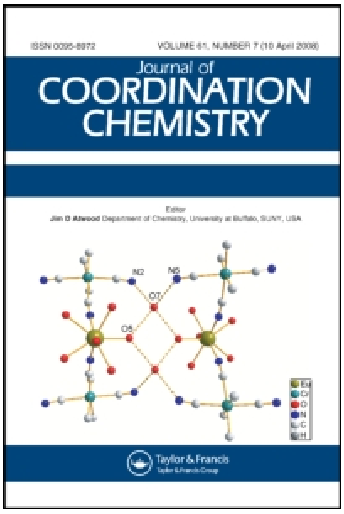

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SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF [Eu($C_{18}H_{18}N_6$)(OAc)$_2$][Cl$^-$] · 7H$_2$O, A TEN-COORDINATE Eu(III) COMPLEX WITH A CLOSE-TO-PLANAR HEXADENTATE $C_{18}H_{18}N_6$ LIGAND: AN INTERESTING CASE OF A STRUCTURE WITH MULTIPLE DISORDER PROBLEMS

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SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$, A TEN-COORDINATE Eu(III) COMPLEX WITH A CLOSE-TO-PLANAR HEXADENTATE $C_{18}H_{18}N_6$ LIGAND: AN INTERESTING CASE OF A STRUCTURE WITH MULTIPLE DISORDER PROBLEMS

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The title compound crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with $a = 8.7080(18)$ Å, $b = 9.2777(14)$ Å, $c = 10.2707(22)$ Å, $\alpha = 77.762(14)°$, $\beta = 77.482(17)°$, $\gamma = 84.735(15)°$, $V = 790.7(3)$ Å^3 and $Z = 1$. The structure was solved and refined to $R = 2.37\%$ and $wR = 3.19\%$ for all 2073 independent reflections. The structure is disordered, with overlapping images of two enantiomeric $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ ions surrounding an inversion center on which lies a Eu(III) cation. These two images correspond to isomers with $\lambda\lambda$ and $\delta\delta$ conformations of their $N{-}CH_2{-}CH_2{-}N$ moieties. The ten-coordinate europium(III) cation has a staggered 2:6:2 coordination geometry, with six equatorial Eu–N bonds to the hexadentate macrocyclic ligand and two *quasi*-axial Eu–O bonds to each of the two bidentate acetate ligands. Further manifestations of disorder occur for the acetate ligands and for H_2O/Cl^- sites in the crystal lattice.

Keywords: Europium(III); ten-coordination; macrocyclic $C_{18}H_{18}N_6$ ligand; Schiff base; crystal structure; disorder

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INTRODUCTION

Reports of the template synthesis[1,2] of Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} complexes of the macrocyclic $C_{22}H_{26}N_6$ Schiff-base ligand (I) were soon followed by the synthesis[3] of the analogous La^{3+} complex; the crystal structure of the 12-coordinate species $La(C_{22}H_{26}N_6)(NO_3)_3$ was reported.[3,4]

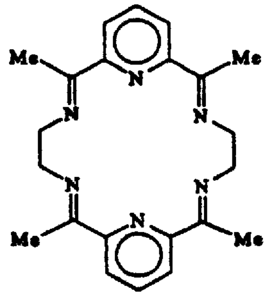
It is interesting to note that NMR studies have shown that all six nitrogen donor atoms of the macrocyclic ring are coordinated to the metal center for the entire series of metal macrocyclic compounds from the largest lanthanide cation (La^{3+}) to the smallest such cation (Lu^{3+}).[5] These macrocyclic metal complexes have been shown to be kinetically inert toward metal dissociation and do not undergo metal loss even under acidic or basic conditions. The stability of these metal-macrocyclic moieties is such that they do not decompose at temperatures up to 240°C. Such stability is very rare for lanthanide bound N-donor organic ligands.[5] In solution, even fluoride ions, which are typically used to precipitate lanthanide ions, fail to remove the lanthanide ion from its macrocyclic ring. This unusual stability probably arises as a result of: (1) the lanthanide cation having the ideal size to fit into the ligand cavity of the 18-crown-6 macrocycle; and, (2) the coordinating ability of the six nitrogen donor atoms. These macrocyclic lanthanide complexes can be solvated intact both in aqueous and organic solvents. It is interesting to note that if the pyridine units in the macrocycle are replaced with furan units, the complex will then rapidly decompose in water.[6] The exocyclic ligands associated with these complexes are usually labile and can easily be exchanged.

Several crystallographic studies have been reported on lanthanide (or the closely related yttrium) complexes of the $C_{22}H_{26}N_6$ ligand, including $La(C_{22}H_{26}N_6)(NO_3)_3$,[3,4] $[Ce(C_{22}H_{26}N_6)(NO_3)_2(H_2O)^+]$,[4] $[Nd(C_{22}H_{26}N_6)(NO_3)(H_2O)_2^{2+}]$,[4] $[\{Eu(C_{22}H_{26}N_6)(OAc)\}_2(\mu\text{-}CO_3)^{2+}](OH^-)_2 \cdot 7H_2O$,[7] $[Gd(C_{22}H_{26}N_6)(OAc)_2^+][Cl^-] \cdot 4H_2O$,[8] $[Y(C_{22}H_{26}N_6)(OAc)_2^+][ClO_4^-]$,[9] $[Y(C_{22}H_{26}N_6)(OAc)(H_2O)^{2+}]$,[9] $[Tb(C_{22}H_{26}N_6)(OAc)_2]Cl \cdot 4H_2O$[10] and $[Eu(C_{22}H_{26}N_6)(OAc)_2^+]$.[11] The complexes range from nine-coordinate (for Y^{3+}) to 12-coordinate (for La^{3+}), with the coordination number steadily increasing as a function of the ionic radius of the M^{3+} cation (see compilation of ionic radii by R.D. Shannon[12]).

The six nitrogen donor atoms of the macrocyclic ligand are located in a *pseudo*-equatorial arrangement around the lanthanide metal center in all of the above structures. The 18-membered macrocyclic hexaaza ligand is, in each case, folded into a butterfly conformation. The fold angles can be as large as 69° (in the dimeric Eu(III) complex).[7] The fold in these macrocyclic ligands always occurs at the flexible ethylenediamine linkages and the direction of the fold is determined by asymmetry in the location of the exocyclic ligands. The atoms in each of the pyridinediimine units of the macrocyclic ligands are planar. The fold angles may be calculated by examining the angle of intercept of the two pyridine units.

We have been interested in the elucidation of the structure of lanthanide (and yttrium) derivatives of high coordination number and have reported the characterization of the eight-coordinate lanthanum(III) species $[La\{C_8H_{16}N_4(CH_2CH_2CONH_2)_4\}^{3+}]$,[13] the nine-coordinate yttrium(III) species $[Y\{C_6H_{12}N_3(CH_2CONH_2)_3\}(CF_3SO_3)_2(H_2O)^+]$,[14] the nine-coordinate europium(III) species $[Eu\{C_8H_{16}N_4(CH_2CH(OH)CH_3)_4\}(H_2O)^{3+}]$[15] and $[Eu\{C_8H_{16}N_4(CH_2CONH_2)_4\}(H_2O)^{3+}]$,[16] the ten-coordinate lanthanum(III) species $[La\{C_8H_{16}N_4(CH_2CONH_2)_4\}(CF_3SO_3)(EtOH)^+]$[17] and the 12-coordinate terbium species $[Tb(C_{22}H_{26}N_6)(OAc)^+]$.[10] We have also characterized the free protonated octadentate ligand $[C_{10}H_{22}N_4(CH_2\text{-}CH_2OH)_4^{2+}]$.[18]

We now report the synthesis and crystal structure of a europium(III) complex of the *unsubstituted* hexaaza macrocyclic ligand $C_{18}H_{18}N_6$ (II).



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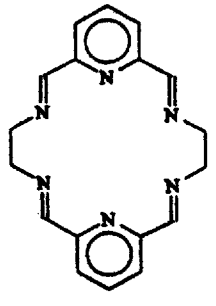

II

EXPERIMENTAL SECTION

The complex $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-]\cdot nH_2O$ was prepared by following syntheses developed by Vallarino *et al.*[5] and Fenton *et al.*[6] The procedure was carried out under nitrogen gas. (It is not an absolute requirement but it improves yields and purity of product.) $Eu(CH_3COO)_3\cdot nH_2O$ (0.3114 g, 9.46 mmol) was stirred in 19 mL of degassed absolute methanol. A solution of 0.12 mL of ethylenediamine (1.85 mmol) and 0.04 mL concentrated HCl in 5 mL of methanol was added to the europium acetate. 2,6-pyridinedicarboxaldehyde (0.255 g, 1.89 mmol) was dissolved in 19 mL of methanol and added to the reaction flask. The solution was refluxed for four hours during which time the solution became dark yellow in color.

Refluxing was discontinued and the solvent was removed *in vacuo* with gentle heating. The nitrogen atmosphere was no longer maintained. An off-white solid remained. It was dissolved in chloroform and filtered. Diethylether was added to precipitate the product. This procedure was repeated. The cream-colored product was collected on a Buchner funnel and rinsed with ether. It was air dried and stored in a desiccator. ^{1}H NMR in D_2O (ppm, J in Hz): 4.86 t, $J = 7.6$, 2H (N–C(C)–CH–*CH*); 3.42 broad, 6H (*CH_3*–COO); 3.00 d, $J = 6.4$, 4H (N–C(C)–*CH*); 0.03 broad, 8H (N–*CH_2CH_2*–N); –16.93 broad, 4H, (imine). IR (cm^{-1}, KBr): 1593 s, $\nu_{C=N_{imine}}$; 1659 s, $\nu_{C-N_{pyridine}}$.

Crystals were obtained from a solution of the complex in $CHCl_3$ and contain (necessary) adventitious water; the formula of these was shown to be $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$ by means of a crystal structure analysis (q.v.).

Collection of the X-ray Diffraction Data

A suitable equidimensional crystal was sealed into a 0.3 mm-diameter thin-walled capillary. It was then mounted and aligned on a Siemens R3 m/V diffractometer. Details of data collection appear in Table I. The crystal belongs to the triclinic system, possible space groups being P1 (No. 1) or $P\bar{1}$ (No. 2).[19] The latter has a far greater frequency of occurrence and is far more common than the former for compounds synthesized from achiral precursors;[20,21] however, see below. A complete sphere of diffraction data was collected in the manner described previously[22] with Mo Kα radiation for the 2θ range 5°–45°. In all, 4146 reflections were measured. These data were corrected for Lorentz and polarization effects and for absorption, and were merged to a unique data set with a merging index of $R_{int} = 1.20\%$ for 2073 averaged pairs of reflections.

Solution of the Crystal Structure

The structure was solved under the SHELXTL PLUS system of crystallographic programs[23,24] on a VAXstation 3100 computer. Calculations were based upon the analytical form of the scattering factors for neutral atoms;[25a] corrections were made for both real and imaginary components of

TABLE I Experimental data for the x-ray diffraction study on $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$

Empirical formula	$C_{22}H_{38}Cl\ EuN_6O_{11}$
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a = 8.7080(18)$ Å $b = 9.2777(14)$ Å $c = 10.2707(22)$ Å $\alpha = 77.762(14)°$ $\beta = 77.482(17)°$ $\gamma = 84.735(15)°$
Volume	$790.7(3)$ Å^3
Z	1
Formula weight	750.0
Density (calc.)	$1.576\,g \cdot cm^{-3}$
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Absorption coeff., μ	$2.12\,mm^{-1}$
2θ range	5.0–45.0°
Index ranges	$-10 \leq h \leq 10, -10 \leq k \leq 10, -12 \leq l \leq 12$
Reflections collected	4146
Independent reflections	2073 ($R_{int} = 1.20\%$)
Reflections above 6σ	2038
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0057F^2$
Number of parameters refined	250
Final R indices (6σ data)	$R = 2.24\%, wR = 2.38\%$
R indices (all data)	$R = 2.37\%, wR = 3.19\%$
Largest and mean Δ/σ	0.001, 0.000
Data-to-parameter ratio	8.3 : 1
Largest difference peak	$0.43\,e$ Å^{-3}
Largest difference hole	$-0.74\,e$ Å^{-3}

anomalous dispersion.[25b] Hydrogen atoms attached to the carbon atoms were placed in calculated positions based upon $d(C-H) = 0.96$ Å.[26]

Determination of Space Group and the Solution to a Severe Disorder Problem

Finding a satisfactory solution to this structure was extremely difficult and extended (with long periods of inactivity) over a three-year period. The unit cell contains only one formula unit. Intensity statistics favored the non-centrosymmetric space group P1; this space group is, however, extremely rare for a synthetic achiral (or racemic) product.[21] Our attempts to solve the structure followed a path of three essential steps:

(1) We initially solved the structure in space group $P\bar{1}$. This suggested an approximately planar $Eu(C_{18}H_{18}N_6)$ moiety with crystallographically-required C_i ($\bar{1}$) symmetry and with two-fold disorder of the acetate groups above and below the plane. A problem of distinguishing between water molecules and chloride ions in the lattice was encountered. Nevertheless, the

structure refined to $R = 4.5\%$, but certain C–C and N–C bond lengths exhibited alarmingly large excursions from their accepted values.

(2) We next tried to refine the structure in the non-centrosymmetric space group P1. Refinement was very slow, many correlation coefficients were close to unity, and disorder persisted in certain portions of the structure. Although the structure refined to $R = 3.53\%$, the range of C–C and of N–C distances now became alarmingly large (*e.g.*, C–C distances of 1.1–1.8 Å were found within the pyridine rings!). These features are all symptomatic of a centrosymmetric structure refined erroneously in a non-centrosymmetric space group. We discontinued this approach.

(3) After a long hiatus (and armed now with the results of two further structural studies) we had an epiphany. A structural study of $[Eu\{C_8H_{16}N_4(CH_2CH(OH)CH_3)_4\}(H_2O)^{3+}]_2[CF_3SO_3^-]_6 \cdot 2EtOH \cdot H_2O$ had shown the crystal to contain an *ordered* array of four different stereoisomers (two enantiomeric pairs).[15] A second study of $[Eu\{C_8H_{16}N_4(CH_2CONH_2)_4(H_2O)^{3+}][CF_3SO_3^-]_3 \cdot 2MeOH$ had revealed a *disordered* array of four different stereoisomers in which two stereoisomers, interrelated by different ligand conformation, are present at each site.[16] The crucial point here is that the disorder manifested itself primarily as disorder in the (N)–CH_2–CH_2–(N) "ruffles" of a 12-membered 1,4,7,10-tetraazacyclododecane ring.[16] We now returned to the present study and were able to obtain a satisfactory, self-consistent, solution to the present structure in the more probable, centrosymmetric, space group $P\bar{1}$.

Careful study of difference-Fourier maps showed that the saturated portion of the $C_{18}H_{18}N_6$ ligand suffered from two-fold disorder, as did the coordinated acetate groups. This is shown in Figure 1. Thus, two different conformations of the macrocyclic ligand are superimposed upon one another. We were able to define a molecule containing an 18-membered $C_{12}N_6$ ring which included the C(7)–N(8)–C(9)–C(10)–N(11)–C(1a) system and an independent C(7a)–N(8′)–C(9′)–C(10′)–N(11′)–C(1) system. [A second molecule, related to this by inversion, may be defined. The two molecules superposed upon one another provide the overall complex disordered image of the macrocyclic ligand.] It seems probable that atoms C(1) and C(7) are also disordered (their thermal ellipsoids are elongated in a direction perpendicular to the plane of the macrocyclic ligand), but we cannot resolve the two possible sites for each atom since they are too close together (probably < 0.6 Å). Overall, we believe that each molecular site has a statistically disordered array of the $\lambda\lambda$ and $\delta\delta$ conformational isomers of the $C_{18}H_{18}N_6$ ligand. [Although a $\lambda\delta$ conformer is possible, the $\lambda\lambda$ and $\delta\delta$ conformers provide two different notches appropriate for the two observed

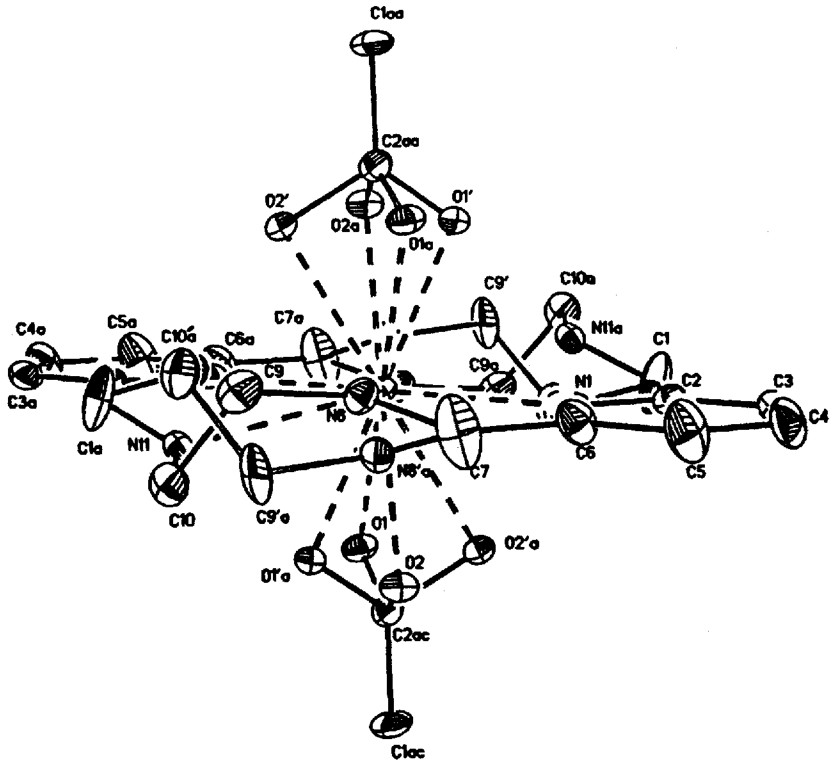

FIGURE 1 The disorder in the $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cation. Within the disordered portions, one image is shown with solid bonds, the other with hollow bonds.

orientations of the disordered acetate groups.] There is also some disorder of water of solvation and chloride ions; specifically, O(4S) and Cl(1) occupy sites separated by only 1.003(9) Å, so that either O(4S) or Cl(1) (but not both) may be present at any given site; the occupancy of each of these atoms was fixed at 0.5.

With the incorporation of these three features of disorder (different conformations of the macrocyclic ring, different orientations of the acetate ligands and H_2O/Cl^- scrambling), the structural refinement converged $[(\Delta/\sigma)_{max} = 0.001]$ with the surprisingly and unexpectedly low discrepancy indices of $R = 2.37\%$ and $wR = 3.19\%$ for all 2073 independent reflections (and $R = 2.24\%$, $wR = 2.38\%$ for those 2038 reflections with $|F_o| > 6\sigma(F_o)$). All bond distances are now within the accepted and expected ranges. A final difference-Fourier syntheses showed features only in the range −0.74 to

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$

	x	*y*	*z*	*U*(eq)
Eu(1)	0	0	0	29(1)
Cl	−1310(4)	4892(5)	−4293(5)	100(2)
O(1)	−1720(6)	1942(6)	−1228(6)	43(2)
O(2)	−2917(6)	528(6)	625(6)	44(2)
O(1′)	2040(6)	−1794(6)	−219(6)	47(2)
O(2′)	2396(6)	−184(6)	946(6)	46(2)
N(1)	−1323(3)	−2610(3)	643(3)	36(1)
N(8)	−872(10)	−1199(10)	2613(9)	38(3)
N(8′)	1612(10)	958(10)	−2423(9)	39(3)
N(11)	−417(9)	1746(8)	1913(7)	36(2)
N(11′)	−529(10)	−1184(8)	−1891(6)	39(2)
C(1)	−728(8)	−2656(7)	−1693(5)	83(3)
C(2)	−1402(5)	−3368(4)	−309(4)	41(1)
C(3)	−2080(5)	−4717(5)	−23(5)	50(2)
C(4)	−2703(7)	−5310(5)	1295(6)	68(2)
C(5)	−2639(8)	−4558(6)	2275(6)	83(2)
C(6)	−1926(6)	−3205(5)	1912(5)	54(2)
C(7)	−1833(9)	−2321(6)	2920(5)	93(3)
C(9)	−707(16)	−404(13)	3693(9)	49(4)
C(9′)	1658(16)	21(14)	−3417(9)	54(4)
C(10)	−1287(11)	1163(11)	3280(8)	49(3)
C(10′)	44(14)	−454(13)	−3297(9)	54(4)
C(1AC)	−4441(5)	2196(5)	−660(6)	63(2)
C(2AC)	−2918(5)	1441(4)	−425(4)	42(1)
O(1S)	−5873(6)	3015(6)	−6478(5)	103(2)
O(2S)	−4051(7)	2657(6)	−4538(6)	114(3)
O(3S)	−4070(11)	−10218(7)	−2986(6)	173(5)
O(4S)	−1914(12)	4150(10)	−3546(9)	90(4)

*Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

0.43 $e^-/Å^3$; the structure is thus both correct and complete. Atomic positional parameters are provided in Table II.

DISCUSSION

Description of the Molecular Structure of $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$

The unit cell contains one disordered $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cation, seven water molecules and one chloride anion. There is a substantial network of hydrogen bonds between water of solvation, the chloride ion and oxygen atoms of the acetate groups in the metal complex. A simplified view of the molecular packing is shown in Figure 2.

The disordered $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cation is pictured in Figure 1. The disorder results, of course, from two molecular arrangements occupying

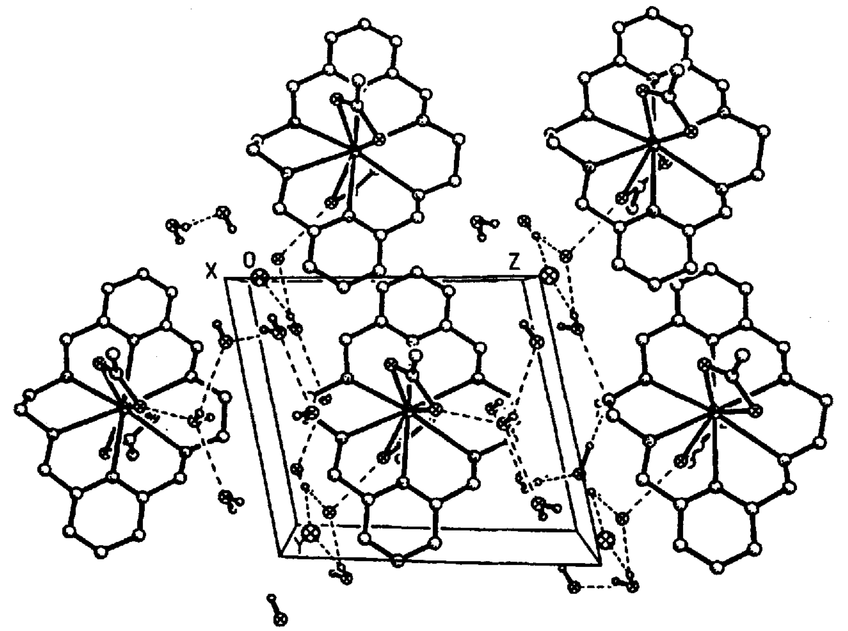

FIGURE 2 Packing within the $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-]\cdot 7H_2O$ crystal, as viewed down *a*; hydrogen bonding is indicated by dashed lines. The diagram has been simplified in the following three ways: (a) the outlined unit cell is the correct shape, but runs from −1/2 to +1/2 in each direction so that the primary Eu(III) atom (true coordinates 0, 0, 0) is in the center of the figure; (b) only one of the two possible images is shown for each $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cation; (c) all hydrogen atoms, other than those found for the water molecules, are omitted. Note that the chloride anions are shown as large cross-hatched circles and all oxygen atoms are indicated with a cross.

sites in the cell on a random basis. The arrangements could, in principle, be two different enantiomeric forms, two different orientations of the same enantiomeric form, or some combination of the two. The pattern shown in Figure 1 can be interpreted as two enantiomeric forms ($\delta\delta$ or $\lambda\lambda$ conformers of the ethylene diamine residues), which require different orientations of the acetate ligands. The two molecular images overlap well except at the ethylenediamine systems and the acetate ligands. The two images of the ethylenediamine ligand have close "separations", with N(8)···N(8′A) = 0.716(13) Å, C(9)···C(9′A) = 0.947(19) Å, C(10)···C(10′A) = 1.216(15) Å and N(11)···N(11′A) = 0.933(11) Å. The disordered acetate ligands are clearly resolved, the closest "separations" between the two distinct ligand images being O(1)···O(1′A) = 1.430(8) Å, O(1)···O(2′A) = 1.730(8) Å, O(2)···O(1′A) = 1.399(8) Å and O(2)···O(2′A) = 1.669(9) Å.

Figures 3 and 4 show the atomic labelling for one of the isomers of $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$. Each isomer is chiral, with C_2 symmetry.

The ten-coordinate Eu^{3+} cation possesses the typical 2,6,2-coordination geometry in which the upper and lower sites are staggered. The primary coordination sphere consists of a hexadentate macrocyclic ligand (for which the average Eu–N distance is 2.645 ± 0.102 Å) and two bidentate acetate groups (for which the average Eu–O distance is 2.460 ± 0.132 Å). Individual distances and angles of note are collected in Table III.

The six nitrogen atoms of the macrocyclic ligand have a root-mean-square deviation from planarity of only 0.28 Å. This leads to ruffle-angles around the EuN_6 system which range from 1.8° for N(11)–Eu(1)–N(1a)/N(1a)–Eu(1)–N(8′) up to 20.4° for N(1a)–Eu(1)–N(8′)/N(8′)–Eu(1)–N(11′) (see Table III); the smallest of these are associated with the pyridine units. The equatorial *cis*-chelate angles range from N(1a)–Eu(1)–N(8′) = 58.8(2)° up to N(8′)–Eu(1)–N(11′) = 64.1(3)°. Cross-ring N ⋯ N distances are provided in Table III. The average value of 5.23 Å is clearly large enough for the europium cation to lie in the plane of the N_6 ring (the deviation of

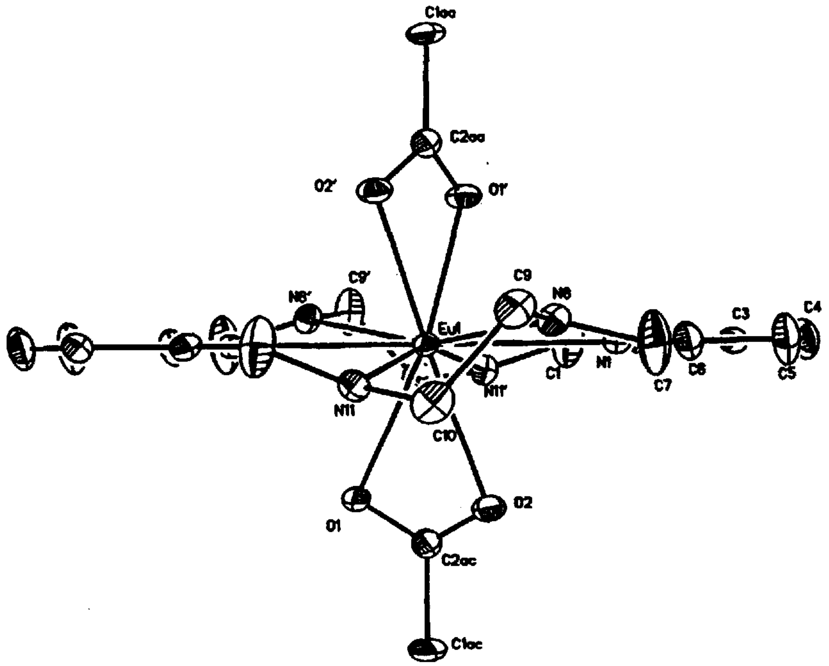

FIGURE 3 One of the images of an ordered $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cation.

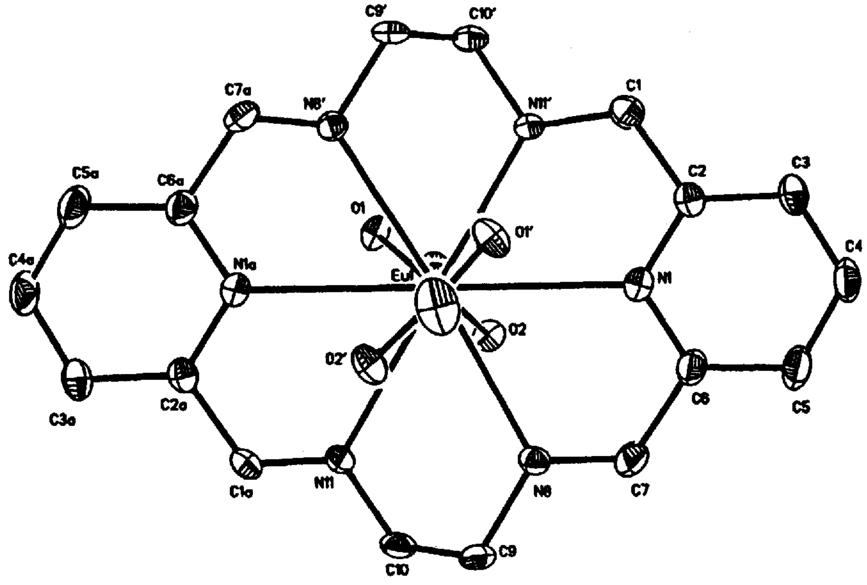

FIGURE 4 An image of one of the $[Eu(C_{18}H_{18}N_6)(OAc)_2^+]$ cations projected onto its N_6 plane.

the Eu^{3+} cation from the least square plane through the N_6 system is only 0.036 Å).

The bidentate acetate ligands occupy *pseudo*-axial sites around the Eu^{3+} cation and are mutually staggered with a dihedral angle of 89.3°. The chelate angles are O(1)–Eu(1)–O(2) = 51.2(2)° and O(1′)–Eu(1)–O(2′) = 54.1(2)°.

General Discussion

The Schiff-base macrocyclic ligands form a structurally interesting series of lanthanide coordination complexes. One of the most intriguing aspects of this study is the fact that the present unsubstituted hexaaza-18-crown-6 macrocyclic ligand $C_{18}H_{18}N_6$ (II) adopts a planar conformation around the europium cation in the structure of $[EuL_2(OAc)_2]^+$. This is very different from the structurally characterized lanthanide complexes containing the tetramethyl-substituted macrocyclic ligand $C_{22}H_{26}N_6$ (I). The macrocyclic ligand $C_{22}H_{26}N_6$ adopts a butterfly arrangement in every case, with the smallest fold angle reported to be 27° in the complex $LaL^1(NO_3)_3$. The only difference between these two ligands is that the methyl groups attached to the imine carbon atoms in $C_{22}H_{26}N_6$ are replaced by hydrogen atoms in the

TABLE III Important dimensions (in Å or °) within the [Eu($C_{18}H_{18}N_6$)$(OAc)_2^+$] cation

(A) *Europium–nitrogen distances*			
Eu(1)–N(1)	2.670(3)	Eu(1)–N(8′)	2.594(8)
Eu(1)–N(1a)	2.670(3)	Eu(1)–N(11)	2.747(7)
Eu(1)–N(8)	2.650(8)	Eu(1)–N(11′)	2.564(8)
(B) *Europium–oxygen distances*			
Eu(1)–O(1)	2.538(5)	Eu(1)–O(1′)	2.328(5)
Eu(1)–O(2)	2.511(5)	Eu(1)–O(2′)	2.464(6)
(C) *Distances within macrocyclic ligand*			
N(1)–C(2)	1.337(6)	N(8)–C(7)	1.337(6)
N(1)–C(6)	1.316(5)	N(11)–C(1a)	1.317(11)
C(2)–C(3)	1.381(6)	N(8′)–C(7a)	1.275(10)
C(3)–C(4)	1.360(7)	N(11′)–C(1)	1.359(10)
C(4)–C(5)	1.353 (9)	C(1)–C(2)	1.453 (6)
C(5)–C(6)	1.394(7)	C(6)–C(7)	1.470(8)
N(8)–C(9)	1.494(16)	N(8′)–C(9′)	1.467(16)
N(11)–C(10)	1.460(10)	N(11′)–C(10′)	1.459(10)
C(9)–C(10)	1.498(15)	C(9′)–C(10′)	1.483(19)
(D) *Distances within acetate ligands*			
O(1)–C(2ac)	1.240(6)	O(1′)–C(2aa)	1.219(8)
O(2)–C(2ac)	1.223(6)	O(2′)–C(2aa)	1.384(7)
C(1ac)–C(2ac)	1.484(6)	C(1aa)–C(2aa)	1.484(6)
(E) *Chelate angles for hexaaza ligand*			
N(1)–Eu(1)–N(8)	62.1(2)	N(1a)–Eu(1)–N(8′)	58.8(2)
N(8)–Eu(1)–N(11)	60.4(2)	N(8′)–Eu(1)–N(11′)	64.1(3)
N(11)–Eu(1)–N(1a)	60.4(2)	N(11′)–Eu(1)–N(1)	60.3(2)
(F) *Chelate angles for acetate groups*			
O(1)–Eu(1)–O(2)	51.2(2)	O(1)–C(2ac)–O(2)	124.8(5)
O(1′)–Eu(1)–O(2′)	54.1(2)	O(1′)–C(2aa)–O(2′)	113.8(5)
(G) *Angles within the* $N–CH_2–CH_2N$ *Fragments*			
C(1a)–N(11)–C(10)	122.0(7)	C(1)–N(11′)–C(10′)	115.5(7)
N(11)–C(10)–C(9)	108.1(7)	N(11′)–C(10′)–C(9′)	108.3(9)
C(10)–C(9)–N(8)	107.0(8)	C(10′)–C(9′)–N(8′)	108.7(9)
C(9)–N(8)–C(7)	119.9(7)	C(9′)–N(8′)–C(7a)	115.6(8)
(H) *N···N distances across the macrocyclic ring*			
N(1)···N(1a)	5.340	N(11)···N(11′)	5.232
N(8)···N(8′)	5.195	N(11a)···N(11′a)	5.232
N(8a)···N(8′a)	5.195		
(I) *Ruffle angles within the* EuN_6 *systems*			
N(1)–Eu(1)–N(8)/N(8)–Eu(1)–N(11)	19.4°		
N(8)–Eu(1)–N(11)/N(11)–Eu(1)–N(1a)	19.7°		
N(11)–Eu(1)–N(1a)/N(1a)–Eu(1)–N(8′)	1.8°		
N(1a)–Eu(1)–N(8′)/N(8′)–Eu(1)–N(11′)	20.4°		
N(8′)–Eu(1)–N(11′)/N(11)–Eu(1)–N(1)	20.0°		
N(11′)–Eu(1)–N(1)/N(1)–Eu(1)–N(8)	3.5°		

macrocyclic ligand $C_{18}H_{18}N_6$. The replacement of the methyl groups with the hydrogen atoms seems to reduce the flexibility of the macrocyclic ring. One possible explanation of this dilemma is that the folded and planar conformations are very similar in energy. The exact conformation adopted would then be determined by packing forces.

In all cases, the hexaaza-18-crown-6 macrocyclic ligand coordinates to the lanthanide cation through all six nitrogen donor atoms. The resulting Eu–N distances are longer than the sum of their ionic radii (predicted Eu–N = 2.52 Å).[5] This trend is seen for many other compounds containing lanthanide–nitrogen interactions. These trends can possibly be explained by hard-soft acid base theory.[27] The lanthanide cations are members of the class (a) hard acids, while the nitrogen donor atoms are soft bases. This describes the oxyphilic tendencies of the lanthanide cations and gives an explanation for the elongation of the Eu–N interactions. Some previous studies have attempted to show a difference between the bonding characteristics of the nitrogen donor atoms of the pyridine groups and those of the nitrogen donor atoms of the imine linkages.[3]

The Eu–N bond distances for the nitrogen donor atoms in the pyridine groups are always among the longer Eu–N distances. This is presumably due to the severe steric restriction of the planar pyridine group as opposed to the more flexible imine linkages. The exocyclic ligands bound to the metal-macrocycle moiety almost invariably contain oxygen donor atoms. They always adopt a configuration that reduces the overall steric strain of the complex. Their Ln–O bond distances are always shorter than that predicted from the sum of their ionic radii (predicted Eu^{3+}–O = 2.58 Å). An interesting fact is that these ligands are always more labile than the macrocyclic ligand even though the lanthanide cations are oxyphilic. The lanthanide-oxygen bonds are usually stronger than a corresponding lanthanide–nitrogen bond, but due to the template synthesis, the macrocylic ligand is hexadentate, with the nitrogen donor atoms at ideal positions. This allows the macrocylic ligand to bind irreversibly to the lanthanide metal center because of the increased stability caused by the hexadentate nature of the ligand.

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Supplementary Materials

Complete listings of interatomic distances, interatomic angles, anisotropic thermal parameters and calculated hydrogen atom parameters for $[Eu(C_{18}H_{18}N_6)(OAc)_2^+][Cl^-] \cdot 7H_2O$ may be obtained, upon request, from one of the authors (M.R.C.).

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