[(Ethylenediamine)Pt(uracilate)]$_4$ – A Metal Analogue of Calix[4]arene: Coordination Chemistry of Its 1,3-Alternate Conformer towards First-Row Transition-Metal Ions

Jorge A. R. Navarro,[a] Eva Freisinger,[a] and Bernhard Lippert*[a]

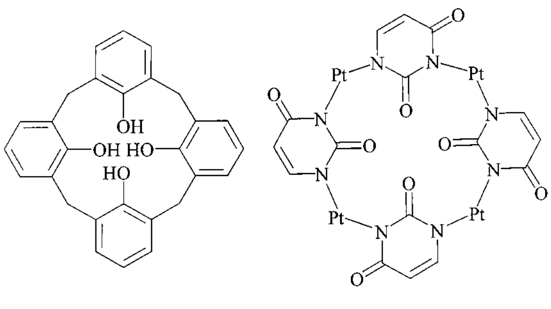
Keywords: Platinum / Uracil / Nucleobase / Host-guest chemistry

The open "molecular box" [(en)Pt(U-N^1,N^3)]$_4$ (**1**) (where en = ethylenediamine, U = uracil dianion) is able to act as an efficient ligand for additional metal ions. Reactions of the 1,3-alternate conformer of **1** with divalent metal ions result in the formation of octanuclear compounds of the general formula [(en)Pt(U-N^1,N^3,O^2,O^4)M]$_4$X$_8$ [M = Cu^{2+}, X = Cl (**2a**), X = (SO$_4$)$_{0.5}$ (**2b**), and M = Co^{2+} (**3**), Ni^{2+} (**4**), Zn^{2+} (**5**) with X = (SO$_4$)$_{0.5}$], in which the heterometals are bound at the exocyclic oxygen atoms of the uracil nucleobases. The structurally characterized heteronuclear compounds show a 1,3-alternate arrangement of the uracil nucleobases. Pt–M contacts are in the range 2.743(2)–2.804(2) Å; the Pt atoms act as weak σ donors to the heterometals. In spite of the high degree of positive charge associated with compounds **2a**–**5**, they do not behave as hosts for anions. This is a consequence of the orientation of the four nucleobases which, in contrast to a cone arrangement, does not produce a sufficiently large cavity for the incorporation of anions.

Introduction

Calixarenes and related cyclic compounds are presently the subject of considerable attention owing to their versatility as hosts for inclusion complexation.[1] In addition to their host-guest chemistry, calixarenes can also act as efficient ligands for metal ions, either through their basic oxo surfaces[2][3] or through the arene π electrons.[4] Analogous macrocyclic coordination compounds are likewise also the focus of considerable research efforts as they may also exhibit host-guest chemistry, which might ultimately be combined with the intrinsic magnetic, optical, catalytic, and structural properties of metal ions.[5]

[(en)Pt(U-N^1,N^3)]$_4$ (**1**) (where en = 1,2-diaminoethane, U = uracil dianion) shows structural similarities to calix[4]arenes (Scheme 1) and is an interesting example of a macrocyclic coordination compound that combines receptor properties analogous to those of classical calixarenes[6] with versatility as a ligand for metal ions.[7]



Scheme 1

In a previous report, we showed **1** to be a very efficient ligand towards metal ions, leading to various stoichiometries depending on the nature of the metal ion and the original conformation of the metallocalixarene.[6] A frequently encountered problem in the structural characterization of such heteronuclear compounds stems from the large number of anions present. Due to anion disorder problems, it proved impossible, in spite of a well-characterized octanuclear cation, to report complete X-ray crystallographic characterizations. Only in one case, namely that of [(en)Pt(U-N^1,N^3,O^2,O^4)Pt(NH$_3$)$_2$]$_4$(NO$_3$)$_8$, was a complete structure determination achieved.[7c] In this communication, we report on the coordination chemistry of **1** towards first row divalent transition metal ions, which has led to the generation of a series of octanuclear compounds having sulfate or chloride anions. In three cases, it has been possible to obtain X-ray quality crystals. In addition, the potential of these compounds to act as anion receptors has been studied.

Results

Reaction of a solution of freshly prepared **1** with 4 equiv. of a divalent transition metal salt at pH = 5−6 results in an immediate color change of the solution (other than in the case of Zn^{2+}), which is accompanied by a drop in the pH by 2−3 units. In the case of Zn^{2+}, addition of the metal salt leads to a significant downfield shift (+0.33 ppm) of the H^5 resonance of uracil in the ^{1}H-NMR spectrum, as well as an upfield shift (−0.10 ppm) of the H^6 resonance, indicating the formation of a thermodynamically stable species. In all other cases (compounds **2a**−**4**), the aforementioned immediate color change of the solution, to green (Cu^{2+}), purple (Co^{2+}), and yellow-green (Ni^{2+}), indicates rapid complexation of the heterometal by **1**. In each case,

---

[a] Fachbereich Chemie, Universität Dortmund,
Otto-Hahn-Straße 6, D-44221 Dortmund, Germany
Fax: (internat.) + 49-(0)231/755-3797
E-mail: lippert@pop.uni-dortmund.de

1434−1948/00/0101−0147 $ 17.50+.50/0

four metal ions are incorporated in the resulting compound, giving $[(en)Pt(U\text{-}N^1,N^3,O^2,O^4)CuCl(H_2O)_2]_4Cl_4$ (**2a**) and $[(en)Pt(U\text{-}N^1,N^3,O^2,O^4)M(H_2O)_3]_4(SO_4)_4$ (M = Cu, **2b**; Co, **3**; Ni, **4**; Zn, **5**). The structures of **2a**, **2b**, and **5** have been fully resolved by X-ray crystallography. The compounds consist of octanuclear cations of approximate S_4 molecular symmetry (see Figures 1 and 2), four chloride (**2a**) or sulfate (**2b**, **5**) counterions, and water molecules of hydration.

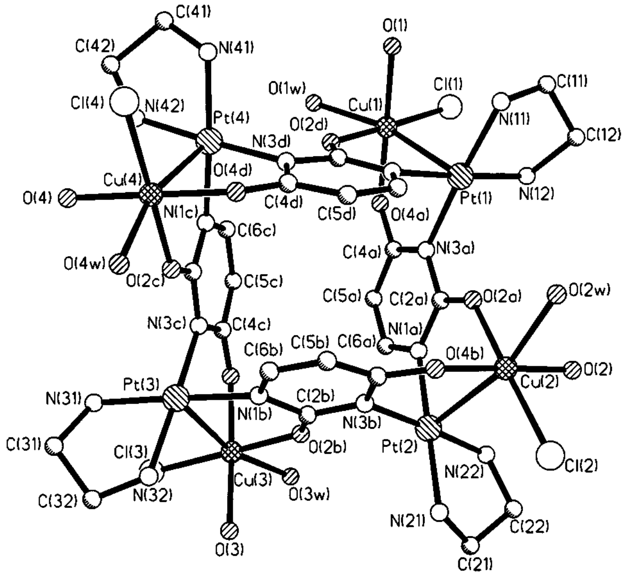


Figure 1. View of the cation $[(en)Pt(U\text{-}N^1,N^3,O^2,O^4)CuCl(H_2O)_2]_4^{4+}$ in **2a**

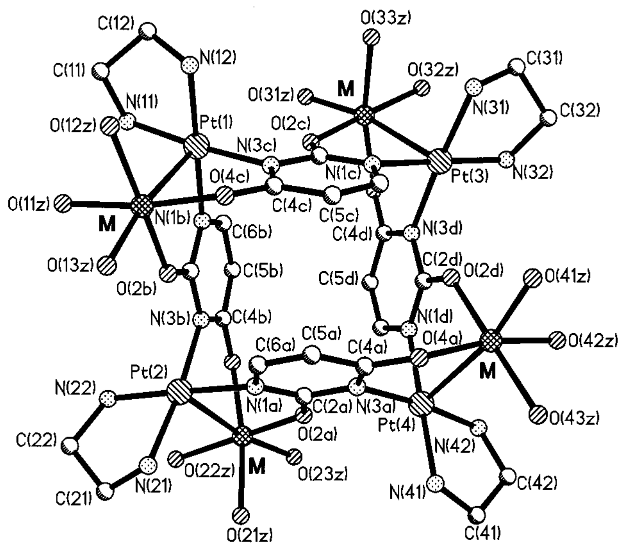


Figure 2. Perspective view of the isomorphous cations of type $[(en)Pt(U\text{-}N^1,N^3,O^2,O^4)M(H_2O)_3]_4^{8+}$ in **2b** (M = Cu^{2+}) and **5** (M = Zn^{2+})

The structures of the cations are similar to that of the original cyclic $[(en)PtHU(N^1,N^3)]_4^{4+}$ framework of **1**, with the uracil N^1 and N^3 sites platinated and a 1,3-alternate arrangement of the uracil nucleobases. There is little variation in the dimensions of the box between the complexes, the starting **1**, and the octanuclear compound $[(en)Pt(U\text{-}N^1,N^3,O^2,O^4)Pt(NH_3)_2]_4(NO_3)_8$.[7c] The mean separation between the platinum centers, which define the sides of the box, is ca. 5.8 Å, while the diagonal measures ca. 8.2 Å. In addition to the four platinum centers, four $[CuCl(H_2O)_2]^+$, $[Cu(H_2O)_3]^{2+}$, or $[Zn(H_2O)_3]^{2+}$ entities are strongly bound to pairs of exocyclic O^2 and O^4 donor atoms of uracil in **2a**, **2b**, and **5**, respectively. The spatial disposition of the four heterometals in the molecular box is 1,3-alternate, with a displacement of ca. 1.9 Å from the plane defined by the four platinum centers (mean deviation ca. 0.05 Å). The four copper ions in both compounds **2a** and **2b** reside in tetragonally distorted octahedral [4+1+1] environments (see Table 1). In the case of **5**, the zinc centers have distorted octahedral [5+1] environments.

Table 1. Metal–metal separations and average Pt^{2+} and M^{2+} environments (Å) in **2a**, **2b**, and **5**

	2a	2b	5
Pt–M	2.764(2) 2.760(2) 2.778(2) 2.770(2)	2.804(3) 2.790(3) 2.767(3) 2.789(3)	2.743(1) 2.788(1) 2.777(1) 2.778(1)
M–O2	1.978(8)	1.95(1)	2.008(5)
M–O4	1.950(8)	1.97(1)	2.048(5)
M–Cl	2.307(4)	–	–
M–O[a]	1.98(1)	2.01(1)	2.103(5)
M–O[b]	2.31(1)	2.31(1)	2.082(5)
Pt–N1	2.02(1)	2.00(2)	2.031(6)
Pt–N3	2.04(1)	2.02(2)	2.027(6)

[a] Water molecules placed in *cis* position to the Pt center. – [b] Water molecule placed in *trans* position to the Pt center.

In **2a**, the equatorial positions of the copper coordination spheres are occupied by uracil O^2 and O^4 donor atoms, a water molecule, and a chloride ion, while the axial positions are occupied by water molecules and Pt^{2+} centers. In **2b** and **5**, the heterometals have coordination environments analogous to those in **2a**, differing only in that the equatorial chloride anion is replaced by a water molecule. The Pt–M separations [2.743(2)–2.804(3) Å, see Table 1] are very similar to those found in related di-[8] or trinuclear[9] complexes containing bridging 1-methyluracilato ligands and *cis*-$Pt(NH_3)_2$ entities, where distances of 2.684(1) Å and 2.765(3) Å have been observed. These distances are significantly longer than those found in heteronuclear complexes derived from *trans*-$Pt(NH_3)_2$,[10] where Pt–M distances as short as 2.49 Å have been found as a consequence of a particularly favourable interaction between the occupied d_{z^2} orbital of Pt^{2+} and the $d_{x^2-dy^2}$ orbitals of Cu^{2+} or Pd^{2+} centers.[11] Nevertheless, the Pt^{2+} centers in **2a**–**5** probably also act as weak σ-donors, as is the situation with other first row transition metals.[12] The weakness of the Pt–M interaction is highlighted by the fact that in compound **5** the axial water ligand is more closely bound to the Zn^{2+} center than the equatorial water ligand, whereas in the case of the copper compounds the tetragonal distortion is always found along the Pt–Cu axis with longer Cu^{2+}–axial water ligand separations. Taking into account the fact that the d^{10}

Zn^{2+} is not subject to a Jahn−Teller effect, in contrast to the d^9 Cu^{2+} ion, it is tentatively concluded that the Pt−Cu interaction is as weak as the Pt−Zn interaction. The tendency of Zn^{2+} to form octanuclear complexes and the weakness of the Pt−Zn donation may be offset by a stronger Zn^{2+}−axial water ligand interaction. The close structural similarities of related di- and trinuclear PtM and Pt_2M complexes (M = Pt^{2+}, Pd^{2+}, Cu^{2+}, Zn^{2+}, etc.) containing bridging uracil nucleobases suggest that the octanuclear frameworks in compounds **3** and **4** may be analogous.[13]

No unusual packing features are observed in **2a**, **2b**, and **5**. Octanuclear cations do not interact directly but are rather separated by counterions and water molecules. Multiple H-bonding interactions are seen between the Cl^- or $SO_4{}^{2-}$ anions and the amino and water ligands coordinated to the metal centers of the cations, although none of these are unusual.

It has previously been reported that compound **1** displays interesting behaviour in solution, with two main species being present, namely the 1,3-alternate and cone conformers. Depending on the experimental conditions, either of the two main species can be stabilized.[7] It is interesting to note that compound **1** in its cone conformation has been shown to be able to incorporate either four[7c] or only one additional metal ion,[6] instead of always four in the case of the 1,3-alternate conformer. Therefore, it may be concluded that the 1,3-alternate form is a much more efficient ligand for divalent metal ions as a result of a more favorable orientation of the exocyclic donor groups of the uracil nucleobases.

The ability of **5** to include anions in its cavity has been studied by means of ^{1}H-NMR spectroscopy using a series of sulfonate anions (see Experimental Section). However, in contrast to the anion host-guest chemistry exhibited by some of the metallated species of the cone conformer of **1**,[6] we found that **5** is unable to include anions in spite of its high positive charge. In fact, the ^{1}H-NMR spectrum of **5** remains unaltered following the addition of anions. Moreover, X-ray analysis results prove beyond doubt that neither chloride (**2a**) nor sulfate anions (**2b**, **5**) are included in the cavity of the compounds. Space-filling representations of the compounds with the 1,3-alternate conformation clearly reveal that the cavity is too small to permit the inclusion of an anion (Figure 3).

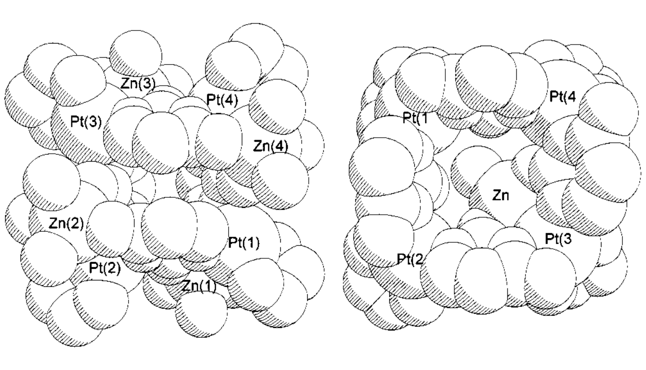


Figure 3. Space-filling representation of the 1,3-alternate-{(en)PtU]$_4$Zn$_4$}$^{8+}$ cation in **5** from the present work and the cone-{(en)PtU]$_4$Zn}$^{2+}$ cation in compound **2b** from ref.[6]

The opening of the cavity, as estimated from the separation between two opposite C^5 atoms of the uracil nucleobases, measures just ca. 3.5 Å in **5** compared to ca. 8.2 Å in cone-{(en)PtU]$_4$Zn(H_2O)}$^{2+}$.[6] Since the metal ions bound to the exocyclic oxygen atoms prevent a 1,3-alternate → cone conversion, this situation does not change with time.

Experimental Section

Materials: enPtCl$_2$,[14] (en)PtCl(UH-N^1)]Cl,[15] and [(en)Pt(UH-N^1,N^3)]$_4$(NO_3)$_4$ (**1**)[7b] were prepared from K_2PtCl_4, ethylenediamine, and uracil (Sigma) as appropriate. Sodium *p*-toluenesulfonate (TS) was purchased from Merck; sodium 3-[tris(methylsilyl)]-1-propanesulfonate (TSP), sodium 1-propanesulfonate (PS), sodium ethylsulfonate (ES), and sodium methylsulfonate (MS) from Aldrich.

Synthesis of [(en)Pt(U-N^1,N^3,O^2,O^4)CuCl(H_2O)$_2$]$_4$Cl$_4$ · *n* H$_2$O (2a): A freshly prepared solution of **1** (150 mg) in 10 mL of H_2O was passed through an anion-exchange column in its Cl^- form. The eluate was concentrated to a volume of 1 mL in a stream of dry N_2 and then $CuCl_2$ (30 mg) in 1 mL of H_2O was added. An immediate color change from pale-green to brown-green was observed. After storage of the solution for a week, brown-green crystals of **2** could be collected. Yield 46 mg (20%). − $C_{24}H_{80}Cl_8Cu_4N_{16}O_{28}Pt_4$ (2359.13): calcd. C 12.22, H 3.42, Cl 12.02, N 9.50; found C 11.8, H 3.3, Cl 11.6, N 9.2.

Synthesis of [(en)Pt(U-N^1,N^3,O^2,O^4)M(H_2O)$_3$]$_4$(SO_4)$_4$ · *n* H$_2$O (2b, 3, 4, 5): The general procedure used for the synthesis of the complexes was as follows: a freshly prepared solution of **1** (0.059 mmol) in 3 mL of H_2O (pH = 4.9) was mixed with a solution of the metal salt (0.24 mmol) in 1 mL of H_2O. Following the addition of the metal salt, the pH value of the respective solutions dropped to 2.5−3 and some turbidity appeared, which was removed by centrifugation. Storage of the resulting solutions (**2a**, green; **3**, purple; **4**, green; **5**, colorless) led to the deposition of crystalline precipitates of the resulting complexes within one day. − **2a:** green, yield 50 mg (34%). − $C_{24}H_{80}Cu_4N_{16}O_{44}Pt_4S_4$ (2459.75): calcd. C 11.72, H 3.28, N 9.11; found C 11.9, H 3.3, N 9.3. − **3:** purple, yield 37 mg (25%). − $C_{24}H_{80}Co_4N_{16}O_{44}Pt_4S_4$ (2441.19): calcd. C 11.81, H 3.30, N 9.18; found C 11.9, H 3.0, N 9.7. − **4:** yellow-green, yield 50 mg (34%). − $C_{24}H_{80}N_{16}Ni_4O_{44}Pt_4S_4$ (2440.38): C 11.81, H 3.30, N 9.18; found C 11.8, H 3.1, N 9.3. − **5:** colorless, yield 50 mg (34%). − $C_{24}H_{80}N_{16}O_{44}Pt_4S_4Zn_4$ (2467.11): calcd. C 11.68, H 3.27, N 9.08; found C 11.9, H 3.1, N 9.6. − ^{1}H NMR (200 MHz, D_2O, pH* = 6.5): δ = 2.75 (s, 4 H, CH_2), 5.67 (d, *J* = 7.0 Hz, 1 H, 5-H), 7.69 (d, *J* = 7.0 Hz, 1 H, 6-H).

Instrumentation: IR spectra (in KBr pellets) were recorded with a Bruker IFs 113v FT-IR spectrometer. − ^{1}H-NMR spectra were recorded with a Bruker AC 200 FT NMR spectrometer in D_2O solution using $NMe_4{}^+$ (δ = 3.18 relative to TMS) as an internal standard.

NMR Titrations: Stock solutions ($1 \cdot 10^{-2}$ M) of the 1,3-alternate conformer of **1** were prepared in D_2O. To a 0.40-mL sample of this solution in a 5-mm NMR tube at pH* = 6.5 was added 4 equiv. of 0.2 M $ZnSO_4$ solution, followed by increasing aliquots of (0.4 M

Table 2. Crystallographic data for compounds **2a**, **2b**, and **5**

Compound	**2a**	**2b**	**5**
Empirical formula	$C_{24}H_{71.8}Cl_8Cu_4N_{16}O_{23.9}Pt_4$	$C_{24}H_{86}Cu_4N_{16}O_{47}Pt_4S_4$	$C_{24}H_{86}N_{16}O_{47}Pt_4S_4Zn_4$
M_r	2285.29	2513.85	2521.17
Crystal system	triclinic	triclinic	triclinic
Space group	$P-1$	$P-1$	$P-1$
a [Å]	16.232(3)	14.256(3)	14.177(3)
b [Å]	16.324(3)	14.187(3)	14.221(3)
c [Å]	16.367(3)	17.895(4)	17.903(4)
α [°]	117.37(3)	92.80(3)	83.58(3)
β [°]	110.49(3)	95.36(3)	86.88(3)
γ [°]	90.87(3)	90.36(3)	89.89(3)
V [Å^3]	3526(1)	3599(1)	3581(1)
Z	2	2	2
ρ(calcd.) [Mg/m^{-3}]	2.153	2.320	2.338
μ(Mo-K_α) [mm^{-1}]	9.459	9.126	9.322
F(000)	2166	2420	2428
Crystal color	green-yellow	green-yellow	colorless
Crystal size [mm]	0.63 × 0.56 × 0.44	0.38 × 0.13 × 0.09	0.63 × 0.15 × 0.14
$2\theta_{max}$[°]	47.3	42	54
Index ranges	$0 \leq h \leq 18$ $-18 \leq k \leq 18$ $-18 \leq l \leq 16$	$0 \leq h \leq 14$ $-14 \leq k \leq 14$ $-17 \leq l \leq 17$	$0 \leq h \leq 18$ $-18 \leq k \leq 18$ $-19 \leq l \leq 19$
Reflns. collected	9862	48399	14410
Independent reflns.	9862	7254	14410
Obsd. reflns. [$I > 2\sigma(I)$]	5755	3783	10336
Parameters refined	808	533	889
R_1[a] (obsd. data)	0.0404	0.0466	0.0372
wR_2[b] (obsd. data)	0.0889	0.0962	0.0940
Goodness of fit (obsd. data)	1.119	1.115	1.118
Residuals [eÅ^{-3}]	0.809/−1.638	1.999/−0.923	1.550/−1.763

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

or 4 M) solutions of NaX (X = TSP, TS, PS, ES, MS) (pH* indicates uncorrected pH meter reading). ^{1}H-NMR spectra were recorded for ten different mixtures and the shifts of the H^5 and H^6 resonances of uracil were analyzed as described previously[6] in order to evaluate the association constants.

X-ray Crystallography: Intensity data for **2a**, **2b**, and **5** were collected with an Enraf−Nonius KappaCCD diffractometer[16] (Mo-K_α, λ = 0.71069 Å, graphite monochromator) with sample-to-detector distances of 30.7, 32.7, and 25.7 mm, respectively. The whole sphere of reciprocal space was covered by measurement of 360 frames rotating about ω in steps of 1° with scan times of 13, 230, and 40 s per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames and were then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.[17] The scaling and the global refinement of crystal parameters were performed by SCALEPACK.[17] Reflections that were partly measured on previous and following frames were used to mutually scale these frames. Merging of redundant reflections partly eliminates absorption effects and, if present, also takes crystal decay into account.

The structures were solved by standard Patterson methods[18] and refined by full-matrix least squares based on F^2 using the SHELXTL-PLUS[19] and SHELXL-93 programs.[20] The atom scattering factors were taken as those given in the SHELXTL-PLUS program. Transmission factors were calculated using SHELXL-97.[21] Hydrogen atoms were placed in calculated positions and refined with a common isotropic temperature factor. In the case of **2a**, only two of the positions of the chloride counterions were found to be fully occupied. For the remaining two anions, seven positions were assumed, as represented by the seven strongest peaks showing a reasonable H-bonding pattern. The residual peaks were assigned to positions fully or partly occupied by water molecules. All non-hydrogen atoms were refined anisotropically, with the exception of a few disordered chloride anions and water molecules. In **2b**, only the heavy atoms, the oxygens of one sulfate, and seven of the eleven water molecules could be anisotropically refined because of the poor reflections-to-parameters ratio. In compound **5**, part of the water molecules and the disorder shown by the oxygens of two sulfate counterions could only be calculated isotropically. Crystal data and data collection parameters are summarized in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101632, -127613, and -127614. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. JARN thanks the University of Granada for a Postdoctoral Fellowship.

---

[1] [1a] C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, **1989**. – [1b] V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713−745. – [1c] A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713−1734.

[2] Some examples of metallated species: [2a] L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, *J. Am. Chem. Soc.* **1997**, *119*, 9198−9210. – [2b] V. C. Gibson, C. Redschaw, W. Clegg, M. R. J. Elsegood, *J.*

Chem. Soc., Chem. Commun. **1995**, 2371–2372. – [2c] G. E. Hofmeister, E. Alvarado, J. A. Leary, D. I. Yoon, S. F. Pedersen, *J. Am. Chem. Soc.* **1990**, *112*, 8843–8851. – [2d] J. A. Acho, T. Ren, J. W. Yun, S. J. Lippard, *Inorg. Chem.* **1995**, *35*, 5226–5532. – [2e] S. R. Dubberley, A. J. Blake, P. Mountford, *Chem. Commun.* **1997**, 1603–1604. – [2f] M. G. Davidson, J. A. K. Howard, S. Lamb, C. W. Lehmann, *Chem. Commun.* **1997**, 1607–1608.

[3] Review: C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93–161.

[4] [4a] M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter, *J. Am. Chem. Soc.* **1997**, *119*, 6324–6335. – [4b] J. W. Steed, R. K. Juneja, J. L. Atwood, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2456–2457. – [4c] H. Iki, T. Kikuchi, S. Shinkai, *J. Chem. Soc., Perkin Trans. 2* **1993**, 205–208. – [4d] A. Ikeda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 3102–3110.

[5] [5a] K. Yamanari, I. Fukuda, T. Kawamoto, Y. Kushi, A. Fuyuhiro, N. Kubota, T. Fukuo, R. Arakawa, *Inorg. Chem.* **1998**, *37*, 5611–5618. – [5b] M. Fujita, J. Yazaki, K. Ogura, *Tetrahedron* **1991**, *32*, 5589–5592. – [5c] R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11813–11814. – [5d] R. Bakthiar, H. Chen, S. Ogo, R. H. Fish, *Chem. Commun.* **1997**, 2135–2136. – [5e] V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwinski, *Prog. Inorg. Chem.* **1996**, *45*, 83–178. – [5f] J. A. Hafen, J. J. Bodwin, V. L. Pecoraro, *Inorg. Chem.* **1998**, *37*, 5416–5417.

[6] [6a] J. A. R. Navarro, M. B. L. Janik, E. Freisinger, B. Lippert, *Inorg. Chem.* **1999**, *38*, 426–432. – [6b] J. A. R. Navarro, B. Lippert, *Coord. Chem. Rev.* **1999**, *185–186*, 653–657.

[7] [7a] H. Rauter, E. C. Hillgeris, B. Lippert, *J. Chem. Soc., Chem. Commun.* **1992**, 1385–1386. – [7b] H. Rauter, E. C. Hillgeris, A. Erxleben, B. Lippert, *J. Am. Chem. Soc.* **1994**, *116*, 616–624. – [7c] H. Rauter, I. Mutikainen, M. Blomberg, C. J. L. Lock, P. Amo-Ochoa, E. Freisinger, L. Randaccio, E. Zangrando, E. Chiarparin, B. Lippert, *Angew. Chem. Int. Ed.* **1997**, *36*, 1296–1301.

[8] [8a] D. Neugebauer, B. Lippert, *J. Am. Chem. Soc.* **1982**, *104*, 6596–6601. – [8b] H. Schöllhorn, U. Thewalt, B. Lippert, *Inorg. Chim. Acta* **1985**, *107*, 77–81.

[9] I. Mutikainen, O. Orama, A. Pajunen, B. Lippert, *Inorg. Chim. Acta* **1987**, *137*, 189–193.

[10] G. Fusch, E. C. Fusch, A. Erxleben, J. Hüttermann, H.-J. Scholl, B. Lippert, *Inorg. Chim. Acta* **1996**, *252*, 167–178 and references cited therein.

[11] C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holthenrich, B. Lippert, *Inorg. Chem.* **1995**, *34*, 3418–3424.

[12] [12a] D. M. L. Goodgame, R. W. Rollins, B. Lippert, *Polyhedron* **1985**, *4*, 829–839. – [12b] D. M. L. Goodgame, M. A. Hitchman, B. Lippert, *Inorg. Chem.* **1986**, *25*, 2191–2194. – [12c] D. M. Duckworth, D. M. L. Goodgame, M. A. Hitchman, B. Lippert, *Inorg. Chem.* **1987**, *26*, 1823–1825.

[13] [13a] B. Lippert, *Prog. Inorg. Chem.* **1989**, *37*, 1–98. – [13b] E. Zangrando, L. Pichierri, L. Randaccio, B. Lippert, *Coord. Chem. Rev.* **1996**, *156*, 275–332.

[14] F. Basolo, J. C. Bailar, Jr., *J. Am. Chem. Soc.* **1950**, *72*, 2433–2438.

[15] B. Lippert, *Inorg. Chem.* **1981**, *20*, 4326–4343.

[16] NONIUS B.V., *KappaCCD Package*, Röntgenweg 1, P. O. Box 811, NL-2600 AV Delft, The Netherlands.

[17] Z. Otwinowsky, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode", *Methods in Enzymology* (Eds.: C. W. Carter, Jr., R. M. Sweet), Academic Press, **1996**, p. 276.

[18] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

[19] G. M. Sheldrick, *SHELXTL-PLUS (VMS)*, Siemens Analytical X-ray Instruments, Inc., Madison WI, **1990**.

[20] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1993**.

[21] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany **1997**.

Received June 25, 1999
[I99231]