110. Crystal Structures of the Lanthanum(III), Europium(III), and Terbium(III) Cryptates of Tris(bipyridine) Macrobicyclic Ligands

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The crystal structures of the La^{III}, Eu^{III}, and Tb^{III} complexes of macrobicyclic [bpy.bpy.bpy] ligands, $[La^{3+} \subset \mathbf{1}]3\,Cl^-$ (= **3**-La), $[Tb^{3+} \subset \mathbf{1}]3\,Cl^-$ (= **3**-Tb), and $[Eu^{3+} \subset \mathbf{2}]3\,Cl^-$ (= **3**-Eu), have been determined. They confirm the cryptate nature of these species, the cations being bound to the eight N-sites of the ligand. The macrobicycle presents two open faces, thus allowing additional coordination of two species, Cl^- ions or H_2O molecules, to the bound cations. These data provide structural support for the photophysical studies of the luminescent properties of the Eu^{III} and Tb^{III} cryptates, which indicated residual coordination of H_2O molecules.

Lanthanide complexes of the macrobicyclic ligand [bpy.bpy.bpy] **1** containing three 2,2′-bipyridine (bpy) units have been prepared [1] [2] from the corresponding NaBr complex [3]. The Eu^{III} and Tb^{III} complexes display pronounced luminescent properties [1] [2] [4–6]. They are of particular interest for the development of luminescent materials and of labels for biological substances, as required, *e.g.*, in immunoassay diagnostic techniques.

On the basis of the structure of the starting NaBr complex and of their analytical and spectral properties, a cryptate structure has been assigned to these lanthanide complexes, in which the Ln^{3+} ion is contained in the intramolecular cavity of the macrobicyclic ligand **1** [1] [2]. Such a structure has been confirmed for the related $[Na^+ \subset$ phen.phen.phen] species by crystal-structure determination [7].

Cation inclusion is of prime importance for the photophysical properties of the Eu^{3+} and Tb^{3+} complexes, since *1*) it makes possible an energy transfer from the three bpy units, functioning as a UV-light collector, to the bound cation, which then emits its characteristic radiation, and *2*) it protects the cation from interaction with solvent molecules, in particular with H_2O, thus leading to high luminescence efficiencies, even in aqueous solution, where it is known that coordination with H_2O strongly decreases light emission.

In order to understand the photophysical properties of these complexes and to be able to optimize them, it is necessary to obtain detailed structural information on the mode of binding of the cations in the cavity and on the ability of the cryptand **1** to shield the bound

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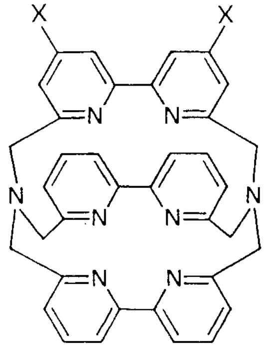
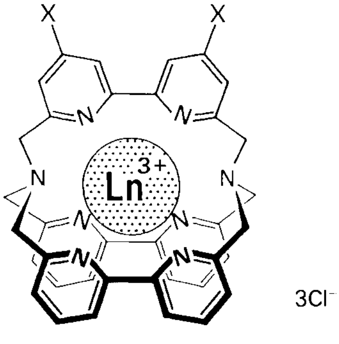


1 X = H
2 X = COOCH$_3$



3-La Ln = La, X = H
3-Eu Ln = Eu, X = COOCH$_3$
3-Tb Ln = Tb, X = H

cations from interaction with the environment. To this end, we have determined and describe here the crystal structures of the La^{3+} and Tb^{3+} complexes of **1**, (**1** · LaCl$_3$ · 2H$_2$O) and (**1** · TbCl$_3$ · 4H$_2$O), and of the Eu^{3+} complex of its substituted derivative **2** (**2** · EuCl$_3$ · 4H$_2$O). Some selected structural parameters are listed in *Tables 1* and *2*.

Common Structural Features of the Three Cryptates [La^{3+} ⊂ 1]3Cl$^-$, [Tb^{3+} ⊂ 1]3Cl$^-$, and [Eu^{3+} ⊂ 2]3Cl$^-$. – The crystal structures show that the LaCl$_3$ and TbCl$_3$ complexes of **1** and the EuCl$_3$ complex of **2** are all three of cryptate type, [La^{3+} ⊂ **1**]3Cl$^-$ (short form, **3**-La), [Tb^{3+} ⊂ **1**]3Cl$^-$ (short form, **3**-Tb), and [Eu^{3+} ⊂ **2**]3Cl$^-$ (short form, **3**-Eu), with the cation contained in the molecular cavity of the macrobicyclic ligands **1** and **2**.

In the three *cryptate cations*, the ligand retains a similar geometry, as shown by the structures viewed along the N,N′ bridgehead axis (*Fig. 1*). It forms as shallow bowl with two bipyridines spread widely open (bpy(A) and bpy(C); dihedral angle, 200°), while the third one, bpy(B), underneath, is tilted to one side towards bpy(A) (mean dihedral angle bpy(A), bpy(B), 30°). The spreading out of the wings reminds strongly of the geometrical features of the structure of the [Li$^+$ ⊂ py.py.bpy] cryptate (see preceding paper). This leaves an empty solid angle on two faces of the macrobicycle so that the anions or the solvent molecules have access to the included cation, thus completing its coordination sphere: 2 Cl$^-$ are bound to La^{3+}; 1 Cl$^-$ and a H$_2$O molecule are bound to Tb^{3+} and Eu^{3+} (*Fig. 1*). Space-filling representations are given in *Fig. 2*.

In all three structures, the plane through the lanthanide cation and its two extra-bonded moieties (Cl or H$_2$O) is perpendicular to the bridghead N,N′ axis. Another common feature is the position of the lanthanide ion. A regular hexagon is formed by 6 N-atoms: 2 from bpy(A), 2 from bpy(C), and the bridgehead N's. These coplanar (within 0.01 Å) N-atoms form a circular cavity of 2.8 Å diameter. Taking into account the *Van der Waals* radius of the N-atom (1.5 Å), the cations La^{3+} (radius, 1.06 Å), Eu^{3+} (0.95 Å), and Tb^{3+} (0.90 Å) are too small; they are not centered and fall inside the core, towards the bpy(B) N-atoms; the LnN$_B$ distances are shorter than the others.

There is always a Cl$^-$ anion in the larger open space between bpy(A) and bpy(C). It does not come into contact with the coplanar N-atoms, but with the H-atoms from the CH$_2$ bridges, as is visible from *Figs. 2a* and *2b*. It occults completely the small lanthanide cation underneath.

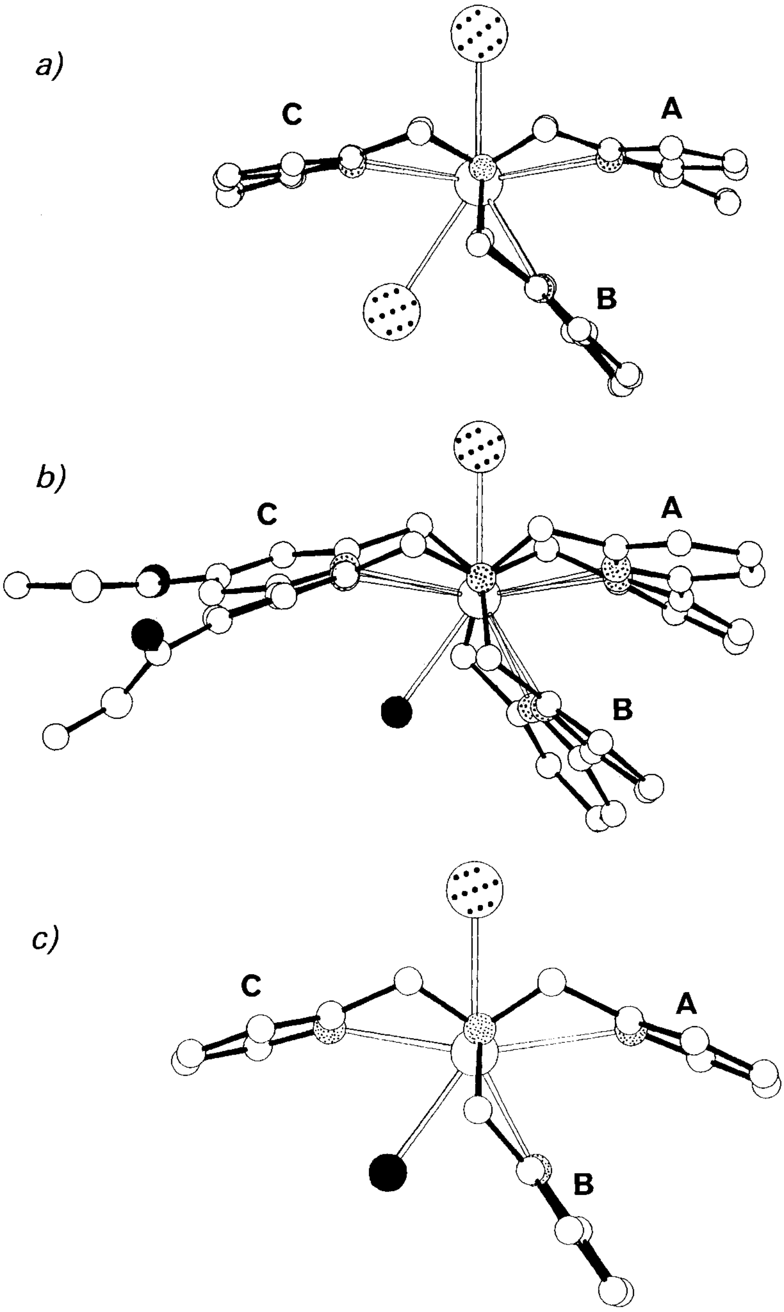


Fig. 1. *Crystal structures of the* a) *lanthanum(III)*, b) *europium(III), and* c) *terbium(III) cryptates* **3**-*La*, **3**-*Eu, and* **3**-*Tb, respectively, with their coordinated* Cl^- *anions* (large dotted circles) *and* H_2O *molecules.*
The view is perpendicular to the mirror plane passing through the cation;
N-atoms, small dotted circles; O-atoms, black circles.

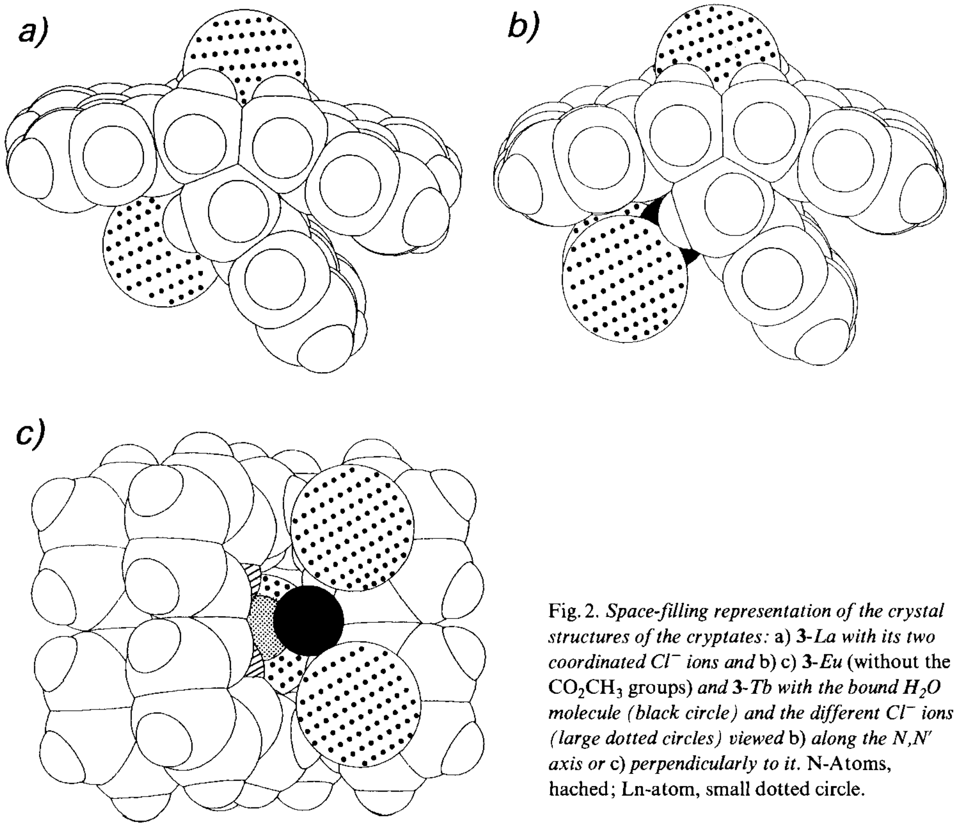


Fig. 2. *Space-filling representation of the crystal structures of the cryptates:* a) **3**-*La with its two coordinated Cl^- ions and* b) c) **3**-*Eu* (without the CO_2CH_3 groups) *and* **3**-*Tb with the bound H_2O molecule (black circle) and the different Cl^- ions (large dotted circles) viewed* b) *along the N,N′ axis or* c) *perpendicularly to it.* N-Atoms, hached; Ln-atom, small dotted circle.

Table 1. *Selected Non-covalent Distances* (< 3.75 Å) *for the Cryptates* **3**-*La*, **3**-*Eu*, *and* **3**-*Tb*

Distances from Ln^{3+} to		**3**-La(X)[a])	**3**-La(Y)[a])	**3**-Eu	**3**-Tb
bpy(A)	$N(1)_A$	2.89	2.91	2.87	2.90
	$N(1)_{A'}$	2.93	2.90	2.85	2.90
bpy(B)	$N(1)_B$	2.69	2.67	2.57	2.55
	$N(1)_{B'}$	2.71	2.69	2.58	2.55
bpy(C)	$N(1)_C$	2.78	2.80	2.78	2.74
	$N(1)_{C'}$	2.80	2.79	2.78	2.74
N		2.79	2.80	2.72	2.73
N′		2.77	2.76	2.73	2.73
Cl(1)		2.85	2.83	2.65	2.65
Cl(2) or H_2O		3.00	2.88	2.55	2.46
Distances from Cl(1) to					
	N	3.71		3.51	3.52
	N′		3.75	3.61	3.52
	$N(1)_A$	3.66	3.61	3.48	3.65
	$N(1)_{A'}$	3.69	3.62	3.64	3.65
	$N(1)_C$	3.69	3.72	3.58	3.52
	$N(1)_{C'}$	3.73		3.51	3.52

Table 1 (cont.)

Distances from Cl(2) or H_2O to	Cl(2) to	Cl(2) to	H_2O to	H_2O to
$N(1)_B$	3.26	3.16	2.96	2.76
$N(1)_{B'}$	3.15	3.13	2.84	2.76
$N(1)_C$	3.33	3.11	2.89	2.92
$N(1)_{C'}$	3.21	3.21	3.03	2.92
Cl(2)			2.98	3.03
Cl(3)			2.98	3.03
Distances N–N				
$N-N(1)_A$	2.84	2.88	2.81 (2)	2.84
$N-N(1)_C$	2.85	2.88	2.82	2.78
$N(1)_{A'}-N(1)_A$	2.72	2.67	2.65	2.65
$N(1)_{A'}-N'$	2.83	2.89	2.85	2.84
$N(1)_{C'}-N(1)_C$	2.69	2.67	2.65	2.68
$N(1)_{C'}-N'$	2.86	2.84	2.80	2.78

[a] X and Y specify the two molecules of the asymmetric unit.

In the empty solid angle between bpy(C) and bpy(B), the supplementary atom (Cl^- or O-atom of H_2O) makes short contacts with their N-atoms (see *Table 1*).

The lanthanide ions display ten-fold coordination in all three cases, to 8 N-atoms, and to two other species, Cl^- or H_2O.

Particular Coordination Features. – *Lanthanum Cryptate* **3**-*La*. The La^{3+} cation is coordinated to 2 Cl^- anions: Cl(1) on the top of the cup is at 2.84 Å from La, and Cl(2) a little further at 2.94 Å (average). The average distance from Cl(1) to the bpy(A) and bpy(C) N-atoms is 3.7 Å, whereas the average distance from Cl(2) to the bpy(B) and bpy(C) N-atoms is 3.2 Å.

Europium and Terbium Cryptates **3**-*Eu and* **3**-*Tb*. These two lanthanide complexes having the same coordination features are described together (see *Figs. 1b, c* and *2b, c*).

Instead of a second Cl^- ion, a H_2O molecule is inserted in the free space between bpy(B) and bpy(C) (*Fig. 1b, c*) with its O-atom bound to the cation Eu^{3+} (Tb^{3+}) at 2.55 Å (2.45 Å) and its two H-atoms forming H-bonds to two Cl^- ions (*Fig. 2b, c*): $H_2O-Cl(2)=H_2O-Cl(3) = 2.98$ Å and $Cl(2)-H_2O-Cl(3) = 110°$. The H_2O molecule makes short contacts with the neighbouring bipyridine groups (H_2O = 2.95 Å (average)).

In **3**-Eu, the two COOMe groups linked to bpy(C) are extended outwards and lie roughly in the bpy plane.

Cryptate **3**-Tb has a mirror plane passing through the middle of each bpy unit and through Tb^{3+}, Cl(1) and H_2O.

Intermolecular Assemblies. – In **3**-La, the two monocations of the asymmetric unit assemble in a very tight manner to form a neutral molecule with a pseudo center of symmetry (*Fig. 3a*). Thus, the two bpy(B) units are parallel and overlap at *van der Waals* separation (3.4 Å). This is expected to stabilize the structure. The two La^{3+} ions of this dimer with their two bound Cl^- ions lie in one plane. The two free Cl^- anions are disordered in five different positions, in a twisted, helical arrangement along the edges of the bpy(B) rings.

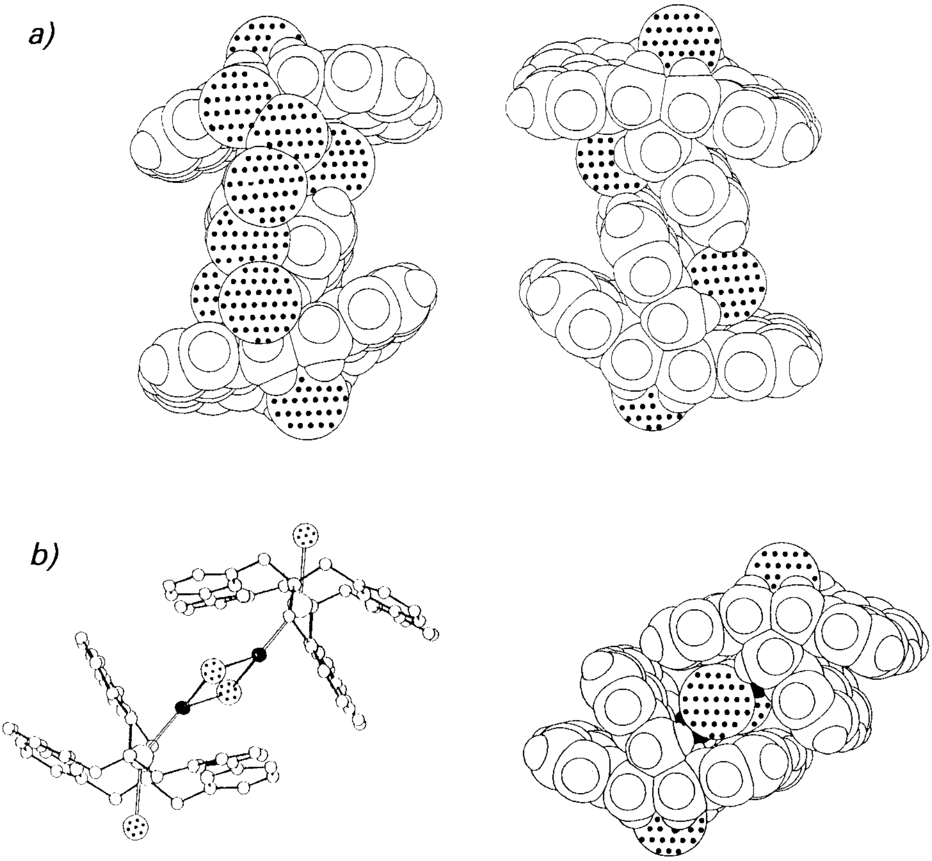


Fig. 3. *Representation of the crystal assemblies for* a) *the dimer of the* La^{III} *cryptate* **3**-*La showing the row of disordered* Cl^- *anions twisted along the edges of the bpy(B) rings* (left) *and the stacking of the bpy(B) rings on the other side* (right) *and* b) *the dimer of the* Tb^{III} *cryptate* **3**-*Tb as an ORTEP plot showing the bridge between the two complexes* (left) *and in space-filling representation* (right)

In **3**-Eu, the neutral system is formed with the two Cl^- ions bound to the H_2O molecule.

In **3**-Tb, a dimer is formed through the two Cl^- ions bound to the H_2O molecule of each complex (*Fig. 3b*), giving a dicationic species. The other two Cl^- counterions have no particular position in the cell. The shape of this dimer is such that the bpy(B) planes of the monomers are parallel and facing each other, thus forming a cavity which contains the anions held at a short distance of *ca.* 4 Å.

Photophysical Properties. – The photophysical properties of Eu^{3+} and Tb^{3+} ions depend markedly on their environment. In particular, their luminescence is strongly decreased by H_2O molecules in the coordination shell. Inclusion of these ions into the cavity of a cryptand may be expected to protect them and hinder the approach of H_2O molecules, thus yielding luminescent complexes of interest both as novel light-emitting materials and as potential labels for biological compounds.

Indeed, it has been found that the Eu^{III} and Tb^{III} cryptates of the macrobicyclic ligand **1** exhibit strong emission [1] [5] [6]. However, a detailed analysis of their photophysical properties showed that the Eu^{3+} ion of cryptate **3**-Eu was not entirely protected and still accessible to an average of 2.5 H_2O molecules as compared to *ca.* 9 in the uncomplexed cation [5] [6]. These results can now be related to the structure of the cryptates described here. As seen in *Figs. 1* and *2*, the ligand in the complex presents open solid angles so that the cryptated cation is accessible and coordinated to two external species (H_2O or Cl^-) in addition to the binding sites provided by the ligand. This suggests that a more complete shielding of the bound cation might be achieved by a more rigid cryptand or by a macrobicycle of [2.2.1] type such as [py.biqi.biqi] which forms a Li^+ complex where the cation is well buried inside the cavity [8]. Another approach is to introduce pyridine *N*-oxide units in the macrobicyclic structure so as to block the faces of the system against the approach of H_2O molecules [9]. The structural information obtained from the present crystallographic data thus suggests pathways towards the design of luminescent cryptates of increased efficiency.

Experimental Part

Synthesis of the Cryptates **3**-La, **3**-Tb, *and* **3**-Eu. See [1] [2] [10].

X-Ray Crystal Structures. The structures were solved by *Patterson* function analysis. Examination of the *Fourier* series showed the ligand, the solvent atoms, and the counter ions. During the refining procedure, the non-H-atoms were anisotropically refined, and the H-atoms introduced at their theoretical position. These and the disordered solvent molecules were treated isotropically. The experimental data and refinement details for the three cryptates are listed in *Table 3*. *Tables 1* and *2* contain some selected distances and angular parameters. The final coordinates as well as a full list of the coordinates of the non-H-atoms and of bond lengths and angles are available[4]).

Table 2. *Relevant Dihedral Angles between Mean Planes for the Cryptates* **3**-*La*[a]), **3**-*Eu, and* **3**-*Tb*

Planes[b])	3-La(X)[a])	3-La(Y)[a])	3-Eu	3-Tb
A/A′	19.2°	8°	23.5°	
B/B′	7.8°	9°	12.7°	
C/C′	9.7°	7.8°	12.9°	
AA′/BB′	33.3°	35.5°	30.5°	34.5°
AA′/CC′	205.8°	205.0°	214.3°	216.5°
BB′/CC′	121.0°	119.8°	118°	109.3°
NAC/MLnM′	90.2°	89.2°	88.4°	90.0°
NAC/NDF	6°	4°		
AA′/DD′	8.4°			
BB′/EE′	5.3°			
CC′/FF′	7.2°			

[a]) X and Y are the two molecules of the asymmetric unit.

[b]) Notation of planes: A, py(A); A′, py(A′); AA′, bpy(AA′); B, py(B); B′, py(B′); BB′, bpy(BB′); C, py(C), C′, py(C′); CC′, bpy(CC′); A, B, and C are replaced by D, E, and F, resp., in 3-La(Y); NAC: $N(1)_A$–$N(1)_{A'}$–$N(1)_C$–$N(1)_{C'}$; NDF: $N(1)_D$–$N(1)_{D'}$–$N(1)_F$–$N(1)_{F'}$; MLnM′: Cl(1)–La–Cl(2) or Cl(1)-Eu-H_2O or Cl(1)–Tb–H_2O.

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[4]) The atomic parameters are available from the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. The list of observed and calculated structure factors is available from the authors at the Institut de Chimie des Substances Naturelles. Any request should be accompanied by the full literature citation.

Table 3. *Experimental Parameters for Data Collection, Structural Data, and Refinement Procedures*

	3-$LaCl_3 \cdot 2H_2O$	**3**-$EuCl_3 \cdot 4H_2O$	**3**-$TbCl_3 \cdot 4H_2O$
Crystal dimensions	0.3 × 0.6 × 0.8 mm	0.3 × 0.3 × 0.2 mm	0.5 × 0.5 × 0.3 mm
Wave length	Mo*Kα*	Mo*Kα*	Mo*Kα*
θ_{max} [°]	26	30	28
Scan speed [°/s]	0.022	0.14	0.10
Scan width [°]	1.4	1.4	0.7
Number of ind. reflexions	13509	10212	4221
No. of I above background	$7312 > 6\sigma$	$5465 > 3\sigma$	$2116 > 4\sigma$
μ cm^{-1}/absorption	12.7	16.2	19.9
Correction	no	no	empirical
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$C2/c$	$Cmca$
Formula	$C_{36}H_{34}Cl_3LaN_8 \cdot 2H_2O$	$C_{40}H_{38}Cl_3EuN_8O_4 \cdot 4H_2O$	$C_{36}H_{34}Cl_3N_8Tb \cdot 4H_2O$
a [Å]	18.602(5)	30.715(8)	25.510(8)
b [Å]	17.342(5)	14.121(5)	10.279(4)
c [Å]	14.130(5)	23.813(8)	31.021(9)
α [°]	99.98(2)	90	90
β [°]	106.26(4)	118.62(4)	90
γ [°]	103.2(3)	90	90
V [Å^3]	4119.8	9066.3	8134.2
$D_{calc.}$	1.35	1.46	1.31
No. mol./cell	4	2	8
Resolution method	*Patterson*	*Patterson*	*Patterson*
Refinement procedure	SHELX 76 [11]	SHELX 76 [11]	SHELX 76 [11]
Thermal parameters	C, N, La, 2 Cl, anisotr.; Cl, $H_2O(1)$, $H_2O(2)$ isotr.	C, N, O, Eu, Cl, $H_2O_{(Eu)}$, $H_2O(3)$ anisotr.; $H_2O(2)$, $H_2O(4)$ disor. = isotr.	C, N, O, Tb, Cl, H_2O(Tb) anistr.
H-atoms	theor. pos. B_{eq} of bonded atom	theor. pos. B_{eq} of bonded atom	theor. pos. B_{eq} of bonded atom
Factor R (R_w)	5.8 (5.6)	5.9 (6.2)	5.0 (7.3)

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