Mono-, Di- and Polymeric Calcium and Gadolinium Complexes of the Tripodal Ligand 2,2′,2′′-Nitrilotribenzoic Acid

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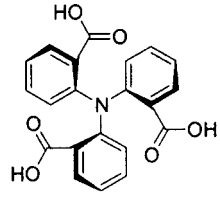
Three novel carboxylate-bridged complexes incorporating the tripodal N,O ligand 2,2′,2′′-nitrilotribenzoic acid H_3L of formula $[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]\cdot 4H_2O$ (**1**), $[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2\cdot 7H_2O$ (**2**) and $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2\cdot 13H_2O$ (**3**) were synthesized and characterized by X-ray crystallography. In all three complexes, the ligand H_3L binds to the metal centre only by its three carboxylate donors, leaving the bridgehead nitrogen atom nonbonding. The calcium(II) ion in the monomeric complex **1** is distorted pentagonal-bipyramidal coordinated, the +1 charge of the complex cation $[Ca^{II}(H_2L)(OH_2)_4]^+$ is balanced by an H_2L^- anion and both units are connected by hydrogen bonds. The polymeric compound **2** displays a one-dimensional chain structure, in which two $[Ca^{II}(L)]^{2-}$ units form a dimeric structure and are connected by hydrated Ca^{II} ions. **3** contains two different $[Gd^{III}(L)(OH_2)_n]$ dimers. In one of them the two Gd^{III} ions are linked by two monoatomic carboxylate O-bridges showing a short Gd···Gd distance of 3.99 Å. In the second, a *syn-anti* carboxylate 1,3-bridge with a longer Gd···Gd distance of 4.96 Å is observed. Magnetic measurements of **3** show paramagnetic behaviour with weak antiferromagnetic coupling.

Introduction

The self-assembly of supramolecular architectures by use of metal ion-ligand interactions is one of the most powerful methods to obtain new molecular structures. The carboxylate group is a versatile ligand and favours the formation of oligomeric and polymeric complexes, it can adopt different binding modes, such as terminal monodentate, chelating to one metal center and various modes of bridging coordination of two, three four or even five metal centres.[1] Metal carboxylates have therefore emerged as an important family of supramolecular coordination compounds and inorganic open framework materials.[2] Organic di- and tricarboxylates broaden the availability of such architectures and provide an effective means to design such structures. While dicarboxylates have been extensively studied in this respect, the supramolecular coordination chemistry of ligands carrying three highly preorganized carboxylate groups has been less well explored.

Here we report mono-, oligo and polymeric complexes of the tricarboxylate ligand 2,2′,2′′-nitrilotribenzoic acid H_3L. We have recently described five-coordinate transition metal complexes of H_3L in which the triphenyl nitrogen atom is involved in metal coordination with exception of an octahedral complex $[Fe^{III}(L)(OH_2)_3]$ in which the "hard" Fe^{III} ion is complexed only by the carboxylate groups of L.[3]



H_3L

This study focuses on Ca^{II} and Gd^{III} complexes, which display higher coordination numbers (> 6) of the metal ion and which tend to form polynuclear structures with various bridging modes of the carboxylate donor of H_3L. Studies of Ca^{II} binding to small molecules have led to generalizations about their corresponding binding preferences. Calcium may coordinate to between five and nine atoms, it exhibits irregular geometries and prefers oxygen donor ligands. The distances of Ca–O bonds show a wide variation of 2.20 to 2.80 Å.

Gadolinium coordination compounds are the subject of intense research efforts due to their applications as MRI contrast agents or as precursors for novel magnetic materials.[4] The number of di- and polynuclear Gd^{III} compounds for which structural and magnetic data are available is restricted. In Gd^{III} dimers usually weak antiferromagnetic interactions are reported.[5]

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Results and Discussion

Synthesis and Characterization

We were able to characterize two new calcium(II) and one gadolinium(III) coordination compound containing the tripodal N,O-ligand H_3L. The synthesis of H_3L was achieved by a copper-catalyzed Ullman-nitrogen-arylation, followed by a standard base hydrolysis as described previously.[6] Compounds **1**–**3** were synthesized by mixing equimolar amounts of the ligand H_3L and the appropriate metal salt in water. $Ca(OH)_2$ was used as a base to deprotonate H_3L. Crystals suitable for X-ray crystallography were obtained by slow evaporation of the solvent after several days at room temperature. A description of the structures **1**–**3**, together with figures of the complexes is given below. Selected bond lengths and angles are given in Table 1 and Table 2. Crystal data and data collection details are presented in Table 3.

$[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]\cdot 4H_2O$ (1)

Complex **1** contains a $[Ca^{II}(H_2L)(OH_2)_4]^+$ cation, a $[H_2L]^-$ anion and four water molecules (Figure 1). The distorted pentagonal-bipyramidal coordination sphere of the calcium(II) core is composed of the $[H_2L]^-$ ligand that coordinates by two COOH and one COO^- to two equatorial and one axial site, and the four remaining sites are occupied by water molecules. The presence of coordinating COOH groups is supported by the unsymmetric bond distances C14–O3 1.222(1) Å, C1–O4 1.315(1) Å and C21–O5 1.221(1) Å, C21–O6 1.317(1) Å, compared with the nearly

Table 1. Selected distances (Å) and angles (°) of **1** and **2**.

1		**2**	
Ca(1)–O(1)	2.347(1)	Ca(1)–O(1)	2.352(1)
Ca(1)–O(3)	2.421(1)	Ca(1)–O(3)	2.292(1)
Ca(1)–O(5)	2.424(1)	Ca(1)–O(5)	2.313(1)
Ca(1)–O(13)	2.336(1)	Ca(1)–O(5a)	2.572(1)
Ca(1)–O(14)	2.468(1)	Ca(1)–O(6a)	2.520(1)
Ca(1)–O(15)	2.388(1)	Ca(1)–O(7)	2.357(1)
Ca(1)–O(16)	2.396(1)	Ca(1)–O(8)	2.404(1)
Ca(1)···N(1)	3.780(1)	Ca(1)···N(1)	3.574(1)
		Ca(1)···Ca(1a)	4.008(1)
O(1)–Ca(1)–O(3)	93.16(3)	O(1)–Ca(1)–O(3)	92.49(4)
O(3)–Ca(1)–O(5)	71.69(3)	O(1)–Ca(1)–O(5)	85.86(4)
O(1)–Ca(1)–O(5)	90.75(3)	O(1)–Ca(1)–O(8)	90.42(5)
O(1)–Ca(1)–O(13)	170.98(4)	O(3)–Ca(1)–O(7)	168.09(5)
O(1)–Ca(1)–O(14)	106.49(3)	O(1)–Ca(1)–O(5a)	143.75(4)
O(1)–Ca(1)–O(15)	80.56(4)	O(1)–Ca(1)–O(7)	81.96(6)

Table 2. Selected distances (Å) and angles (°) of **3**.

Gd(1)···Gd(1′)	4.959(1)	Gd(2)···Gd(2′)	3.996(1)
Gd(1)···N(1)	3.756(2)	Gd(2)···N(2)	3.739(2)
Gd(1)–O(1)	2.293(2)	Gd(2)–O(11)	2.395(2)
Gd(1)–O(2′)	2.422(2)	Gd(2)–O(11′)	2.484(2)
Gd(1)–O(3)	2.368(2)	Gd(2)–O(12′)	2.490(2)
Gd(1)–O(5)	2.385(2)	Gd(2)–O(13)	2.279(2)
Gd(1)–O(7)	2.334(2)	Gd(2)–O(15)	2.303(2)
Gd(1)–O(8)	2.549(2)	Gd(2)–O(17)	2.355(2)
Gd(1)–O(9)	2.499(2)	Gd(2)–O(18)	2.466(2)
Gd(1)–O(10)	2.388(2)	Gd(2)–O(19)	2.409(2)
O(1)–Gd(1)–O(3)	78.79(7)	O(11)–Gd(2)–O(15)	75.78(8)
O(1)–Gd(1)–O(5)	97.04(7)	O(11)–Gd(2)–O(13)	84.32(8)
O(3)–Gd(1)–O(5)	77.79(7)	O(13)–Gd(2)–O(15)	95.35(9)
O(1)–Gd(1)–O(7)	146.92(8)	O(11)–Gd(2)–O(17)	141.98(9)
O(1)–Gd(1)–O(9)	143.24(8)	O(11)–Gd(2)–O(19)	140.11(8)

Table 3. Crystallographic data of $[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]\cdot 4H_2O$ (**1**); $[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2\cdot 7H_2O$ (**2**) and $[Gd^{III}(L)(OH_2)_3]_2$-$[Gd^{III}(L)(OH_2)_4]_2\cdot 13H_2O$ (**3**).

Compound	**1**	**2**	**3**
Empirical formula	$C_{42}H_{44}CaN_2O_{20}$	$C_{44}H_{60}Ca_3N_2O_{28}$	$C_{84}H_{128}Gd_4N_4O_{64}$
M_r	936.87	1185.18	2846.90
Crystal system	monoclinic	triclinic	triclinic
Space group	*Cc*	$P\bar{1}$	$P\bar{1}$
a (Å)	29.790(1)	9.7539(5)	10.8541(4)
b (Å)	9.8802(4)	10.7435(5)	13.0603(5)
c (Å)	15.3957(7)	12.8194(6)	19.9940(8)
α (°)	90	76.799(1)	100.343(1)
β (°)	106.185(1)	76.225(1)	96.564(1)
γ (°)	90	88.223(1)	107.174(1)
V (Å^3)	4351.9(3)	1269.86(11)	2621.4(2)
Z	4	1	1
$\rho_{calcd.}$ (mg/m^{-3})	1.430	1.550	1.803
μ (mm^{-1})	0.229	0.422	2.609
F_{000}	1960	622	1428
T (K)	103(2)	103(2)	103(2)
Crystal size (mm)	0.30 × 0.30 × 0.15	0.40 × 0.18 × 0.17	0.16 × 0.16 × 0.04
$\theta_{max.}$ (°)	32.03	32.00	32.01
Measured reflns.	39387	23496	52091
Unique reflns. (R_{int})	14114 [0.0272]	8612 [0.0244]	17742 [0.0435]
Parameters	763	463	942
Goodness of fit	1.057	1.081	1.044
*R*1 ($I > 2\ \sigma_I$)	0.0328	0.0441	0.0333
*wR*2 (all reflections)	0.0849	0.1277	0.0803
Residuals (e·Å^{-3})	0.492/–0.343	0.617/–1.025	2.244/–1.540

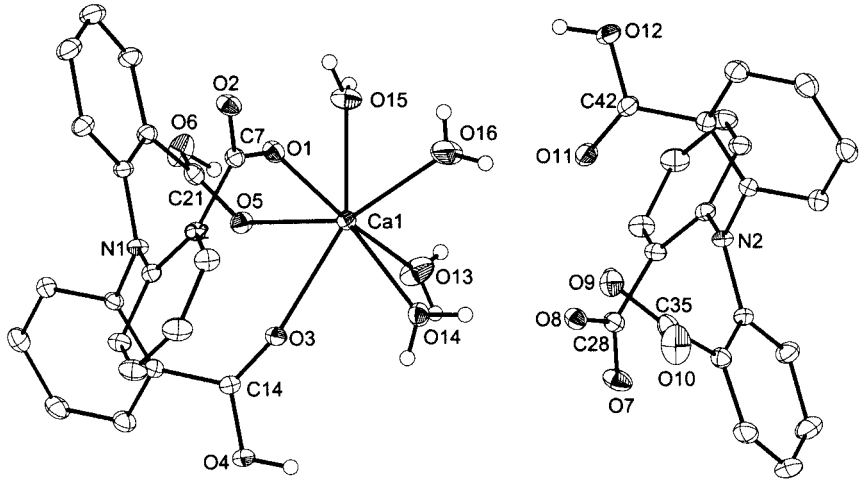

Figure 1. Ellipsoid plot of $[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]$ (**1**). Aryl-H atoms and the H_2O solvent molecules have been omitted for clarity.

symmetric coordinating COO^- group: C7–O1 1.253(1) Å and C7–O2 1.273(1) Å. Also in the nonbonding $[H_2L]^-$ anion two unsymmetric bond distances are found for the COOH group: C35–O9 1.325(1) Å, C35–O10 1.217(1) Å and C42–O11 1.214(1) Å, C42–O12 1.316(1) Å, compared to the nearly symmetric bond distances of the COO^- group: C28–O7 1.265(1) Å and C28–O8 1.260(1) Å. The central nitrogen atom of $[H_2L]^-$ does not coordinate to the calcium ion [Ca1···N1 3.78 Å], resulting in a O3 coordination mode of the ligand. The two equatorial Ca–O bonds are almost identical [2.421(5) and 2.424(1) Å] and the axial Ca–O bond is, as expected, significantly shorter [2.347(1) Å]. The other Ca–O distances lie within the range of 2.336(1) and 2.468(1) Å. Planarization of the triarylamine unit is evident by an average C–N(1)–C angle of 119.0°, underlining the nonbonding property of the nitrogen atom to the calcium ion [average C–N(2)–C angle 118.4 °]. Hydrogen bonds linking $[Ca^{II}(H_2L)(OH_2)_4]^+$ and $[(H_2L)]^-$ are found between H(O16)–O11 [2.023(1) Å] and H(O14)–O8 [1.958(1) Å]. Furthermore, there are other O–H···O interactions between coordinated water and free water molecules.

$[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2\ 7H_2O$ (2)

A second calcium complex $[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2 \cdot 7H_2O$ (**2**) was isolated out of the reaction mixture yielding complex **1**. In contrast to **1**, the complex is a linear polymer and contains dimeric $[Ca^{II}(L)(OH_2)_2]_2^{2-}$ units, which are bridged by hydrated Ca^{II} ions (Figure 2). In the centrosymmetric $[Ca^{II}(L)(OH_2)_2]_2^{2-}$ unit, each Ca^{II} ion is hepta-coordinated and has a distorted pentagonal-bipyramidal coordination sphere, interacting with L^{3-} by three carboxylate donors. The four remaining sites are occupied by two water molecules and a bidentate bridging carboxylate group of the second $[Ca^{II}(L)]^-$ unit. The resulting –2 charge per $[Ca^{II}(L)(OH_2)_2]_2^{2-}$ unit is balanced by a hexacoordinate Ca^{II} cation. The Ca^{II} ion links the dinuclear units by axial coordination of bridging carboxylates, while its octahedral coordination sphere is completed by four equatorial water molecules. The Ca1–O distances lie in the range of 2.292(1) and 2.572(1) Å. The Ca2–O bond distances are similar to the reported ones for six-coordinate calcium complexes: Ca2–O2 2.335(2) Å, Ca2–O9 2.321(1) Å and Ca2–O10

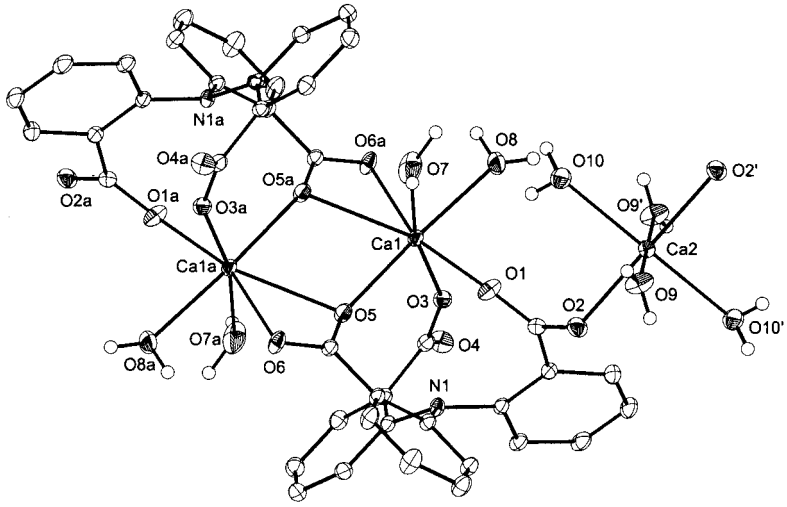

Figure 2. Ellipsoid plot of $[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2$ (**2**). Aryl-H atoms and the H_2O solvent molecules have been omitted for clarity.

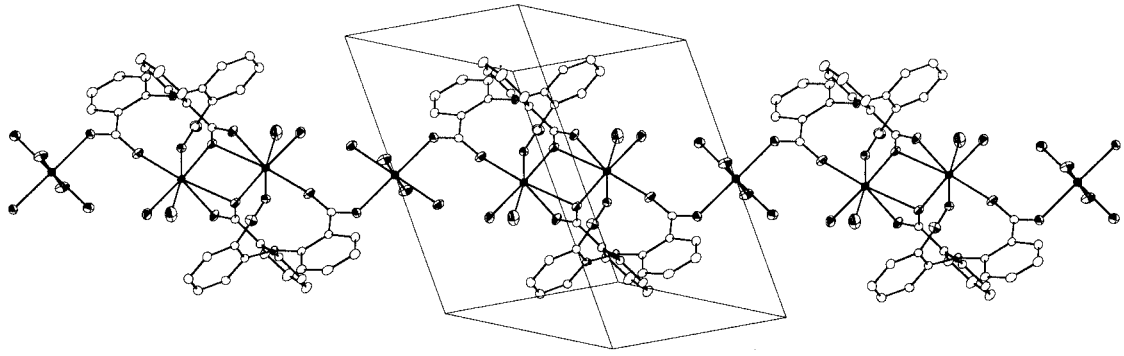

Figure 3. View of the self-assembled one-dimensional supramolecular architecture of **2** emphasizing the catenarian order of the calcium ions; hydrogen atoms and solvate molecules have been omitted for clarity.

2.369(1) Å. The Ca1···Ca1a distance of 4.008(1) Å is relatively long compared to other structurally characterized carboxylate-bridged calcium-dimers with average Ca···Ca distances around 3.8 Å.

$[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2 \cdot 13H_2O$ (3)

H_3L reacts with gadolinium(III) to the complex $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2 \cdot 13H_2O$ (**3**), incorporating two dimers $[Gd^{III}(L)(OH_2)_3]_2$ and $[Gd^{III}(L)(OH_2)_4]_2$ with different Gd^{III} coordination spheres. The structure of **3** is shown in Figure 4. Two $[Gd^{III}(L)]$ moieties are joined via the carboxylate groups of L^{3-}. The gadolinium ions are eight-coordinate in both structures. The coordination geometry of the metal ion can be described as distorted square-antiprismatic. The remarkable structural feature of **3** is that the flexible ligand H_3L adopts two different coordination modes at the gadolinium(III) ions: In $[Gd^{III}(L)(OH_2)_4]_2$ (Figure 4, left) the two metal ions are bridged by two bidentate carboxylate groups in a *syn-anti* fashion, resulting in a large Gd···Gd distance of 4.959(1) Å. In the second dimer (Figure 4, right), in analogy to the Ca^{II} complex **2**, the bridging carboxylate groups are tridentate with formation of a four-membered chelate ring with one gadolinium ion, resulting in a smaller Gd···Gd distance of 3.996(2) Å; this Gd···Gd′ distance is comparable to that found in other complexes containing Gd_2O_2 rings.[7] The Gd–O distances range from 2.293(1) Å to 2.499(1) Å. The average Gd–O distance at Gd1 is 2.407(1) Å and 2.397(1) Å for Gd2, which is close to other reported Gd^{III} dimers.[8] The angles Gd2–O11–Gd2′ and O11–Gd2–O11′ are 109.96° and 70.04°, respectively. Many lanthanide(III) carboxylate complexes reported in the literature have polymeric structures [9] and only a few are dimeric.[10]

Magnetic Properties of 3

The magnetic susceptibility (χ_M) of **3** was measured in the temperature range 2–300 K. The variations of the inverse of the magnetic susceptibility, χ_M^{-1} and $\chi_M T$ of **3** are shown in Figure 6. The μ_{eff} value of 7.83 μ_B at room temperature is close to the calculated spin-only value (7.94 μ_B). The $\chi_M T$ product at 300 K (30.7 $cm^3 \cdot K \cdot mol^{-1}$) is expected for four isolated Gd^{3+} ions ($^8S_{7/2}$) and remains almost constant to 20 K. Below 10 K the $\chi_M T$ product decreases steeply down to 19.7 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. Such behaviour indicates paramagnetic behaviour of the Gd centres in **3** with weak antiferromagnetic coupling, as observed before in several binuclear Gd complexes.[11] The experimental points (7–300 K) obey the Curie–Weiss law with a Weiss constant θ = –0.18 K and Curie constant C = 30.731 which corresponds to four Gd^{3+} ions with the average g value

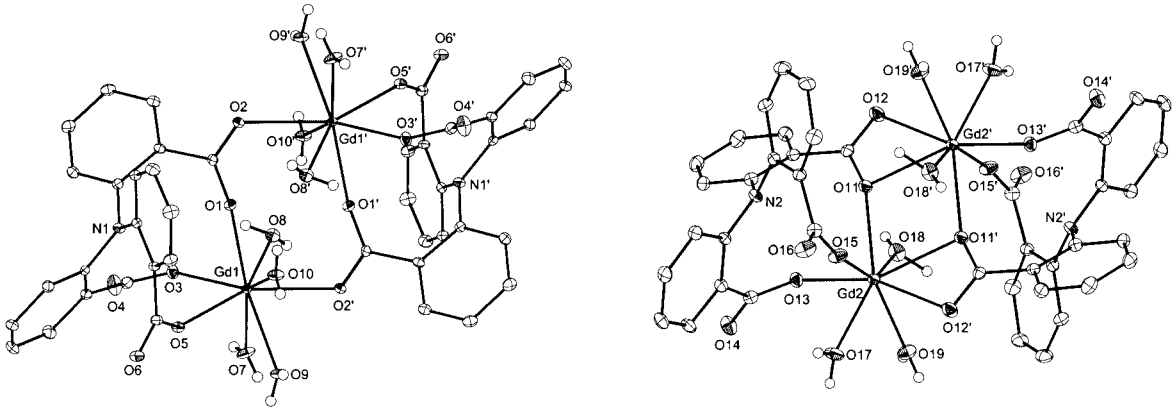

Figure 4. Ellipsoid plot of $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2 \cdot 13H_2O$ (**3**); aryl-H atoms and the H_2O solvent molecules have been omitted for clarity.

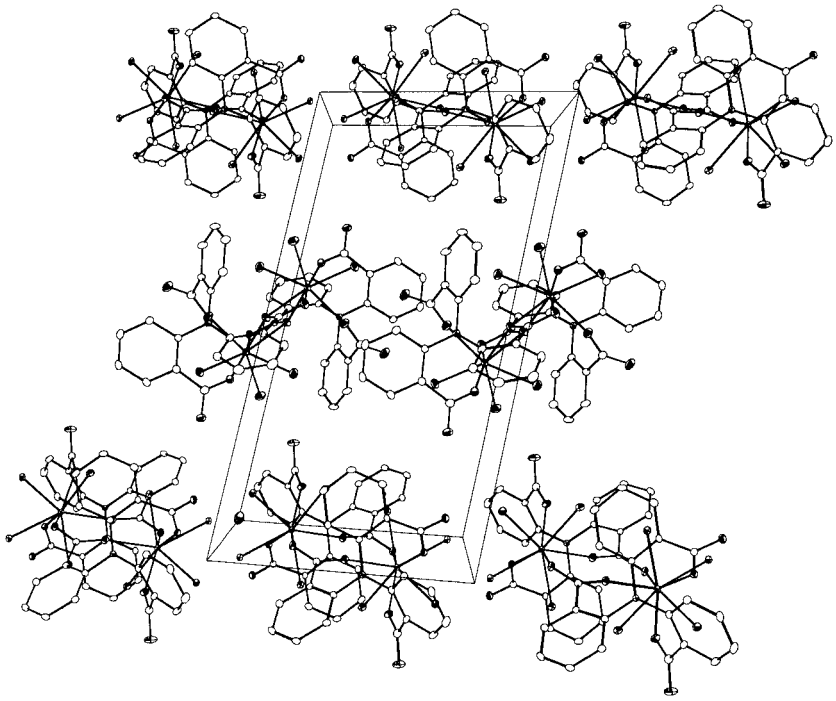

Figure 5. View of $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2{\cdot}13H_2O$ (**3**) showing the discrete arrangement of the $[Gd(L)]_2$ units.

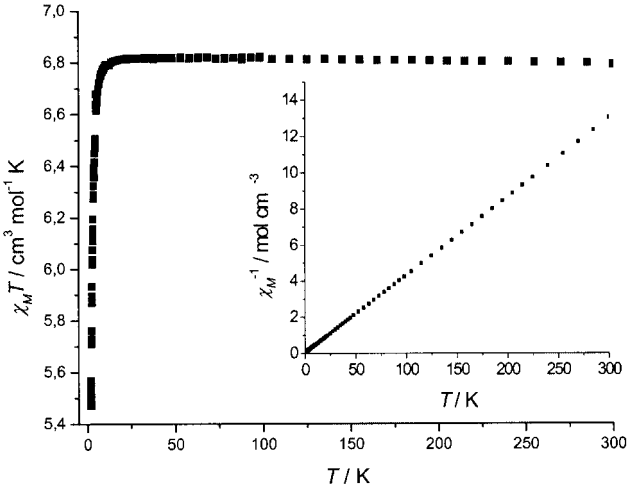

Figure 6. Plot of $\chi_M T$ and χ_M^{-1} vs. T for **3**.

equal to 1.975. Since two inequivalent exchange Gd dimeric units are present and the sample exhibits very weak antiferromagnetic interaction, it is not possible to distinguish the contribution to the observable behaviour from each coupling pattern using an analytical expression. Thus, the susceptibility data were fitted on the basis of the equation deduced from the isotropic Heisenberg model[12] envisaged the presence of an average isotropic coupling parameter $J = (J1 + J2)/2$ ($\boldsymbol{H} = -J \times \boldsymbol{S_1} \times \boldsymbol{S_{1'}} = -J \times \boldsymbol{S_2} \times \boldsymbol{S_{2'}}$, $\boldsymbol{S_1} = \boldsymbol{S_{1'}} = \boldsymbol{S_2} = \boldsymbol{S_{2'}} = 7/2$). A quantitative analysis of the data gave J to be equal to –0.084(2) cm^{-1}, the isotropic g factor to be equal to 1.975. Note, that J values in the range between –0.04 and –0.11 cm^{-1} were reported for other gadolinium dimers.[11,12]

UV/Vis-Spectrophotometric Titrations

Smooth formation of 1:1 complexes is indicated by isosbestic points, when H_3L in water/methanol at pH 7 is titrated with the appropriate metal salts (Figure 7). The UV-band at $\lambda_{max.}$ = 300 nm, that served as a probe for the M···N interaction, is nearly unchanged, in accordance to the crystal structures showing no M···N interactions. Metal coordination of this nitrogen atom is accompanied by a significant decrease of the 300 nm absorbance.[3]

Conclusions

In summary we have characterised new binding modes of lewis-hard metals to the versatile ligand H_3L. With calcium(II) a monomeric species $[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]{\cdot}4H_2O$ (**1**) and a polymeric species $[Ca^{II}(OH_2)_4][Ca^{II}(L)(OH_2)_2]_2{\cdot}7H_2O$ (**2**) is formed, revealing rare examples of calcium(II) complexes with tridentate carboxylate only donor sets in mononuclear complex **1** and in one-dimensional chain-like structure **2**. With gadolinium(III) the complex $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2{\cdot}13H_2O$ (**3**), incorporating two different dimers with Gd···Gd distances of 4.0 and 5.0 Å, respectively, is formed. The magnetic properties of compound **3** have been studied, revealing paramagnetic behaviour of the gadolinium(III) ions with weak antiferromagnetic coupling. In all three compounds there is no interaction between the bridgehead nitrogen and the metal ions, this is in accordance with UV/Vis spectrophotometric titrations in solution. As observed previously for the iron(II) complex of L,[3] two [ML] units tend to dimerize via two carboxylate bridges in the solid state. The nonbridging car-

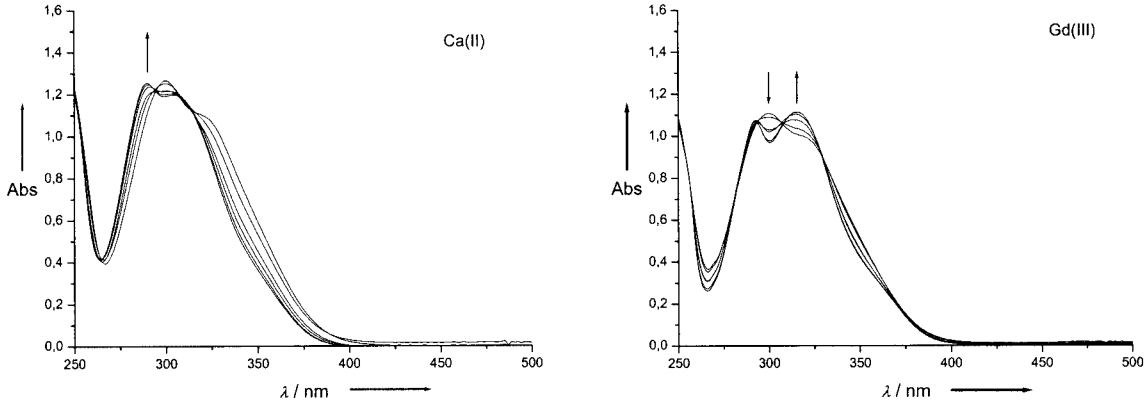

Figure 7. Spectrophotometric titration of H_3L (0.1 mM in MeOH/H_2O, pH 7, 20 mM buffer 3-(*N*-morpholino)propanesulfonic acid, T = 25 °C) with solutions of $Ca(NO_3)_2$ and $Gd(NO_3)_3$, in 0.2 equiv. steps. No further absorbance changes are observed on addition of >1 equiv. metal salt.

boxylate groups in each [ML] unit are available for interaction with "free" metal ions which link the dimers to extended structures, as exemplified by the linear-chain polymer **2**.

Experimental Section

General Remarks: All reactions were carried out in open flasks without exclusion of O_2 or H_2O. Chemicals were purchased from commercial sources (Aldrich and Acros) and were used as received without any further purifications. Electrospray ionization (ESI) mass spectra were recorded with a Q-TOF Micromass/Waters spectrometer. Absorbance UV/Vis spectra were recorded with a Specord S100 spectrophotometer (Carl Zeiss Jena). Magnetic susceptibility data were collected on ground crystals with use of a SQUID-based sample magnetometer (QUANTUM-Design, MPMS-XL-5) in the temperature range 2–300 K with an applied field of 1 T.

Preparation of the Complexes: The ligand 2,2′,2′′-nitrilotribenzoic acid H_3L was synthesised according to published methods.[6]

Synthesis of $[Ca^{II}(H_2L)(OH_2)_4][(H_2L)]\cdot 4H_2O$ (1) and $[Ca^{II}(OH_2)_4]$-$[Ca^{II}(L)(OH_2)_2]_2\cdot 7H_2O$ (2): H_3L (15.0 mg, 0.04 mmol) was dissolved in water (3 mL) and reacted with $Ca(OH)_2$ (4.4 mg, 0.06 mmol). After several days colourless crystals of **1** (monoclinic) and some of **2** (triclinic) were obtained. Yield: 13 mg (72 %). HR-ESI: *m/z*: for **1**: calcd. for $C_{21}H_{14}CaNO_6$ $[Ca(H_2L)]^+$: 416.0447; found: 416.0462; and $C_{42}H_{29}CaN_2O_{12}$ $[\{Ca(H_2L)\}\{H_2L\} + H]^+$: 793.1346; found: 793.1336; and in case of **2**: calcd. for $C_{42}H_{25}Ca_2N_2O_{12}$ $[\{CaL\}_2 + H]^-$: 829.0659; found 829.0655.

Synthesis of $[Gd^{III}(L)(OH_2)_3]_2[Gd^{III}(L)(OH_2)_4]_2\cdot 13H_2O$ (3): H_3L (15.0 mg, 0.04 mmol) was dissolved in water (3 mL) and deprotonated with $Ca(OH)_2$ (4.4 mg, 0.06 mmol). $Gd(NO_3)_3\cdot 6H_2O$ (17.9 mg, 0.04 mmol) in water (3 mL) was added to the solution and after several days colourless crystals were obtained. Yield: 18 mg (65 %). HR-ESI: *m/z*: calcd. for $C_{42}H_{26}GdN_2O_{12}$ $[(GdL)(H_2L)]^-$: 908.0727; found: 908.0725.

X-ray Crystallographic Study: Crystal data and refinement results of complexes **1**–**3** are listed in Table 3. Intensity data were collected with a BRUKER AXS Smart 1000 CCD area detector (Mo-K_α radiation, λ = 0.71073 Å, ω-scan). An empirical absorption correction was applied (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 with all measured reflections.[13] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined isotropically. Some of the solvent molecules in **2** and **3** were disordered. CCDC-243383 (for **1**), -243384 (for **2**) and -243385 (for **3**) contain 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.

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