# Unusual Hexameric Structure in the Crystal of Sodium Propylenediaminetetraacetatoeuropium(III)

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The unique hexameric crystal structure of the title complex, hexasodium bis{cyclotris[propylenediaminetetraacetato-μ-*O,O′*-diaquaeuropium(III)]}, has been shown by X-ray analysis.

Among various chiral lanthanoid NMR shift reagents, sodium propylenediaminetetraacetatoeuropium(III), 'Na[Eu$^{III}$(*R*- or *S*-pdta)]' [pdta = $(^-O_2CCH_2)_2NCH(Me)CH_2N(CH_2CO_2^-)_2$] **1**‡ showed a remarkably consistent correlation between the shifts it induced for a series of organic substrates and their absolute configurations in aqueous solution. In the course of a study of the mechanism of chiral differentiation by **1**, we carried out an X-ray analysis on racemic **1** and found it had

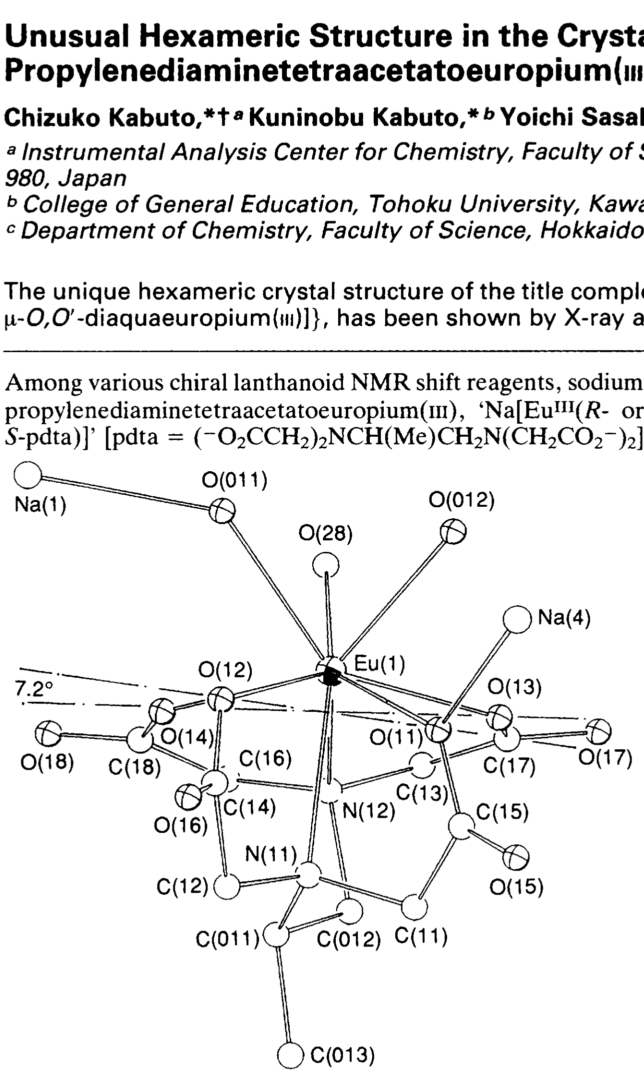

**Fig. 1** Molecular structure of **1** projected through the mean plane of the four oxygen atoms. Atoms are shown as circles of arbitrary size, with the labelling scheme for one molecule. Selected bond lengths (Å) and angles (°), averaged over the six complexes, are as follows: Eu(1)–O(011) 2.53, Eu(1)–O(012) 2.46, Eu(1)–O(28) 2.42, Eu(1)–O(11) 2.39, Eu(1)–O(12) 2.39, Eu(1)–O(13) 2.39, Eu(1)–O(14) 2.38, Eu(1)–N(11) 2.66, Eu(1)–N(12) 2.69, C=O: 1.25–1.30, C–N 1.48–1.50, C–C 1.51–1.54, Na(1)–O(011) 2.47, Na(4)–O(11) 2.36–2.58, O(11)–Eu(1)–O(12) 71.2, O(13)–Eu(1)–O(14) 126.2, O(12)–Eu(1)–O(14) 75.4, O(11)–Eu(1)–O(13) 73.7, O(12)–Eu(1)–O(14) 75.4, O(11)–Eu(1)–O(14) 137.2, O(12)–Eu(1)–O(13) 142.6, O(11)–Eu(1)–N(11) 65.7, O(12)–Eu(1)–N(11) 67.3, O(13)–Eu(1)–N(12) 62.7, O(13)–Eu(1)–N(11) 86.8, O(14)–Eu(1)–N(11) 77.2, O(11)–Eu(1)–N(12) 116.2, O(12)–Eu(1)–N(12) 124.0, O(14)–Eu(1)–N(12) 63.7, N(11)–Eu(1)–N(12) 67.5.

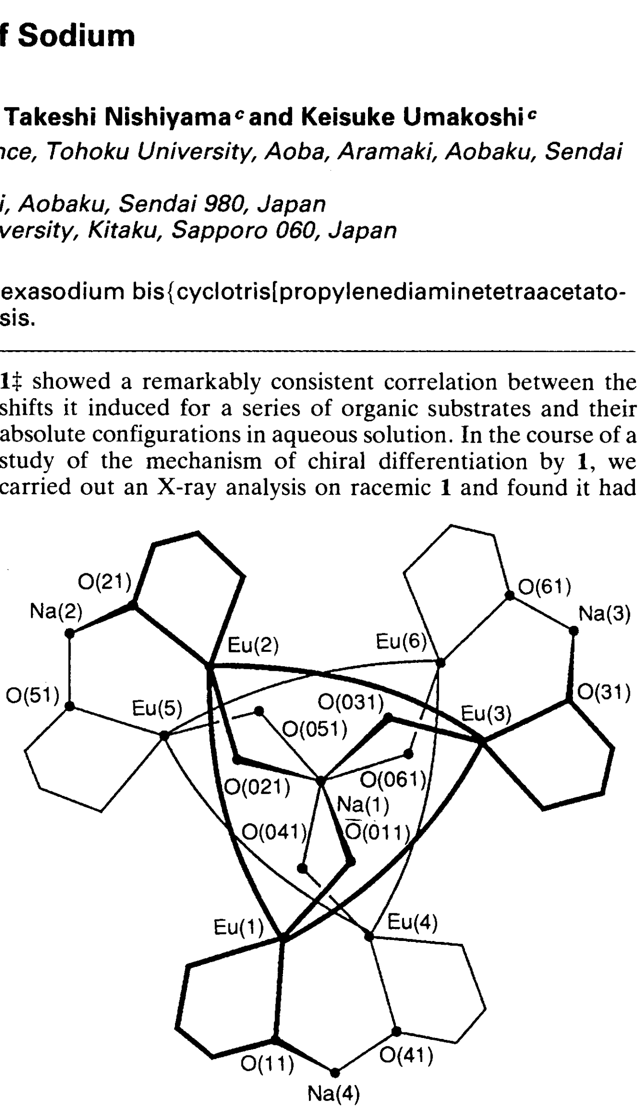

**Fig. 2** Formation of the hexamer units from two trimer units

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† For crystallographic enquiries.

‡ The chemical formula of **1** with three aqua ligands is given by analogy with the corresponding edta (ethylenediaminetetraacetato) complexes of La and Tb (ref. 3; also footnotes in J. I. Stezowski, R. Countryman and J. L. Hoard, *Inorg. Chem.*, 1973, **12**, 1749). The complex **1** was prepared as follows: a mixture of europium oxide (0.500 g, 1.42 mmol) and propylenediaminetetraacetic acid (0.870 g, 2.84 mmol) in 20 ml of water was heated at 70 °C for 1.5 h with stirring. The mixture was filtered and the acidic filtrate was neutralized by the addition of 0.198 mol dm$^{-3}$ sodium hydroxide (14.5 ml). After removal of water under aspirator vacuum followed by drying *in vacuo*, 1.355 g of **1** was obtained as a glassy solid: m.p. >300 °C (decomp.); Found: C, 24.5; H, 3.8; N, 5.1; Na 4.3%. These values indicate that this glassy sample contained *ca.* 3.5 water molecules [Calc. for $C_{11}H_{14}N_2O_8EuNa \cdot nH_2O$ ($n$ = 3.5): C, 24.5; H, 3.9; N, 5.2; Na, 4.3].

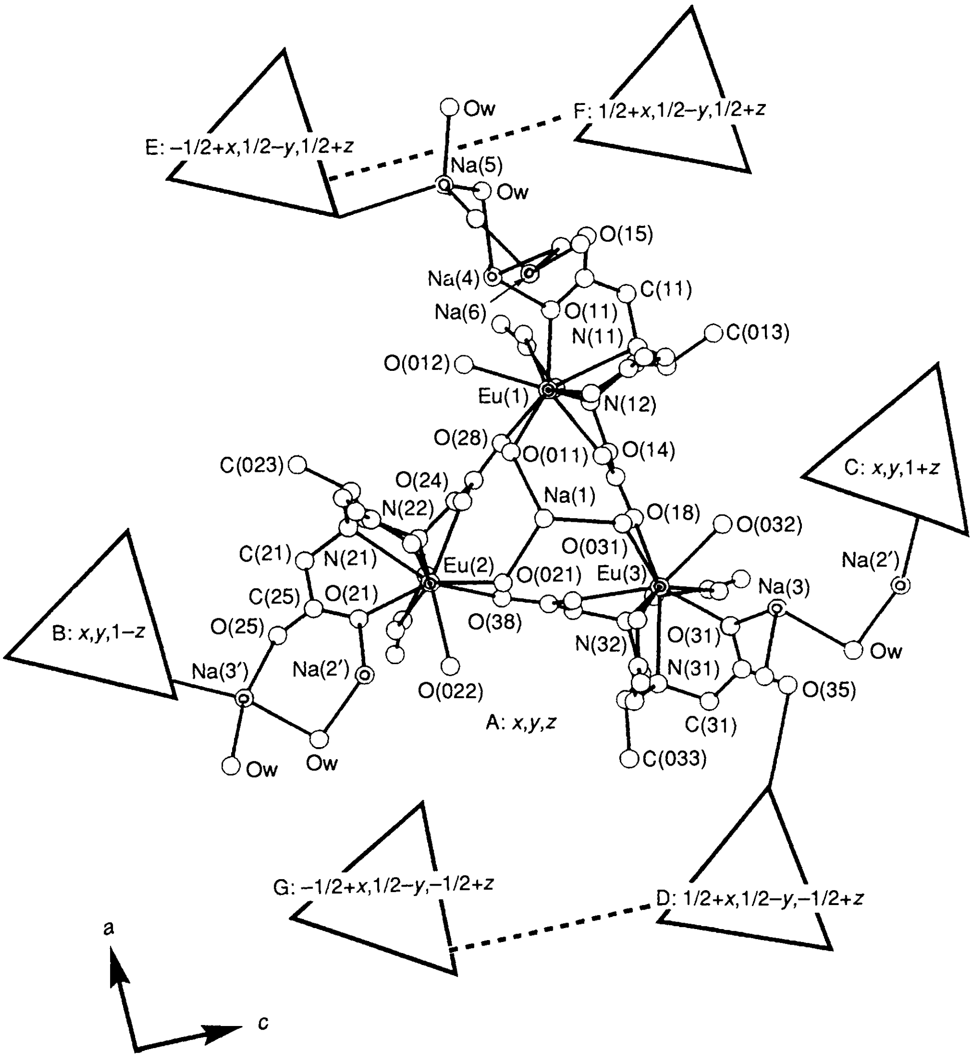

**Fig. 3** The intermolecular connection scheme of **1** in the crystal structure. Only one triangle linkage of the pair forming a hexamer unit is shown for clarity. Two trimer units combine to form a hexamer unit as shown in Fig. 2. The central Na(1)$^+$ ion coordinates to six water oxygens of O(011)–O(061). One hexamer (A) is connected to four neighbouring hexamers (B, C, D, E) *via* Na$^+$···Ow(water)···Na$^+$ linkages, A, B and C hexamers lie in the same plane, while D and E are approximately 4.7 Å (1/8 of *b* axis) out of this plane. The crystal structure, as a whole, consists of two dimensionally expanded zigzag sheet networks parallel to the crystallographic *ac* plane.

unusual crystal and molecular structures,§ which should be of more general interest than our original purpose.

Crystals of **1** contain six independent complex molecules in the asymmetric unit cell. Three molecules form a triangular linkage in such a way that each pair of europium complexes is bridged by an acetate group of a pdta ligand. The structure of the monomeric unit is illustrated in Fig. 1. Equivalent structural parameters for the six molecules do not differ meaningfully within experimental error. The Eu$^{3+}$ ion is nine-coordinated with six donor atoms from the pdta ligand, two water molecules [O(011) and O(012)], and the oxygen of pdta in an adjacent Eu complex [O(28)]. The coordination polyhedron is best described in terms of a distorted monocapped square antiprism.[2]¶ The characteristics of this geometry are the presence of a quasi-mirror symmetry plane through Eu(1), N(11), N(12) and O(28) atoms and a trapezoidal array of four chelating oxygen atoms.[3]

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§ Transparent crystals of suitable size (*ca.* 0.4 × 0.2 × 0.6 mm) were obtained from water–acetone solution using the vapour diffusion method in a refrigerator at 5 °C for a week. The crystals rapidly turned opaque and crumbled under ambient conditions and so were sealed in intimate contact with the mother liquor.

*Crystal data:* $[Na\{EuC_{11}N_2O_8H_{16}\}(H_2O)_2]_6 \cdot nH_2O$ ($n = 22$), $M_r$ = 3487.75; $a$ = 25.782(3), $b$ = 36.802(6), $c$ = 14.678(12) Å, $\beta$ = 90.286(8)°, $V$ = 13927(5) Å$^3$; space group $P2_1/n$; $Z$ = 4; $D_c$ = 1.66 g cm$^{-3}$; $\mu$(Mo-K$\alpha$) = 27.81 cm$^{-1}$; Rigaku AFC5PR diffractometer; graphite monochromated Mo-K$\alpha$ radiation; three exchanged crystals; 23 580 measured reflections with $2\theta \leq 53°$; 12 850 independent reflections with $F_o > 3\sigma(F_o)$. A total of 144 atoms of the six molecules were refined anisotropically. Six Na atoms and 22 water oxygens (seven with O···Na$^+$ bonds and others with OH···O bonds) were refined isotropically. No significant final difference electron density peaks were found. The number of water molecules is not determined definitively, but should be close to the above number. After including hydrogen atoms on carbon atoms (calculated positions and not refined), the final $R$ factor is 0.079 ($R_w$ = 0.082). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The monocapped antiprism consists of eight vertices of two square bases and one axial position; two oxygen atoms [O(11) and O(12)] are in one square and O(13) and O(14) are in the other with N(11); the remaining nitrogen atom N(12) is in the axial position. The coordination sphere is completed by two water molecules and one carboxylate oxygen atom of another linked complex. This type of geometry is generally observed in lanthanoid complexes of ligands exhibiting a 'square' conformation such as $Na[Eu(dota)(H_2O)]$ (dota = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate). See for example, M. Spirlet, J. Rebizant, J. F. Desreux and M. Loncin, *Inorg. Chem.*, 1984, **23**, 357.

A further characteristic of the coordination structure is the non-planarity of the four coordinated carboxy oxygen atoms. The propylenediamine chelate ring of **1** is strongly puckered by steric requirements (torsion angle of N–C–C–N: 67.7°). Consequently, the four oxygen atoms deviate significantly from planarity, with deviations from the mean plane of −0.12, 0.12, 0.08 and −0.08 Å for O(11), O(12), O(13) and O(14), respectively, and the $Eu^{3+}$ atom is displaced by 0.55 Å from this plane. The angle of twist between the two O(11)–O(12) and O(13)–O(14) axes is 7.2°.‖ We consider this twisting, the direction of which is determined by the chirality of the propylenediamine moiety, plays a key role in differentiating enantiomer signals through paramagnetic anisotropy.[1d]

The most striking feature is the crystal structure (Figs. 2 and 3). One $Na^+$ ion is located between two parallel triangles, forming coordination bonds with six water oxygens from six complexes in the two trimers. The remaining five $Na^+$ ions connect the two trimers by the $O \cdots Na^+ \cdots O$ linkages. Thus, the complex anion of **1** forms a hexamer linkage unit through the $Na^+ \cdots O$ bonds (Fig. 2). The hexamer unit has, as a whole, quasi-$D_{3h}$ symmetry with one threefold axis and three twofold axes, because of the quasi-symmetrical locations of the central and three side $Na^+$ ions. In addition, one hexamer unit is connected to four neighbouring hexamer units *via* the $Na^+ \cdots O(water) \cdots Na^+$ linkages as shown in Fig. 3. Thus a two-dimensional zigzag ribbon network of hexamer units is present on the crystallographic *ac* plane. This hexameric structure was not observed in crystals of $K[La(edta)(H_2O)_3]$ and $Na[Tb(edta)(H_2O)_3]$ ($H_4edta$ = ethylenediaminetetraacetic acid),[3a] complexes which are similar to **1**. These complexes crystallize isomorphously, forming a linear infinite chain by $O \cdots M^+ \cdots O$ (M = K or Na; O = oxygen of coordinated water) bonding through a cation located between two adjacent molecules.[4] At present we cannot put forward clear reasons for the formation of the unusual hexamer unit of **1**. It is also notable that all pdta ligands within each hexamer exhibit the same chirality.

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‖ X-Ray structures of lanthanoid complexes having edta type ligands have so far been reported only in refs 3 and 4. These reports described preliminary features of the structures of the ten-coordinate $La(Hedta)(H_2O)_4$ and nine-coordinate $K[La(edta)(H_2O)_3]$. The four chelating carboxy oxygens in the former are coplanar to within 0.01 Å, while a detailed discussion was not given for the latter. We recalculated the geometry for the latter based on the atomic coordinates given in ref. 4. Results indicate a similar deviation of the four oxygen atoms from planarity to that found for **1**, although rapid crystal decay led to some uncertainty in the data.

## References

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2 D. L. Kepert, in *Inorganic Chemistry Concepts*, Springer-Verlag, Heidelberg, 1982, vol. 6, ch. 14.

3 (*a*) M. D. Lind, B. Lee and J. L. Hoard, *J. Am. Chem. Soc.*, 1965, **87**, 1612; (*b*) J. L. Hoard, B. Lee and M. D. Lind, *J. Am. Chem. Soc.*, 1965, **87**, 1611.

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