Rational Design of the First Closed Coordination Capsule with Octahedral Outer Shape

Iris M. Müller,*[a] Susanne Spillmann,[a] Holger Franck,[a] and Rudolf Pietschnig[b]

Abstract: The rational synthesis of an octahedral coordination capsule in which the triangular faces are covered by single ligands is described herein. Starting with tris(2-hydroxybenzylidene)triaminoguanidinium chloride $[H_6L]Cl$, we observed an oxidative cyclization of this ligand in the presence of PPh_4^+ ions resulting in the complex $[Pd(H_2L')(PPh_3)]$ (**1**). The use of 5,5-diethylbarbiturate (bar^{2-}) as a bridging ligand in the presence of $[Co(en)_3]^{3+}$ (en = ethylenediamine) leads to the formation of a rectangular box with the formula $(Et_4N)_6[\{Co\{(PdCl)(Pd)L\}_2(\mu\text{-}bar)\}_2]$ (**2**). The analysis of the architecture of compounds **1** and **2** enables the development of a self-assembly strategy for the synthesis of an octahedral coordination cage **3** with the formula $Na_4(Et_3NH)_{12}[(Pd_3L)_8\{\mu\text{-}(bar)\}_{12}]\cdot x\,H_2O$. Compound **3** was characterized by ^{13}C-MAS-NMR spectroscopy and single-crystal structure analysis.

Keywords: cage compounds · NMR spectroscopy · octahedron · self-assembly · supramolecular chemistry

Introduction

Self-assembly processes leading to the formation of polymers are already well known because of the application of such compounds as new materials, heterogeneous catalysts, and ion exchangers.[1] The rational design of discrete cage molecules can be carried out following the molecular library method.[2,3] In this method molecular fragments are combined, in which the stochiometry and symmetry elements (e.g. a C_3 axis) of the resulting cage are already predestined. For example, there are four different ways to generate a cage with the overall symmetry of a tetrahedron (Figure 1).

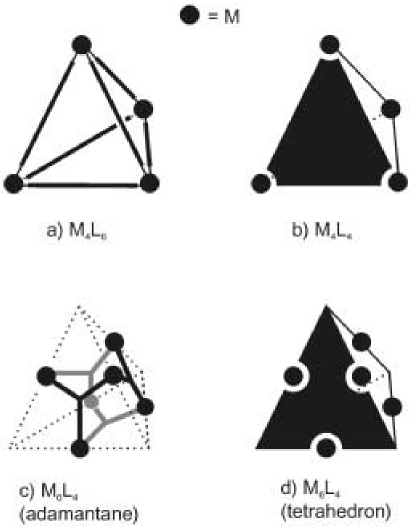

Figure 1. Tetrahedral cage molecules with different topologies and connectivities.

Most of the tetrahedra described in the literature have M_4L_6 topology. The metal centers are located at the corners, and the edges are formed by bridging ligands (Figure 1 a). These systems have been reviewed several times.[2] The formation of tetrahedral cages in which the faces are covered by ligands with threefold symmetry is far more rare. These faces are connected by metal centers forming the corners (Figure 1 b) or the middle of the edges (Figure 1 c, d). The known M_4L_4 systems have also been recently reviewed.[2,4] Up to now the published M_6L_4 systems can be classified as adamantanoid or truncated tetrahedra (Figure 1 c).[2b,d–f,5] The ligands, for example 2,4,6-tri-4-pyridyl-1,3,5-triazine derivatives,[5a,e,g] 1,3,5-tri(ethynylpyridyl)benzene,[5b] triphos,[5d] or trimesic acid,[5h] have threefold symmetry and coordinate three metal centers, but they cover only a small part of the triangular face. To our knowledge there is only one M_6L_4 tetrahedral cage known in which the faces are almost completely covered by a threefold chelating ligand (Figure 1 d).[6] In this case M denotes a $(CdO)_2$ four-membered ring. Additionally there are two tetrahedral cages known with ligands representing the triangular faces but showing M_8L_4 topolo-

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gy.[3,7] Four of the six edges are each formed by two metal centers.

Triangular faces are also found in another platonic body, the octahedron. Coordination cages with this geometry should show an $A^{3}_{8}B^{2}_{12}$ topology. A^{3} stands for a three-connecting knot, while B^{2} is the symbol for a twofold bridging fragment. Figure 2 shows four different possible geometries of cage molecules with this $A^{3}_{8}B^{2}_{12}$ formula.

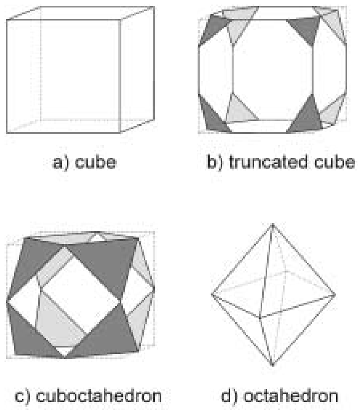

a) cube
b) truncated cube
c) cuboctahedron
d) octahedron

Figure 2. Different possible geometries for cage molecules with $A^{3}_{8}B^{2}_{12}$ topology.

In a cube-shaped cage the eight threefold connecting knots sit at the corners, the edges are formed by the twelve twofold bridging units (Figure 2a). Compounds of this type are known, for which, for example, the corners are represented by ([9]aneS$_3$)Ru^{III} or Cp*Rh^{III} units bridged by ligands such as CN^{-} or 4,4′-bipyridine.[8] In 1999 R. Robson et al. published an example of a truncated cube (Figure 2b). Eight hexadentate and threefold bridging ligands are bound to twelve Cu^{II} centers, which are coordinated in a square-planar manner by two chelating ligands so as to form a linear bridging unit.[9] In the same year the first two cuboctahedra were published (Figure 2c),[10] and these were followed by another example in which the triangular faces have different sizes.[11] To our knowledge there is no known coordination cage with the $A^{3}_{8}B^{2}_{12}$ topology in the shape of an octahedron (Figure 2d). Herein we present the first rationally designed and synthetically realized representative of such an octahedrally shaped capsule.

Results and Discussion

We employed tris(2-hydroxybenzylidene)triaminoguanidinium chloride [H$_6$L]Cl as a threefold chelating ligand (Figure 3a) to form the triangular faces of the cage. The use of square-planar coordinating metal centers leads to a free coordination site for the bridging ligand in the middle of the edge. This bridging ligand connecting the faces of the octahedron has to exhibit the same bridging angle as the dihedral angle observed in an ideal octahedron (109.5°). We therefore decided to use 5,5-diethylbarbiturate (bar^{2-}) for this purpose (Figure 3b). Up to now there are two complexes known in which two metal centers are bridged by bar^{2-},(M = Au[12] M = Zn[13]). In these compounds bridging angles of $\alpha = 108$–$117°$ are observed so that bar^{2-} would seem to be a suitable connecting unit for the synthesis of an octahedral cage. The expected formula would be $[(Pd_3L)_8\{\mu\text{-}(bar)\}_{12}]^{16-}$. In the first attempts to prepare such a coordination complex we employed Na^{+}, Et$_4$N^{+}, Et$_3$NH^{+}, and Ph$_4$P^{+} as counter cations. The reaction of [H$_6$L]Cl, NaHbar, PdCl$_2$, Et$_4$NCl, and PPh$_4$Br in acetonitrile in the presence of Et$_3$N leads to the formation of red needles of [Pd(H$_2$L′)(PPh$_3$)] (**1**). The crystal structure of **1** shows an unexpected result (Figure 4).[14]

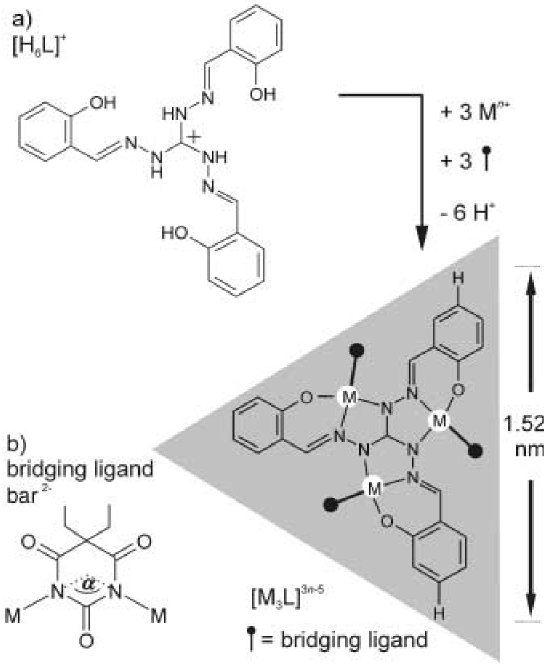


Figure 3. a) $[M_3L]^{3n-5}$ unit as triangular face; b) bridging 5,5-diethylbarbiturate (bar)$^{2-}$ ligand.

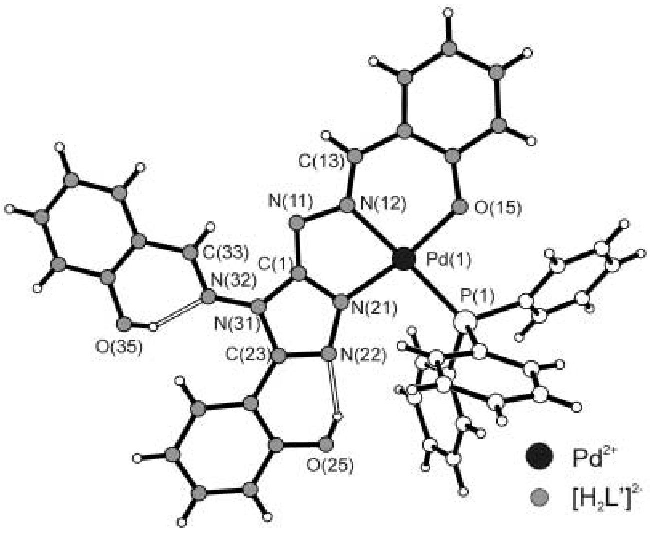
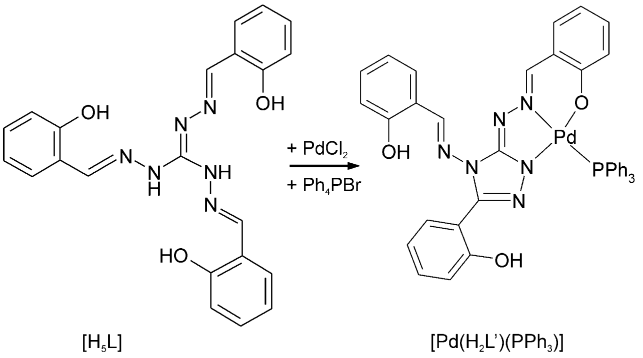


Figure 4. Structure of [Pd(H$_2$L′)(PPh$_3$)] (**1**).

Instead of coordinating three Pd^{II} centers the ligand L^{5-} underwent an oxidative cyclization. Such a reaction of L^{5-} has been described only once before.[15] Unlike the previously reported cyclization, in the present case the ligand is oxidized, while PPh_4^+ is reduced to PPh_3 (Scheme 1).

Nevertheless $[H_2L']^{2-}$ is able to chelate one Pd^{II} center in the same manner as L^{5-} would do. $[H_2L']^{2-}$ has a propeller-like conformation; the dihedral angles between the central CN_6^{2-} core and the phenyl groups are 4.9°, 24.0°, and 15.4°. All bond lengths (Table 1) are within the expected range, and L′ shows no further distortion. Therefore it should be possible to occupy the free coordination site at the metal centers in a $[M_3L]$ unit by using ligands with a steric demand as high as that of PPh_3.



Scheme 1. Formation of $[Pd(H_2L')(PPh_3)]$ (**1**).

Table 1. Selected bond lengths in **1** and **2**. Bond lengths in the triazol of L′ in **1** are in italics.

	1	2
Pd–N(1, L)[a]	2.001(9)	2.00(2)
Pd–N(2, L)[b]	1.98(1)	1.97(2)
Pd–O(L)	2.004(9)	2.03(2)
Pd–N(bar)	–	2.11(3)
Pd–X(coligand)	2.033(9)	2.34(5)
C(1)–N(11)	1.322(7)	1.40(3)
N(11)–N(12)	1.391(7)	1.39(2)
N(12)–C(13)	1.291(7)	1.27(2)
C(1)–N(21)	*1.329(8)*	1.33(2)
N(21)–N(22)	*1.392(6)*	1.47(2)
N(22)–C(23)	*1.310(8)*	1.39(2)
C(1)–N(31)	*1.381(7)*	1.41(2)
N(31)–N(32)	1.387(7)	1.43(2)
N(31)–C(23)	*1.387(8)*	–
N(32)–C(33)	1.270(8)	1.23(2)
Co–N(1, L)[a]	–	2.00(2)
Co–N(2, L)[b]	–	1.94(2)
Co–O(L)	-	1.92(2)

[a] First N in each arm of the ligand L, L′. [b] Second N in each arm of the ligand L, L′.

In the next attempts to prepare an octahedral cage we used $[Co(en)_3]Br_3$ (en = ethylenediamine) as an octahedral counter cation. The reaction of $[H_6L]Cl$, NaHbar, $PdCl_2$, Et_4NCl, and $[Co(en)_3]Br_3$ in acetonitrile in the presence of Et_3N at room temperature leads to the formation of black crystals. The X-ray analysis was difficult due to rapid solvent loss and resulting crystal deterioration during the measurement. Nevertheless the quality of the X-ray analysis data was adequate to enable the unequivocal establishment of the connectivity in the complex with the formula $(Et_4N)_6[\{Co\{(PdCl)(Pd)L\}_2(\mu\text{-bar})\}_2]$ (**2**). The structure is shown in Figure 5.[16]

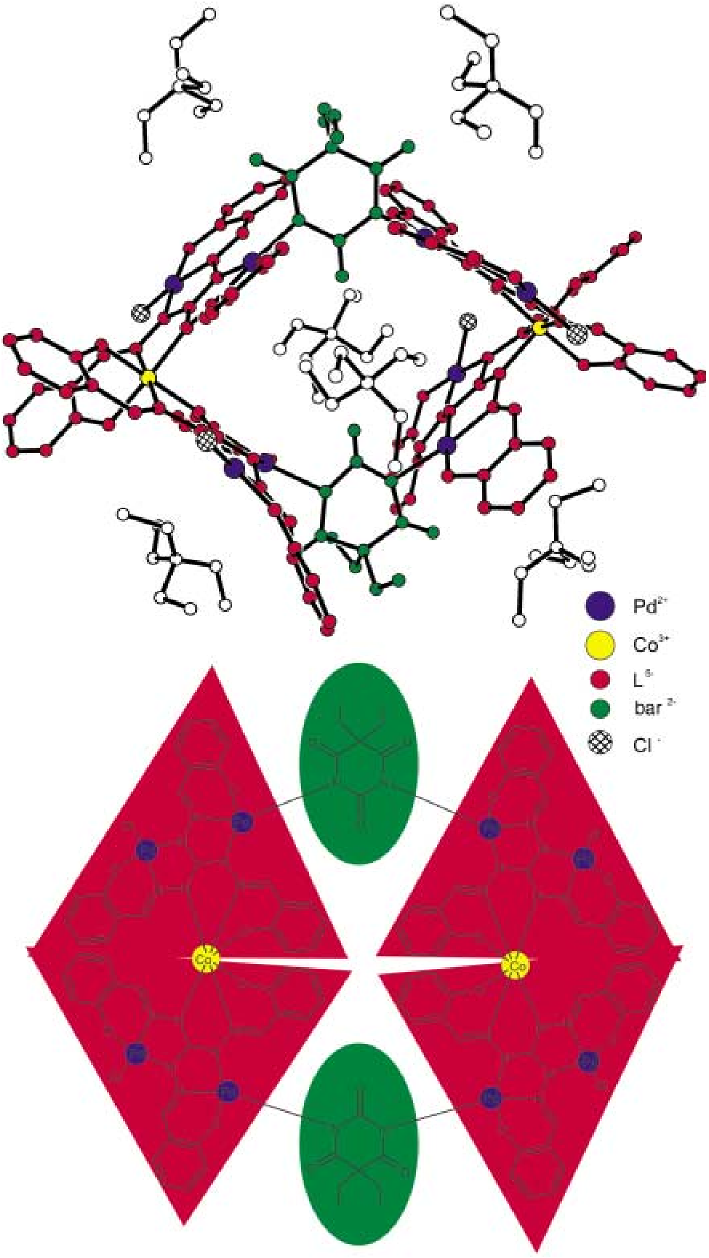


Figure 5. Structure of $(Et_4N)_6[\{Co\{(PdCl)(Pd)L\}_2(\mu\text{-bar})\}_2]$ (**2**) (protons omitted for clarity).

Complex **2** does not have the expected octahedral structure but rather a rectangular boxlike shape. The Et_4N^+ ions are completely embedded in the central cavity and the depressions in the outer faces. The rectangular box is formed by four L and two bar ligands, which bond to a total of eight

Pd^{II} and two Co^{III} centers. The ligands exhibit no significant distortion (Table 1). The Co^{III} centers are octahedrally coordinated by two L ligands orientated perpendicular to one other. Each L ligand also bonds to two further square-planar Pd^{II} centers. One of these carries a chloride ligand, whilst the other is fixed at the free coordination side to a barbiturate, bridging two Pd^{II} centers. The observed bridging angles between two Pd^{II} centers are 109(2)° and 115(2)°. The structures of **1** and **2** allow the following conclusions:

1) Sterically it is possible to bind a barbiturate ligand to a M_3L unit.
2) The bridging angle of bar^{2-} is relatively flexible and can adopt a value close to 109.5°.
3) Because of the observed oxidative cyclization, the use of PPh_4^+ as counter cation should be avoided.
4) Despite its octahedral geometry, $[Co(en)_3]^{3+}$ is not a viable counter cation for the postulated $[(Pd_3L)_8\{\mu\text{-}(bar)\}_{12}]^{16-}$ ion. Because of the substitution reaction of L for en, the $[Co(en)_3]^{3+}$ complex is not stable enough under the reaction conditions.

The reaction of $PdCl_2$, Et_4NCl, $[H_6L]Cl$, NaHbar, and Et_3N in acetonitrile at room temperature leads to the formation of orange-red cubic crystals of **3** after a couple of days. The solid-state ^{13}C-MAS-NMR (MAS = magic angle spinning) spectrum shows sharp signals, indicating that complex **3** must exhibit high symmetry (Figure 6). The detailed analysis of the spectrum confirms that the characteristic signals for both ligands are in good agreement with literature values (Table 2).[6,12,17]

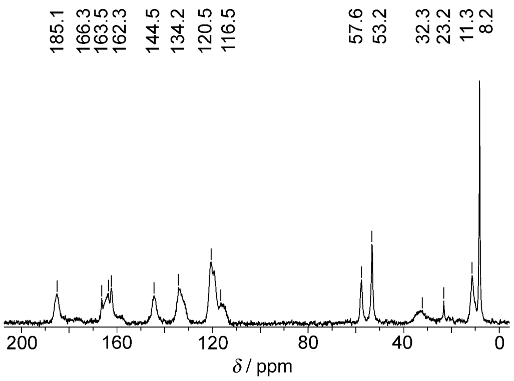


Figure 6. ^{13}C-MAS-NMR spectrum of **3** ($\upsilon_{rot} = 15$ kHz).

Contrary to the tetrahedral cage described in the literature, there are no differences between the counter cations inside and outside of the capsule.[6] The ^1H-MAS-NMR spectrum provides only limited information due to the broadness of the signals. Nevertheless the absence of signals in the region of $\delta = 8.5–14$ ppm allows the conclusion that all ligands are fully deprotonated. The determination of the crystal structure was challenging. All investigated crystals diffracted very weakly and lost solvent during data collection. By using a modern diffractometer with very intense primer radiation (Oxford diffraction Xcalibur3, Enhanced ultra Cu radiation) we were able to obtain a satisfactory data set.[18] Complex **3** crystallizes in the cubic space group *P*23. Two Pd^{II} centers can be found in the asymmetric unit, which are not related by a mirror plane or twofold axes. The two central CN_6^{2-} cores, the coordinated metal centers, and the N and O donor atoms bonded to these metals could be localized in the difference map and freely refined ($R_1 = 0.2769$; $wR_2 = 0.5898$). Because of the poor data to parameter ratio of 15:1 and the low resolution of 1.82 Å ($2\theta_{max} = 50°$) all other non-hydrogen atoms were fixed at geometrically calculated positions. As a starting point we used the coordinates of L and bar^{2-} observed in **2**. The completed ligands were refined later as rigid groups ($R_1 = 0.2454$; $wR_2 = 0.5268$). The whole complex anion $[(Pd_3L)_8\{\mu\text{-}(bar)_{12}\}]^{16-}$ (**3**) is shown as a schematic drawing in Figure 7.

Table 2. ^{13}C-MAS-NMR signals of **3** (sh = shoulder), $\upsilon_{rot} = 15$ kHz.

δ [ppm]	Assignment	Literature
185.07	bar	182.7[12]
166.26	bar	165.2[12]
163.48	L	168.0[6]
162.34	L	167.8[6]
144.49	L	147.5[6]
134.15 sh	L	133.3/131.7[6]
120.55 sh	L	125.7/123.6[6]
116.45	L	117.7[6]
57.62	bar	60.7[12]
53.18	Et_4N^+/Et_3NH^+	53.6[6]/45.8[17]
32.28	bar	34.4[12]
11.31	bar	11.7[12]
8.21	Et_4N^+/Et_3NH^+	9.1[6]/8.4[17]

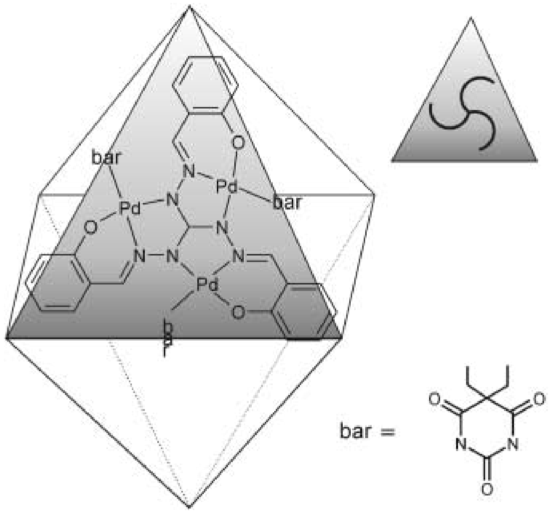


Figure 7. Schematic structure and chirality of $[\{Pd_3L\}_8\{\mu\text{- }(bar)\}_{12}]^{16-}$ (**3**).

The charge compensation can be achieved by using Na^+, Et_4N^+, or Et_3NH^+ ions. The resolution was good enough to allow us to localize four sodium ions within the capsule. The other twelve ions could be located outside and partly (as N of Et_4N^+ or Et_3NH^+) refined ($R_1 = 0.2395$; $wR_2 = 0.5086$). This assignment is in accordance with the results of the ^{13}C-MAS-NMR measurement. The X-ray data were corrected for the influence of the disordered counter cations and solvent molecules by employing the squeeze routine of PLATON ($R_1 = 0.1495$; $wR_2 = 0.3542$).[19] The resulting structure of the complex anion **3** is shown in Figure 8.

The free inside volume of the cage can be estimated to be 1600 Å^3, thereby providing enough space for four water-coordinated sodium ions. A weak interaction between the carbonyl oxygen atom of bar^{2-} and one of the Na$^+$ ions is indicated (d(O···Na) = 2.84(7) Å). Outside the octahedral capsule there is a volume of about 5200 Å^3—or 40 % of the cell volume—occupied by the other counter cations and solvent molecules. We expect the solvent to be water, since no organic solvent signals can be seen in the ^{13}C-MAS-NMR spectra. For the possible formulas $Na_4(Et_4N)_{12}[(Pd_3L)_8\{\mu\text{-}(bar)\}_{12}]\cdot x\,H_2O$ (**A**) and $Na_4(Et_3NH)_{12}[(Pd_3L)_8\{\mu\text{-}(bar)\}_{12}]\cdot x\,H_2O$ (**B**), the elemental analysis data for **A** [and **B**] were calculated as follows for $x = 20$: C 43.99 [42.55 %], H 5.22 [4.90 %], and N 11.71 [12.12 %]. The elemental analysis values measured were C 42.64, H 5.57, and N 12.05 %, which indicates the presence of Et_3NH^+ ions—a fact that was justified experimentally. Reactions containing only Et_4NOH as the base do not result in crystalline products, whereas in reaction mixtures containing Et_3N the formation of red crystals of **3** can always be observed.

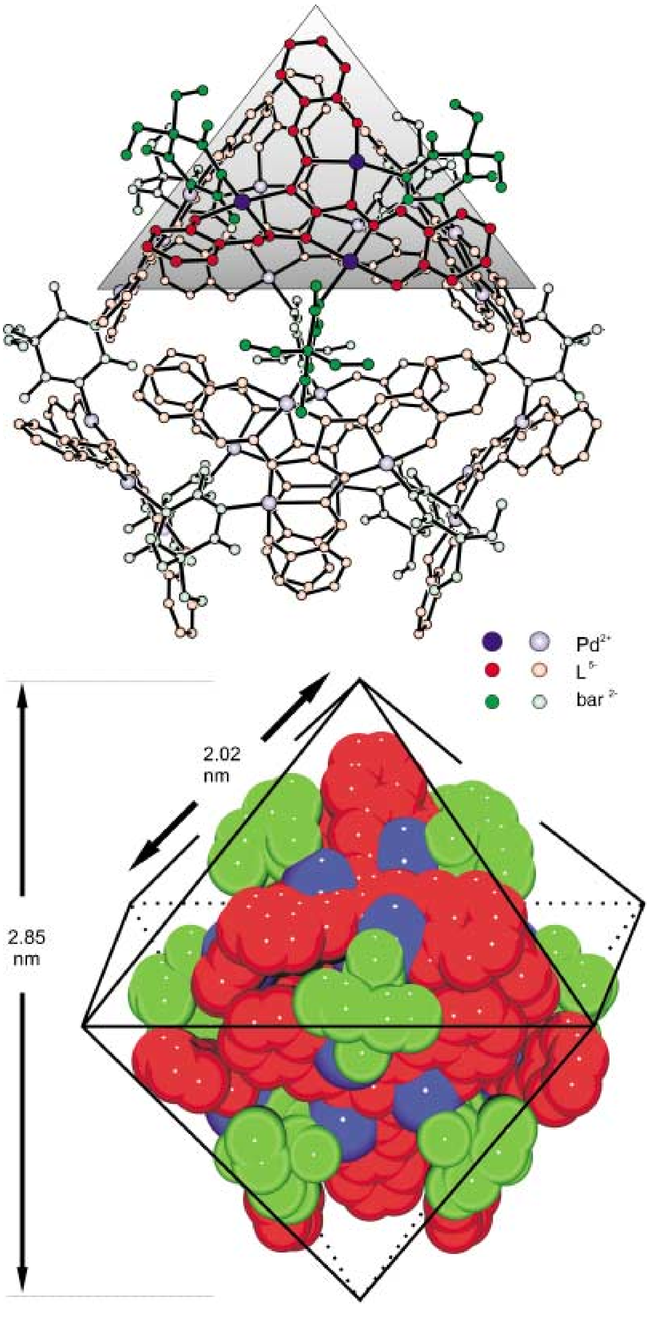


Figure 8. Crystal structure of $[\{Pd_3L\}_8\{\mu\text{-}(bar)\}_{12}]^{16-}$(**3**): Top: stick-and-ball model; bottom: space-filling model (counter cations and protons omitted for clarity).

The complex anion in **3** is chiral. The propeller-like shape of the ligand can be seen in the schematic representation of one of the faces of the octahedral cage shown in Figure 7. Inside the capsule all the ligands have the same screw sense. The observed space group $P23$ is also chiral. In the crystal there is a disorder of both enantiomers (twin refinement). The cage has crystallographic T symmetry. The screwlike distortion of half of the ligands prevents O symmetry. The different degrees of distortion can be gauged by the dihedral angles between the central CN_6^{2-} core and the aromatic systems; the absolute values are 2.2° and 31.9°. The distortion is necessary to avoid close contacts between the protons of the aromatic rings. The closest H···H contacts observed (2.5, 4.6, and 8.6 Å) are shown in the space-filling model of **3** (Figure 9). In this way each corner is sealed off tightly.

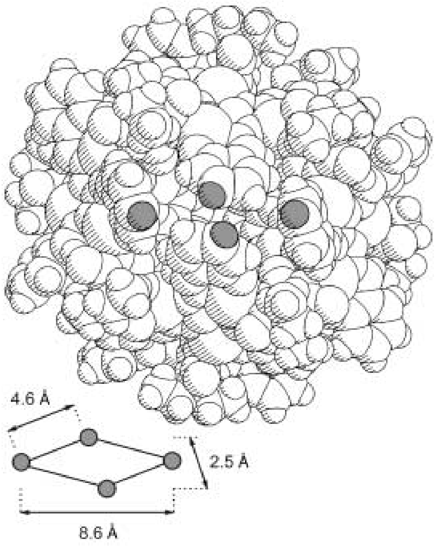


Figure 9. Space-filling model of $[\{Pd_3L\}_8\{\mu\text{-}(bar)\}_{12}]^{16-}$ (**3**) with closest H···H contacts at the corner of the octahedron (counter cations omitted for clarity).

The radius of an imaginary inner sphere in the octahedral capsule can be estimated by using the positions of the central carbon atoms of L (8.25 Å). This leads to the dimensions of the edge (20.2 Å) and height (28.5 Å, Figure 8) of the octahedron. The edge of the triangular face covered by the ligand has a length of 15.2 Å (Figure 3 a) or 75 % of the octahedron face in **3**. In this way **3** represents the first example of a closed coordination cage with the shape of an octahedron, in which most of the triangular faces are occupied by a single ligand.

Experimental Section

Tris(2-hydroxybenzylidene)triaminoguanidinium chloride $[H_6L]Cl$ and tris(ethylenediamine)cobalt(III) bromide $[Co(en)_3]Br_3$ were prepared by literature methods.[15,20] Sodium 5,5-diethylbarbiturate (NaHbar) was purchased and used without further purification.

$[H_2Pd\{P(C_6H_5)_3\}(C_{22}H_{14}N_6O_3)]$ (1): $PdCl_2$ (24.7 mg, 0.14 mmol) and Et_4NCl (54.7 mg, 0.33 mmol) were dissolved in acetonitrile (4.5 mL). Solutions of $[H_6L]Cl$ (44.3 mg, 0.098 mmol), NaHbar (14.8 mg, 0.072 mmol), and PPh_4Br (120.0 mg, 0.286 mmol) in acetonitrile (1.5 mL each) were added slowly to this solution to yield a deep red solution. Then triethylamine (1.0 mL) was slowly diffused into the reaction mixture. After three weeks red crystals of **1** were formed. Yield: 11.3 mg (0.0145 mmol, 15%). Elemental analysis calcd (%) for $C_{40}H_{31}N_6O_3PPd$ (781.11): C 61.51, H 4.00, N 10.76; found: C 60.9, H 4.8, N 10.3; ^1H NMR (400 MHz, $[D_6]DMSO$, 22 °C): $\delta = 7.98$ (m, 3H) 7.84 (m, 6H), 7.75 (m, 6H), 7.67 (m, 1H), 7.08, 6.83, 6.61, 6.47 (all m, together 11H), 3.21 ppm (m, 2H).

$[(C_2H_5)_4N]_6[\{Co\{(PdCl)(Pd)(C_{22}H_{15}N_6O_3)\}_2(\mu\text{-}(C_8H_{10}N_2O_3))\}_2]$ (2): $PdCl_2$ (22.6 mg, 0.128 mmol), $Et_4NCl{\cdot}2H_2O$ (53.6 mg, 0.266 mmol), and Et_4NOH (0.2 mL, 40% in water) were dissolved in acetonitrile (3 mL). Solutions of $[H_6L]Cl$ (21.8 mg, 0.0481 mmol), NaHbar (14.1 mg, 0.0684 mmol), and $[Co(en)_3]Br_3$ (84.3 mg, 0.176 mmol) in acetonitrile (2 mL each) were added to this solution. Then triethylamine (1.0 mL) was slowly diffused into the reaction mixture. After three weeks black crystals of **2** were formed. Yield: 13.6 mg (3.5×10^{-3} mmol, 29%). Elemental analysis calcd (%) for $Co_2Pd_8Cl_4C_{152}H_{200}N_{34}O_{18}$ (3902.47): C 46.78, H 5.17, N 12.20; found: C 47.8, H 4.8, N 11.9.

$Na_4[C_6H_{16}N]_{12}[\{Pd_3(C_{22}H_{15}N_6O_3)\}_8\{\mu\text{-}(C_8H_{10}N_2O_3)\}_{12}]{\cdot}x\,H_2O$ (3): $PdCl_2$ (48.4 mg, 0.273 mmol) and $Et_4NCl{\cdot}2H_2O$ (42.5 mg, 0.211 mmol) were dissolved in a mixture of acetonitrile (4 mL) and water (1 mL). Solutions of $[H_6L]Cl$ (42.5 mg, 0.0934 mmol) and NaHbar (26.6 mg, 0.129 mmol) in acetonitrile (2 mL each) were added. Then triethylamine (1.0 mL) was slowly diffused into the reaction mixture. After two weeks orange-red crystals of **3** were formed. Yield: 20.5 mg (2.11×10^{-3} mmol, 19%). Elemental analysis calcd (%) for $Na_4Pd_{24}C_{344}H_{432}N_{84}O_{60}{\cdot}20H_2O$ (9709.99): C 42.55, H 4.90, N 12.12; found: C 42.64, H 5.57, N 12.05; ^1H-MAS-NMR ($v_{rot} = 15$ kHz, 22 °C): $\delta = 1.0$, 1.3, 2.0, 3.0, 3.3, 4.2, 7.0, 7.9 ppm; ^{13}C-MAS-NMR ($v_{rot} = 15$ kHz, 22 °C): $\delta = 8.2$, 11.3, 23.2, 32.3, 53.2, 57.6, 116.5, 120.6(sh), 134.2(sh), 144.5, 162.3, 163.5, 166.3, 185.1 ppm.

X-ray analysis: Intensity data for **1** were collected on an Siemens P4 four-circle diffractometer ($Mo_{K\alpha}$ radiation) employing the ω scan method, for **2** on an AXS Smart/CCD diffractometer ($Mo_{K\alpha}$ radiation) employing the ω scan method, and for **3** on an Oxford Diffraction Xcalibur3 ($Cu_{K\alpha}$ radiation). All data were corrected for Lorentz and polarization effects. Absorption corrections were performed for **1** on the basis of ψ-scan data, for **2** by SADABS, and for **3** by the Gauss method. Complexes **1**–**3** were solved by using direct methods (SHELXS-97)[21] and refined by using a full-matrix least-squares refinement procedure (SHELXL-97).[22] The protons were placed at geometrically estimated positions. CCDC-219713 (**1**), CCDC-219714 (**2**), CCDC-219715 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

Solid-state NMR spectroscopy: Solid-state ^1H and ^{13}C MAS (magic-angle spinning) NMR spectra were recorded at 22 °C on a Bruker DSX 400 spectrometer at 399.9 MHz (^1H) and 100.6 MHz (^{13}C) with bottom layer rotors of ZrO_2 (diameter 4 mm) containing about 75 mg of sample, using rotation frequencies of 10 kHz and 15 kHz and a cross polarization pulse sequence with a ramp-shaped contact pulse.

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$0.634\,\mathrm{mm}^{-1}$, semiempirical absorption correction, $T_{\mathrm{min}}=0.325$, $T_{\mathrm{max}}=0.413$, 460 parameters, $R_1(I>2\sigma(I))=0.0582$, wR_2(all data) = 0.1537, max./min. residual electron density $1.223/-1.149\,\mathrm{e\AA^{-3}}$.

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[16] Crystal data for **2**: $0.32\times0.38\times0.42\,\mathrm{mm}^3$, monoclinic, $C2/c$, $a=23.82(6)$, $b=27.34(7)$, $c=30.58(7)$ Å, $\beta=108.85(4)°$, $V=18838(79)$ Å^3, $\rho_{\mathrm{calcd}}=1.376\,\mathrm{g\,cm^{-3}}$, $2\theta_{\mathrm{max}}=50.04°$, $\lambda=0.71073$ Å, $T=203$ K, 32808 measured reflections, 15092 independent reflections ($R_{\mathrm{int}}=0.1287$), 5701 observed reflections ($I>2\sigma(I)$), $\mu=1.035\,\mathrm{mm}^{-1}$, numerical absorption correction, $T_{\mathrm{min}}=0.6704$, $T_{\mathrm{max}}=0.7330$, 539 parameters, $R_1(I>2\sigma(I))=0.1464$, wR_2(all data) = 0.2830, max./min. residual electron density $1.164/-1.078\,\mathrm{e\AA^{-3}}$.

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[18] Crystal data for **3**: $0.096\times0.096\times0.096\,\mathrm{mm}^3$, cubic, $P23$, $a=b=c=23.510(3)$ Å, $V=12994(3)$ Å^3, $\rho_{\mathrm{calcd}}=1.195\,\mathrm{g\,cm^{-3}}$, $2\theta_{\mathrm{max}}=49.98°$, $\lambda=1.54178$ Å, $T=100$ K, 2269 measured reflections, 765 independent reflections ($R_{\mathrm{int}}=0.1467$), 666 observed reflections ($I>2\sigma(I)$), $\mu=7.03\,\mathrm{mm}^{-1}$,numerical absorption correction, $T_{\mathrm{min}}=0.3105$, $T_{\mathrm{max}}=0.6022$, 42 parameters, $R_1(I>2\sigma(I))=0.1495$, wR_2(all data) = 0.3542, max./min. residual electron density $0.808/-0.634\,\mathrm{e\AA^{-3}}$.

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