Poulsen, J. K. M. Sanders, *Chem. Commun.* **1999**, 1575; j) S. J. Rowan, P. S. Lukeman, D. J. Reynolds, J. K. M. Sanders, *New J. Chem.* **1998**, *22*, 1015; k) P. A. Brady, R. P. Bonar-Law, S. J. Rowan, C. J. Suckling, J. K. M. Sanders, *Chem. Commun.* **1996**, 319.

[10] J. E. Baldwin, *J. Chem. Soc. Chem. Commun.* **1976**, 734.

[11] K. A. Connors, *Binding Constants*, Wiley, New York, **1987**.

[12] C. J. Chandler, L. W. Deady, J. A. Reiss, *J. Heterocycl. Chem.* **1981**, *18*, 599.

[13] K. E. Krakowiak, J. S. Bradshaw, W. Jiang, N. K. Dalley, G. Wu, R. M. Izatt, *J. Org. Chem.* **1991**, *56*, 2675.

Lanthanide [15]Metallacrown-5 Complexes Form Nitrate-Selective Chiral Cavities

Annabel D. Cutland, Roneil G. Malkani,
Jeff W. Kampf, and Vincent L. Pecoraro*

In 1989 we described a strategy using a metal salt and a bifunctional hydroxamic acid for the synthesis of metallomacrocycles known as metallacrowns.[1a] Metallacrowns are preorganised molecules that can be prepared in a variety of structure types[1b–f] in yields ranging from 60% to quantitative. Remarkably, the molecules are robust: they retain their structure in solution and carry out cation and anion exchange reactions without decomposition.[1g,h] Recently, we have shown that resolved amino hydroxamic acids[1i–k] can be used as precursors for the preparation of macrocycles that can have molecular weights greater than 1500 Daltons,[1k] contain multiple resolved centers, and may be amphiphilic. There is current interest in developing materials capable of anion recognition, particularly through the use of macromolecules such as calixarenes,[2a,b] porphyrins,[3a,b] and macropolycyclic polyammonium molecules[4a–c] which can require multiple step syntheses. Herein we show for the first time that one can exploit the asymmetry of the chiral metallacrown motif to realize molecular cavities that are capable of selective anion recognition by using molecules that are made in a one-step reaction from simple starting materials.

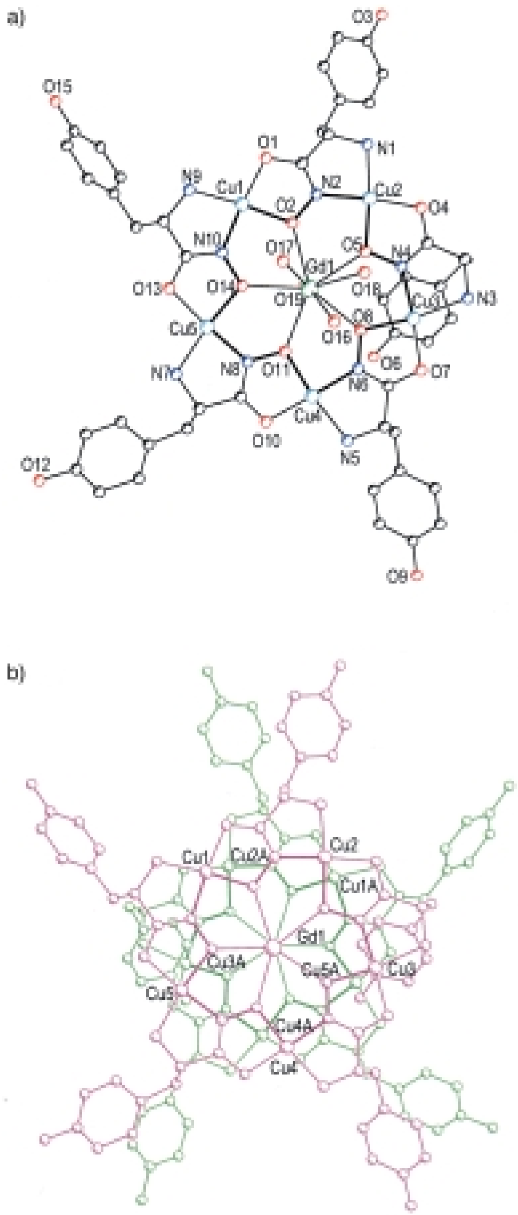

Figure 1. PLUTO diagram of $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ with chloride ions removed for clarity. a) Monomer and b) dimer shown looking down the psuedo fivefold axis, with the C_2 axis in the plane of the page.

The metallacrown dimer $[(\mathbf{1})\mathrm{Cl}_2]^{4+}$[5] (Figures 1 and 2a, Table 1)[6, 7] is prepared using L-tyrosinehydroxamic acid (H_2tyrha) as a ligand.[8] The molecule contains five tyrosinehydroximate ligands and five $\mathrm{Cu^{II}}$ ions in each of the two [15]metallacrown-5 (15MC-5) disks, with a $\mathrm{Gd^{III}}$ ion captured in the core of each metallamacrocycle to give a stoichiometry of $[\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd}]^{3+}$. The metallacrowns have rotational symmetry, and therefore, the use of L-tyrosinehydroxamic acid provides face differentiation as the side chains are all oriented to the same "hydrophobic" face. The metallacrowns in the dimer are related to one another by a C_2 axis that is parallel to the plane of the disc, and thus are orientated with the hydrophobic faces towards each other. As viewed down the pseudo fivefold axis the MC that is on top has clockwise (C) rotational symmetry (Cu-O-N-Cu); therefore, the bottom metallacrown is anticlockwise (A) when viewed from this perspective, thus giving a C/A isomer. While four phenol groups from each metallacrown are extended into solution, the remaining two wrap into the cavity and bond to a ring copper ion from the opposite metallacrown ($\mathrm{Cu{-}O_{tyr}} = 2.872$ Å). The ring oxygen atoms are nearly perfectly staggered, with an O–O twist angle (defined as the torsion angle O2-Gd1-Gd1A-O2A) between the two metallacrowns of the dimer of 35.7°. However, because the metallacrowns have C/A rotational symmetry, the Cu–Cu twist angle (Cu1-Gd1-Gd1A-Cu2A) is 11.4°, which makes the ring copper ions closer to being eclipsed than staggered. The result is a weakly

---

[*] Prof. V. L. Pecoraro, A. D. Cutland, R. G. Malkani, J. W. Kampf
Department of Chemistry
Willard H. Dow Laboratories
The University of Michigan, Ann Arbor, MI 48109-1055 (USA)
Fax: (+1) 734-647-4865
E-mail: vlpec@umich.edu

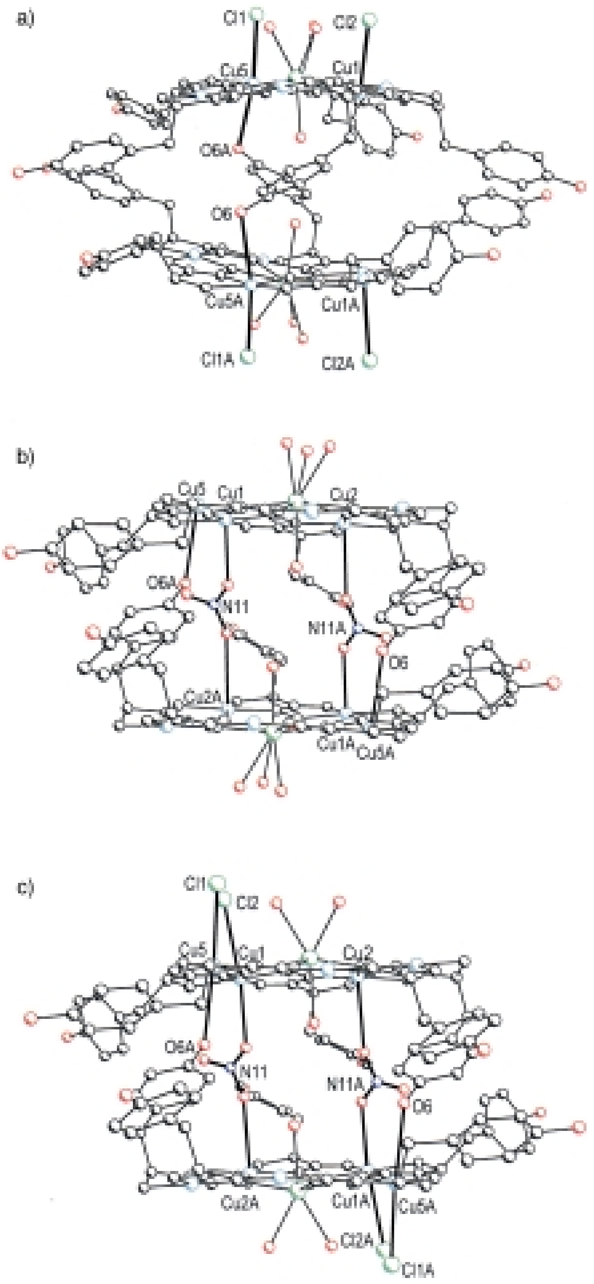

Figure 2. PLUTO diagrams of a) $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$, b) $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$, and c) $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$. The structures in b and c are viewed down the C_2 axis while a is rotated 90° from this view.

associated dimer with the Gd ions separated by 8.34 Å and a metallacrown cavity of 776 Å^3. Thus, through an exceedingly simple reaction, one can isolate a crystalline compound of molecular weight 2963 Daltons that contains 12 metal atoms, 10 defined carbon centers, and a nearly nanometer sized cavity in 60.5 % yield.

In the preceding structure there are two chloride ions per dimer that are weakly bound to ring copper ions on the outer face of each metallacrown. The same basic structure and chloride localization is obtained if La$^{\mathrm{III}}$ is substituted for Gd$^{\mathrm{III}}$ in the synthesis. We conclude that while chloride ions are capable of binding to the Cu$^{\mathrm{II}}$ ions, they do so only to the outer face of the metallacrown.

Table 1. Selected metrical parameters for $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$, $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$, and $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$.

Distance [Å]/angle [°]	Metallacrown		
	$[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$	$[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$	$[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$
across the dimer cavity			
Cu1-Cu2A	7.55	7.26	7.47
Cu3-Cu5A	7.76	8.00	7.90
Cu4-Cu4A	6.68	7.90	7.26
Gd1-Gd1A	8.34	8.39	8.49
O-O twist	35.7	40.6	38.6
Cu-Cu twist	11.4	15.1	14.6
axial Cu distances			
Cu1-$\mathrm{O_{(tyr)}}$	2.87	2.83	2.86
Cu1-$\mathrm{O_{(NO3)}}$	N/A[a]	2.48	2.64
Cu2-$\mathrm{O_{(NO3)}}$	N/A[a]	2.96	2.97
Cu5-Cl1	2.86	N/A[a]	2.89
Cu1-Cl2	3.14	N/A[a]	3.14
inter-dimer			
Gd1-Gd1B	8.19	8.52	8.28
Cu1-Cu1B	6.26	6.67	6.25
Cu5-Cu5B	5.71	6.07	5.77

[a] Not available.

We have also prepared $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ (Figure 2 b) in approximately 80 % yield.[9, 10] The basic structural features of $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ and $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ are essentially identical except that two nitrate anions are captured in the cavity and bridge the dimer by binding to ring copper ions. The nitrate shortens the Cu1–Cu2A distances by 0.29 Å in $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ relative to that in $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ and the twist angles increase by 4–5°. Additional anions required for charge balance are found in the lattice. Thus, the cavity can act as a host for nitrate but not chloride in the solid state. We have tested the selectivity of the tyrosine metallacrown dimer for nitrate versus chloride ions in two ways. First, we assessed whether there was a binding preference for nitrate over chloride ions during the initial assembly of the metallacrown. In syntheses that contained a 10:3:1 ratio of chloride:nitrate:metallacrown a complex is isolated that contains two nitrate and two chloride ions per dimer.[11] Therefore, despite biasing the synthesis toward chloride ions, nitrate ions continue to bind inside the cavity. An X-ray analysis of $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$ (Figure 2 c)[12] reveals a hybrid structure of $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ and $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ with metrical parameters midway between these two structures (Table 1). Of interest is the observation that the Cu1–$\mathrm{O_{nitrate}}$ bond in $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$ is nearly 0.16 Å longer than that in $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$. This difference is a result of the chloride ions binding to Cu1 in $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$. Note that Cl1 and Cl2 are *always* bound to Cu5 and Cu1, respectively, in the presence or absence of nitrate, while the nitrate ion is *always* bound between Cu1 and Cu2A, whether or not chloride is present (see Figure 2). Next, we added four equivalents of sodium nitrate to an aqueous solution of $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ to test whether the metallacrown $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ could be converted into $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$. A blue crystalline solid was obtained that is identical in all respects to $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$.[13] Therefore, we have shown that the pre-formed metallacrown can selectively incorporate nitrate ions directly into the cavity with minor structural perturbations. Surprisingly, despite repeated attempts to sequester acetate, in the presence and absence of nitrate, we have not observed acetate ligands bound to **1**.

While the guest, in this case, is achiral, we hope in the future to exploit the chirality of metallacrowns by building larger cavities that may show recognition of chiral anions.

In conclusion, we have shown that a chiral metallamacrocycle can be prepared in excellent yield in a one-step synthesis using commercially available starting materials. The resultant metallacrown binds nitrate ions, complexing this anion with minor perturbations to a cavity with dimensions approaching 1 nm^3. In contrast, acetate ions have not been seen to bind to the metallacrown, while chloride ions only bind to the outer face. These observations of the solid state are consistent with selective anion recognition; however, they do not directly address the solution behavior. Future studies to define and quantify the binding interactions of nitrate in solution are planned. We suggest that these metallacrowns form a new class of selective anion recognition agents that can be prepared by simple modification of the side chains of α-aminohydroxamic acids to alter the size, charge, or topology of the resultant supramolecular species. Through such variation, selective recognition of anions containing differing charge, shape, size, or chirality may be achieved.

Experimental Section

$[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$: Prepared by the reaction of L-tyrosinehydroxamic acid (H_2tyrha, 0.395 g, 2.00 mmol) with $\mathrm{CuCl_2\cdot 2H_2O}$ (0.342 g, 2.00 mmol), $\mathrm{GdCl_3\cdot 6H_2O}$ (0.150 g, 0.40 mmol), and pyridine (0.5 ml, 6.00 mmol) in water (50 mL). Blue-violet crystals of $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ were obtained by slow evaporation of the solvent.

$[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$: Prepared as for $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ using $\mathrm{Gd(NO_3)_3\cdot 5H_2O}$ and $\mathrm{Cu(OAc)_2\cdot H_2O}$, without pyridine. Blue-violet crystals of $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ were obtained by slow evaporation of the solvent.

$[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$: Prepared as for $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ using $\mathrm{Gd(NO_3)_3\cdot 5H_2O}$ and $\mathrm{CuCl_2\cdot 2H_2O}$ in water and methanol. Blue-violet crystals of $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$ were obtained by slow evaporation of the solvent.

Received: October 10, 1999 [Z14099]
Publication delayed at authors' request

---

[1] a) M. S. Lah, V. L. Pecoraro, *J. Am. Chem. Soc.* **1989**, *111*, 7258; b) V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwinski, *Progress in Inorganic Chemistry, Vol. 45* (Ed.: K. D. Karlin), Wiley, New York, **1997**, pp. 83–177; c) B. Kwak, H. Rhee, S. Park, M. S. Lah, *Inorg. Chem.* **1998**, *37*, 3599; d) G. Psomas, C. Dendrinou-Samara, M. Alexiou, A. Tsohos, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **1998**, *37*, 6556; e) R. W. Saalfrank, N. Löw, F. Hampel, H.-D. Stachel, *Angew. Chem.* **1996**, *108*, 2353; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2209; f) R. W. Saalfrank, N. Löw, S. Kareth, V. Seitz, F. Hampel, D. Stalke, M. Teichert, *Angew. Chem.* **1998**, *110*, 182; *Angew. Chem. Int. Ed.* **1998**, *37*, 172; g) B. R. Gibney, H. Wang, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1996**, *35*, 6184; h) A. J. Stemmler, J. W. Kampf, V. L. Pecoraro, *Angew. Chem.* **1996**, *108*, 3011; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2841; i) J. Halfen, J. J. Bodwin, V. L. Pecoraro, *Inorg. Chem.* **1998**, *37*, 5416; j) A. J. Stemmler, A. Barwinski, M. J. Baldwin, V. Young, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 11962; k) A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi, V. L. Pecoraro, *Inorg. Chem.* **1999**, *38*, 2807.

[2] a) W. Xu, J. J. Vittal, R. J. Puddephatt, *J. Am. Chem. Soc.* **1993**, *115*, 6456; b) N. Pelixxi, A Casnati, R. Ungaro, *Chem. Comm.* **1998**, *23*, 2607.

[3] a) J. L. Sessler, M. Cyr, H. Furuta, V. Kral, T. Mody, T. Morishima, M. Shionoya, S. Weghorn, *Pure Appl. Chem.* **1993**, *65*, 393; b) R. C. Jagessar, M. Shang, W. R. Scheidt, D. H. Burns, *J. Am. Chem. Soc.* **1998**, *120*, 11684.

[4] a) S. Mason, T. Clifford, L. Seib, K. Kuczera, K. Bowman-James, *J. Am. Chem. Soc.* **1998**, *120*, 8899; b) G. Papoyan, K. Gu, J. Wiorkiewicz-Kuczera, K. Kuczera, K. Bowman-James, *J. Am. Chem. Soc.* **1996**, *118*, 1354; c) J.-M. Lehn, *Science* **1985**, *227*, 849.

[5] Compound **1** refers to the core dimer $[\{\mathrm{Gd15MC_{Cu(II)(L\text{-}tyrha)}\text{-}5}\}_2]^{6+}$, while $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$, $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$, and $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$ indicate the anion-bound forms of the metallacrown. The empirical formula for each molecule is given with the X-ray parameters.

[6] General crystallographic data: Data were collected on a SMART-CCD 3-circle diffractometer equipped with LT-2 low-temperature device and $\mathrm{Mo_{K\alpha}}$ ($\lambda = 0.71073$ Å) radiation. Crystals were coated with inert oil to prevent solvent loss and frozen to a teflon fiber. The data were processed using the SAINT processing package (v4.05) with a narrow-frame algorithm. A correction for absorption was performed by SADABS (R. Blessing, *Acta Cryst.* **1995**, *A51*, 33). Structure solution and refinement was performed by direct methods using the SHELXTL program suite (v5.10) operating on a SGI Octane workstation. 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-135202–135204. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] Crystal data for $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$: ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5GdCl\cdot 2OH\cdot 12H_2O}$), $M_r = 1731.56$, monoclinic, space group *C*2 (no. 5), $a = 18.6666(2)$, $b = 29.58500(10)$, $c = 14.58100(10)$ Å, $\alpha = 90.000$, $\beta = 122.6680(10)$, $\gamma = 90.000°$, $V = 6778.59(9)$ Å^3, $Z = 4$; $\rho_{\mathrm{calcd}} = 1.697$ g cm^{-1}; $2.44 < \theta < 26.41°$; crystal dimensions, $0.22 \times 0.32 \times 0.38$ mm^3; $\mu = 26.31$ cm^{-1}; $T = 158(2)$ K; 13731 unique of 31544 reflections collected. 12844 reflections and 803 parameters were used for the full matrix, least-squares refinement on F^2, $R1 = 0.0551$, $wR2 = 0.1539$. Two hydroxide anions are inferred for charge balance, but have not been located.

[8] Elemental analysis calcd for $[\mathbf{1}\cdot(\mathrm{Cl})_2]^{4+}$ ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5GdCl\cdot 2OH\cdot 5H_2O}$): C 33.67, H 3.89, N 8.72; found: C 33.61, H 3.62, N 8.72. positive ion FAB-MS (in methanol with a 3-nitrobenzyl alcohol matrix): m/z: 1443.6 $[\mathrm{M}]^+$.

[9] Elemental analysis calcd for $[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$ ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd\cdot 1.5NO_3\cdot 1.5OH\cdot 1.5H_2O}$): C 33.96, H 3.45, N 10.12; found: C 33.68, H 3.57, N 10.47. positive-ion FAB-MS (in methanol in a 3-nitrobenzyl alcohol matrix): m/z: 1443.7 $[\mathrm{M}]^+$.

[10] Crystal data for ($[\mathbf{1}\cdot(\mathrm{NO_3})_2]^{4+}$): ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd\cdot 1.5NO_3\cdot 1.5OH\cdot 9H_2O}$), $M_r = 1726.57$, monoclinic, space group *I*2 (no. 5), $a = 15.02060(10)$, $b = 28.9110(2)$, $c = 16.42480(10)$ Å, $\alpha = 90.000$, $\beta = 103.9510(10)$, $\gamma = 90.000°$, $V = 6922.24(8)$ Å^3, $Z = 4$; $\rho_{\mathrm{calcd}} = 1.657$ g cm^{-1}; $2.47 < \theta < 29.44°$; crystal dimensions, $0.14 \times 0.34 \times 0.44$ mm^3; $\mu = 25.43$ cm^{-1}; $T = 158(2)$ K; 16913 unique of 3718 reflections collected. 15095 reflections and 851 parameters were used for the full matrix, least-squares refinement on F^2, $R1 = 0.0649$, $wR2 = 0.1682$. One and a half hydroxide anions are inferred for charge balance, but have not been located.

[11] Elemental analysis calcd for $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$ ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd\cdot NO_3\cdot Cl\cdot OH\cdot 12H_2O}$): C 30.42, H 4.26, N 8.67, Cu 17.9; found: C 29.73, H 4.05, N 8.92, Cu 17.4. positive-ion FAB-MS (in methanol with a 3-nitrobenzyl alcohol matrix): m/z: 1444.6 $[\mathrm{M}]^+$.

[12] Crystal data for $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$: ($\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd\cdot NO_3\cdot Cl\cdot OH\cdot 7.5H_2O}$), $M_r = 1754.59$, monoclinic, space group C2 (no. 5), $a = 19.1017(4)$, $b = 29.1994(6)$, $c = 14.7861(3)$ Å, $\alpha = 90.000$, $\beta = 123.9670(10)$, $\gamma = 90.000°$, $V = 6839.8(2)$ Å^3, $Z = 4$; $\rho_{\mathrm{calcd}} = 1.647$ g cm^{-1}; $1.39 < \theta < 26.40°$; crystal dimensions, $0.38 \times 0.42 \times 0.68$ mm^3; $\mu = 26.03$ cm^{-1}; $T = 158(2)$ K; 13909 unique of 61978 reflections collected. 13354 reflections and 800 parameters were used for the full matrix, least-squares refinement on F^2, $R1 = 0.0499$, $wR2 = 0.1453$. One hydroxide anion is inferred for charge balance, but has not been located.

[13] Elemental analysis calcd for $\mathrm{C_{45}H_{50}N_{10}O_{15}Cu_5Gd\cdot NO_3\cdot Cl\cdot OH\cdot 10H_2O}$: C 31.05, H 4.11, N 8.85, Cu 18.3; found: C 30.75, H 3.82, N 9.06, Cu 17.5. positive ion FAB-MS (in methanol with a 3-nitrobenzyl alcohol matrix): m/z: 1443.9 $[\mathrm{M}]^+$. The structure was solved by X-ray crystallography and shown to be identical to $[\mathbf{1}\cdot(\mathrm{Cl})_2(\mathrm{NO_3})_2]^{2+}$.