Synthesis and Characterization of Some Metal Complexes with New Nitrogen–Oxygen Donor Macrocyclic Ligands – X-ray Crystal Structures of a 26-Membered Reduced Monoprotonated Macrocycle and a 20-Membered Pendant-Arm Schiff-Base Macrocyclic Cadmium(II) Complex

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New series of macrocyclic Schiff-base lanthanide(III), yttrium(III), and cadmium(II) complexes, [M(**1**)]X$_n$ (X = NO_3^-, M = Y, Ln = La–Yb except Pm and Dy; X = ClO_4^-, M = Cd, La, Ce, Pr, Sm, Gd, or Er) and [M(**3**)]X$_n$ (X = NO_3^-, M = Dy; X = ClO_4^-, M = Er and Cd), have been prepared by cyclocondensation of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane with *O*^{1},*O*^{7}-bis(2-aninyl)-1,4,7-trioxaheptane (**1**) or tris(2-aminoethyl)amine (**3**) in the presence of the appropriate metal salt as a template agent. The Schiff-base macrocycles **1** and **3** are also formed in the absence of a metal ion. Treatment of **1** with $NaBH_4$ in methanol gives the diamine macrocycle **2**. The reactions of Ln^{III}, Cd^{II}, and Y^{III} ions with **2** have also been investigated. The crystal structures of the monoprotonated ligand **2** and of the complex [Cd(**3**)]$(ClO_4)_2$ have been determined by X-ray diffraction analysis.

Introduction

Enormous progress in macrocyclic chemistry has been made in the past decade.[1–4] The number of new macrocyclic ligand molecules designed and synthesized has increased significantly and their structures have become much more complex. One reason for the interest in this field is that it offers exciting possibilities for creative minds to construct novel supramolecular assemblies that are capable of performing highly specific molecular functions. The precise molecular recognition between macrocyclic ligands and their guests provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine, and related science and technology.

In the course of our research programme on the synthesis and characterization of new coordination complexes of lanthanides, we have reported the synthesis of lanthanide(III) complexes with several N_xO_y-donor macrocyclic ligands containing aromatic, head, and lateral units.[5–10] The compound *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane has been used as a dicarbonyl precursor in the design of macrocyclic ligands incorporating mixed donor atoms. Most efforts to date have focused on its use in the synthesis of oxaazapolyamine macrocycles as complexing agents for transition metal or heavy metal ions.[11–14] In contrast, little has been reported on its use in the synthesis of Schiff-base macrocycles and their metal complexes.[15–17]

An important aspect of the present work has been the synthesis of two novel dibenzo-substituted Schiff-base macrocycles derived from *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane, specifically the 26-membered N_2O_6-donor macrocycle **1** and the 20-membered N_4O_3-donor pendant-arm macrocycle **3** (Scheme 1).

The coordination abilities of **1** and **3** towards lanthanide(III) ions have been investigated and, as an extension of these studies, a comparative investigation of the interactions of Y^{III} and Cd^{II} with these ligands has also been carried out. In macrocycle **3**, the role of the amine moiety as an axial coordinating pendant arm has been confirmed by X-ray structural analysis of the complex [Cd(**3**)]$(ClO_4)_2$. The Schiff-base ligand **1** has been reduced to the corresponding saturated macrocycle **2** in order to increase its flexibility and the complexation behaviour of **2** towards the aforementioned metal ions has also been investigated. We also report the X-ray crystal structure of the monoprotonated macrocycle **2**.

Results and Discussion

Macrocycle 1 and Its Metal Complexes

The non-template reaction of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane and *O*^{1},*O*^{7}-bis(2-aninyl)-1,4,7-trioxa-

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the author.

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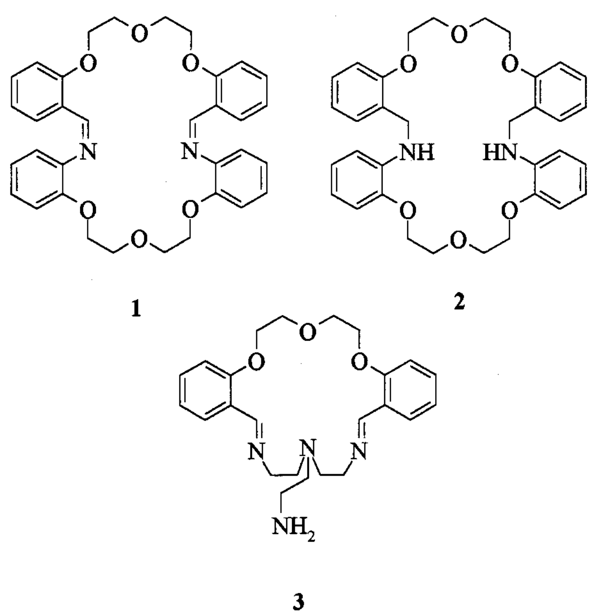


Scheme 1. Macrocycle **1**: 12,13,15,16,29,30,32,33-octahydrotetrabenzo[*h*,*l*,*u*,*y*][1,4,7,14,17,20,10,24]hexaoxadiazacyclohexacosine; macrocycle **2**: 5,6,12,13,15,16,22,23,29,30,32,33-dodecahydrotetrabenzo[*h*,*l*,*u*,*y*][1,4,7,14,17,20,10,24]hexaoxadiazacyclohexacosine, macrocycle **3**: 2-(8,9,10,11,19,20,22,23-octahydro-7*H*-dibenzo[*h*,*s*][1,4,7,11,14, 17]trioxatriazacycloicosin-9-yl)-1-ethylamine

heptane in methanol yields the Schiff-base macrocycle **1**. It was not found necessary to carry out this ring-closure under high-dilution conditions. The product was isolated as an air-stable orange-yellow solid in 75% yield and was characterized by elemental analysis, FAB MS, IR, and ^{1}H-NMR spectroscopy. The FAB mass spectrum shows the parent-ion peak at m/z = 567, confirming the [1+1] cyclic nature of the Schiff-base ligand. The IR spectrum features a strong band at 1620 cm^{-1} attributable to the azomethine group. The ^{1}H-NMR spectrum in CD_3CN solution is complicated and shows more than the expected number of signals; a signal at $\delta = 8.91$ can be attributed to the CH=N- proton. The complexity may be due to hydration and hydrolysis of imine bonds leading to carbinolamine formation and reversal of the Schiff base reaction.[18]

Cyclocondensation reactions carried out in the presence of metal salts (M = Y, Ln, Cd) yielded solids, which were characterized as the metal complexes $[M(\mathbf{1})]X_n \cdot x\,H_2O$ ($X = NO_3^-$, M = Y, La–Yb except Pm and Dy; $X = ClO_4^-$, M = Cd, La, Ce, Pr, Sm, Gd, or Er). Their analytical and conductivity data are presented in Table 1. The molar conductivities of the nitrate complexes in acetonitrile fall within the range reported for 2:1 electrolytes in this solvent.[19] This implies that one anion must be coordinated, at least in MeCN solution, and most probably in the solid state as well. The perchlorate complexes of La, Ce, Pr, Sm, and Er have conductivities between those for 2:1 and 3:1 electrolytes and the Gd and Cd complexes have values corresponding to 2:1 electrolytes, reflecting the weak coordination ability of the perchlorate anion. The FAB mass spectral results confirm the monomeric [1+1] (dicarbonyl + diamine) nature of the complexes, the most intense peak corresponding to $[\mathbf{1} + H]^+$. The spectra of the complexes frequently show peaks due to $[Ln(\mathbf{1})X_2]^+$ and for the cadmium complex peaks corresponding to $[Cd(\mathbf{1})(ClO_4)]^+$ at m/z = 779 and $[Cd(\mathbf{1})]^+$ at m/z = 680 are seen.

The complexes have similar IR spectra and the data are again consistent with the presence of imine bonds, each complex exhibiting the ν(C=N) mode at ca. 1644 cm^{-1},[20] while no bands attributable to C=O or NH_2 groups are detected. The shift of the imine band to higher wavenumbers upon complexation suggests coordination through the imine nitrogen atoms.[21,22] In the complexes derived from La^{III} nitrate and Cd^{II} and Sm^{III} perchlorates, a ν(C=N) band at ca. 1624 cm^{-1} is also seen, suggesting that in these cases only one imine N atom may be bound to the metal. The water present in the majority of the complexes (giving broad absorption bands at ca. 3450 cm^{-1}) is probably lattice and/or coordinated water.[23] All nitrate complexes exhibit absorption bands characteristic of both coordinated [ca. 1450 (ν_5), 1300 (ν_1), and 1030 (ν_2) cm^{-1}] and ionic (ca. 1380 cm^{-1}) nitrate.[24–26] The magnitude of the separation of the nitrate stretching vibrations ($\nu_5 - \nu_1$) of ca. 160 cm^{-1} is indicative of bidentate coordination.[27]

The IR spectra of the perchlorate complexes feature split bands attributable to the asymmetric Cl–O stretching mode at ca. 1080 cm^{-1} (ν_3) and the asymmetric Cl–O bending mode (ν_4) at ca. 620 cm^{-1}, suggesting that both bound and free anions are present.[28,29] The highest-energy band comprises three well-resolved maxima at ca. 1140, 1120, and 1080 cm^{-1}. However, as ν_{as}(C–O–C) for the polyether chains of the ligand also falls in this region it is not possible to precisely define the coordination mode.

The UV/visible spectra of macrocycle **1** and the corresponding metal complexes were recorded using 10^{-3}–10^{-6} M solutions in acetonitrile. For the complexes, the spectra were recorded immediately after preparation of the solutions and again after these solution had been set aside for periods of one day and one week. The spectra were found to be reproducible and no loss of the metal ion in solution could be detected. The positions of the absorption maxima, the extinction coefficients, and the linear correlation coefficients are available as Supporting Information. The free macrocycle exhibits two strong, broad absorption bands at ca. 251 and 320 nm, corresponding to the π-π* transitions of benzene rings and azomethine groups.[30] In the spectra of the metal complexes, the π-π* absorption bands are red-shifted with respect to their positions in the spectrum of **1**. The perchlorate complexes of La^{III} and Ce^{III} exhibit three strong absorptions at around 274, 317, and 391 nm; the spectra of the other complexes are similar, featuring four absorptions around 246, 291, 315, and 391 nm; the band around 246 nm may arise from charge-transfer transitions.[31,32]

Room temperature emission spectra were recorded using 10^{-6} M acetonitrile solutions of the free ligand **1** and of the $[Ln(\mathbf{1})]X_3$ (Ln = La, Nd, Eu, Gd, Tb, Lu; $X = NO_3^-$) and $[Cd(\mathbf{1})](ClO_4)_2$ complexes. The spectrum of the free ligand was recorded following excitation at 265 nm, which resulted

Table 1. Analytical, yield and molar conductance (in MeCN) data for the complexes $[M(\mathbf{1})]X_n \cdot x\,H_2O$ (calculated values are given in parentheses)

M	x	Analysis (%) C	N	H	Yield (%)	Λ_M (Ω^{-1} cm^{2}mol^{-1})	Colour
$X = NO_3^-$							
Y[a]	3	47.85 (48.35)	6.70 (6.70)	5.25 (5.80)	31	225	pale brown
La	7	40.30 (40.15)	6.85 (6.90)	4.55 (4.75)	41	289	yellow/orange
Ce	3	43.60 (43.15)	7.05 (7.40)	4.85 (4.25)	51	278	orange
Pr[b]	–	47.00 (47.20)	7.30 (7.25)	4.70 (4.60)	34	220	orange
Nd	8	38.80 (39.25)	7.25 (6.80)	4.65 (4.85)	55	296	yellow/orange
Sm	2	43.10 (43.50)	7.40 (7.45)	3.95 (4.10)	44	246	yellow/green
Eu	4	42.30 (41.80)	7.00 (7.15)	4.40 (4.30)	27	237	orange
Gd	3	41.65 (42.35)	7.75 (7.30)	3.95 (4.20)	52	270	orange
Tb	5	40.25 (40.75)	7.20 (7.00)	3.90 (4.45)	18	229	dark orange
Ho	2	42.00 (42.80)	7.65 (7.35)	4.05 (4.00)	78	284	brown
Er	3	42.10 (41.95)	6.70 (7.20)	4.10 (4.15)	46	291	pale orange
Tm	7	38.90 (39.00)	6.45 (6.70)	4.10 (4.60)	50	279	orange
Yb	8	37.95 (38.20)	6.40 (6.55)	4.40 (4.70)	58	244	orange
$X = ClO_4^-$							
Cd	8	39.40 (39.90)	2.80 (2.75)	4.75 (4.90)	64	291	yellow
La	5	37.40 (37.40)	2.60 (2.55)	4.10 (4.05)	87	369	orange
Ce	5	37.25 (37.35)	2.75 (2.55)	3.75 (4.05)	51	409	dark orange
Pr	2	39.05 (39.20)	2.50 (2.70)	3.90 (3.70)	30	433	dark green
Sm	11	33.75 (33.65)	2.20 (2.30)	5.10 (4.65)	68	386	red-orange
Gd	1	39.90 (39.30)	2.40 (2.70)	4.55 (3.50)	62	277	orange
Er	6	35.55 (35.85)	2.55 (2.45)	3.85 (4.05)	64	386	orange

[a] $[M(\mathbf{1})]X_n \cdot x\,H_2O \cdot 2\,Et_2O$. – [b] $[M(\mathbf{1})]X_n \cdot Et_2O$.

in a low fluorescent emission. It was not possible to observe an antenna effect[33] and the luminescent quantum yield could not be calculated because of the low residual intensity of the emission.

Macrocycle 2 and Its Metal Complexes

It has previously been reported that diamine-containing oxaazamacrocyclic ligands derived from *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane can be prepared by a non-template cyclocondensation of the precursor dialdehyde and the appropriate diamine, followed by in situ reduction with sodium borohydride.[12] We have found that a similar procedure may successfully be employed for the preparation of the reduced macrocycle **2**. The FAB mass spectrum shows a highest molecular weight peak at $m/z = 571$, corresponding to $[\mathbf{2} + H]^+$, while the IR spectrum features a secondary amine N–H stretching band at ca. 3410 cm^{-1} and no imine band at ca. 1620 cm^{-1}. Comparison of the ^{1}H-NMR spectra of macrocycles **1** and **2** reveals the disappearance of the signal at δ = ca. 8.91 due to the imine proton and the appearance of a new broad singlet signal at δ = 3.65 corresponding to the N*H*CH$_2$ amine protons.

Complexation reactions of macrocycle **2** with hydrated metal salts ($X = NO_3^-$, M = Y, La, Ce, Pr, Sm, Gd, Er, or Lu; $X = ClO_4^-$, M = Cd, La, Pr, Gd, or Er) were carried out in order to investigate the coordination capability of this more flexible and hydrolytically stable ligand towards the Ln^{III}, Y^{III}, and Cd^{II} ions. In most cases, the microana-

Table 2. Analytical, yield and molar conductance (in MeCN) data for the complexes $[M_m(\mathbf{2})]X_n \cdot x\,H_2O$ (calculated values are given in parentheses)

M	m	x	Analysis (%) C	N	H	Yield (%)	Λ_M (Ω^{-1} cm^{2}mol^{-1})	Colour
$X = NO_3^-$								
Y[a]	1	–	41.50 (41.60)	7.20 (6.85)	4.15 (3.95)	93	283	yellow
La[b]	1	–	38.50 (38.10)	6.30 (6.20)	3.40 (3.55)	84	251	pale yellow
Ce[c]	1	–	35.70 (35.40)	5.65 (5.60)	3.55 (3.30)	85	274	yellow
Pr	1	9	38.05 (38.55)	6.70 (6.60)	5.60 (5.35)	63	219	pale yellow
Sm	1	9	38.80 (38.20)	6.40 (6.55)	5.70 (5.30)	51	290	pale yellow
Gd[d]	2	–	32.90 (32.85)	8.25 (8.30)	3.75 (3.70)	77	375	pale yellow
Er[e]	2	–	32.30 (32.10)	8.60 (8.55)	3.25 (3.25)	31	295	yellow
Lu	2	7	29.80 (29.10)	7.85 (8.00)	3.95 (3.75)	19	315	pale yellow
$X = ClO_4^-$								
Cd	1	2	44.55 (44.50)	3.05 (3.05)	4.60 (4.60)	14	220	yellow
La	1	3	38.90 (38.45)	2.90 (2.65)	4.35 (4.20)	20	225	pale yellow
Pr	1	2	38.50 (39.05)	3.00 (2.70)	4.05 (4.05)	41	388	yellow
Gd	2	9	24.95 (24.85)	1.80 (1.70)	4.00 (3.45)	79	395	orange
Er	2	2	26.65 (26.55)	1.70 (1.80)	2.55 (2.75)	50	339	orange

[a] $[M_m(\mathbf{2})]X_n \cdot 1.5\,CHCl_3$. – [b] $[M_m(\mathbf{2})]X_n \cdot 2\,CHCl_3$. – [c] $[M_m(\mathbf{2})]X_n \cdot 3\,CHCl_3$. – [d] $[M_m(\mathbf{2})]X_n \cdot 3\,CH_3OH$. – [e] $[M_m(\mathbf{2})]X_n \cdot CH_3OH$.

lytical data (Table 2) were in accord with the formation of mononuclear complexes of the type $[M(\mathbf{2})]X_n \cdot x\,H_2O$ ($X = NO_3^-$, M = Y, La, Ce, Pr, Sm; $X = ClO_4^-$, M = Cd, La, Pr). However, in contrast to the complexes of macrocycle **1**, elemental analyses of complexes of the heavier lanthanides Gd, Er (NO_3^-, ClO_4^-), and Lu (NO_3^-) were indicative of dinuclear complexes of the general formula $[Ln_2(\mathbf{2})]X_6$. These may arise from the increased flexibility of the reduced macrocycle, allowing the accommodation of the smaller cations; attempts to obtain the corresponding mononuclear complexes were unsuccessful. The molar conductivities of the complexes $[M(\mathbf{2})]X_n \cdot x\,H_2O$ in acetonitrile were found to fall in the range reported for 2:1 electrolytes in this solvent.[19]

The FAB mass spectra of the complexes invariably show the peak corresponding to the free macrocycle. The spectra of the yttrium, cerium, and cadmium complexes also show peaks corresponding to $[Y(\mathbf{2})(NO_3)]^+$ (m/z = 721), $[Ce(\mathbf{2})(NO_3)_2]^+$ (m/z = 834) and $[Cd(\mathbf{2})(ClO_4)]^+$ (m/z = 783).

The IR spectra of the nitrate complexes feature several bands in the region associated with nitrate vibrations, from which it is evident that these species contain both coordinated and ionic nitrate groups.[24,25] The two most intense nitrate absorptions, associated with $\nu(N{=}O)$ and $\nu_a(NO_2)$, appear at ca. 1450 and 1300 cm^{-1}. The $\Delta\nu$ separations between the two highest frequency bands fall in the range 154–213 cm^{-1}, suggesting bidentate coordination of the nitrate anions.[27] In the spectra of the perchlorate complexes, the higher-energy band (ν_3) consists of three maxima at ca. 1137, 1120, and 1080 cm^{-1}. The ν_4 band also shows splitting with maxima at ca. 636 and 624 cm^{-1}. The splitting of these bands is indicative of coordination of at least one of the perchlorate anions to the metal,[28,29] but as with the complexes of macrocycle **1** a full assignment is hindered by the presence of ligand bands.

The UV/visible spectra of macrocycle **2** and the corresponding metal complexes were recorded using 10^{-3}–10^{-6} M acetonitrile solutions. The free macrocycle exhibits three broad absorption bands at ca. 250, 277, and 293 nm, corresponding to the π-π^* transitions of benzene rings and azomethine groups.[30] In the spectra of the metal complexes, the π-π^* absorption bands are red-shifted with respect to their positions in the spectrum of macrocycle **2**. Emission spectra of the free ligand **2** and some of its metal complexes were recorded using 10^{-6} M acetonitrile solutions. Low fluorescent emissions were observed, similar to those seen with macrocycle **1** and its metal complexes.

Crystal Structure of $[(\mathbf{2})H](ClO_4) \cdot CHCl_3$

Single crystals of $[(\mathbf{2})H](ClO_4) \cdot CHCl_3$ suitable for X-ray analysis were obtained by slow crystallization from a solution of the complex $[Cd(\mathbf{2})](ClO_4)_2 \cdot 2\,H_2O$ in diethyl ether/chloroform open to the atmosphere. The crystal structure of the cation is shown in Figure 1. There are two $[(\mathbf{2})H](ClO_4) \cdot CHCl_3$ groups in the asymmetric unit. Only one of the two amine nitrogen atoms in the ligand is protonated and the flexibility of the macrocycle allows it to adopt a folded conformation. This is reinforced by intramolecular hydrogen-bond interactions. The perchlorate ions and the solvent molecules are not involved in hydrogen-bond interactions with macrocycle **2**. The bond lengths and angles fall within the expected ranges.

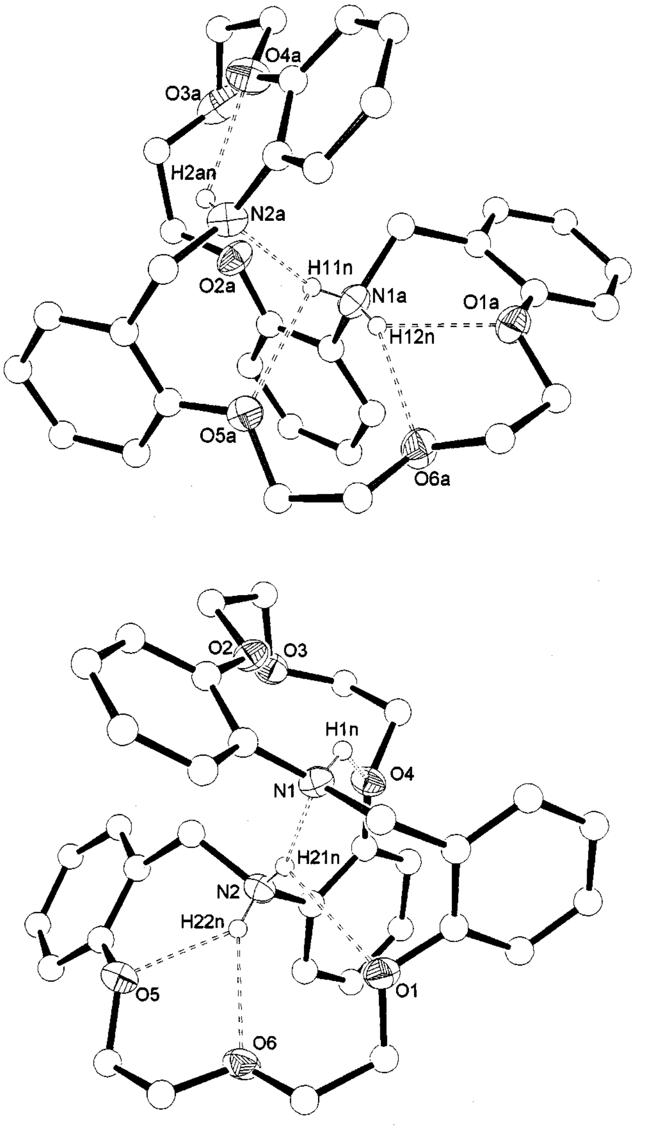


Figure 1. Molecules 1 and 2 of the protonated macrocycle **2** in the asymmetric unit of $[(\mathbf{2})H](ClO_4) \cdot CHCl_3$

Macrocycle 3 and Its Metal Complexes

Reactions of heterocyclic dialdehydes with tris(2-aminoethyl)amine give cryptands,[34–36] while the reaction of 2,6-diacetylpyridine with tris(2-aminoethyl)amine in the presence of metal templates gives a [2+2] pendant-armed Schiff-base macrocycle resulting from the condensation of two molecules of each precursor.[37] It was therefore extremely interesting to find that the non-template reaction of O^1,O^7-bis(2-formylphenyl)-1,4,7-trioxaheptane and tris(2-aminoethyl)amine in acetonitrile produced a rare example of an amino pendant-armed [1+1] Schiff-base macrocycle, i.e. **3**.

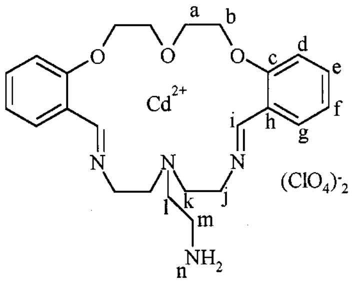
The compound was isolated as a yellow solid, and was found to be stable in air and moderately soluble in most common organic solvents. The IR spectrum features a strong peak at 1636 cm^{-1} due to C=N while no bands attributable to C=O groups are detectable. The primary amine stretching modes of the *pendant-arm* NH_2 group cannot be assigned owing to the presence of an intense broad band centred at ca. 3400 cm^{-1}. The latter is consistent with the presence of water, as is also suggested by the microanalytical data. The FAB mass spectrum shows the parent peak at m/z = 425, confirming the [1+1] cyclic nature of the Schiff base. The ^1H-NMR spectrum recorded in $CDCl_3$ solution features two imine proton singlets at δ = 8.79 and δ = 8.77, suggesting the possible presence of conformers in solution. The C_6H_4 protons give rise to a multiplet at δ = 7.96–6.84, while the CH_2CH_2 chains give rise to four multiplets in the aliphatic region. The complex nature of these signals could stem from the presence of related conformers in solution or from the magnetic inequivalence of the geminal hydrogen pairs caused by restricted rotation about the C–C bond.[38,39] In the pendant arm, this restriction could possibly be due to hydrogen-bonding effects. The broad singlet at δ = 1.84–1.95 may be assigned to the NH_2 group, as was confirmed by deuterium exchange when D_2O was added to the $CDCl_3$ solution. No change in the spectrum of the macrocycle was observed after 24 h, demonstrating a greater stability of this ligand compared with macrocycle **1**.

Metal-template reactions between equimolar amounts of O^1,O^7-bis(2-formylphenyl)-1,4,7-trioxaheptane and tris(2-aminoethyl)amine in the presence of hydrated lanthanide nitrates or perchlorates gave analytically pure products formulated as $[Ln(\mathbf{3})]X_3 \cdot x\,H_2O$ only for Er (X = ClO_4^-) and Dy (X = NO_3^-). Attempts to obtain other Ln^{III} complexes by changing the experimental conditions were unsuccessful and it was possible to identify complexes derived from the precursor amine as the major components of the products. The complexes cannot be prepared by a two-step procedure involving preparation of the free macrocycle followed by a complexation reaction with the requisite lanthanide salt.

The IR spectra of $[Er(\mathbf{3})](ClO_4)_3 \cdot 2\,H_2O$ and $[Dy(\mathbf{3})](NO_3)_3 \cdot H_2O$ show the imine band at ca. 1638 cm^{-1}. This band is slightly shifted in comparison to its position in the spectrum of the free ligand. The $\nu(NH_2)$ band is masked by a broad band at ca. 3400 cm^{-1} due to the water present in the complexes. Bands attributable to the perchlorate groups are present in the spectrum of the Er complex at ca. 1120, 1109, and 1088 cm^{-1} (ν_3) and at 627 and 637 cm^{-1} (ν_4), suggesting the presence of coordinated perchlorate groups. The spectrum of the Dy complex features bands at ca. 1458 (ν_5), 1298 (ν_1), and 1030 (ν_2) cm^{-1}, indicative of bidentate nitrate groups, as well as a band at 1383 cm^{-1} due to ionic nitrate. The molar conductance of the Dy complex in dimethylformamide (71 $\Omega^{-1}cm^2mol^{-1}$) is in the range reported for 1:1 electrolytes in this solvent,[19] indicating strong coordination of the nitrate ions. The very limited solubility of the Er complex in various solvents prohibited the measurement of conductivity. The FAB mass spectra of the complexes feature a peak corresponding to the free macrocycle **3** at m/z = 425; in neither case was the molecular ion observed.

When the template reaction was carried out in the presence of hydrated cadmium perchlorate, $[Cd(\mathbf{3})](ClO_4)_2$ was isolated as a white solid. It was found that direct reaction of macrocycle **3** with the metal salt could also be exploited for the synthesis of the complex. The molar conductivity in acetonitrile (307 $\Omega^{-1}cm^2mol^{-1}$) indicates that the complex is

Table 3. ^1H- and ^{13}C-NMR data (250 MHz) for $[Cd(\mathbf{3})](ClO_4)_2$ in CD_3CN



Assignment	Shift (δ value)	Integration	J/Hz	Assignment	Shift (δ value)
H_i	8.37 (s)	2 H	^3J (^1H,$^{111,113}Cd$) 43	C_a	66.7
H_f	7.50 (t)	1 H	^3J (H_e,H_f) 7.5	C_b	67.2
H_d	7.19 (t)	1 H	^4J (H_d,H_f) 1.8	C_c	156.1
H_e	7.36 (dd)	1 H	^3J (H_e,H_d) 7.9	C_d	113.9
H_g	6.86 (d)	1 H	^3J (H_g,H_f) 8.3	C_e	134.7
H_a, H_b, H_j, H_k, H_l, H_m	4.59–4.49 (m)	2 H		C_f	121.1
	4.21–3.99 (m)	6 H		C_g	133.8
	3.93–3.81 (m)	2 H		C_h	122.5
	3.64–3.53 (m)	2 H		C_i	169.9
	3.03–2.96 (m)	8 H		C_j	57.2
H_n	3.39–3.22 (br. s)	2 H		C_k	55.0
				C_l	54.2
				C_m	37.5

a 2:1 electrolyte, hence the ClO_4^- anion is not coordinated in solution. In the IR spectrum of the complex, the strong absorption at 1642 cm^{-1} corresponds to the expected C=N vibration of the Schiff base; this band is shifted to higher wavenumber than in the free ligand. Two strong peaks at 3354 and 3274 cm^{-1} can be attributed to the vibration of the primary amine, and the spectrum also features single bands attributable to ionic ClO_4^- anions at 1080 cm^{-1} (ν_3) and 620 cm^{-1} (ν_4). The FAB mass spectrum shows peaks attributable to $[Cd(\mathbf{3})ClO_4]^+$ at m/z = 637 and $[Cd(\mathbf{3})]^+$ at m/z = 537. The ^{1}H-NMR spectrum (Table 3), recorded immediately after dissolution in CD_3CN, features only a single imine proton peak at δ = 8.37, along with two cadmium satellites [$^3J(^1H,^{111,113}Cd) \approx 43$ Hz]. A broad signal is observed at δ = ca. 3.39, corresponding to the pendant-amine protons. A spectrum recorded after 24 h showed no significant changes, demonstrating the stability of the cadmium perchlorate complex in solution. Recrystallization of the complex from acetonitrile resulted in the formation of crystals suitable for an X-ray crystallographic study.

Description of the Structure of $[Cd(3)](ClO_4)_2$

The X-ray crystal structure of complex $[Cd(\mathbf{3})](ClO_4)_2$ is shown in Figure 2, together with selected bond lengths and angles at the metal, and confirms that a single cadmium cation is coordinated by macrocycle **3**. The perchlorate anions do not interact with the metal. The flexibility of the macrocycle allows it to adopt a folded cleft-like conformation that encapsulates the metal, giving an irregular 7-coordinated N_4O_3 complex in which the Cd ion interacts with all heteroatoms of the ligand. Similar 7-coordination of Cd^{II} has been observed in other macrocyclic complexes.[40,41] The cadmium–nitrogen bond lengths range from 2.254(4) Å [Cd–pendant amine nitrogen N(4)] to 2.492(4) Å [Cd–tertiary amine nitrogen N(2)], with the distances between the metal and the two imino nitrogens and the pendant amino nitrogen N(4) being shorter than the standard Cd–N bond length of 2.33 ± 0.005 Å,[42] thus indicating strong coordinative bonds between these N atoms and the metal. The three Cd–ether oxygen bonds appear to be somewhat elongated, although they fall within the range of 2.36–2.84 Å reported for similar bonds in other cadmium(II) complexes.[43–45] The distances and angles in the ligand are normal. The folding of the macrocycle to achieve the hepta-coordination results in an almost coplanar arrangement of the two phenyl rings [interplanar angle 19.9(2)°].

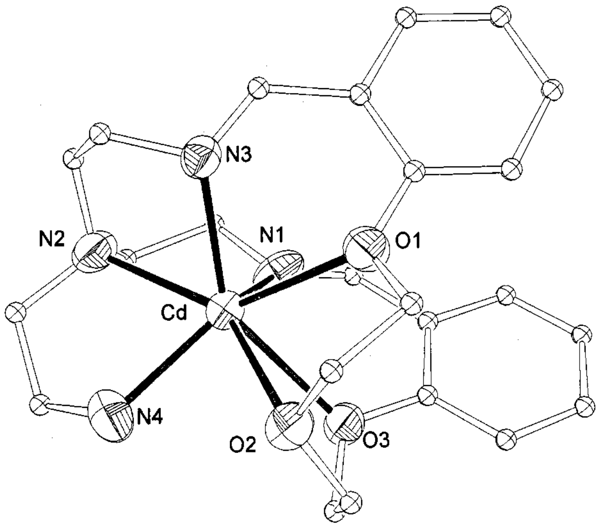


Figure 2. Crystal structure of the cation in $[Cd(\mathbf{3})](ClO_4)_2$: selected bond lengths (Å) and angles (°) at the metal: Cd–N4, 2.254(4), Cd–N1 2.268(4), Cd–N3 2.309(3), Cd–N2 2.492(4), Cd–O1 2.558(3), Cd–O3 2.581(3), Cd–O2 2.605(3); N4–Cd–N1 123.73(18), N4–Cd–N3 119.48(17), N1–Cd–N3 93.73(12), N4–Cd–N2 74.42(16), N1–Cd–N2 75.57(14), N3–Cd–N2 71.56(12), N4–Cd–O1 135.57(15), N1–Cd–O1 96.73(13), N3–Cd–O1 69.55(11), N2–Cd–O1 139.71(11), N4–Cd–O3 95.23(16), N1–Cd–O3 70.56(118), N3–Cd–O3 144.46(10), N2–Cd–O3 130.12(11), O1–Cd–O3 80.58(10), N4–Cd–O2 75.00(15), N1–Cd–O2 132.22(11), N3–Cd–O2 115.41(10), N2–Cd–O2 147.45(12), O1–Cd–O2 63.44(9), O3–Cd–O2 63.76(9)

Conclusions

The cyclocondensation of O^1,O^7-bis(2-formylphenyl)-1,4,7-trioxaheptane with O^1,O^7-bis(2-aninyl)-1,4,7-trioxaheptane gives the oxa-aza Schiff-base macrocycle **1**, which, on reaction with $NaBH_4$, is readily reduced to macrocycle **2**. Mononuclear lanthanide complexes have been prepared from both macrocycles, with dinuclear complexes being formed only by the more flexible ligand **2** and the smaller lanthanide ions. Most interestingly, the reaction of O^1,O^7-bis(2-formylphenyl)-1,4,7-trioxaheptane with tris(2-aminoethyl)amine has been found to give a rare example of an amino pendant-armed [1+1] Schiff-base macrocycle **3** rather than a cryptand or a [2+2] macrocycle. The integrity of the macrocycle **3** has been confirmed by a crystal structure determination of the complex $[Cd(\mathbf{3})](ClO_4)_2$. This type of functionalized macrocycle should provide opportunities for the synthesis of a wide range of derivatives suitable as precursors for polynuclear complexation.

Experimental Section

Measurements: Elemental analyses were carried out by the University of Santiago de Compostela Microanalytical Service on Carlo Erba 1108 and Leco CNHS-932 microanalysers. – Infrared spectra were recorded with samples between KBr discs using a Mattson Cygnus 100 spectrophotometer. – Proton NMR spectra were recorded on a Bruker WM-300 spectrometer. – Positive-ion FAB mass spectra were recorded on a Kratos MS50TC spectrometer using a 3-nitrobenzyl alcohol (*m*NBA) matrix. Conductivity measurements were carried out on 10^{-3} mol dm^{-3} acetonitrile solutions at 20 °C using a WTW LF-3 conductivimeter. The electronic absorption spectra of the complexes (10^{-3}–10^{-6} M acetonitrile solutions) were measured in the range 300–900 nm using Hitachi U-3200 and Perkin–Elmer Lambda 6 spectrophotometers. Emission spectra were recorded on a SPEX F111 Fluorolog spectrofluorimeter.

Chemicals and Starting Materials: O^1,O^7-Bis(2-formylphenyl)-1,4,7-trioxaheptane was prepared according to a literature method;[17] O^1,O^7-bis(2-aninyl)-1,4,7-trioxaheptane was prepared by reduction of the corresponding dinitro precursor using a procedure similar to that described previously.[46–49] Tris(2-aminoethyl)amine and the metal salts were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. ***Caution:*** Perchlorate salts are potentially explosive! Only small amounts of material should be prepared and handled with great care; particular caution must be exercised when they are heated in vacuo.

Condensation of *O*^{1},*O*^{7}-Bis(2-formylphenyl)-1,4,7-trioxaheptane with *O*^{1},*O*^{7}-Bis(2-aninyl)-1,4,7-trioxaheptane in the Absence of Metal Ions: A solution of *O*^{1},*O*^{7}-bis(2-aninyl)-1,4,7-trioxaheptane (0.28 g, 1 mmol) in hot methanol (50 mL) was added dropwise to a refluxing solution of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane (0.31 g, 1 mmol) in hot methanol (50 mL). The resulting solution was gently refluxed with magnetic stirring for ca. 5 h. The colour changed to yellow and an orange-brown powder precipitated, which was filtered off. The solution was then concentrated using a rotary evaporator; on leaving the concentrated filtrate to stand, an orange-yellow powder precipitated, which was filtered off, washed with diethyl ether, and dried in vacuo. This product was characterized as the macrocyclic ligand. Yield 75%; m.p. 160 °C. – IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=N)$_{\mathrm{imi}}$, 1590 (C=C). – MS (FAB; *m*NBA): *m*/*z* = 567 [**1** + H]$^+$.– HR MS: *m*/*z* = 566 (100%) $C_{34}H_{34}N_2O_6$. – ^{1}H NMR (CD_3CN): δ = 8.9 (s, 2 H, HC=N$_{\mathrm{imi}}$). – $C_{34}H_{34}N_2O_6 \cdot 0.5\,H_2O$: calcd. C 70.95, H 6.15, N 4.90; found C 70.80, H 6.10, N 5.25.

Reaction of *O*^{1},*O*^{7}-Bis(2-formylphenyl)-1,4,7-trioxaheptane and *O*^{1},*O*^{7}-Bis(2-aninyl)-1,4,7-trioxaheptane in the Presence of Metal Ions: General Procedure for [M(1)][X]$_n$: To a refluxing solution of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane (1 mmol) in hot methanol (25 mL) was added a solution of the hydrated metal salt (1 mmol) (M = Y, Cd, Ln = La–Yb except Pm and Dy) in methanol (15 mL). The resulting solution was magnetically stirred and heated while a methanolic solution of *O*^{1},*O*^{7}-bis(2-aninyl)-1,4,7-trioxaheptane (1 mmol) was slowly added. Following the addition, refluxing was continued for ca. 4–5 h. The solution was then concentrated in a rotary evaporator to a volume of ca. 10–15 mL. An equal volume of acetonitrile/diethyl ether was slowly infused into the solution, which led to the deposition of a powdery precipitate. The product was filtered off, washed with absolute ethanol, and dried in vacuo. Microanalytical data are given in Table 1. The compounds were found to be air-stable, soluble in methanol, dimethylformamide, dimethyl sulfoxide, acetonitrile, pyridine, dichloromethane, nitrobenzene, and nitromethane, moderately soluble in absolute ethanol, and insoluble in diethyl ether, water, chloroform, and cyclohexane.

Synthesis of Macrocycle 2: The reduction was carried out according to a modification of a literature method.[49,50] *O*^{1},*O*^{7}-Bis(2-aninyl)-1,4,7-trioxaheptane (4.0 mmol) in warm methanol (150 mL) was slowly added to a solution of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane (4.0 mmol) in warm methanol (300 mL). The resulting mixture was refluxed for 1 h, cooled, and then solid $NaBH_4$ (65 mmol) was carefully added portionwise with stirring. When effervescence had ceased, a white precipitate was observed, which was collected by filtration. This product was washed with water and characterized as the macrocycle. The filtrate was concentrated to dryness in a rotary evaporator and the residue was taken up in dichloromethane (150 mL). The resulting solution was stirred for ca. 72 h. A grey precipitate was removed by filtration and the solution was dried over anhydrous sodium sulfate. It was then concentrated to a volume of ca. 10–15 mL in a rotary evaporator whereupon diethyl ether was added, which led to the deposition of a white product. This was filtered off, washed with absolute ethanol, and dried in vacuo to give a second crop of the macrocyclic product. The compound was found to be air-stable, soluble in warm chloroform/benzene (1:1); moderately soluble in hot methanol and chloroform, and insoluble in acetonitrile, absolute ethanol, diethyl ether, dimethylformamide, dimethyl sulfoxide, pyridine, and water. Yield 40%; m.p. 179–181 °C. – IR (KBr): $\tilde{\nu}$ = 3364 cm^{-1} (NH), 1601 (C=C). – MS (FAB; *m*NBA): *m*/*z* = 571 [**2** + H]$^+$. – HR MS: *m*/*z* = 570 (100%) $C_{34}H_{38}N_2O_6$.– ^{1}H NMR ($CDCl_3$): δ = 7.42–6.67 (m, 16 H, C_6H_4), 4.75 (s, 4 H, C*H*$_2$NH), 4.23–3.87 (m, 16 H, OC*H*$_2$C*H*$_2$), 3.65 (br. s, 2 H, NH). – $C_{34}H_{38}N_2O_6 \cdot H_2O$: calcd. C 69.40, H 6.50, N 8.10; found C 69.50, H 6.75, N 7.95.

Crystal Structure of [(2)H](ClO$_4$) · CHCl$_3$: A yellow plate-like crystal of $[C_{34}H_{39}N_2O_6](ClO_4) \cdot CHCl_3$ (790.48), dimensions 0.5 × 0.5 × 0.2 mm, crystallized from diethyl ether/chloroform, was used for the structure determination. The chosen crystal was mounted on a glass fibre using an epoxy resin. Data were collected by means of a Bruker Smart CCD area detector with an Oxford Cryosystems low-temperature system held at 150 K. Cell parameters were refined from the setting angles of 140 reflections (θ range 1.35–28.48). Reflections were measured from a hemisphere of data composed of frames each covering 0.3° in ω. Of the 24613 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption (maximum and minimum transmission coefficients of 0.893 and 0.223), 9824 independent reflections exceeded the significance level $F/\sigma(F) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed in geometrically idealized positions and refined with a riding model (including torsional freedom for methyl groups) with U_{iso} restrained as 1.2 (or 1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final $R = 0.0745$ ($wR2 = 0.2321$ for all 16888 unique data, 943 parameters, mean and maximum Δ/σ 0.000, 0.0001) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density –0.816 and 0.987 eÅ^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1408P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the SHELXTL program package[51] as implemented on a Viglen Pentium computer, while molecular graphics were derived from ORTEP-3.[52] A summary of the experimental and structure solution procedure is given in Table 4.

Metal Complexes of Macrocycle 2. – General Procedure: The appropriate metal salt (0.15 mmol) was dissolved in methanol (10 mL) and added to a stirred solution of the ligand **2** (0.15 mmol) in chloroform/benzene (20 mL + 20 mL). An immediate colour change was usually observed and a precipitate began to deposit. The mixture was then stirred for 3 days at room temperature. The product was subsequently filtered off and dried in vacuo. The filtrate was concentrated in a rotary evaporator to leave an oil. On treatment with diethyl ether, a solid was obtained, which was filtered off and dried in vacuo. This reaction was attempted with $Cd(ClO_4)_2 \cdot x\,H_2O$ and $Y(NO_3)_3 \cdot x\,H_2O$, the nitrates of La, Ce, Pr, Sm, Gd, Er, and Lu, and the perchlorates of La, Pr, Gd, and Er. Microanalytical data of the relevant products are given in Table 2. The complexes were found to be air-stable, soluble in acetonitrile, chloroform, dimethylformamide, and dimethyl sulfoxide, moderately soluble in methanol and dichloromethane, and insoluble in absolute ethanol, cyclohexane, diethyl ether, and water.

Reaction of *O*^{1},*O*^{7}-Bis(2-formylphenyl)-1,4,7-trioxaheptane and Tris(2-aminoethyl)amine in the Absence of Metal Ions: A solution of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane (0.31 g, 1 mmol)

Table 4. Crystal data and structure refinement for $[C_{34}H_{39}N_2O_6](ClO_4) \cdot CHCl_3$

Empirical formula	$C_{35}H_{40}Cl_4N_2O_{10}$
Formula weight	790.48
Temperature [K]	423(2)
Wavelength [Å]	0.71073
Crystal system, space group	triclinic, *P*-1
Unit cell dimensions:	
a [Å]	10.4438(11)
b [Å]	11.9470(12)
c [Å]	30.724(3) Å
α [°]	90.619(2)
β [°]	99.485(2)
γ [°]	102.441(2)
Volume [Å^3]	3688.1(7)
Z	4
Calculated density [Mg/m^3]	1.328
Absorption coefficient [mm^{-1}]	0.243
F(000)	1528
Crystal size [mm]	0.5 × 0.5 × 0.2
θ range for data collection [°]	1.35 to 28.48
Index ranges	$-13 \le h \le 9$
	$-14 \le k \le 15$
	$-40 \le l \le 40$
Reflections collected/unique	24613/16888 [*R*(int) = 0.0464]
Completeness to 2θ	28.48°; 90.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16888/0/943
Goodness-of-fit on F^2	0.990
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0745$, $wR2 = 0.1982$
R indices (all data)	$R1 = 0.1200$, $wR2 = 0.2321$
Largest diff. peak and hole	0.987 and –0.816 e · Å^{-3}

in hot acetonitrile (100 mL) was added dropwise to a refluxing solution of tris(2-aminoethyl)amine (0.15 mL, 1 mmol) in hot acetonitrile (300 mL). The resulting solution was gently refluxed with magnetic stirring for ca. 3 h. The colour of the reaction mixture changed to yellow and first an unidentified precipitate was deposited, which was removed by filtration. The filtrate was then concentrated to a volume of ca. 10 mL and a yellow product was obtained. This was collected by filtration, washed with diethyl ether, and dried in vacuo to give macrocycle **3** in 25% yield; m.p. 115 °C (dec.) – IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1} (C=N)$_{imi}$. – ^{1}H NMR (CDCl$_3$): δ = 8.79–8.77 (s, 2 H, HC=N$_{imi}$), 7.96–6.84 (m, 8 H, C_6H_4), 4.24–4.14 (m, 4 H, CH_2O), 4.00–3.84 (m, 4 H, CH_2O-aryl), 3.71–3.62 (m, 4 H, C*H*$_2$N=CH), 2.92–2.60 (m, 8 H, CH$_2$-N$_{ternary}$), 1.94–1.85 (br. s, 2 H, NH$_2$). – MS (FAB; *m*NBA): *m*/*z* = 425 [**3** + H]$^+$. – MS(EI): P$^+$ = 394 [**3** – CH$_2$NH$_2$]$^+$. – $C_{24}H_{32}N_4O_3 \cdot 1.5\ H_2O$: calcd. C 63.85, H 7.75, N 12.45; found C 64.40, H 7.50, N 12.40.

Reaction of *O*^{1},*O*^{7}-Bis(2-formylphenyl)-1,4,7-trioxaheptane and Tris(2-aminoethyl)amine in the Presence of Metal Ions: General Procedure for [M(3)][X]$_n$: To a refluxing solution of tris(2-aminoethyl)amine (1 mmol) in either hot methanol, acetonitrile, or absolute ethanol (50 mL) was added a solution of the hydrated lanthanide salt (1 mmol) (X = ClO_4^-, Ln = La, Ce, Gd, Er or Ho; X = NO_3^-, Ln = La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu) in the same solvent (50 mL). The resulting mixture was magnetically stirred and heated for 1 h, during which a methanolic or ethanolic solution (50 mL) of *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane (1 mmol) was slowly added. Refluxing was continued for ca. 3–4 h. The solution was then concentrated in a rotary evaporator to a volume of ca. 10–15 mL. An equal volume of diethyl ether was slowly infused into the concentrated solution, which led to the deposition of a yellow powdery precipitate. The product was filtered off and dried in vacuo. The products thus obtained gave unsatisfactory analytical results. When the methanol/diethyl ether or ethanol/diethyl ether solution was concentrated to dryness once more and further diethyl ether was added, a second product was isolated by filtration and identified as the metal complex only in the cases of the reactions with erbium perchlorate and dysprosium nitrate. In the reactions with the other Ln^{III} nitrates or perchlorates, no analytically pure products could be isolated. The compounds were found to be air-sensitive. When the same reaction was carried out with Cd^{II} perchlorate in absolute ethanol, the product isolated was characterized as the [Cd(**3**)](ClO$_4$)$_2$ complex; recrystallization from acetonitrile resulted in the formation of crystals suitable for X-ray crystallographic analysis.

[Er(3)](ClO$_4$)$_3$ · 2 H$_2$O: Solvent: Methanol. Yield: 16%. – IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} (C=N)$_{imi}$, 1600 (C=C), 1120, 1109, 1088, 627, and 636 (ClO_4^-). – MS (FAB; *m*NBA): *m*/*z* = 425 [**3** + H]$^+$. – $C_{24}H_{36}N_4O_{17}Cl_3Er$: calcd. C 31.10, H 3.90, N 6.05; found C 30.60, H 3.75, N 6.80. The yellow complex was found to be moderately soluble in acetonitrile, dimethylformamide, and acetone, but insoluble in methanol, chloroform, absolute ethanol, dimethyl sulfoxide, diethyl ether, and water.

[Dy(3)](NO$_3$)$_3$ · H$_2$O: Solvent: Acetonitrile. Yield: 63%. – IR (KBr): $\tilde{\nu}$ = 1638 cm^{-1} (C=N)$_{imi}$, 1600 (C=C), 1458, 1383, 1298, 1046, and 1030 (NO_3^-). – MS (FAB; *m*NBA): *m*/*z* = 425 [**3** + H]$^+$. – Λ_M (DMF): 71 Ω^{-1}cm^{2}mol^{-1}. – $C_{24}H_{34}N_7O_{13}Dy$: calcd. C 37.55, H 4.50, N 12.75; found C 37.50, H 4.80, N 12.55. The yellow complex was found to be soluble in dimethylformamide and dimethyl sulfoxide, moderately soluble in acetonitrile, methanol, chloroform, absolute ethanol, and acetone, and insoluble in diethyl ether and water.

[Cd(3)](ClO$_4$)$_2$: Solvent: Absolute ethanol; the order of addition of tris(2-aminoethyl)amine and *O*^{1},*O*^{7}-bis(2-formylphenyl)-1,4,7-trioxaheptane was reversed. The white precipitate obtained directly from the reaction mixture was filtered off and dried in vacuo. Yield: 36%. – IR (KBr): 1642 cm^{-1} (C=N)$_{imi}$, 1116, 1083, 1039, and 620 (ClO_4^-). – ^{1}H- and ^{13}C-NMR spectra; see Table 3. – MS (FAB; *m*NBA): *m*/*z* = 637 [Cd(**3**)(ClO$_4$)]$^+$, 537 [Cd(**3**)]$^+$. – $C_{24}H_{32}N_4O_{11}Cl_2Cd$: calcd. C 39.20, H 4.40, N 7.60; found C 39.35,

Table 5. Crystal data and structure refinement of [Cd(**3**)](ClO$_4$)$_2$

Empirical formula	$C_{24}H_{32}CdCl_2N_4O_{11}$
Formula weight	735.84
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	*P*21/*n*
Unit cell dimensions:	
a [Å]	11.7207(2)
b [Å]	18.2691(2)
c [Å]	13.5708(2)
β [°]	100.3439(3)
Volume [Å^3]	2858.64(7)
Z	4
Calculated density [Mg/m^3]	1.710
Absorption coefficient [mm^{-1}]	1.017
F(000)	1496
Crystal size [mm]	0.55 × 0.30 × 0.05
θ range for data collection [°]	1.89 to 28.29
Index ranges	$-14 \le h \le 15$
	$-24 \le k \le 12$
	$-18 \le l \le 16$
Reflections collected/unique	20796/7078 [*R*(int) = 0.0360]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7078/0/387
Goodness-of-fit on F^2	1.022
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0472$, $wR_2 = 0.1179$
R indices (all data)	$R_1 = 0.0722$, $wR_2 = 0.1335$
Largest diff. peak and hole	1.151 and -0.749 eÅ^{-3}

H 4.40, N 7.30. The complex was found to be air-stable, soluble in acetonitrile, dimethylformamide, and dimethyl sulfoxide, but insoluble in methanol, chloroform, absolute ethanol, acetone, diethyl ether, and water. Recrystallization from acetonitrile resulted in the formation of crystals suitable for an X-ray crystallographic study.

Crystal Structure of [Cd(3)](ClO_4)$_2$: A colorless, plate-like crystal of [Cd($C_{24}H_{32}N_4O_3$)](ClO_4)$_2$ (735.84), crystallized from acetonitrile solution, with dimensions 0.55 × 0.30 × 0.05 mm, was used for the structure determination. The chosen crystal was mounted on a glass fibre using an epoxy resin. Data were collected using a Siemens SMART CCD area detector single-crystal diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Preliminary unit cell constants were determined from a set of 45 narrow-frame scans (0.3 in ω). A total of 1420 frames of intensity data were collected with a width of 0.3° per frame and a counting time of 20 s/frame at a crystal-to-detector distance of 4.5 cm. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans and refined using Siemens SAINT[53] software on all observed reflections. Absorption corrections were applied by means of the SADABS[54] program (maximum and minimum transmission coefficients, 1.0000 and 0.7650). The integration process yielded 20796 reflections, of which 7078 were independent. The structure was solved using SHELX-97[55] by the heavy atom method (Cd atom) and subsequent Fourier difference synthesis, and refined by full-matrix least-squares methods on F^2. The amine hydrogen atoms were located on a Fourier map. All other hydrogen atoms were included in calculated positions and refined in riding mode with U(H) equal to 1.2 times U_{eq} of the parent atom. Molecular graphics were generated using ORTEP-3.[52] A summary of the experimental and structure solution procedure is given in Table 5.

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-135465 for [(2)H](ClO_4) · $CHCl_3$ and CCDC-135464 for [Cd(**3**)](ClO_4)$_2$. 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 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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