Japan and the Global COE Program for Chemistry Innovation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108197.

two Pt(pyridine)$_4$ planes of cage **1b** placed in parallel approximately 1.7 nm apart. As the concave shape of the rigid ligands creates a spherical cavity, we envisioned the possibility of an alternately stacked arrangement of the composition $\{[PtX_4][PtY_4][PtX_4]\}^{2-}$ in between these two positively charged Pt(pyridine)$_4$ planes.

Indeed, ^{1}H NMR spectroscopy indicated the formation of the host–guest complex in solution (Figure 2). Initially, cage **1b** in CD_3CN (Figure 2a) was titrated with 1 equivalent of guest $[Pt(NH_2nBu)_4]^{2+}$ (Figure 2b). As expected, no significant interactions were found between the positively charged guest and the tetracationic host. Upon subsequent addition of two equivalents of the negatively charged guest $[PtCl_4]^{2-}$, however, a significant shift of certain NMR resonances indicated the formation of a quaternary host–guest complex of stoichiometry $\{[Pt(NH_2nBu)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}^{2+}$ (Figure 2c and d). In accordance with our previous findings, the incorporation of the (net) negatively charged guests inside cage **1** resulted in a characteristic downfield shift of the cage's inward pointing hydrogen atom H_i (purple in Figure 1 and Figure 2). In addition, all four signals attributed to the butyl chains of guest $[Pt(NH_2nBu)_4]^{2+}$ were found to shift upfield as expected.[14a] Interestingly, the nitrogen-bound protons of guest $[Pt(NH_2nBu)_4]^{2+}$ were found to undergo a slight downfield shift, thus suggesting an interaction with the closely packed $[PtCl_4]^{2-}$ units nearby.

It should be noted that the addition of two equivalents of $[PtCl_4]^{2-}$ to the mixture, $[Pt(NH_2nBu)_4]^{2+}+\mathbf{1b}$, was necessary to achieve full incorporation of one equivalent of guest $[Pt(NH_2nBu)_4]^{2+}$ as expected for the formation of a supramolecular assembly of the stoichiometry $[Pt(NH_2nBu)_4]^{2+}/[PtCl_4]^{2-}/\mathbf{1b}=1:2:1$.

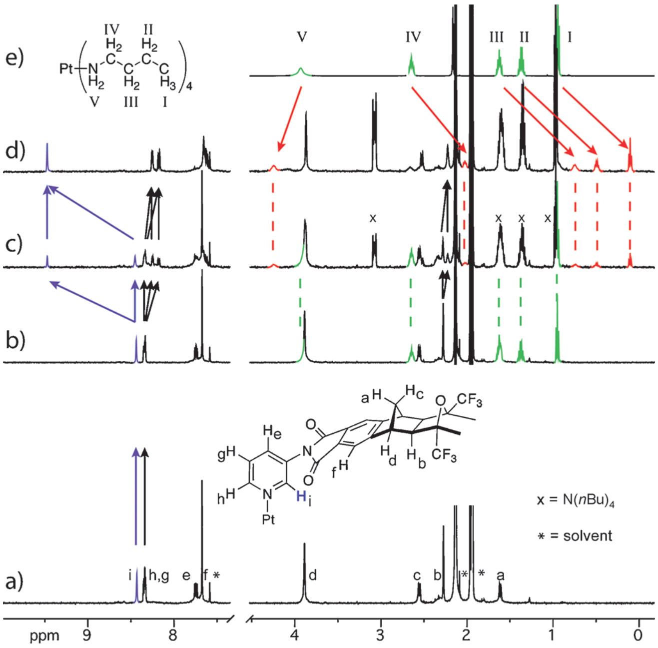

Figure 2. ^{1}H NMR titration of $[Pt(NH_2nBu)_4](BF_4)_2$ and $(NnBu_4)_2[PtCl_4]$ inside a 0.7 mM solution of cage **1b** in CD_3CN (500 MHz, 298 K). a) Pure cage **1b**, b) addition of 1 equivalent of $[Pt(NH_2nBu)_4](BF_4)_2$, subsequent addition of c) 1 equivalent and d) 2 equivalents of $(NnBu_4)_2[PtCl_4]$, e) pure $[Pt(NH_2nBu)_4](BF_4)_2$ (0.7 mM) in CD_3CN. Purple: inward pointing hydrogen atom H_i of cage **1b**, green and red: signals of free and encapsulated $[Pt(NH_2nBu)_4]^{2+}$, respectively.

Throughout the titration, no splitting of NMR signals was observed and all signals remained relatively sharp, thus supporting our interpretation of a linear and alternating stack inside the cage without loss of the initial fourfold symmetry of the cage.

Furthermore, it is interesting to note that the same result was obtained when the titration was commenced with the addition of $[PtCl_4]^{2-}$, followed by addition of $[Pt(NH_2nBu)_4]^{2+}$. In this case, however, NMR spectroscopy and ESI mass spectrometry indicated that the guest $[PtCl_4]^{2-}$, which was added first, was already incorporated alone as a weak binding guest molecule inside cage **1b** in a 1:1 fashion. Similarly, using the guest compounds $[Pt(pyridine)_4]^{2+}$ and $[PtBr_4]^{2-}$ also resulted in the formation of host–guest complexes of the Magnus' salt type (see the Supporting Information).

Further data supporting the formation of soluble compounds, having a discrete architecture similar to Magnus' salt, inside **1b** were obtained from ESI-TOF mass spectrometry. Figure 3a–c show the resulting mass spectra of three different guest combinations, each featuring the expected signal for $\{[PtY_4]\cdot[PtX_4]_2@\mathbf{1b}\}^{2+}$ as the most prominent peak. In all cases, the resolved isotope patterns of the measurement are in very good agreement with the simulated patterns for the expected molecular composition.

Using cage **1b** and a combination of $[PtCl_4]^{2-}$ and $[Pt(pyridine)_4]^{2+}$ as guests, we were successful in growing single crystals suitable for X-ray crystal structure determination (Figure 4). In contrast to the X-ray structure of "free" palladium-based cage $[\mathbf{1a}](BF_4)_4$, which adopts a D_{4h} sym-

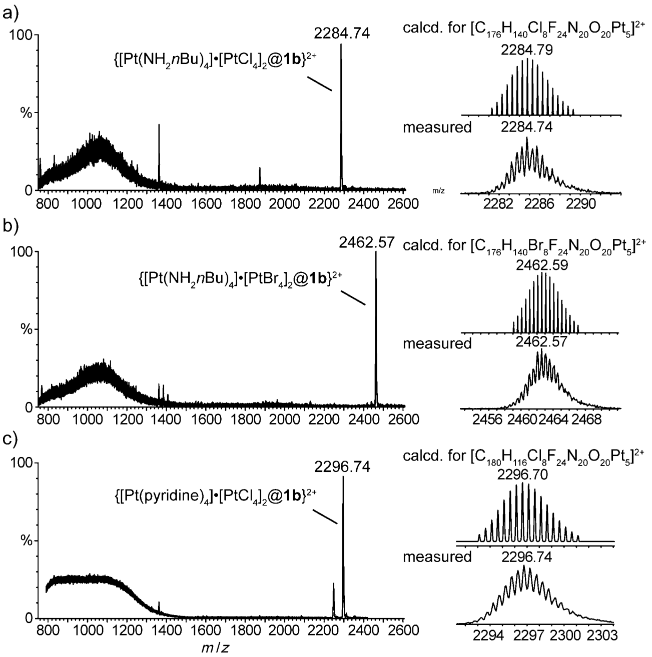

Figure 3. ESI-TOF mass spectra of acetonitrile solutions of the host–guest complexes: a) $\{[Pt(NH_2nBu)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}^{2+}$, b) $\{[Pt(NH_2nBu)_4]\cdot[PtBr_4]_2@\mathbf{1b}\}^{2+}$, and c) $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}^{2+}$.

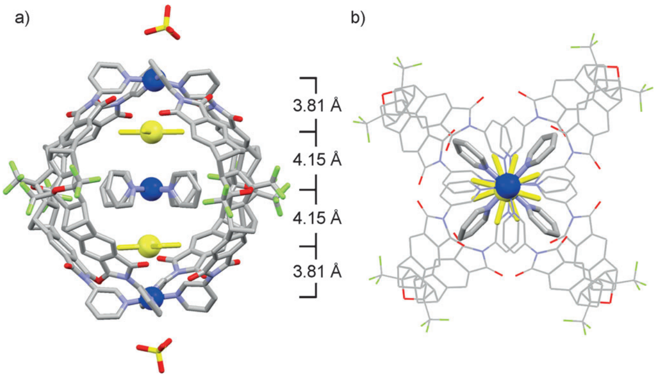

Figure 4. X-ray structure of $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}(ClO_4)_2$. a) Side view of one of the two enantiomeric complexes found in the crystal, b) top view with Pt^{II} ions highlighted as large spheres showing the staggered arrangement of the five square-planar platinum complexes and the slight trapezoid distortion of the cage structure owing to packing effects (C: gray, N: light blue, O: red, F: green, Cl: yellow, Pt in $[Pt(pyridine)_4]$: dark blue, Pt in $[Pt(Cl)_4]$: yellow; H atoms, solvent molecules and ClO_4^- counter ions in (b) are omitted for clarity.[21]

metry in the solid state,[14a] the cage substructure in $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}^{2+}$ was found to show an approximated C_4 symmetry with all four ligands twisting in a helical manner around the line connecting the Pt atoms. Both enantiomers of the chiral cage were found in the crystal in a 1:1 ratio. A slight trapezoid distortion from the ideal C_4 symmetry can be attributed to packing effects (see the Supporting Information for discussion of the packing).

As expected from the solution experiments, all cages were found to contain two molecules of $[PtCl_4]^{2-}$ and one molecule of $[Pt(pyridine)_4]^{2+}$ alternately stacked along the line connecting the cage's two platinum centers (Figure 4). The resulting nearly linear stack of five platinum complexes comprising the cage's two $[Pt(ligand)_4]^{2+}$ moieties and the three guests is highlighted in Figure 4a. The Pt–Pt distance between the outer complexes and the $[PtCl_4]^{2-}$ units is 3.81 Å and the distances between the $[PtCl_4]^{2-}$ units and the central $[Pt(pyridine)_4]^{2+}$ molecule is 4.15 Å. Both distances are thus larger than the sum of van der Waals radii for two Pt^{II} ions (3.50 Å) and also larger than the Pt–Pt distances found in Magnus' Green salt (3.25 Å).[1] Therefore, no strong *d–d* interaction is to be expected in the present case; this finding is in agreement with the faint yellow color of the crystals. Accordingly, also the UV/Vis examination of the slightly yellow solution of $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}(BF_4)_2$ in acetonitrile indicated no remarkable spectral features. To the best of our knowledge, no X-ray structure of the parent polymeric compound $\{[Pt(pyridine)_4][PtCl_4]\}_n$ has ever been reported in the literature, however, the X-ray structure of a compound containing the related stacked motif $\{[Pt(pyrazole)_4][PtCl_4]\}_n$ was found to show a comparable Pt–Pt distance of 3.94 Å.[18]

Figure 4b shows the structure viewed along the Pt–Pt line with the guests $[Pt(pyridine)_4]^{2+}$ and $[PtCl_4]^{2-}$ highlighted by thicker bonds. The square-planar complexes adopt a staggered arrangement showing slight deviations from coplanarity. The pyridine rings of the central $[Pt(pyridine)_4]^{2+}$ units are directly pointing towards the inner side of the norbornane-framework of the cage's four ligands. The resulting close proximity between the hydrogen atoms in the 4-position of these pyridine rings and the cage's protons H_b explains the upfield shift of the H_b resonances upon assembly of the quaternary host–guest complex.

The packing of the cages in the X-ray structure reveals a circular arrangement of six cages in a chairlike fashion around a central cavity containing counter anions and solvent (Figure 5a). The columnar stacking of these rings into tubes is shown schematically in Figure 5b and a partial breakdown of the cages, Pt stacks and ClO_4^- ions in the central channel is shown in Figure 5c. In each ring, the cages shown in blue and red are of opposite chirality (from one ring to the next, the sense of chirality is reversed). The main driving force for this aggregation pattern remains unclear, but the assembled structure is characterized by the fact that some fluorine atoms of the ligand moieties of neighboring cages are close to each other (2.81–2.99 Å; see the Supporting Information Figure S7).

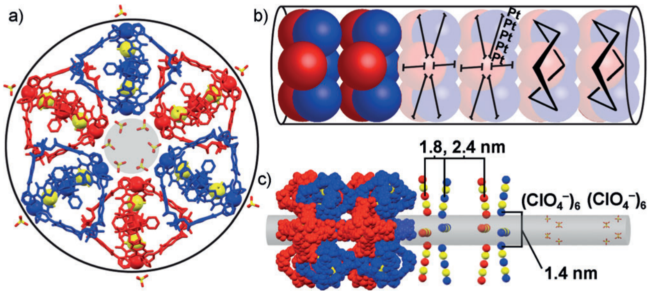

Figure 5. a) The top view of the packing in the X-ray structure reveals the circular, chairlike arrangement of six cages with their Pt_5 axis pointing towards a central channel (gray) that contains ClO_4^- counter anions and disordered solvent (upper cages: blue, lower cages: red, Pt in $[Pt(Cl)_4]$: yellow, Pt ions highlighted as large spheres). b) Schematic side view showing the stacking of rings to give hollow tubes and c) breakdown of the assembly around the inner channel showing: whole cages (left), only Pt ions (middle), and only inner ClO_4^- ions (right).

In conclusion, our results show that the coplanar arrangement of two cationic, square-planar Pt^{II} complexes by four rigid, concave ligands into a supramolecular cage, templates the formation of a discrete stretch of an alternating stack of platinum complexes of the Magnus' salt type, in solution and in the solid state.[19] This principle of charge-based molecular arrangement in spatially restricted spaces has proven to be remarkably versatile, thus allowing various combinations of cationic and anionic guests to be coencapsulated. Noteworthy is the fact, that the coencapsulated guest trimer $\{[PtX_4][PtY_4][PtX_4]\}^{2-}$ binds much stronger inside cage **1b** than the small, monomeric guest $[PtX_4]^{2-}$ alone (although they carry the same charge), an effect that was recently also observed by Fujita and co-workers for the encapsulation of uncharged electron-rich/poor guest trimers.[20] This concept has future potential in the fields of molecular electronics and catalysis. As the channels (1.4 nm in diameter) spanning the solid-state structure are flanked by the outer $[Pt(pyridine)_4]$ faces of the discrete Pt_5-stacks, interaction with (redox active) substrates or functional guests in these channels might lead to the development of new materials with interesting properties. Furthermore, the use of paramagnetic metal ions and mixed (valence) metal assemblies might have impact on the fields of information storage and molecular spintronics.

Currently, we are exploring the potential to fine-tune the metal–metal separation and create extended stacks by altering the cage's backbone structure to deduce a relationship between structural and spectroscopic features.

Experimental Section

The synthesis of cages **1a**,[14a] **1b**,[16] and the guest compounds $(NnBu_4)_2[PtX_4]$ ($X = Cl^-$ or Br^-) and $[PtY_4](BF_4)_2$ ($Y = NH_2nBu$ or pyridine) is described in the Supporting Information. For a typical titration experiment, a 0.7 mM solution of cage **1b** (500 μL) in CD_3CN was treated with 8.75 mM solution of the respective guest freshly prepared in CD_3CN in steps of 0.25 equiv (10 μL) followed by an equilibration time of 5 min prior to the NMR measurement (500 MHz, 298 K). Pale yellow single crystals of $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@\mathbf{1b}\}(ClO_4)_2$ suitable for X-ray crystal structure determination were grown by slow evaporation of the mixture of **1b** (0.35 μmol), $(NnBu_4)_2[PtCl_4]$ (1.4 μmol), $[Pt(pyridine)_4](BF_4)_2$ (1.05 μmol), and $NnBu_4ClO_4$ (20 μmol) in CH_3CN (2.0 mL) for two weeks at room temperature. Crystal data: $C_{180}H_{116}Cl_{10}F_{24}N_{20}O_{28}Pt_5$, $Fw = 4792.96$, crystal dimensions $0.2 \times 0.2 \times 0.1$ mm, trigonal, space group $R\bar{3}c$, $a = 55.13(2)$, $c = 49.517(18)$ Å, $V = 130339(81)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.099\ g\,cm^{-3}$, $\mu = 25.51\ cm^{-1}$, $F(000) = 42048.00$, $T = 296$ K, $\lambda(Mo_{K\alpha}) = 0.71075$ Å, $2\theta_{max} = 29.4°$, 47135/5369 reflections collected/unique ($R_{int} = 0.1494$), $R_1 = 0.0954$ ($I > 2\sigma(I)$), $wR_2 = 0.2820$ (for all data), GOF = 1.046, largest diff. peak and hole 0.73/−0.82 e Å^{-3}. The contribution of solvent electron density was removed by the SQUEEZE function.[21]

Received: November 22, 2011

Keywords: cage compounds · host–guest systems · metal stacking · platinum · supramolecular chemistry

---

[1] a) M. Atoji, J. Richardson, R. Rundle, *J. Am. Chem. Soc.* **1957**, *79*, 3017; b) T. Thomas, A. E. Underhill, *Chem. Soc. Rev.* **1972**, *1*, 99; c) M. Fontana, H. Chanzy, W. Caseri, P. Smith, A. Schenning, E. Meijer, F. Grohn, *Chem. Mater.* **2002**, *14*, 1730; d) W. Caseri, *Platinum Met. Rev.* **2004**, *48*, 91; e) J. Casas, Y. Parajo, Y. Romero, A. Sanchez-Gonzalez, J. Sordo, E. Vazquez-Lopez, *Z. Anorg. Allg. Chem.* **2004**, *630*, 980.
[2] a) K. Krogmann, *Angew. Chem.* **1969**, *81*, 10; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 35; b) J. M. Williams, *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 235.
[3] a) J. Bremi, V. Gramlich, W. Caseri, P. Smith, *Inorg. Chim. Acta* **2001**, *322*, 23; b) K. Sakai, E. Ishigami, Y. Konno, T. Kajiwara, T. Ito, *J. Am. Chem. Soc.* **2002**, *124*, 12088; c) J. K. Bera, K. R. Dunbar, *Angew. Chem.* **2002**, *114*, 4633; *Angew. Chem. Int. Ed.* **2002**, *41*, 4453; d) Y. Sun, K. Ye, H. Zhang, J. Zhang, L. Zhao, B. Li, G. Yang, B. Yang, Y. Wang, S.-W. Lai, C.-M. Che, *Angew. Chem.* **2006**, *118*, 5738; *Angew. Chem. Int. Ed.* **2006**, *45*, 5610; e) B. M. Anderson, S. K. Hurst, *Eur. J. Inorg. Chem.* **2009**, 3041.
[4] R. Mas-Ballesté, O. Castillo, P. J. Sanz Miguel, D. Olea, J. Gomez-Herrero, F. Zamora, *Eur. J. Inorg. Chem.* **2009**, 2885.
[5] G. Clever, M. Shionoya, *Coord. Chem. Rev.* **2010**, *254*, 2391.
[6] K. Tanaka, K. Kaneko, Y. Watanabe, M. Shionoya, *Dalton Trans.* **2007**, 5369.
[7] K. Matsumoto, K. Sakai, K. Nishio, Y. Tokisue, R. Ito, T. Nishide, Y. Shichi, *J. Am. Chem. Soc.* **1992**, *114*, 8110.
[8] a) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509; b) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825; c) D. Tranchemontagne, Z. Ni, M. O'Keeffe, O. Yaghi, *Angew. Chem.* **2008**, *120*, 5214; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136.
[9] a) D. Cram, M. Tanner, R. Thomas, *Angew. Chem.* **1991**, *103*, 1048; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1024; b) K. Goto, R. Okazaki, *Liebigs Ann./Recueil* **1997**, 2393; c) F. Hapiot, S. Tilloy, E. Monflier, *Chem. Rev.* **2006**, *106*, 767; d) R. J. Hooley, J. Rebek, Jr., *Chem. Biol.* **2009**, *16*, 255; e) *Molecular Encapsulation: Organic Reactions in Constrained Systems* (Eds.: U. H. Brinker, J. Mieusset), Wiley, Hoboken, **2010**.
[10] a) D. Vriezema, M. Aragones, J. Elemans, J. Cornelissen, A. Rowan, R. Nolte, *Chem. Rev.* **2005**, *105*, 1445; b) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem.* **2009**, *121*, 3470; *Angew. Chem. Int. Ed.* **2009**, *48*, 3418; c) A. Lützen, *ChemCatChem* **2010**, *2*, 1212; d) M. J. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem.* **2011**, *123*, 118; *Angew. Chem. Int. Ed.* **2011**, *50*, 114.
[11] J. K. Klosterman, Y. Yamauchi, M. Fujita, *Chem. Soc. Rev.* **2009**, *38*, 1714.
[12] M. Yoshizawa, K. Ono, K. Kumazawa, T. Kato, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 10800.
[13] a) K. Ono, M. Yoshizawa, T. Kato, M. Fujita, *Chem. Commun.* **2008**, 2328; b) K. Ono, M. Yoshizawa, M. Akita, T. Kato, Y. Tsunobuchi, S. Ohkoshi, M. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 2782.
[14] a) G. H. Clever, S. Tashiro, M. Shionoya, *Angew. Chem.* **2009**, *121*, 7144; *Angew. Chem. Int. Ed.* **2009**, *48*, 7010; for further examples of related $[M_2Ligand_4]$ cages see: b) D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3495; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295; c) D. K. Chand, K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 1652; d) C. Su, Y. P. Cai, C. Chen, M. D. Smith, W. Kaim, H. C. zur Loye, *J. Am. Chem. Soc.* **2003**, *125*, 8595; e) N. L. S. Yue, D. J. Eisler, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2004**, *43*, 7671; f) P. Liao, B. W. Langloss, A. M. Johnson, E. R. Knudsen, F. S. Tham, R. R. Julian, R. J. Hooley, *Chem. Commun.* **2010**, *46*, 4932; g) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438; h) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem.* **2008**, *120*, 718; *Angew. Chem. Int. Ed.* **2008**, *47*, 706; i) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem.* **2011**, DOI: 10.1002/ange.201107184; *Angew. Chem. Int. Ed.* **2011**, DOI: 10.1002/anie.201107184.
[15] G. H. Clever, W. Kawamura, M. Shionoya, *Inorg. Chem.* **2011**, *50*, 4689.
[16] G. H. Clever, M. Shionoya, *Chem. Eur. J.* **2010**, *16*, 11792.
[17] G. H. Clever, S. Tashiro, M. Shionoya, *J. Am. Chem. Soc.* **2010**, *132*, 9973.
[18] K. Sakai, Y. Tomita, T. Ue, K. Goshima, M. Ohminato, T. Tsubomura, K. Matsumoto, K. Ohmura, K. Kawakami, *Inorg. Chim. Acta* **2000**, *297*, 64.
[19] For a recent example of the encapsulation of a stacked dimer of *cis*-platinum inside an $[M_2L_4]$ cage see: J. E. M. Lewis, E. L. Gavey, S. A. Cameron, J. D. Crowley, *Chem. Sci.* **2011**, DOI: 10.1039/c2sc00899h.
[20] K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita, *Angew. Chem.* **2007**, *119*, 1835; *Angew. Chem. Int. Ed.* **2007**, *46*, 1803.
[21] CCDC 846887 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.