Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrated hexacyanometallate(III) salts of triaqua(18-crown-6)lanthanoid(III) and tetraaqua(18-crown-6)-lanthanoid(III) cations containing nine- and ten-coordinate lanthanoids

Phalguni Misra,[a] Rajesh Koner,[a] Malabika Nayak,[a] Sasankasekhar Mohanta,[a]‡ John N. Low,[b] George Ferguson[c] and Christopher Glidewell[c]*

[a]Department of Chemistry, University of Calcutta, 92 A. P. C. Ray Road, Kolkata 700 009, India, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

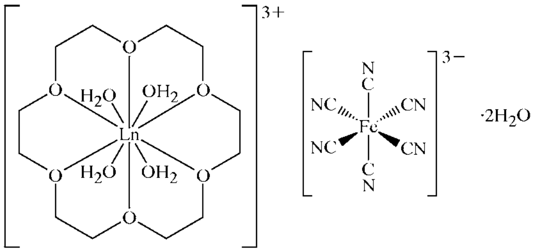
Received 13 August 2007
Accepted 14 August 2007
Online 1 September 2007

Tetraaqua(18-crown-6)cerium(III) hexacyanoferrate(III) dihydrate, $[Ce(C_{12}H_{24}O_6)(H_2O)_4][Fe(CN)_6]\cdot 2H_2O$, and tetraaqua(18-crown-6)neodymium(III) hexacyanoferrate(III) dihydrate, $[Nd(C_{12}H_{24}O_6)(H_2O)_4][Fe(CN)_6]\cdot 2H_2O$, are isomorphous and isostructural in the $C2/c$ space group, where the cations, which contain ten-coordinate lanthanoid centres, lie across twofold rotation axes and the anions lie across inversion centres. In these compounds, an extensive series of $O—H\cdots O$ and $O—H\cdots N$ hydrogen bonds links the components into a continuous three-dimensional framework. Triaqua(18-crown-6)lanthanoid(III) hexacyanoferrate(III) dihydrate, $[Ln(C_{12}H_{24}O_6)(H_2O)_3][Fe(CN)_6]\cdot 2H_2O$, where Ln = Sm, Eu, Gd or Tb, are all isomorphous and isostructural in the $P\overline{1}$ space group, as are triaqua(18-crown-6)gadolinium(III) hexacyanochromate(III) dihydrate, $[Gd(C_{12}H_{24}O_6)(H_2O)_3][Cr(CN)_6]\cdot 2H_2O$, and triaqua(18-crown-6)gadolinium(III) hexacyanocobaltate(III) dihydrate, $[Gd(C_{12}H_{24}O_6)(H_2O)_3][Co(CN)_6]\cdot 2H_2O$. In these compounds, there are two independent anions, both lying across inversion centres, and the lanthanoid centres exhibit nine-coordination; in the crystal structures, an extensive series of hydrogen bonds links the components into a three-dimensional framework.

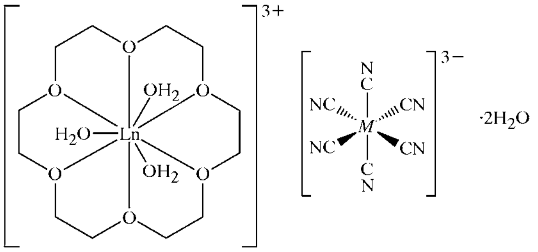
Comment

We report here the molecular and supramolecular structures of a number of lanthanoid complexes of the macrocyclic ligand 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as hydrated hexacyanometallate salts, which are formed by the reactions in aqueous solution between 18-crown-6 and the appropriate neutral dinuclear precursor complexes $[Ln(DMF)_4(H_2O)_3(\mu\text{-}CN)M(CN)_5]\cdot nH_2O$ (DMF is dimethylformamide; Ln = Ce, Nd, Sm, Eu, Gd or Tb; M = Cr, Fe or Co) (see scheme). In these ligand-substitution reactions, the hexadentate macrocyclic ether displaces not only the hexacyanometallate(III) unit, which acts in the dinuclear precursors as a monodentate ligand, but also all of the DMF ligands.

$$[Ln(OCHNMe_2)_4(H_2O)_3NCM(CN)_5]\cdot nH_2O \xrightarrow{\text{18-crown-6}} [Ln(\text{18-crown-6})(H_2O)_{3\text{-}4}]^{3+}\,[M(CN)_6]^{3-}\cdot 2H_2O$$



(I) Ln=Ce
(II) Ln=Nd



(III) Ln=Sm, M=Fe
(IV) Ln=Eu, M=Fe
(V) Ln=Gd, M=Cr
(VI) Ln=Gd, M=Fe
(VII) Ln=Gd, M=Co
(VIII) Ln=Tb, M=Fe

When the lanthanoid is either Ce^{3+} or Nd^{3+} and M is Fe^{3+}, the isomorphous hexacyanoferrate(III) salts $[Ce(\text{18-crown-6})(H_2O)_4)][Fe(CN)_6]\cdot 2H_2O$, (I), and $[Nd(\text{18-crown-6})(H_2O)_4)][Fe(CN)_6]\cdot 2H_2O$, (II), are formed (Fig. 1). When the lanthanoid cation is Sm^{3+}, Eu^{3+} or Tb^{3+}, and M is again Fe^{3+}, the salts $[Ln(\text{18-crown-6})(H_2O)_3)][Fe(CN)_6]\cdot 2H_2O$, with Ln = Sm, (III), Eu, (IV), and Tb, (VIII), are formed, all of which are isomorphous with the Gd analogue, (VI), whose structure was reported recently (Koner *et al.*, 2005). Finally, when the lanthanoid cation is Gd^{3+} and M is either Cr^{3+} or Co^{3+}, the salts $[Gd(\text{18-crown-6})(H_2O)_3)][Cr(CN)_6]\cdot 2H_2O$, (V), and $[Gd(\text{18-crown-6})(H_2O)_3)]Co(CN)_6]\cdot 2H_2O$, (VII), are obtained, and these two salts are also isomorphous with compound (VI). The crystal quality for compound (VIII) was consistently poor, and the quality of the X-ray diffraction data was correspondingly poor; accordingly, we do not discuss the metrical properties of this compound.

The isomorphous pair of compounds (I)/(II) crystallize in the space group $C2/c$, with the $[Ln(\text{18-crown-6})(H_2O)_4]^{3+}$ unit

---

‡ Additional correspondence author, e-mail: sm_cu_chem@yahoo.co.in.

lying across a twofold rotation axis, selected as that along $(0, y, \frac{1}{4})$, and the $[Fe(CN)_6]^{3-}$ anion lying across an inversion centre, selected as that at $(\frac{1}{4}, \frac{1}{4}, 0)$; the composition is completed by a noncoordinated water molecule lying in a general position. The isomorphous set of compounds (III)–(VIII), within which the structure is invariant to changes of either the 4*f* or the 3*d* metal, all crystallize in the space group $P\overline{1}$, with the $[Ln(18\text{-crown-}6)(H_2O)_3]^{3+}$ cation and two noncoordinated water molecules all lying in general positions, and two independent $[M(CN)_6]^{3-}$ anions, where M = Cr in compound (V), Fe in compounds (III), (IV), (VI) and (VIII), and Co in compound (VII), each lying across centres of inversion, selected as those at $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$. These specifications of the special positions provide compact and connected asymmetric units for both types of salt.

In compounds (I) and (II), the lanthanoid cation exhibits ten-coordination with a geometry best described as a bicapped square antiprism, while in each of (III)–(VIII), the lanthanoid cation exhibits nine-coordination, with a monocapped square-antiprismatic geometry (Koner *et al.*, 2005). The patterns of the O—C—C—O torsion angles, beginning at O1 and increasing monotonically, are $g^+g^-g^+g^-g^+g^+$ in (I) and (II), and $g^-g^-g^+g^-g^+g^-$ in (III)–(VIII), indicative of the folding of the macrocycle around the Ln cation (Forsellini *et al.*, 1985). In compounds (I) and (II), the patterns of the Ln—O bond distances (Table 3) are very similar, with the distances to water O atoms somewhat less than those to the crown ether O atoms. Likewise, within the isomorphous set (III)–(VIII), the patterns of the Ln—O distances (Table 4) are consistent from one compound to another, with again the distances to the water O atoms less than those to the crown ether O atoms. Regardless of whether we consider the mean values of all the Ln—O distances, or just the mean of those involving the crown ether, there is a monotonic decrease from left to right across the 4*f* series, exactly as expected and consistent with the change in coordination number from ten to nine between Nd [compound (I)] and Sm [compound (III)]. Within the subseries (V)–(VII), where the Ln—O distances are virtually identical, the mean values of the M—C distances in the anions are 2.072 (5) Å when M = Cr, 1.940 (2) Å when M = Fe and 1.893 (2) Å when M = Co; inasmuch as the anions when M = Fe or Co are expected to adopt low-spin configurations, the minimum M—C distance is expected for the d^6 anion $[Co(CN)_6]^{3-}$, as observed.

The independent components in each of compounds (I) and (II) are linked into a three-dimensional framework structure by a combination of two O—H···O hydrogen bonds and four O—H···N hydrogen bonds, where each water molecule acts as a double donor of hydrogen bonds, and each N atom acts as an acceptor, with atom N11 acting as a double acceptor (Tables 1 and 2); it may be noted that the O atoms of the crown ether component play no part in the hydrogen bonding. Despite the number of independent hydrogen bonds, which is amplified by the symmetry properties of the ionic components, the formation of the framework structure is readily analyzed in terms of simple substructures in one and two dimensions.

The anion and the two symmetry-related water molecules of the cation, those containing atom O19, generate a chain of spiro-fused $R_6^6(20)$ rings (Bernstein *et al.*, 1995) running parallel to the [010] direction. Chains of this type are further linked by O—H···N hydrogen bonds to form a hydrogen-bonded sheet of anions and water molecules lying parallel to (100) and built from alternating ribbons of $R_5^5(18)$ and $R_6^6(20)$ rings (Fig. 2). The reference (100) sheet, of which water atom O20 is a component, contains the Fe atoms lying on centres of inversion at $x = \frac{1}{4}$. This sheet is related by the twofold rotation axes at $x = 0$ and $x = \frac{1}{2}$ to the sheets generated by Fe atoms lying on inversion centres at $x = -\frac{1}{4}$ and $x = \frac{3}{4}$, respectively. Since atoms O20 and O20^{i} [symmetry code: (i) $-x, y, \frac{1}{2} - z$] are both coordinated to the reference Ln atom at $x = 0$, these two water molecules are components of adjacent sheets which are thereby linked. In addition, adjacent sheets are also linked by a further O—H···O hydrogen bond, and these two interactions combine to generate a continuous three-dimensional framework.

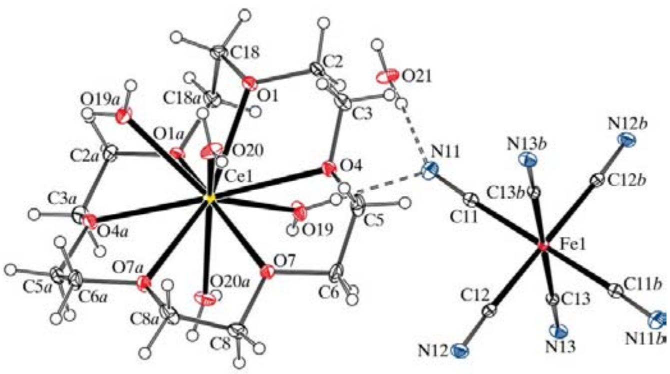


Figure 1
The independent components of (I), showing the atom-labelling scheme. Atoms marked *a* and *b* are at the symmetry positions $(-x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$, respectively. Displacement ellipsoids are drawn at the 30% probability level. Compound (II) is isomorphous and isostructural with (I).

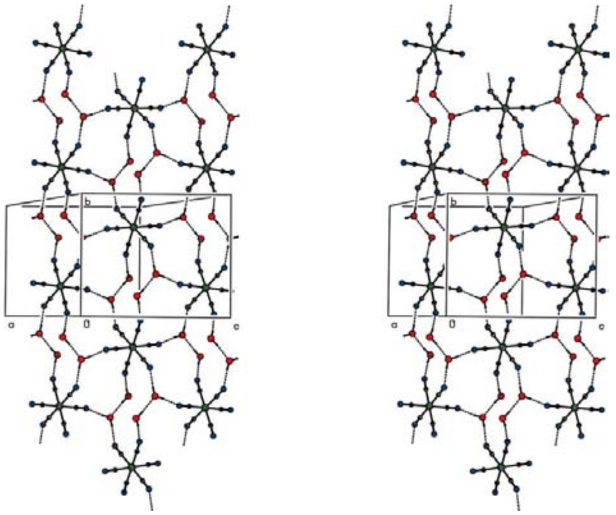


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet parallel to (100) and built from hexacyanoferrate(III) anions and water molecules only.

Acta Cryst. (2007). C**63**, m440–m444 Misra *et al.* • Five $[Ln(C_{12}H_{24}O_6)(H_2O)_x][M(CN)_6]\cdot 2H_2O$ complexes **m441**

The supramolecular structure of compound (VI) has already been described (Koner *et al.*, 2005), so that the structures of the isomorphous analogues (III), (V), (VII) and (VIII) need little further discussion. However, we may note here that the one-dimensional substructures in (VI) were described erroneously (Koner *et al.*, 2005) as double helices; they are, in fact, chains of spiro-fused rings, with the points of ring fusion lying on centres of inversion, thus precluding the development of any helical structures which are necessarily chiral.

Experimental

The dinuclear precursor compounds $[\mathrm{Ln(DMF)_4(H_2O)_3}(\mu\text{-CN})\text{-}M\mathrm{(CN)_5}]\cdot n\mathrm{H_2O}$ (Ln = Ce, Nd, Sm, Eu, Gd or Tb; M = Cr, Fe or Co) were prepared using a published method (Figuerola *et al.*, 2003). For the synthesis of (I), a solution of 18-crown-6 (0.066 g, 0.25 mmol) in water (5 ml) was added dropwise to a solution of $[\mathrm{Ce(DMF)_4(H_2O)_3}\text{-}(\mu\text{-CN})M\mathrm{(CN)_5}]\cdot\mathrm{H_2O}$ (0.18 g, 0.25 mmol) in water (5 ml). The mixture was stirred for 10 min and then filtered; the yellow filtrate was then set aside to crystallize at ambient temperature. After a few days, golden-yellow crystals suitable for single-crystal X-ray diffraction were deposited and collected by filtration. Compounds (II)–(V), (VII) and (VIII) were prepared in entirely analogous ways by use of the appropriate dinuclear precursor complexes. (I), golden yellow, yield 85%; analysis found: C 29.6, H 5.1, N 11.7%; $\mathrm{C_{18}H_{36}CeFeN_6O_{12}}$ requires: C 29.8, H 5.0, N 11.6%; IR (KBr, $\mathrm{cm^{-1}}$): 2122 (*m*, CN) and 1081 (*s*, CO); μ_{eff} (300 K) 3.00 BM. (II), golden yellow, yield 80%; analysis found: C 29.5, H 4.9, N 11.6%; $\mathrm{C_{18}H_{36}FeN_6NdO_{12}}$ requires: C 29.7, H 5.0, N 11.5%; IR (KBr, $\mathrm{cm^{-1}}$): 2122 (*m*, CN) and 1081 (*s*, CO); μ_{eff} (300 K) 3.92 BM. (III), yellow, yield 75%; analysis found: C 30.3, H 4.7, N 11.8%; $\mathrm{C_{18}H_{34}FeN_6O_{11}Sm}$ requires: C 30.2, H 4.8, N 11.7%; IR (KBr, $\mathrm{cm^{-1}}$): 2124 (*s*, CN) and 1073 (*s*, CO); μ_{eff} (300 K) 2.55 BM. (IV), yellow, yield 88%; analysis found: C 30.2, H 4.7, N 11.6%; $\mathrm{C_{18}H_{34}EuFeN_6O_{11}}$ requires: C 30.1, H 4.8, N 11.7%; IR (KBr, $\mathrm{cm^{-1}}$): 2124 (*m*, CN) and 1073 (*s*, CO); μ_{eff} (300 K) 3.76 BM. (V), pale yellow, yield 82%; analysis found: C 29.9, H 4.7, N 11.8%; $\mathrm{C_{18}H_{34}CrGdN_6O_{11}}$ requires: C 30.0, H 4.8, N 11.7%; IR (KBr, $\mathrm{cm^{-1}}$): 2138 (*m*, CN) and 1073 (*s*, CO); μ_{eff} (300 K) 8.72 BM. (VII), colourless, yield 90%; analysis found: C 29.9, H 4.6, N 11.6%; $\mathrm{C_{18}H_{34}CoGdN_6O_{11}}$ requires: C 29.8, H 4.7, N 11.6%; IR (KBr, $\mathrm{cm^{-1}}$): 2137 (*s*, CN) and 1073 (*s*, CO); μ_{eff} (300 K) 7.62 BM. (VIII), yellow, yield 80%; analysis found: C 29.7, H 4.7, N 11.7%; $\mathrm{C_{18}H_{34}FeN_6O_{11}Tb}$ requires: C 29.8, H 4.7, N 11.6%; IR (KBr, $\mathrm{cm^{-1}}$): 2125 (*m*, CN) and 1072 (*s*, CO); μ_{eff} (300 K) 9.78 BM.

Compound (I)

Crystal data

$[\mathrm{Ce(C_{12}H_{24}O_6)(H_2O)_4}]\text{-}[\mathrm{Fe(CN)_6}]\cdot\mathrm{2H_2O}$
$M_r = 724.50$
Monoclinic, $C2/c$
$a = 19.8534\ (6)$ Å
$b = 11.5705\ (2)$ Å
$c = 14.0258\ (4)$ Å
$\beta = 113.3930\ (13)^\circ$
$V = 2957.09\ (13)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.07\ \mathrm{mm^{-1}}$
$T = 120\ (2)$ K
0.20 × 0.10 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.682$, $T_{\max} = 0.820$
15557 measured reflections
3385 independent reflections
3079 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.049$
$S = 1.09$
3385 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.81$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O19—H19A···O21$^{\mathrm{i}}$	0.81	1.91	2.700 (2)	163
O19—H19B···N11	0.81	2.14	2.917 (2)	161
O20—H20A···O21$^{\mathrm{ii}}$	0.82	1.96	2.768 (2)	168
O20—H20B···N12$^{\mathrm{iii}}$	0.82	1.92	2.739 (2)	171
O21—H21A···N13$^{\mathrm{ii}}$	0.82	1.94	2.757 (2)	173
O21—H21B···N11	0.82	2.07	2.888 (2)	175

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, -y+1, z+\frac{1}{2}$; (iii) $x, -y, z+\frac{1}{2}$.

Compound (II)

Crystal data

$[\mathrm{Nd(C_{12}H_{24}O_6)(H_2O)_4}]\text{-}[\mathrm{Fe(CN)_6}]\cdot\mathrm{2H_2O}$
$M_r = 728.62$
Monoclinic, $C2/c$
$a = 19.9552\ (6)$ Å
$b = 11.5063\ (2)$ Å
$c = 13.9706\ (3)$ Å
$\beta = 113.4189\ (11)^\circ$
$V = 2943.55\ (12)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.30\ \mathrm{mm^{-1}}$
$T = 120\ (2)$ K
0.34 × 0.34 × 0.25 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.478$, $T_{\max} = 0.561$
21701 measured reflections
3360 independent reflections
3168 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.043$
$S = 1.06$
3360 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.83$ e Å^{-3}
$\Delta\rho_{\min} = -1.07$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O19—H19A···O21$^{\mathrm{i}}$	0.81	1.92	2.697 (2)	161
O19—H19B···N11	0.84	2.09	2.904 (2)	161
O20—H20A···O21$^{\mathrm{ii}}$	0.83	1.96	2.773 (2)	166
O20—H20B···N12$^{\mathrm{iii}}$	0.84	1.90	2.734 (2)	169
O21—H21A···N13$^{\mathrm{ii}}$	0.83	1.93	2.753 (2)	173
O21—H21B···N11	0.80	2.10	2.893 (2)	175

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, -y+1, z+\frac{1}{2}$; (iii) $x, -y, z+\frac{1}{2}$.

Compound (III)

Crystal data

$[\mathrm{Sm(C_{12}H_{24}O_6)(H_2O)_3}]\text{-}[\mathrm{Fe(CN)_6}]\cdot\mathrm{2H_2O}$
$M_r = 716.71$
Triclinic, $P\overline{1}$
$a = 10.9324\ (2)$ Å
$b = 11.0996\ (2)$ Å
$c = 14.0119\ (4)$ Å
$\alpha = 67.9012\ (13)^\circ$
$\beta = 70.7291\ (13)^\circ$
$\gamma = 65.7231\ (14)^\circ$
$V = 1404.77\ (6)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.65\ \mathrm{mm^{-1}}$
$T = 120\ (2)$ K
0.10 × 0.06 × 0.04 mm

m442 Misra *et al.* • Five $[\mathrm{Ln(C_{12}H_{24}O_6)(H_2O)_x}][M\mathrm{(CN)_6}]\cdot\mathrm{2H_2O}$ complexes *Acta Cryst.* (2007). C**63**, m440–m444

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.836$, $T_{\max} = 0.900$
28348 measured reflections
6453 independent reflections
5624 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.067$
$S = 1.01$
6453 reflections
334 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.95$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}

Compound (IV)

Crystal data

$[\mathrm{Eu}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)(\mathrm{H}_2\mathrm{O})_3]$-$[\mathrm{Fe}(\mathrm{CN})_6]\cdot2\mathrm{H}_2\mathrm{O}$
$M_r = 718.32$
Triclinic, $P\overline{1}$
$a = 10.9125$ (3) Å
$b = 11.0947$ (4) Å
$c = 14.0119$ (3) Å
$\alpha = 67.8201$ (18)°
$\beta = 70.635$ (2)°
$\gamma = 65.743$ (2)°
$V = 1400.57$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.80$ mm^{-1}
$T = 120$ (2) K
$0.25 \times 0.20 \times 0.20$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.509$, $T_{\max} = 0.568$
27604 measured reflections
6420 independent reflections
5973 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.212$
$S = 1.10$
6420 reflections
334 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 11.43$ e Å^{-3}
$\Delta\rho_{\min} = -3.03$ e Å^{-3}

Compound (V)

Crystal data

$[\mathrm{Gd}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)(\mathrm{H}_2\mathrm{O})_3]$-$[\mathrm{Cr}(\mathrm{CN})_6]\cdot2\mathrm{H}_2\mathrm{O}$
$M_r = 719.76$
Triclinic, $P\overline{1}$
$a = 11.0563$ (2) Å
$b = 11.1562$ (2) Å
$c = 14.2127$ (3) Å
$\alpha = 68.3494$ (11)°
$\beta = 70.0959$ (12)°
$\gamma = 66.0299$ (12)°
$V = 1450.92$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.70$ mm^{-1}
$T = 120$ (2) K
$0.16 \times 0.15 \times 0.04$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.672$, $T_{\max} = 0.899$
34884 measured reflections
6646 independent reflections
6382 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.04$
6646 reflections
334 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 3.60$ e Å^{-3}
$\Delta\rho_{\min} = -1.63$ e Å^{-3}

Compound (VII)

Crystal data

$[\mathrm{Gd}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)(\mathrm{H}_2\mathrm{O})_3]$-$[\mathrm{Co}(\mathrm{CN})_6]\cdot2\mathrm{H}_2\mathrm{O}$
$M_r = 726.69$
Triclinic, $P\overline{1}$
$a = 10.8604$ (2) Å
$b = 11.0724$ (3) Å
$c = 13.9909$ (2) Å
$\alpha = 67.5857$ (10)°
$\beta = 70.5870$ (8)°
$\gamma = 65.5666$ (9)°
$V = 1385.20$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 3.03$ mm^{-1}
$T = 120$ (2) K
$0.60 \times 0.54 \times 0.42$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.187$, $T_{\max} = 0.280$
27907 measured reflections
6348 independent reflections
6022 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.047$
$S = 1.09$
6348 reflections
334 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 1.00$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}

Table 3
Ln—O distances (Å) in (I) and (II).

	(I)	(II)
Ln1—O1	2.5784 (13)	2.5515 (12)
Ln1—O4	2.6811 (14)	2.6620 (13)
Ln1—O7	2.5619 (13)	2.5312 (12)
Ln1—O19	2.5389 (14)	2.5062 (12)
Ln1—O20	2.4962 (14)	2.4615 (12)

Table 4
Ln—O distances (Å) in (III)–(VII).

	(III)	(IV)	(V)	(VI)	(VII)
Ln1—O1	2.602 (2)	2.590 (5)	2.581 (3)	2.5790 (17)	2.5769 (14)
Ln1—O4	2.505 (2)	2.502 (6)	2.489 (4)	2.4882 (19)	2.4863 (16)
Ln1—O7	2.563 (2)	2.553 (5)	2.548 (3)	2.5476 (17)	2.5437 (15)
Ln1—O10	2.529 (2)	2.511 (5)	2.504 (3)	2.5007 (17)	2.4989 (15)
Ln1—O13	2.552 (2)	2.550 (5)	2.543 (3)	2.5361 (17)	2.5347 (15)
Ln1—O16	2.481 (2)	2.467 (6)	2.476 (3)	2.4608 (17)	2.4573 (15)
Ln1—O19	2.327 (2)	2.318 (6)	2.307 (3)	2.3088 (17)	2.3042 (15)
Ln1—O20	2.409 (2)	2.405 (5)	2.381 (3)	2.3884 (17)	2.3887 (15)
Ln1—O21	2.408 (2)	2.392 (5)	2.377 (3)	2.3881 (17)	2.3883 (15)

Note: data for compound (VI) are taken from Koner *et al.* (2005).

For compounds (I) and (II), the systematic absences permitted *Cc* and *C*2/*c* as possible space groups; *C*2/*c* was selected and confirmed by the subsequent structure analyses. Crystals of compounds (III)–(V), (VII) and (VIII) are all triclinic; space group $P\overline{1}$ was selected for each and confirmed by the subsequent structure analyses. All H atoms were located in difference maps. Those bonded to C atoms were treated as riding atoms with a C—H distance of 0.99 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C); those bonded to O atoms were allowed to ride at the positions deduced from difference maps, with a common $U_{\rm iso}$(H) value for each compound, giving a range of O—H distances of 0.80–0.89 Å. In compounds (II), (IV), (V) and (VII), atoms C2 and C18 bonded to O1 are each disordered over two sites. This was allowed for with both components of these atoms refined isotropically; the final linked occupancy parameters for these disordered atoms are as follows: (III) 0.815 (7):0.185 (7), (IV) 0.762 (14):

Acta Cryst. (2007). C**63**, m440–m444 Misra *et al.* • Five $[\mathrm{Ln}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{O}_6)(\mathrm{H}_2\mathrm{O})_x][M(\mathrm{CN})_6]\cdot2\mathrm{H}_2\mathrm{O}$ complexes **m443**

0.238 (14), (V) 0.542 (7):0.458 (7) and (VII) 0.777 (6):0.223 (6). The maximum difference density in compound (IV) is located 0.91 Å from the Eu atom. For compound (VIII), with unit-cell dimensions a = 11.1302 (4) Å, b = 11.2341 (4) Å, c = 13.9408 (5) Å, α = 69.778 (2)°, β = 68.585 (3)° and γ = 62.425 (2)°, we were unable to reduce the R factor below 11%, although (VIII) is clearly isostructural with compounds (III)–(VII); no attempt was made to model any disorder of the macrocyclic ligand, and we do not report any further structural details here.

For all compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC National Crystallography Service, University of Southampton, UK. The authors thank the staff for all their help and advice. Financial support from the Department of Science and Technology, Government of India (SR/S1/IC-27/2002), and CSIR, Government of India (Fellowships to MN and RK), is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3119). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Figuerola, A., Diaz, C., Ribas, J., Tangoulis, V., Granell, J., Lloret, F., Mahfa, J. & Maestro, M. (2003). *Inorg. Chem.* **42**, 641–649.

Forsellini, F., Benetollo, F., Bombieri, G., Cassol, A. & De Paoli, G. (1985). *Inorg. Chim. Acta*, **109**, 167–171.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Koner, R., Nayak, M., Ferguson, G., Low, J. N., Glidewell, C., Misra, P. & Mohanta, S. (2005). *CrystEngComm*, **7**, 129–132.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

m444 Misra *et al.* • Five [Ln($C_{12}H_{24}O_6$)(H_2O)$_x$][M(CN)$_6$]·2H_2O complexes *Acta Cryst.* (2007). C**63**, m440–m444