Highly Polydentate Ligands. Part 4.[1] Crystal Structures of Neodymium(III) and Erbium(III) Complexes of 3,12-Bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioate(4−)†

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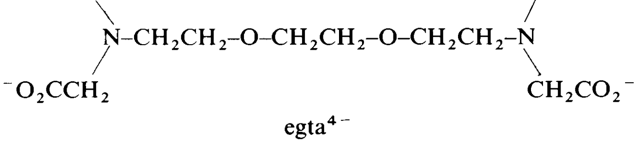
The structures of calcium salts of the erbium(III) and neodymium(III) chelates of the calcium-selective octadentate ligand egta^{4-} [H_4egta = 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid] have been determined, in order to identify the structural changes that occur in a calcium-selective binding site when lanthanides are substituted for calcium. Ca[Er(egta)$(OH_2)]_2\cdot12H_2O\cdot(CH_3)_2CO$ (**1**) crystallizes in the monoclinic space group $P2_1$ ($Z = 2$), with $a = 12.710(2)$, $b = 12.157(2)$, $c = 17.765(3)$ Å, and $\beta = 105.79(1)°$; $R = 0.027$, $R' = 0.035$. Ca[Nd(egta)$(OH_2)]_2\cdot9H_2O$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ ($Z = 2$), with $a = 10.776(2)$, $b = 18.218(4)$, $c = 12.560(2)$ Å, and $\beta = 112.14(1)°$; $R = 0.028$, $R' = 0.040$. The full octadentate chelating capability of egta^{4-} is utilized in both chelates. In contrast to the eight-co-ordinate calcium ions in [Ca(egta)]$^{2-}$, the Er^{III} ions in (**1**) are nine-co-ordinate; the ninth co-ordination site is occupied by a water molecule. Of the three ligand atom types, the carboxylate oxygen atoms are bound at the shortest distance [Er–O(carboxylate)$_{av}$ = 2.31(3) Å], followed by the ether oxygen atoms [Er–O(ether)$_{av}$ = 2.42(5) Å], and the amine nitrogen atoms [Er–N$_{av}$ = 2.57(4) Å]. The Nd^{III} ions in (**2**) are ten-co-ordinate; ten-co-ordination is achieved in the solid state by binding a water molecule, as well as a carboxylate oxygen atom from an adjacent complex ion. The order of metal–ligand bond distances observed for Nd^{III} is the same as that observed for Er^{III}: Nd–O(carboxylate)$_{av}$ = 2.46(1), Nd–O(ether)$_{av}$ = 2.67(3), Nd–N$_{av}$ = 2.81(7) Å.

The octadentate ligand egta^{4-} [H_4egta = 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid] binds Ca^{2+} more strongly than Mg^{2+}($K\{[Ca(egta)]^{2-}\} \approx 10^6 \times K\{[Mg(egta)]^{2-}\}$).[2] This high degree of calcium-binding selectivity suggested use of egta^{4-} as a model for the metal binding sites in intracellular calcium-binding proteins.[3]



egta^{4-}

Information regarding the structures of the binding sites in calcium-binding proteins is difficult to obtain using techniques other than *X*-ray crystallography, due to the calcium ion's lack of useful spectroscopic properties. Consequently, spectroscopic probe ions with sizes similar to that of Ca^{2+}, such as Cd^{2+} [4,5] or Ln^{3+} ions (Ln^{3+} = a lanthanide ion) have been utilized in attempts to obtain information about the calcium-binding sites. A variety of experiments may be carried out with Ln^{3+}-substituted proteins; such investigations have exploited optical absorption, fluorescence/luminescence, and magnetic properties of these centres.[6–10]

Despite size similarities, it is possible that metals such as Cd^{2+} and Ln^{3+} may bind to a calcium-binding site in a significantly different manner than does the calcium ion. In fact, *X*-ray crystallographic studies of Tb^{3+}-substituted parvalbumin showed that to be the case.[11,12] Our recent study of the Ca^{2+} and Cd^{2+} complexes of egta^{4-} allowed assessment of the nature and magnitude of the structural changes associated with substitution of a Cd^{2+} ion into the calcium-selective environment provided by egta^{4-}.[3] Eight-co-ordinate Ca^{2+} and Cd^{2+} ions possess similar ionic radii (r_{Ca} = 1.12, r_{Cd} = 1.10 Å),[13] and the two complexes exhibited very similar structures. The Ca^{2+} and Cd^{2+} ions did, however, display distinct bonding preferences among the different base types within egta^{4-}.

This report extends this structural comparison to two representative chelates of Ln^{3+} ions. The results of single-crystal *X*-ray diffraction studies of the calcium salts of the Er^{III} and Nd^{III} complexes of egta^{4-}, Ca[Er(egta)$(OH_2)]_2\cdot12H_2O\cdot(CH_3)_2CO$ (**1**) and Ca[Nd(egta)$(OH_2)]_2\cdot9H_2O$ (**2**) are described. Metal ions in the lanthanide series range in size from La^{III} (r_{La} = 1.22 Å, nine-co-ordinate) to Lu^{III} (r_{Lu} = 0.98 Å, eight-co-ordinate).[13] Our decision to study the structures of the egta^{4-} chelates involving the relatively large Nd^{III} ion (r_{Nd} = 1.16 Å for nine-co-ordination) and the much smaller Er^{III} ion (r_{Er} = 1.00 Å for eight-co-ordination) was based on the expectation of a co-ordination number difference between the two chelates. Among [Ln(edta)]$^-$ chelates [H_4edta = 3,6-bis(carboxymethyl)-3,6-diazaoctanedioic acid], those complexes containing metal ions larger than Ho^{III} were nine-co-ordinate in the solid state,[14] while those containing smaller metal ions were eight-co-ordinate.[15] The results reported below regarding the conformations adopted by the egta^{4-} ligand in the Er^{III} and Nd^{III} chelates, and the ligand atom preferences exhibited by Er^{III} and Nd^{III} in those chelates, may now be compared to the corresponding parameters for the [Ca(egta)]$^{2-}$complex.

Experimental

All chemicals were used as purchased: H_4egta (J. T. Baker), Ca$(OH)_2$ (Fisher), $Er_2(CO_3)_3$ (17.8% H_2O, Alfa), and $Nd_2(CO_3)_3$ (1.0% H_2O, Alfa). All preparations were performed in aqueous solution utilizing distilled water.

Preparation of Ca[Er(egta)$(OH_2)]_2\cdot12H_2O\cdot(CH_3)_2CO$ (**1**).— $Er_2(CO_3)_3$ (17.8% H_2O) (0.626 g, 1.00 mmol) and H_4egta (0.760

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

g, 2.00 mmol) were dissolved in boiling water (500 cm^3). $Ca(OH)_2$(0.074 g, 1.00 mmol) was added, and the volume reduced to 8 cm^3. Vapour diffusion of acetone into the filtered solution yielded crystalline (**1**). Crystals suitable for study by *X*-ray diffraction were obtained by vapour diffusion of acetone into 2.5 cm^3 of a 0.02 mol dm^{-3} solution of (**1**). δ_H[200 MHz; solvent D_2O, pH 7; standard dss (dss = sodium 2,2-dimethyl-2-silapentane-5-sulphonate)] -14.1 (2 H, $\Delta\nu_{\frac{1}{2}} \approx 440$), 4.5 (4 H, $\Delta\nu_{\frac{1}{2}} \approx 510$), 11.5 (2 H, $\Delta\nu_{\frac{1}{2}} \approx 560$), 19.8 (2 H, $\Delta\nu_{\frac{1}{2}} \approx 310$), 23.2 (2 H, $\Delta\nu_{\frac{1}{2}} \approx 310$), 34.5 (6 H, $\Delta\nu_{\frac{1}{2}} \approx 570$), and 51.3 (2 H, $\Delta\nu_{\frac{1}{2}} \approx 940$ Hz).

Preparation of $Ca[Nd(egta)(OH_2)]_2 \cdot 9H_2O$ (**2**).—$Nd_2(CO_3)_3$ (0.956 g, 2.00 mmol) and H_4egta (1.520 g, 4.00 mmol) were added to water (350 cm^3). The suspension was heated, with stirring, at reflux temperature overnight to effect dissolution and reaction of the reagents. After addition of $Ca(OH)_2$ (0.148 g, 2.00 mmol) and filtration, the volume of the solution was reduced to 10 cm^3. Vapour diffusion experiments with solutions of varying concentrations initially yielded non-crystalline (**2**). Lavender crystals suitable for study by *X*-ray diffraction were eventually obtained by vapour diffusion of acetone into 3 cm^3 of a 0.020 mol dm^{-3} solution of (**2**) (prepared from the isolated non-crystalline material) over a period of one month. δ_H(200 MHz; solvent D_2O, pH 8; standard dss) -1.10 (4 H, $\Delta\nu_{\frac{1}{2}} \approx 18$), 0.84(4 H, $\Delta\nu_{\frac{1}{2}} \approx 42$), 2.38 (4 H, $\Delta\nu_{\frac{1}{2}} \approx 42$), 3.22 (4 H, $\Delta\nu_{\frac{1}{2}} \approx 24$), 6.73 (4 H, $\Delta\nu_{\frac{1}{2}} \approx 51$ Hz).

Structure Determination of $Ca[Er(egta)(OH_2)]_2 \cdot 12H_2O \cdot (CH_3)_2CO$ (**1**).—*Crystal data.* $C_{28}H_{40}CaEr_2N_4O_{20} \cdot 14H_2O \cdot (CH_3)_2CO$, $M = 1\,437.5$, monoclinic, $a = 12.710(2)$, $b = 12.157(2)$, $c = 17.765(3)$ Å, $\beta = 105.79(1)°$, $U = 2\,641.5$ Å^3 [by least-squares refinement on diffractometer angles for 25 automatically centred reflections ($2\theta_{av} = 21.46°$), $\lambda = 0.7107$ Å, $T = 143$ K], space group $P2_1$ (no. 4), $Z = 2$, $D_c = 1.81$ g cm^{-3}, $F(000) = 1\,428$. Pink parallelepipeds. Crystal dimensions: 0.48 (010—$0\bar{1}0$) × 0.08 (001—$00\bar{1}$) × 0.14 (100—$\bar{1}00$) mm, μ(Mo-K_α) = 35.45 cm^{-1}.

Data collection and processing. Nicolet *R*3*m* diffractometer, $\theta/2\theta$ mode, scan width = $2\theta(K_{\alpha2}) - 2\theta(K_{\alpha1}) + 2.00$, scan speed variable (4—29° min^{-1}), graphite-monochromated Mo-K_α radiation; 5 075 reflections measured ($3.5 \leqslant 2\theta \leqslant 50°$, $\pm h$, $-k$, $+l$), 4 905 unique, absorption correction, giving 4 711 with $I > 2\sigma(I)$. Lorentz and polarization corrections, no crystal decay in the beam.

Structure analysis and refinement. Choice of space group $P2_1$ supported by: (*a*) statistical analysis ($|E^2 - 1|_{av} \approx 0.75$ for $0.15 < \sin\theta/\lambda < 0.50$) and (*b*) Patterson synthesis (indicated two heavy atoms of similar scattering power in the asymmetric unit). Europium(III) positions from the Patterson map, followed by normal heavy-atom procedures. Block, weighted $\{w = [\sigma^2(F_o) + 0.000\,49F_o{}^2]^{-1}$, $\sigma(F_o)$ from counting statistics$\}$ least-squares refinement (97—103 parameters per cycle, 664 parameters total, data:parameters = 7.1) on *F* minimized $w(|F_o| - |kF_c|)^2$; neutral atom scattering factors with anomalous scattering contributions[16] used in all computations.[17] Enantiomorph checked; refinement gave $-1.01(2)$ for multiplicative factor on imaginary components, $\Delta f''$; atomic co-ordinates transformed. Anisotropic thermal parameters for non-H atoms; H atoms on C in idealized positions [C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$]. At convergence [$(\text{shift/e.s.d.})_{av} < 0.01$ over the last seven cycles] highest peak in difference map (1.7 e Å^{-3}) close to Er^{III}; minimum -0.7 e Å^{-3}. Final values: $R\,[= (\Sigma|F_o - F_c|)/\Sigma F_o] = 0.027$, $R'\{=[\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}\} = 0.035$, goodness of fit $\{=[\Sigma w(F_o - F_c)^2/(N_{data} - N_{parameters})]^{\frac{1}{2}}\} = 1.21$, slope of normal probability plot = 1.05.[18]

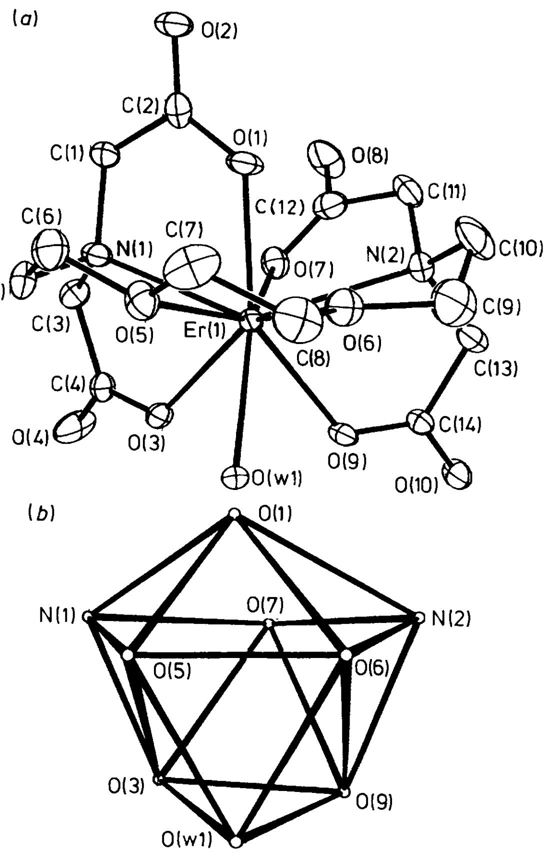

Figure 1. (*a*) Thermal ellipsoid plot (35%) of the $[Er(egta)(OH_2)]^-$ complex ion involving Er(1). The numbering scheme for the complex ion involving Er(2) may be derived as follows: for C(*x*), *x* = 14 + *a*; for O(*x*), *x* = 10 + *a*; for N(*x*), *x* = 2 + *a*; *a* = atom number in the complex involving Er(1). (*b*) View of the co-ordination polyhedron formed by the ligand atoms about Er(1)

Structure Determination of $Ca[Nd(egta)(OH_2)]_2 \cdot 9H_2O$ (**2**).—*Crystal data.* $C_{28}H_{40}CaN_4Nd_2O_{20} \cdot 11H_2O$, $M = 1\,279.4$, monoclinic, $a = 10.776(2)$, $b = 18.218(4)$, $c = 12.560(2)$ Å, $\beta = 112.14(1)°$, $U = 2\,284.0$ Å^3 [by least-squares refinement on diffractometer angles for 25 automatically centred reflections ($2\theta_{av} = 29.76°$), $\lambda = 0.7107$ Å, $T = 293$ K], space group $P2_1/c$ (no. 14), $Z = 2$, $D_c = 1.86$ g cm^{-3}, $F(000) = 1\,292$. Lavender parallelepipeds. Crystal dimensions: 0.51 × 0.16 × 0.20 mm, μ(Mo-K_α) = 24.57 cm^{-1}.

Data collection and processing. Nicolet *R*3*m* diffractometer, $\theta/2\theta$ mode, scan width = $2\theta(K_{\alpha2}) - 2\theta(K_{\alpha1}) + 2.00$, scan speed variable (5—29° min^{-1}), graphite-monochromated Mo-K_α radiation; 4 419 reflections measured ($3.5 \leqslant 2\theta \leqslant 50°$, $-h$, $-k$, $\pm l$), 4 047 unique, empirical absorption correction (ψ scan data on 15 reflections), 3 746 with $I > 2\sigma(I)$. Lorentz and polarization corrections, linear and approximately isotropic crystal decay (*ca.* 4%) corrected during processing.

Structure analysis and refinement. Neodymium(III) positions from Patterson map, Ca^{2+} on inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), remaining non-H atoms found by normal heavy-atom procedures. Block, weighted $\{w = [\sigma^2(F_o) + 0.000\,22F_o{}^2]^{-1}$, $\sigma(F_o)$ from counting statistics$\}$ least-squares refinement (97—103 parameters per cycle, 304 parameters total, data:parameters = 12.3) on *F* minimized $w(|F_o| - |kF_c|)^2$; neutral atom scattering factors with anomalous scattering contributions[16] used in all computations.[17] Anisotropic thermal parameters for non-H atoms; H atoms on C in idealized positions [C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$]. Site occupancy factor for O(w6) fixed at 0.5 after refinement. At convergence [$(\text{shift/e.s.d.})_{av} < 0.06$ over the last three cycles] highest peak in difference map

Table 1. Atomic co-ordinates (fractional, × 10^4) for $Ca[Er(egta)(OH_2)]_2 \cdot 12H_2O \cdot (CH_3)_2CO$, (**1**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Er(1)	2 966(1)	3 896	1 534(1)	O(2)	257(4)	2 897(5)	−466(3)
Er(2)	7 329(1)	5 017(1)	4 668(1)	O(3)	2 603(4)	4 647(4)	2 642(3)
Ca	4 452(1)	5 144(1)	3 436(1)	O(4)	1 505(4)	4 738(6)	3 426(3)
C(1)	268(6)	3 677(7)	754(4)	O(5)	2 433(4)	5 479(4)	641(3)
C(2)	836(6)	3 240(6)	168(5)	O(6)	4 068(4)	4 124(5)	650(3)
C(3)	724(6)	4 299(7)	2 103(4)	O(7)	2 248(4)	2 358(5)	1 963(3)
C(4)	1 674(6)	4 597(7)	2 787(4)	O(8)	1 615(5)	666(5)	1 658(4)
C(5)	878(6)	5 583(7)	1 109(5)	O(9)	4 425(4)	3 460(4)	2 620(3)
C(6)	1 299(7)	5 772(8)	409(5)	O(10)	5 585(4)	2 268(5)	3 350(3)
C(7)	2 902(7)	5 502(8)	−20(5)	O(11)	9 040(4)	5 100(4)	5 533(3)
C(8)	4 052(7)	5 112(8)	234(5)	O(12)	10 258(4)	5 750(5)	6 582(3)
C(9)	4 890(8)	3 327(9)	624(7)	O(13)	5 780(4)	6 080(4)	4 514(3)
C(10)	4 423(8)	2 214(8)	648(6)	O(14)	5 040(4)	7 707(4)	4 633(3)
C(11)	3 088(6)	1 257(7)	1 159(5)	O(15)	7 252(4)	3 912(5)	5 808(3)
C(12)	2 261(6)	1 427(7)	1 634(5)	O(16)	7 918(4)	3 192(4)	4 608(3)
C(13)	4 818(7)	1 810(8)	2 028(5)	O(17)	7 924(4)	6 656(4)	4 334(3)
C(14)	4 945(6)	2 555(6)	2 724(4)	O(18)	9 334(5)	7 654(5)	4 226(4)
C(15)	8 499(5)	6 559(6)	6 274(5)	O(19)	6 372(3)	5 013(4)	3 344(3)
C(16)	9 319(6)	5 724(7)	6 123(5)	O(20)	6 251(4)	5 133(5)	2 079(3)
C(17)	6 694(6)	7 245(7)	5 567(4)	O(w1)	4 197(4)	5 458(4)	2 007(3)
C(18)	5 745(5)	6 993(6)	4 853(4)	O(w2)	5 663(3)	3 873(4)	4 354(3)
C(19)	6 843(6)	5 592(7)	6 335(4)	O(w3)	3 507(4)	5 045(5)	4 393(3)
C(20)	7 384(6)	4 472(7)	6 535(4)	O(w4)	3 951(4)	7 004(5)	3 210(3)
C(21)	7 889(6)	2 888(6)	5 918(5)	O(w5)	2 453(7)	7 584(7)	8 417(5)
C(22)	7 695(6)	2 365(6)	5 129(5)	O(w6)	3 827(4)	5 141(5)	6 001(3)
C(23)	8 434(7)	2 826(7)	4 020(5)	O(w7)	2 771(6)	8 812(8)	9 775(4)
C(24)	9 204(5)	3 732(7)	3 950(4)	O(w8)	1 643(4)	4 702(5)	5 753(4)
C(25)	9 378(6)	5 740(7)	3 981(5)	O(w9)	6 248(4)	2 653(5)	8 304(3)
C(26)	8 832(6)	6 759(7)	4 192(5)	O(w10)	441(5)	6 367(8)	8 119(4)
C(27)	8 007(5)	4 866(8)	2 926(4)	O(w11)	2 853(7)	792(7)	9 108(4)
C(28)	6 784(5)	5 027(7)	2 777(4)	O(w12)	8 209(4)	3 665(5)	8 947(4)
N(1)	986(5)	4 406(6)	1 356(4)	O(w13)	422(5)	3 465(7)	7 152(4)
N(2)	3 946(5)	2 093(5)	1 322(4)	O(w14)	1 276(11)	2 246(10)	−1 563(6)
N(3)	7 361(4)	6 243(5)	5 837(3)	C(29)	3 481(8)	3 037(9)	7 407(7)
N(4)	8 627(4)	4 802(5)	3 775(3)	C(30)	3 723(7)	3 987(8)	7 964(5)
O(1)	1 884(4)	3 231(4)	376(3)	C(31)	2 880(7)	4 825(9)	7 926(6)
				O(21)	4 614(5)	4 074(6)	8 453(4)

* Estimated standard deviations in the least significant digits are given in parentheses.

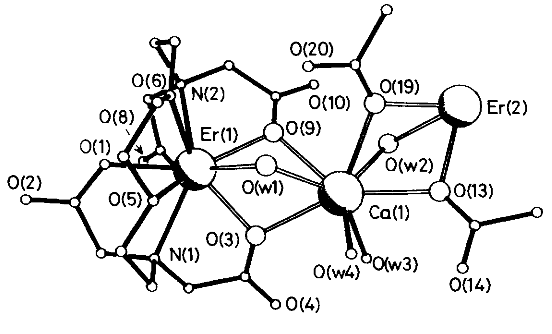

Figure 2. Ball and stick plot (arbitrarily chosen radii) depicting the interionic interactions in the solid state for (**1**). The oxygen atoms that are involved in bridging interactions are enlarged. Hollowed bonds highlight the bridging pathways between the $[Er(egta)]^-$ anions and the calcium counter ions

(1.1 e Å^{-3}) close to Nd^{III}; minimum −0.5 e Å^{-3}. Final values: $R = 0.028$, $R' = 0.040$, goodness of fit = 1.88, slope of normal probability plot = 1.46.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Structures of the Er^{III} *Chelates in* $Ca[Er(egta)(OH_2)]_2 \cdot 12\ H_2O \cdot (CH_3)_2CO$ (**1**).—Final fractional atomic co-ordinates for all the non-hydrogen atoms of (**1**) may be found in Table 1 and bond lengths and angles in Table 2.

The calcium salt of $[Er(egta)]^-$ crystallizes with two Er^{III} complexes [(**1a**) for Er(1), (**1b**) for Er(2)] per asymmetric unit. In both, Er^{III} is nine-co-ordinate [see Figure 1(*a*)], and egta^{4-} exhibits its full octadentate character. The ninth co-ordination site is occupied by a water molecule, which is also bound to the Ca^{2+} ion (see below). The ligand atoms about the Er^{3+} ions occupy the vertices of a distorted tricapped trigonal prism in each case. In (**1a**), the trigonal faces are formed by O(1), O(5), and O(6), as well as by O(7), O(3), and O(9). The square faces [O(1)–O(3)–O(5)–O(7), O(1)–O(7)–O(9)–O(6), and O(5)–O(3)–O(9)–O(6)] are capped by N(1), N(2), and O(w1), respectively [see Figure 1(*b*)]. Complex (**1b**) has the same arrangement of ligand atoms and the same absolute configuration as (**1a**).

Two carboxylate groups of each $[Er(egta)]^-$ complex ion bridge to the single Ca^{2+} counter ion (see Figure 2), utilizing the carboxylate oxygen atom that is co-ordinated to Er^{III}. Other linkages between the complex anions and the counter ion occur through bridging water molecules [O(w1) and O(w2)]. In addition, the eight-co-ordinate Ca^{2+} counter ion is co-ordinated by the oxygen atoms of two non-bridging water molecules.

Table 2. Metal–ligand distances (Å) and angles (°)* for $Ca[Er(egta)(OH_2)]_2 \cdot 12H_2O \cdot (CH_3)_2CO$, (**1**)

(*a*) Complex ions

Complex (**1a**)				Complex (**1b**)			
Er(1)–N(1)	2.526(6)	Er(1)–O(6)	2.389(6)	Er(2)–N(3)	2.548(6)	Er(2)–O(16)	2.353(5)
Er(1)–N(2)	2.599(7)	Er(1)–O(7)	2.299(6)	Er(2)–N(4)	2.595(7)	Er(2)–O(17)	2.267(6)
Er(1)–O(1)	2.288(5)	Er(1)–O(9)	2.344(4)	Er(2)–O(11)	2.298(4)	Er(2)–O(19)	2.335(4)
Er(1)–O(3)	2.327(5)	Er(1)–O(w1)	2.459(5)	Er(2)–O(13)	2.309(5)	Er(2)–O(w2)	2.466(5)
Er(1)–O(5)	2.468(5)			Er(2)–O(15)	2.453(5)		
N(1)–Er(1)–N(2)	133.6(2)	O(3)–Er(1)–O(7)	81.4(2)	N(3)–Er(2)–N(4)	133.3(2)	O(13)–Er(2)–O(17)	79.1(2)
N(1)–Er(1)–O(1)	68.9(2)	O(5)–Er(1)–O(7)	141.5(2)	N(3)–Er(2)–O(11)	68.1(2)	O(15)–Er(2)–O(17)	142.0(2)
N(2)–Er(1)–O(1)	76.5(2)	O(6)–Er(1)–O(7)	132.0(2)	N(4)–Er(2)–O(11)	76.7(2)	O(16)–Er(2)–O(17)	133.2(2)
N(1)–Er(1)–O(3)	65.8(2)	N(1)–Er(1)–O(9)	134.1(2)	N(3)–Er(2)–O(13)	66.0(2)	N(3)–Er(2)–O(19)	135.2(2)
N(2)–Er(1)–O(3)	131.8(2)	N(2)–Er(1)–O(9)	68.0(2)	N(4)–Er(2)–O(13)	130.3(2)	N(4)–Er(2)–O(19)	68.2(2)
O(1)–Er(1)–O(3)	133.7(2)	O(1)–Er(1)–O(9)	143.8(2)	O(11)–Er(2)–O(13)	132.5(2)	O(11)–Er(2)–O(19)	144.4(2)
N(1)–Er(1)–O(5)	68.8(2)	O(3)–Er(1)–O(9)	71.8(2)	N(3)–Er(2)–O(15)	69.1(2)	O(13)–Er(2)–O(19)	71.8(2)
N(2)–Er(1)–O(5)	128.5(2)	O(5)–Er(1)–O(9)	136.3(2)	N(4)–Er(2)–O(15)	128.6(2)	O(15)–Er(2)–O(19)	134.7(2)
O(1)–Er(1)–O(5)	72.8(2)	O(6)–Er(1)–O(9)	95.4(2)	O(11)–Er(2)–O(15)	73.4(2)	O(16)–Er(2)–O(19)	92.2(2)
O(3)–Er(1)–O(5)	98.9(2)	O(7)–Er(1)–O(9)	80.8(2)	O(13)–Er(2)–O(15)	100.4(2)	O(17)–Er(2)–O(19)	81.8(2)
N(1)–Er(1)–O(6)	129.2(2)	N(1)–Er(1)–O(w1)	111.9(2)	N(3)–Er(2)–O(16)	130.8(2)	N(3)–Er(2)–O(w2)	109.7(2)
N(2)–Er(1)–O(6)	67.2(2)	N(2)–Er(1)–O(w1)	114.5(2)	N(4)–Er(2)–O(16)	67.3(2)	N(4)–Er(2)–O(w2)	117.0(2)
O(1)–Er(1)–O(6)	76.5(2)	O(1)–Er(1)–O(w1)	138.6(2)	O(11)–Er(2)–O(16)	79.5(2)	O(11)–Er(2)–O(w2)	140.7(2)
O(3)–Er(1)–O(6)	142.9(2)	O(3)–Er(1)–O(w1)	70.3(2)	O(13)–Er(2)–O(16)	142.6(2)	O(13)–Er(2)–O(w2)	68.7(2)
O(5)–Er(1)–O(6)	66.1(2)	O(5)–Er(1)–O(w1)	69.8(2)	O(15)–Er(2)–O(16)	66.8(2)	O(15)–Er(2)–O(w2)	69.8(1)
N(1)–Er(1)–O(7)	76.7(2)	O(6)–Er(1)–O(w1)	72.7(2)	N(3)–Er(2)–O(17)	76.5(2)	O(16)–Er(2)–O(w2)	73.9(2)
N(2)–Er(1)–O(7)	67.1(2)	O(7)–Er(1)–O(w1)	142.0(2)	N(4)–Er(2)–O(17)	67.4(2)	O(17)–Er(2)–O(w2)	139.7(2)
O(1)–Er(1)–O(7)	79.4(2)	O(9)–Er(1)–O(w1)	66.8(2)	O(11)–Er(2)–O(17)	79.3(2)	O(19)–Er(2)–O(w2)	65.8(2)

(*b*) Counter ion

Ca–O(3)	2.466(4)	Ca–O(w1)	2.501(5)	Ca–O(9)	2.504(5)	Ca–O(w2)	2.458(5)
Ca–O(13)	2.459(5)	Ca–O(w3)	2.336(6)	Ca–O(19)	2.494(5)	Ca–O(w4)	2.355(6)
O(3)–Ca–O(9)	66.9(2)	O(w1)–Ca–O(w2)	130.8(2)	O(3)–Ca–O(13)	154.7(2)	O(3)–Ca–O(w3)	78.8(2)
O(9)–Ca–O(13)	136.7(2)	O(9)–Ca–O(w3)	116.8(2)	O(3)–Ca–O(19)	138.1(2)	O(13)–Ca–O(w3)	80.6(2)
O(9)–Ca–O(19)	76.7(2)	O(19)–Ca–O(w3)	138.6(2)	O(13)–Ca–O(19)	66.7(2)	O(w1)–Ca–O(w3)	142.8(2)
O(3)–Ca–O(w1)	67.4(2)	O(w2)–Ca–O(w3)	80.7(2)	O(9)–Ca–O(w1)	63.8(2)	O(3)–Ca–O(w4)	88.1(2)
O(13)–Ca–O(w1)	126.3(2)	O(9)–Ca–O(w4)	136.6(2)	O(19)–Ca–O(w1)	78.6(2)	O(13)–Ca–O(w4)	77.6(2)
O(3)–Ca–O(w2)	123.6(2)	O(19)–Ca–O(w4)	105.9(2)	O(9)–Ca–O(w2)	77.2(2)	O(w1)–Ca–O(w4)	74.1(2)
O(13)–Ca–O(w2)	66.5(2)	O(w2)–Ca–O(w4)	143.9(2)	O(19)–Ca–O(w2)	63.7(2)	O(w3)–Ca–O(w4)	90.3(2)

* Estimated standard deviations in the least significant digits are given in parentheses.

Since the two complex anions of the asymmetric unit interact with the same Ca^{2+} ion, discrete cation–anion trinuclear units are formed. The eight ligand atoms about Ca^{2+} occupy the vertices of a distorted square antiprism, with square faces defined by O(w2)–O(w3)–O(9)–O(3) and by O(w1)–O(w4)–O(13)–O(19). The discrete, trinuclear $CaEr_2$ units are connected by hydrogen bonding that links water molecules and all of the carboxylate oxygen atoms not co-ordinated to metal ions.

The bridging water molecules are nearly symmetrically bound between the Ca^{2+} and Er^{3+} ions [Ca–O(w)$_{av}$ = 2.48(3), Er–O(w)$_{av}$ = 2.462(5) Å]. The Er–O(w) distances are longer than those seen in eight-co-ordinate $[Er(edta)(OH_2)_2]^-$ [Er–O(w) = 2.32(3) Å][15] and in eight-co-ordinate $[Er(HOCH_2COO)_2(H_2O)_4]^+$ [Er–O(w) = 2.37(1), 2.28(1) Å],[19] where the water molecules are not involved in bridging interactions. The non-bridging water molecules are bound to Ca^{2+} at shorter distances than are the bridging water molecules [Ca–O(w)(non-bridging) = 2.35(1) Å]. A bridging water molecule has been previously observed to link two calcium ions.[20]

In all cases, the carboxylate oxygen atom involved in a bridge to Ca^{2+} is bound at a shorter distance to the chelated Er^{3+} ion than to Ca^{2+} [Er–O$_{av}$ = 2.33(1), Ca–O$_{av}$ = 2.48(3) Å]. As was typical of the bridging interactions of similar type in $Ca[Ca(egta)] \cdot \frac{22}{3}H_2O$ (**3**),[3] the bridging carboxylate oxygen atoms are bound to Er^{III} at longer distances than are any of the other carboxylate oxygen atoms (see Table 2).

The mean Er–ligand distances for all three classes of donor atoms in (**1**) are shorter than or similar in length to the mean Ca–ligand distances of similar type in (**3**) [Er/Ca–N$_{av}$ = 2.57(4)/2.60(2), Er/Ca–O(carboxylate)$_{av}$ = 2.31(3)/2.38(2), Er/Ca–O(ether)$_{av}$ = 2.42(5)/2.50(3) Å]. The mean Er–O(carboxylate) and Er–N distances are similar to those observed in $[Er(edta)(OH_2)_2]^-$ [Er–N$_{av}$ = 2.57(5), Er–O(carboxylate)$_{av}$ = 2.27(5) Å].[15] The Er–O(ether) distances in the nine-co-ordinate $[Er(oda)_3]^{3-}$ complex[21] [Er–O(carboxylate)$_{av}$ = 2.35, Er–O(ether)$_{av}$ = 2.49 Å, H_2oda = oxydiacetic acid] are longer than those seen in (**1**). It appears, however, that the Er–O(ether) distances in the oda^{2-} complex are anomalously long, since they are approximately 0.05 Å longer than would be expected, based on the isomorphous Ce^{III} structure.[22]

Despite the fact that no mean metal–ligand distances are longer for Er^{3+} than for Ca^{2+}, the erbium complex is nine-co-ordinate, while $[Ca(egta)]^{2-}$ in (**3**) is eight-co-ordinate.[3] On comparing the structures of $[Ca(egta)]^{2-}$ and $[Er(egta)(OH_2)]^-$ (see Figure 3), it appears that the room for the ninth ligand in (**1**) is provided by conformational rearrangement of the N–O(ether)–O(ether)–N belt. The four ligand atoms in this belt adopt a relatively planar configuration in (**1**), as a result of co-

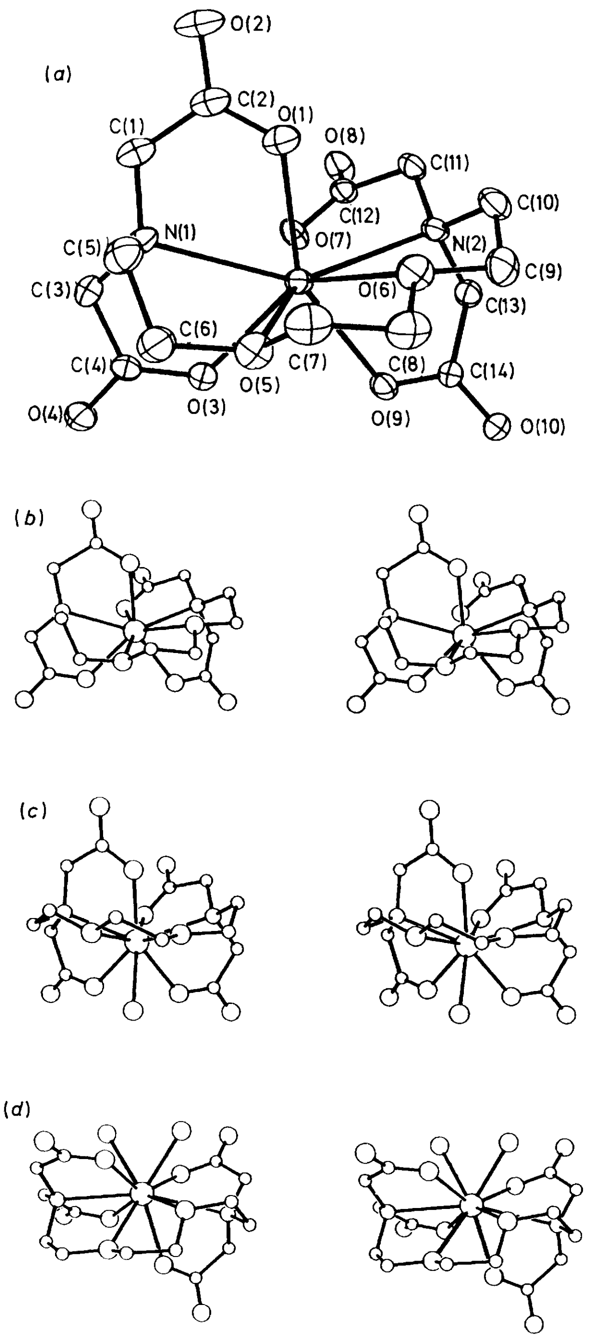

Figure 3. (*a*) Reference complex anion with numbering scheme. Stereoviews of (*b*) $[Ca(egta)]^{2-}$, (*c*) $[Er(egta)(OH_2)]^-$, and (*d*) $[Nd(egta)(OH_2)]^-$

ordination of O(6) and O(16) to the Er^{III} ions in a 'planar' fashion.

This mode of co-ordination results in displacements of Er^{III} from the planes containing C(8)–O(6)–C(9) and C(22)–O(16)–C(23) of only 0.34 and 0.17 Å, respectively. These displacements are quite different from displacements from similar planes containing O(5) and O(15) (both 1.53 Å). The angle between the Er–O(ether) vector and the normal to these C–O–C planes should be 90° if the ether oxygen atom is utilizing both lone pairs in co-ordinating to the metal ion, and approximately 125° if the ether oxygen atom is utilizing only a single lone pair. In (**1**), these angles range from 85° [O(16)] and 98° [O(6)] to 128° [O(5), O(15)]. Additionally, the ether oxygen atoms bound in the 'planar' mode exhibit shorter Er–O(ether) distances than do those that are not bound in that fashion [$Er–O(6)/O(16)_{av}$ = 2.37(3), $Er–O(5)/O(15)_{av}$ = 2.46(1) Å].

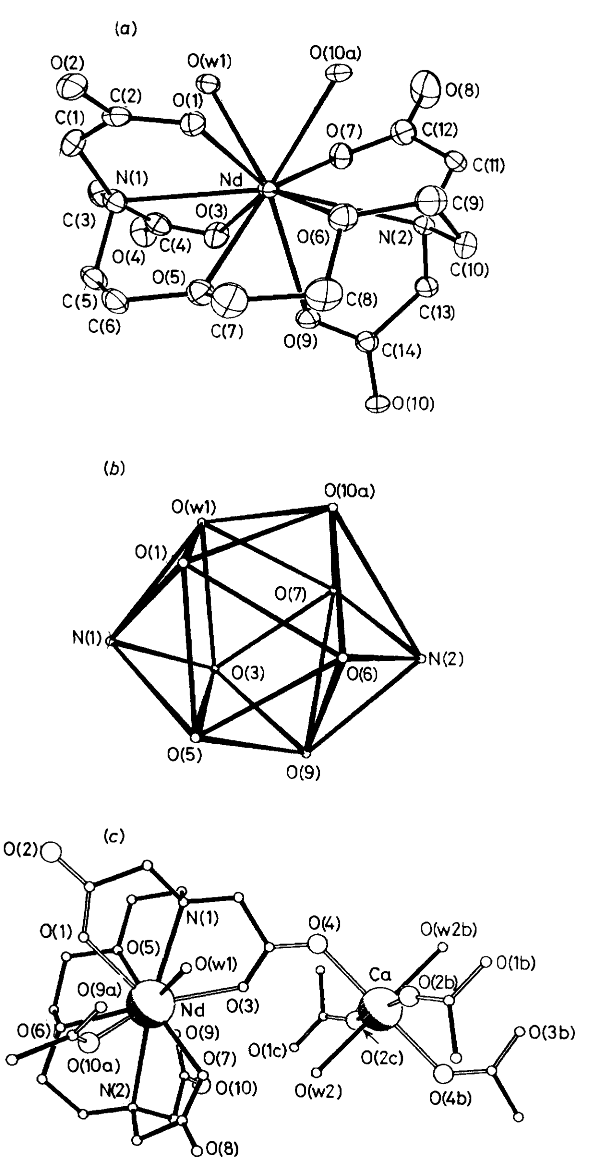

Figure 4. (*a*) Thermal ellipsoid plot (30%) of the $[Nd(egta)(OH_2)]^-$ complex ion. (*b*) View of the co-ordination polyhedron formed by the ligand atoms about Nd. (*c*) Ball and stick plot depicting interionic interactions in the solid state for (**2**). Conventions are the same as in Figure 2

The two aminodiacetate termini co-ordinate Er^{III} in very different manners. The Er^{3+} ion is approximately coplanar with N(1), O(1), and O(3) at one end of the $egta^{4-}$ ligand, but does not lie near the plane formed by N(2), O(7), and O(9) at the other end of the ligand. These conformations are similar to those observed for $[Ca(egta)]^{2-}$ in (**3**) (see Figure 3).[3]

The inequivalencies in chemically equivalent bond lengths in (**1a**) and (**1b**) follow the same patterns. Of the two amine nitrogen atoms in each complex anion, the nitrogen atoms N(2) and N(4) are bound at longer distances than are N(1) and N(3) [$Er–N(2)/N(4)_{av}$ = 2.597(3), $Er–N(1)/N(3)_{av}$ = 2.54(2) Å]. This may be associated with the 'planar' conformation at the

Table 3. Atomic co-ordinates (fractional, × 10^4) for $Ca[Nd(egta)(OH_2)]_2 \cdot 9H_2O$, (**2**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nd	2 322(1)	2 324(1)	2 582(1)	N(2)	−330(3)	2 631(2)	2 467(3)
Ca	5 000	5 000	5 000	O(1)	3 037(2)	1 323(1)	1 645(2)
C(1)	5 365(4)	1 592(2)	2 575(3)	O(2)	4 505(3)	538(1)	1 424(2)
C(2)	4 211(4)	1 112(2)	1 825(3)	O(3)	3 838(3)	3 198(1)	3 940(2)
C(3)	5 782(4)	2 726(2)	3 694(3)	O(4)	5 722(3)	3 854(2)	4 599(2)
C(4)	5 059(4)	3 302(2)	4 128(3)	O(5)	3 132(3)	1 125(1)	3 912(2)
C(5)	5 334(4)	1 619(2)	4 504(3)	O(6)	634(3)	1 214(1)	2 223(2)
C(6)	4 524(4)	934(2)	4 359(3)	O(7)	1 377(3)	3 559(1)	2 113(2)
C(7)	2 311(4)	478(2)	3 547(4)	O(8)	−208(3)	4 193(2)	769(3)
C(8)	879(4)	700(2)	3 139(4)	O(9)	1 843(3)	2 341(1)	4 365(2)
C(9)	−772(4)	1 389(2)	1 663(3)	O(10)	837(3)	2 725(1)	5 533(2)
C(10)	−1 158(4)	1 969(2)	2 322(3)	O(w1)	3 550(2)	2 968(1)	1 481(2)
C(11)	−878(4)	3 135(2)	1 501(3)	O(w2)	2 761(3)	4 724(2)	3 731(2)
C(12)	168(4)	3 673(2)	1 451(3)	O(w3)	4 250(3)	4 423(2)	1 826(3)
C(13)	−189(4)	3 003(2)	3 544(3)	O(w4)	1 894(3)	5 185(2)	1 194(3)
C(14)	909(4)	2 656(2)	4 565(3)	O(w5)	1 101(3)	394(2)	15(3)
N(1)	5 031(3)	2 027(2)	3 421(3)	O(w6)	2 615(9)	9 160(5)	1 553(8)

* Estimated standard deviations in the least significant digits are given in parentheses.

Table 4. Metal–ligand distances (Å) and angles (°)* for $Ca[Nd(egta)(OH_2)]_2 \cdot 9H_2O$, (**2**)

(*a*) Complex ion			
Nd–N(1)	2.757(3)	Nd–O(6)	2.642(3)
Nd–N(2)	2.862(3)	Nd–O(7)	2.449(2)
Nd–O(1)	2.446(3)	Nd–O(9)	2.481(3)
Nd–O(3)	2.453(2)	Nd–O(w1)	2.533(3)
Nd–O(5)	2.687(2)	Nd–O(10a)	2.468(2)
N(1)–Nd–N(2)	161.9(1)	O(1)–Nd–O(9)	130.9(1)
N(1)–Nd–O(1)	63.8(1)	O(3)–Nd–O(9)	71.0(1)
N(2)–Nd–O(1)	127.7(1)	O(5)–Nd–O(9)	65.1(1)
N(1)–Nd–O(3)	62.0(1)	O(6)–Nd–O(9)	78.4(1)
N(2)–Nd–O(3)	107.4(1)	O(7)–Nd–O(9)	89.8(1)
O(1)–Nd–O(3)	124.8(1)	N(1)–Nd–O(w1)	66.7(1)
N(1)–Nd–O(5)	63.5(1)	N(2)–Nd–O(w1)	126.8(1)
N(2)–Nd–O(5)	105.9(1)	O(1)–Nd–O(w1)	76.0(1)
O(1)–Nd–O(5)	66.8(1)	O(3)–Nd–O(w1)	74.4(1)
O(3)–Nd–O(5)	96.9(1)	O(5)–Nd–O(w1)	127.0(1)
N(1)–Nd–O(6)	118.5(1)	O(6)–Nd–O(w1)	136.8(1)
N(2)–Nd–O(6)	62.0(1)	O(7)–Nd–O(w1)	72.4(1)
O(1)–Nd–O(6)	70.7(1)	O(9)–Nd–O(w1)	144.7(1)
O(3)–Nd–O(6)	148.3(1)	N(1)–Nd–O(10a)	124.6(1)
O(5)–Nd–O(6)	61.7(1)	N(2)–Nd–O(10a)	73.2(1)
N(1)–Nd–O(7)	123.8(1)	O(1)–Nd–O(10a)	70.7(1)
N(2)–Nd–O(7)	59.4(1)	O(3)–Nd–O(10a)	138.5(1)
O(1)–Nd–O(7)	138.3(1)	O(5)–Nd–O(10a)	123.4(1)
O(3)–Nd–O(7)	71.2(1)	O(6)–Nd–O(10a)	70.1(1)
O(5)–Nd–O(7)	154.8(1)	O(7)–Nd–O(10a)	74.6(1)
O(6)–Nd–O(7)	117.7(1)	O(9)–Nd–O(10a)	131.9(1)
N(1)–Nd–O(9)	102.0(1)	O(w1)–Nd–O(10a)	73.4(1)
N(2)–Nd–O(9)	60.0(1)		
(*b*) Counter ion			
Ca–O(4)	2.348(3)	Ca–O(w2)	2.390(3)
Ca–O(2a)	2.273(3)		
O(4)–Ca–O(w2)	90.2(1)	O(4)–Ca–O(2a)	91.1(1)
O(w2)–Ca–O(2a)	92.5(1)		

* Estimated standard deviations in the least significant digits are given in parentheses.

ether oxygen atoms, O(6) and O(16), which are adjacent to N(2) and N(4) in the two complexes.

The conformations of the five-membered chelate rings were analysed by a method used to assess ring conformations in other polyamino-polycarboxylate complexes.[23] The amino-ether rings exhibiting the planar mode of oxygen co-ordination showed unusual conformational parameters, as expected. The conformations of all other rings fell within the normal patterns.

Structure of the Nd^{III} *Chelate in* $Ca[Nd(egta)(OH_2)]_2 \cdot 9H_2O$ (**2**).—Final fractional atomic co-ordinates for all the non-hydrogen atoms of (**2**) may be found in Table 3 and bond lengths and angles in Table 4.

As expected (see above), an increase in co-ordination number from nine to ten is observed on going from the Er^{III} to the Nd^{III} chelate of $egta^{4-}$. Ten-co-ordination for Nd^{III} in (**2**) is achieved in the solid state by co-ordination of the octadentate $egta^{4-}$ ligand, a carboxylate oxygen atom from an adjacent complex ion, and a water molecule [see Figure 4(*a*)]. The structure of (**2**) is such that only one complex anion resides in the asymmetric unit. The ligand atoms about the Nd^{3+} ion occupy the vertices of a distorted bicapped square antiprism [see Figure 4(*b*)], with the two square faces of the antiprism made up of O(1)–O(w1)–O(3)–O(5) and O(10a)–O(7)–O(6)–O(9). The nitrogen atoms, N(1) and N(2), cap the square faces.

Each Nd^{III} chelate engages in three carboxylate bridging interactions; each of these bridges employs a carboxylate oxygen atom that is not co-ordinated to Nd^{III}. Two of these interactions involve bridging to two different Ca^{2+} counter ions [see Figure 4(*c*)], while the third interaction involves bridging to the Nd^{III} atom of an adjacent complex anion. This complex anion–cation network is propagated in the *yz* plane to produce polymeric sheets, which are linked together by hydrogen bonds with water molecules.

The crystallographically required $\bar{1}$ symmetry about the Ca^{2+} counter ion is satisfied by a distorted octahedral co-ordination array. In addition to the oxygen atoms of four bridging carboxylate groups, two water molecules are co-ordinated to Ca^{2+}. The Ca–O(4) bridging distance [2.348(3) Å] is similar to corresponding distances seen in (**3**), while the Ca–O(2) bridging distance [2.273(3) Å] is considerably shorter.[3] The single water molecule is bound at a typical distance.[20]

The wrapping of $egta^{4-}$ about Nd^{III} is not a simple perturbation on the $[Er(egta)(OH_2)]^-$ structure above. The tenth co-ordination site in the Nd^{III} complex is obtained by twisting the meridional aminodiacetate end of the $egta^{4-}$ ligand about the Nd–N bond (see Figure 3). As a result, an ether oxygen atom occupies the co-ordination site that was occupied by the water molecule in the erbium chelate. The water molecule and the bridging carboxylate group occupy sites vacated by this twisting. The conformations that characterized the aminodiacetate termini of the egta^{4-} ligand in (**1**) [and (**3**)] are maintained in (**2**), despite these changes in orientation.

The oxygen atom donated through a carboxylate bridge is bound at a distance intermediate in the range of intra-chelate Nd–O(carboxylate) distances [Nd–O(carboxylate) = 2.446(3)–2.481(3), Nd–O(10a) = 2.468(2) Å]. These distances are similar to those observed in $[Nd(edta)(OH_2)_3]^-$ [Nd–N = 2.8, Nd–O(carboxylate) = 2.5 Å][24] and about the nine-co-ordinate Nd^{III} ion in $Ba[Nd(dtpa)(OH_2)]\cdot 2H_2O$ [Nd–O(carboxylate)$_{av}$ = 2.45(6) Å, H_5dtpa = 3,6,9-tris(carboxymethyl)-3,6,9-triazaundecanedioic acid].[23]

The Nd–N distance in the nine-co-ordinate $[Nd(ida)(OH_2)_3]^+$ complex (H_2ida = iminodiacetic acid) is 2.67(2) Å.[25] For the nine-co-ordinate Nd^{III} ion in $Na_3[Nd(oda)_3]$, Nd–O(ether) = 2.52(1) Å and Nd–O(carboxylate) = 2.428(6) Å.[26] In the $[Nd(dtpa)(OH_2)]^{2-}$ complex mentioned above, Nd–N$_{av}$ = 2.76(7) Å. Although the carboxylate oxygen atoms in (**2**) thus appear to be bonded at normal distances, the amine nitrogen atoms and ether oxygen atoms appear to be bonded at longer distances than would be expected [Nd–N$_{av}$ = 2.81(7), Nd–O(ether)$_{av}$ = 2.67(3) Å in (**2**)].

The difference in the ionic radii of nine-co-ordinate Er^{III} and ten-co-ordinate Nd^{III} is 0.14 Å.[13] The difference in the mean metal–carboxylate bond distances between the Er^{III} and Nd^{III} chelates (0.15 Å) is consistent with this difference in ionic radii, but the differences in mean M–N and M–O(ether) distances between the two chelates are considerably larger (0.24 and 0.25 Å, respectively). Apparently the binding preferences of the favoured ligands are satisfied to the detriment of the weaker ligands.

The difference between the chemically equivalent Nd–N distances, relative to the Er–N difference in the Er^{III} chelate, is larger; the difference in the Nd–O(ether) distances is smaller for Nd^{3+} than for Er^{3+}. These changes must result from the constraints of wrapping the egta^{4-} ligand around the relatively small ten-co-ordinate metal ion.

Relevance to Calcium-binding Proteins.—The conformational flexibility of a chelating ligand like egta^{4-} is, presumably, considerably greater than that of a metal ion binding site in a protein. Thus, it seems unlikely that the substantial conformational rearrangement observed for the egta^{4-} ligand on going from Er^{III} to Nd^{III} would be possible in a protein. Nevertheless, this study has shown that lanthanides have a preference for a higher co-ordination number when bound to the highly calcium-selective egta^{4-} ligand. This effect must be taken into account when using lanthanide ions to probe the structure at and about calcium binding sites in calcium-building proteins.

Acknowledgements

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