Structures of the Yttrium Complexes of 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetic acid (H_4dota) and *N,N″*-Bis(benzylcarbamoylmethyl)diethylenetriamine-*N,N′,N″*-triacetic acid and the Solution Structure of a Zirconium Complex of H_4dota†

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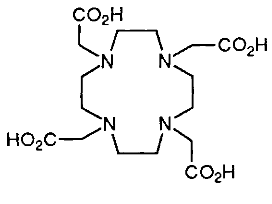
The solid-state crystal structure of Na[Y(dota)(H_2O)]·4H_2O (H_4dota = 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetic acid) at 115 K has been obtained together with the solution structure of the neutral zirconium complex. The yttrium complex shows a mono-capped (H_2O) square-antiprismatic structure while the solution ^1H NMR spectra of [Zr(dota)(H_2O)] suggest that a structure of lower symmetry is adopted and a minor isomer is observed. The crystal structure of the yttrium complex of *N,N″*-bis(benzylcarbamoylmethyl)diethylenetriamine-*N,N′,N″*-triacetic acid has revealed amide carbonyl ligation in a distorted mono-capped square-antiprismatic structure, with one metal-bound water molecule.

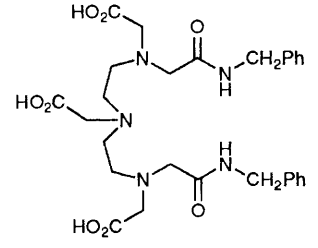
The complexation chemistry of yttrium has been the subject of renewed interest in recent years because of the need to find yttrium complexes which are sufficiently stable *in vivo* for radioimmunotherapy with ^{90}Y-labelled antibody conjugates.[1–3] Following the work of Desreux and co-workers[4] on stable lanthanide complexes of H_4dota (1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetic acid, H_4L^1), it was soon apparent that dota was a suitable ligand both for gadolinium {Na[Gd(dota)(H_2O)][5] is a commercially available magnetic resonance imaging (MRI) contrast agent used in patients in multigram quantities} and for yttrium.[6] The crystal structures of the complexes of H_4dota with europium and gadolinium have been published[5,7] which reveal that dota acts as an octadentate ligand with a ninth co-ordination site occupied by a water molecule. When the β-emitting isotope ^{90}Y decays ($t_{\frac{1}{2}}$ 64 h, E_{max} 2.24 MeV, $\approx 3.58 \times 10^{-13}$ J) it yields a stable zirconium daughter. The product therefore of the radioactive decay of Na[^{90}Y(dota)(H_2O)] is the neutral complex [Zr(dota)(H_2O)]. This complex is quite difficult to prepare because of the strong tendency of Group 4 complexes or complex precursors to hydrolyse in aqueous media.

We report the accurate low-temperature crystal structure of Na[Y(dota)(H_2O)]·4H_2O and the preparation and NMR solution structure of [Zr(dota)(H_2O)]. In addition, the structure of the yttrium complex of *N,N″*-bis(benzylcarbamoylmethyl)diethylenetriamine-*N,N′,N″*-triacetic acid, H_3L^2, is reported. The gadolinium complexes of related (*e.g.* methyl-, ethyl- rather than benzyl-carbamoyl) ligands are being studied actively as low osmolality paramagnetic contrast agents for MRI,[8] although the lack of *in vivo* stability of such complexes, compared to the complexes of H_4dota and related phosphinates (revealed by measurable deposition of Gd in the bone and liver) has been noted.[9,10]

Results and Discussion

The complexes of yttrium and zirconium with H_4dota were prepared using established methods.[3,11] In the latter case, $Zr(OH)_4$ was generated by controlled hydrolysis of $ZrOCl_2$ and


H_4dota, H_4L^1


H_3L^2

the neutral complex separated from unreacted ligand by anion exchange chromatography. The structure of Na[Y(dota)(H_2O)]·4H_2O, determined at 115 K, is shown in Fig. 1. Crystals were isomorphous with the related europium complex[7] and the yttrium ion is in a nine-co-ordinate ligand environment comprising the four ring nitrogens, the four carboxylate oxygens and a water molecule. The four nitrogens and four ligand oxygens are almost in an antiprismatic geometry, the prism being twisted by 40° instead of the ideal 45°. The antiprism is mono-capped by the water molecule. The average Y–N distance [2.645(18) Å] is much longer than the average Y–O [2.326(5) Å] value. This trend was noted in the structure of Na[Eu(dota)(H_2O)]·4H_2O and has been generally observed in a variety of polyaminopolycarboxylate complexes.[8,12–15]

The sodium atom is irregularly co-ordinated by three carboxylate groups (two chelating and one monodentate) belonging to three different $[Y(dota)(H_2O)]^-$ moieties, and additionally by one water molecule. The remaining three water molecules in the asymmetric unit are molecules of crystallisation. The twelve-membered ring adopts the usual 'square' [3333] conformation[16] with all of the nitrogen atoms coplanar to within 0.008 Å and average torsion angles of τ = 164(3), β = −59(1) and ψ = −79(3)°. The local four-fold symmetry of yttrium co-ordination is hardly perturbed by crystal packing effects.

In the crystal, the $[Y(dota)(H_2O)]^-$ ions are linked by sodium cations into double ribbons stretched parallel to the *b* axis. These ribbons and non-co-ordinated water molecules are

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

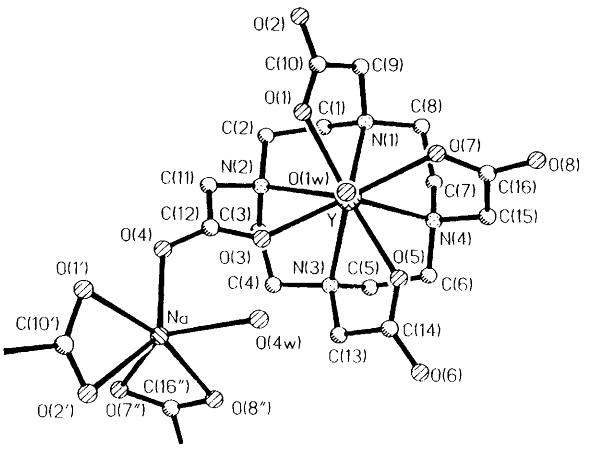

Fig. 1 Co-ordination of yttrium and sodium ions in the structure of Na[Y(dota)(H_2O)]·$4H_2O$

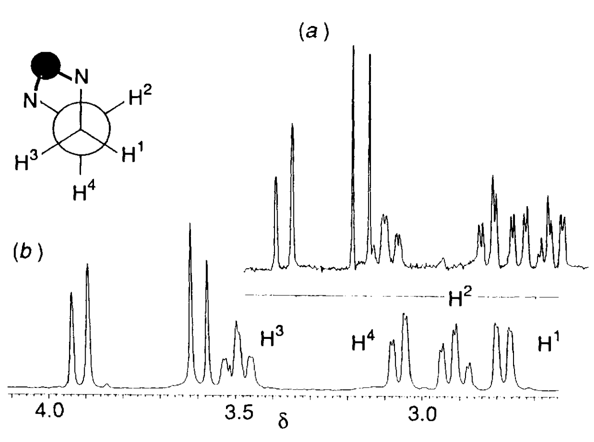

Fig. 3 ^1H NMR spectra of [Zr(dota)(H_2O)] (293 K, D_2O) at 250 (*a*) and 400 MHz (*b*)

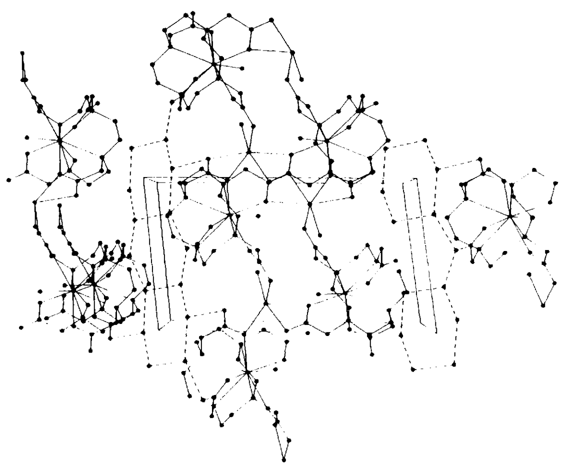

Fig. 2 Crystal packing and hydrogen-bonding network in Na[Y(dota)(H_2O)]·$4H_2O$. The projection shown is down the *x* axis

linked into a three-dimensional network by O–H···O hydrogen bonds (O···O distances of 2.71–2.82 Å) in which all active hydrogen atoms participate except H(42W) of the sodium-bound water molecule (Fig. 2). In the room-temperature structure of Na[Eu(dota)(H_2O)]·$4H_2O$,[7] it had been suggested that each non-co-ordinated water molecule had two possible orientations with a statistical disorder of hydrogen atoms. In Y[Eu(dota)(H_2O)]·$4H_2O$ no such disorder was found.

The zirconium complex of H_4dota was found to be insoluble in most common polar solvents (dimethyl sulfoxide, dimethylformamide, MeCN, Me_2CO, MeOH) limiting the nature and range of solution-state NMR experiments that could be undertaken. It was sparingly soluble in D_2O, and the ^{13}C NMR spectrum (293 K, 101 MHz) consisted of the expected four resonances at δ 182.2 (acetate carbonyl), 70.3 (acetate methylene groups) and 59.64, 59.56 (ethylenic carbons of the tetraaza ring). In the temperature range 288–328 K no significant changes were observed consistent with an apparent retention of time-averaged C_4-symmetry. Unfortunately it was not possible to carry out further solution studies at lower temperatures (*e.g.* by adding CD_3OD to lower the freezing point of the aqueous mixture) because of the insolubility of the complex.

It has previously been noted with [Ln(dota)(H_2O)]$^-$ (Ln = Pr, La, Nd, Yb or Eu] and [Y(dota)(H_2O)]$^-$, that a second minor isomer exists in solution at very low concentration (*ca.* 5%) which is in exchange with the major species[17] (T_c *ca.* 0 °C in the ^1H NMR spectrum at 400 MHz). Although not detected in the ^{13}C NMR studies, there is evidence in the ^1H NMR spectra of [Zr(dota)(H_2O)] to suggest the existence of such an isomer (Fig. 3). At 400 MHz and at 293 K, the minor isomer is apparent as a series of broad resonances, *e.g.* at δ 3.12, 3.0 and 2.75. On cooling to 278 K, these sharpen somewhat and represent about 8% of the total signal intensity. In the range 303 to 343 K, the two species are in fast exchange on the NMR time-scale and an averaged signal is observed.

Analysis of the room-temperature ^1H spectrum (Fig. 3) (NB still exchange broadened at 400 MHz), reveals that the acetate methylene protons appear as a pair of doublets at δ 3.92 and 3.59 ($J = -17.2$ Hz). The ethylenic ring protons resonate as two double triplets (labelled as H^3 and H^2 in Fig. 3) at δ 3.49 and 2.91 for the 'axial' protons, and two 'double' doublets for the 'equatorial' protons (H^4 and H^1) at δ 3.06 and 2.78. The geminal coupling constant is 14 Hz and the '*trans*-antiperiplanar' coupling constant is 14.7 Hz. A two-dimensional correlation (COSY) spectrum confirmed the assignments given.

The apparent 'doubling' of certain ring resonances evident in Fig. 3 was more readily interpreted following analysis of the ^1H spectrum in the temperature range 5–75 °C (D_2O, 400 MHz). At 60 °C, the diastereotopic methylene protons of the acetate groups appeared as three closely spaced ($\Delta\delta_H \approx 0.01$ ppm) pairs of doublets (ratio 1 : 1 : 2) and as two broadened pairs of doublets in the temperature range 30–60 °C (ratio 1 : 1). Similarly the 'triplets' for H^3 and H^2 (appearing as a pair of closely-spaced triplets at 293 K, Fig. 3) appeared as three closely spaced sets of triplets (in ratio 1 : 1 : 2) at 60–75 °C. Evidently, there is a loss of 'time-averaged' C_2 symmetry in the NMR solution structure at elevated temperatures which is not apparent in the corresponding ^{13}C NMR spectra presumably because the shift non-equivalence of, for example, the different acetate carbons is too small to be resolved.

In the yttrium complex of *N*,*N*″-bis(benzylcarbamoylmethyl)-*N*,*N*′,*N*″-diethylenetriaminetriacetic acid there was a marked co-ordination shift in the infrared stretching frequency of the amide carbonyl band (37 cm^{-1} co-ordination shift) consistent with amide oxygen ligation.

The molecular structure of [YL^2(H_2O)]·$3H_2O$ was established by an X-ray single crystal diffraction study, and is shown in Fig. 4. The chelating octadentate ligand co-ordinates the Y atom in a square-antiprismatic mode. Three nitrogen atoms and one carboxylate oxygen, O(2), comprise one square base of the antiprism, while oxygen atoms of the two remaining (also monodentate) carboxylate groups and two amide groups from another base. The latter is capped by an aqua ligand. The bonding of negatively charged carboxylate and formally neutral amide groups with yttrium has essentially the same character, as indicated by similar average distances Y–O [2.33(1) *vs.* 2.35(1) Å] and C–O(Y) [1.26(2) *vs.* 1.24(2) Å], because the electronic delocalisation within an amide O–N–C moiety also gives a significant negative charge on the oxygen atom. The purely donor–acceptor Y–OH_2 of 2.402(2) Å is only marginally longer than the above mentioned ionic bonds. On the contrary, three

Y–N bond distances vary in a wide range (0.2 Å), notwithstanding the chemical equivalence of two of the three nitrogen atoms, and on average are longer than the Y–O bonds by 0.3 Å, while the ionic radius of N is only by 0.11 Å larger than that of O (for co-ordination numbers of four and two, respectively).[18] Both elongation and variation of lanthanide–nitrogen bonds have been observed earlier for the complexes with LnN_4O_4 and LnN_4O_5 co-ordination polyhedra,[8,11–15] and demonstrate the comparative weakness and lability of the less polar Ln–N bonds in these strongly ionic complexes. Similar observations in particular were noted in the structure of the gadolinium complex of the bis(ethylcarbamoyl) analogue of L^2 (ref. 8).

The asymmetric unit of the crystal contains three molecules of crystallisation water (besides the one co-ordinated to Y), one of which, O(4W), is disordered by two positions (A and B) with estimated occupancies of 60 and 40%. Short distances between positions A and B (1.35 Å), B and its inversion partner B′ (1.76 Å), show that both positions cannot be occupied within the same asymmetric unit, but rather the inversion centre $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is locally violated. Then, simultaneous occupation of positions A and B′, B and A′, or A and A′ only, result in reasonable intermolecular distances and hydrogen-bonding geometry.

All independent water molecules (including the capping one) and their equivalents *via* the inversion centre $(\frac{1}{2}\,0\,0)$ are sandwiched between the molecules of the complex, related by the same inversion centre, and link them through a system of O–H $\cdots$ O hydrogen bonds (O $\cdots$ O 2.61–2.85 Å). Hydrogen bonds formed by the disordered water molecules link these groupings into an infinite chain parallel to the *x* axis, supported also by N(3)–H $\cdots$ O(6) bonds (N $\cdots$ O 2.79 Å), while N(5)–H $\cdots$ O(3) bonds (N $\cdots$ O 2.87 Å) link the chains into a layer parallel to the $(0\,\bar{1}\,1)$ plane (Fig. 5).

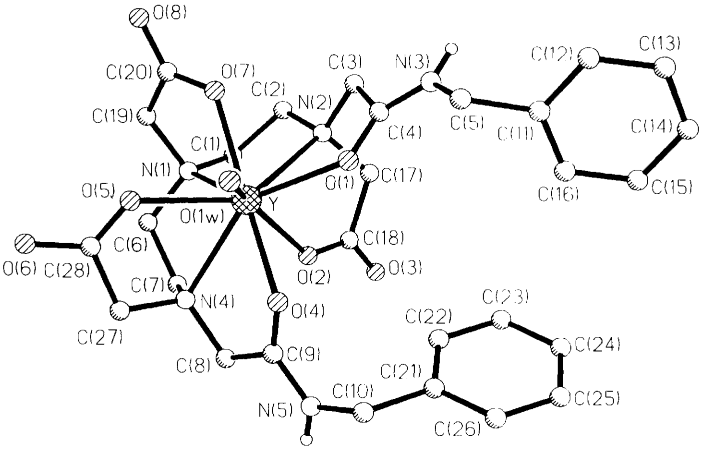

Fig. 4 Molecular structure of $[YL^2(H_2O)]\cdot 3H_2O$ with hydrogens omitted except for the amide group

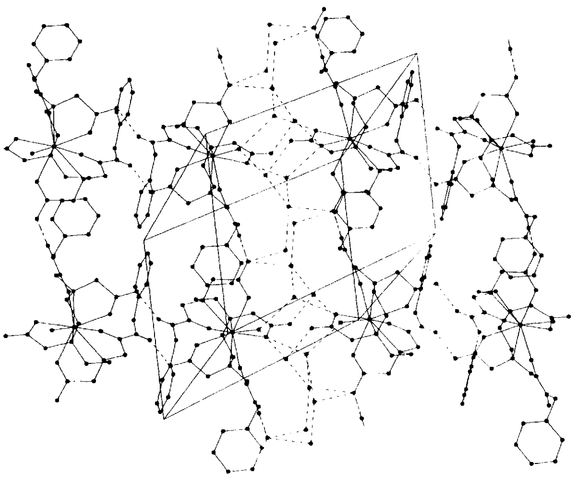

Fig. 5 Hydrogen-bonding network in the structure of $[YL^2(H_2O)]\cdot 3H_2O$; projection of the $(0\,\bar{1}\,1)$ plane

Experimental

Commercial solvents were dried from an appropriate drying agent prior to use according to standard procedures. Water was purified by the MilliQ or Purite system. Proton and carbon-13 NMR spectra were recorded on a Bruker AC-250 (250.1 and 62.9 MHz respectively) and a Varian VXR-400 spectrometer. Yttrium-89 spectra were recorded on a Bruker AM-500 operating at 24.5 MHz. Shifts are given to higher frequency of YCl_3 (1 mol dm^{-3}, $\delta = 0$). Mass spectra were recorded with a VG 7070E spectrometer operating in desorption chemical ionisation (DCI) or fast-atom bombardment (FAB) mode. Glycerol or *m*-nitrobenzyl alcohol was used as the FAB matrix. Infrared spectra were recorded as KBr discs or as a mull in Nujol with a Mattson Sirius 100 Fourier transform spectrometer.

Preparations.—$[Zr(dota)(H_2O)]\cdot 4H_2O$. To a solution of $ZrOCl_2$ (0.5 g, 1.56 mmol) in water (5 cm^3) was added ammonia solution (0.88 specific gravity) until complete precipitation had occurred. The white precipitate was isolated by centrifugation and washed repeatedly with water (10 x 2 cm^3) to remove excess ammonia. To the resultant wet solid was added H_4dota (0.62 g, 1.56 mmol) and water (20 cm^3) and the mixture was heated under reflux for 72 h. After filtering the cooled sample and removing the water the residue was dissolved in the minimum quantity of cold water and passed down an anion exchange column [Amberlite IRA G16 (Cl^- form)]. The product eluted with water and the resultant solid was recrystallised from hot water to give colourless needles of the product (0.45 g, 50%). Mass spectrum (DCI): *m/z* 493 (M^+ + 1, 18) and 492 (M^+, 100%) (Found: C, 33.1; H, 6.10; N, 9.55%. $C_{16}H_{24}N_4O_8Zr\cdot 5H_2O$ requires C, 33.5; H, 5.95; N, 9.80%); $\delta_C(D_2O)$ 182.22 (CO), 70.26 (CH_2CO), 59.64 and 59.56 (CH_2N); $\delta_H(D_2O)$ 3.92 (4 H, d, $CHH'CO_2$, J = 17.3), 3.59 (4 H, d, $CHH'CO_2$), 3.49 (4 H, br dt, H^3, ring $CHH'N$, J = 14.7 and 14), 3.06 (4 H, br dd, H^4, $CH''H'''N$, J = 14.4 Hz), 2.91 (4 H, br dt, H^2, $CH''H'''N$) and 2.78 (4 H, br dd, H^1, $CHH'N$).

$Na[Y(dota)(H_2O)]\cdot 4H_2O$. This complex was prepared as described in the literature[3] and was recrystallised from aqueous solution as the pentahydrate salt, $\delta_Y(D_2O)$ = +111.8.

N,N″-*Bis*(*benzylcarbamoylmethyl*)*diethylenetriamine*-N,N′,N″-*triacetic acid*, H_3L^2. To the *N*,*N*″-dianhydride of diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (0.357 g, 1 mmol) in pyridine (3 cm^3) was added benzylamine (0.32 g, 3 mmol) and dimethylaminopyridine (5 mg). An immediate white precipitate was observed which dissolved after 30 min. The mixture was heated at 50 °C for 14 h, solvent removed under reduced pressure and water added (1 cm^3) to give a solution at pH 4.5. Dilute hydrochloric acid (0.1 mol dm^{-3}) was added slowly until the pH was 3.5 when a white solid formed which was filtered, washed with dilute hydrochloric acid (pH 3.5, 3 x 2 cm^3) and dried under reduced pressure to yield a white solid (0.41 g, 72%), m.p. 112–113 °C (Found: C, 55.3; H, 6.75; N, 11.3%. $C_{28}H_{37}N_5O_8\cdot 2H_2O$ requires C, 55.4; H, 6.75; N, 11.5%); R_f 0.40 [silica gel, CH_2Cl_2–MeOH (95.5)]. Mass spectrum (DCI) for the trimethyl ester: *m/z* 614 (M^+ + 1), 237, 150 and 108; $\delta_H[(CD_3)_2SO]$ 8.60 (2 H, t, NHCO), 7.28 (10 H, m, aromatic H), 4.31 (4 H, d, CH_2Ph), 3.39 (6 H, s, CH_2CO_2H), 3.32 (4 H, s, CH_2CO), 2.90 (4 H, br t, CH_2N) and 2.83 (4 H, t, CH_2N); $\delta_C[(CD_3)_2SO]$ 172.6 (CONH), 170.4 (CO_2H), 169.7 (CO_2H), 139.5 (q, aromatic C), 128.3, 127.2, 126.7 (aromatic CH), 57.41, 55.11, 52.10, 50.89 and 41.9 (CH_2N); ν_{max}(KBr)

Table 1 Atomic coordinates (× 10^4) for $Na[Y(dota)(H_2O)]\cdot 4H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Y	953(1)	2509(1)	3065(1)	N(4)	1472(2)	1386(2)	1548(1)
Na	−1283(1)	8229(1)	4001(1)	C(1)	4921(3)	1348(3)	2885(2)
O(1)	1849(2)	1634(2)	4433(1)	C(2)	4830(3)	2623(3)	3433(2)
O(2)	3007(2)	−154(2)	5369(1)	C(3)	3866(3)	4755(3)	2426(2)
O(3)	389(2)	4785(2)	3637(1)	C(4)	2440(3)	5605(2)	1997(2)
O(4)	1018(2)	6656(2)	4282(1)	C(5)	2084(3)	3907(3)	972(1)
O(5)	−1241(2)	3256(2)	2272(1)	C(6)	1328(3)	2583(3)	802(1)
O(6)	−2591(2)	4704(2)	1249(1)	C(7)	3053(3)	496(3)	1464(1)
O(7)	118(2)	192(2)	3096(1)	C(8)	3516(3)	−407(3)	2309(2)
O(8)	−1126(2)	−1300(2)	2449(1)	C(9)	3528(3)	−389(2)	3862(1)
O(1W)	−1324(2)	2537(2)	4074(1)	C(10)	2762(3)	423(2)	4612(1)
O(2W)	5269(2)	−2832(3)	776(1)	C(11)	3047(3)	4690(3)	4954(2)
O(3W)	7063(2)	−706(3)	986(1)	C(12)	1359(3)	5452(2)	3957(1)
O(4W)	−2712(3)	6236(3)	3804(2)	C(13)	−180(3)	5402(3)	1597(2)
O(5W)	6318(3)	2324(3)	688(2)	C(14)	−1439(3)	4381(2)	1707(1)
N(1)	3509(2)	560(2)	3018(1)	C(15)	248(3)	419(3)	1535(2)
N(2)	3462(2)	3776(2)	3226(1)	C(16)	−285(3)	−296(2)	2423(1)
N(3)	1393(2)	4573(2)	1767(1)				

Table 2 Selected bond lengths (Å) and angles (°) for $Na[Y(dota)(H_2O)]\cdot 4H_2O$

Y–O(1)	2.330(2)	Y–N(3)	2.633(2)
Y–O(5)	2.319(2)	Y–N(4)	2.666(2)
Y–O(3)	2.328(2)	Na–O(4)	2.315(2)
Y–O(7)	2.328(2)	Na–O(4W)	2.409(2)
Y–O(1W)	2.424(2)	Na–O(1′)	2.461(2)
Y–N(1)	2.628(2)	Na–O(2′)	2.385(2)
Y–N(2)	2.654(2)		
O(1)–Y–O(3)	83.8(1)	O(1W)–Y–N(1)	129.6(1)
O(1)–Y–O(5)	145.2(1)	O(1)–Y–N(2)	72.8(1)
O(1)–Y–O(1W)	73.1(1)	O(4)–Na–O(4W)	94.2(1)
O(1)–Y–N(1)	66.7(1)	O(4)–Na–O(1′)	90.1(1)
O(3)–Y–N(1)	131.7(1)		

3736m, 3315s, 3034m, 2550br, 1720br, 1653 (sh), 1630vs (CO_2^-), 1559s, 1375, 1222, 1101 (CO), 738 and 695 cm^{-1}.

$[YL^2(H_2O)]\cdot 3H_2O$. To a solution of H_3L^2 (0.1 g, 0.175 mmol) in water (0.5 cm^3) was added a solution of yttrium nitrate (0.064 g, 0.175 mol) in dilute hydrochloric acid (1 cm^3, pH 2) and the mixture was heated under reflux until the solution was completely clear. After cooling to room temperature, the pH was adjusted to 4 and crystals formed on standing which were filtered, washed with cold water (3 × 1 cm^3) and dried under vacuum (0.095 g, 74%). Mass spectrum (FAB): *m*/*z* 658 (M^+ + 1), 600, 367, 267 and 241 (Found: C, 46.35; H, 5.40; N, 9.50. $C_{28}H_{34}N_5O_8Y\cdot 4H_2O$ requires C, 46.05; H, 5.80; N, 9.60%); ν_{max}(KBr) 3407br (OH), 3250s, 3089m, 1616vs, br, 1497m, 1384vs, 1255m, 1097, 1029, 995, 931, 825, 705 and 619; $\delta_H(D_2O)$ 7.37 (10 H, m, aromatic H), 4.45 (4 H, br m, CH_2Ph), 4.12 (2 H, br, CH_2CO), 3.61–3.38 (10 H, br m, CH_2N) and 2.9–2.3 (8 H, br m, CH_2N).

Crystallography.—$Na[Y(dota)(H_2O)]\cdot 4H_2O$, $C_{16}H_{34}N_4NaO_{13}Y$, *M* = 602.4, triclinic, space group $P\bar{1}$, *a* = 8.676(5), *b* = 9.120(10), *c* = 15.556(13) Å, α = 82.97(9), β = 85.53(6), γ = 81.36(8)°, *U* = 1206(2) $Å^3$, *Z* = 2, D_c = 1.66 g cm^{-3}, *F*(000) = 624. 6998 Independent reflections with $2\theta < 60°$ were collected at 115 K from a colourless prismatic crystal (0.20 × 0.25 × 0.55 mm) using a Rigaku AFC 6S four-circle diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.710 793 Å). Data were corrected for absorption (μ = 25.1 cm^{-1}) by a semiempirical method based on 108 ψ-scans from three reflections (minimum to maximum transmission ratio 0.8605 : 1). The structure was solved by direct methods and refined by a full-matrix least-squares analysis (non-hydrogen atoms with anisotropic, all H atoms with isotropic displacement parameters) to *R* = 0.033, *R′* = 0.034, goodness of fit = 1.25 for 5580 reflections with $|F| > 4\sigma(F)$ and 452 variables using a $w^{-1} = \sigma^2(F) + 0.0001F^2$ weighting scheme. The SHELXTL PLUS programs were used.[19] The residual Fourier map contained no features exceeding the range −0.50 to +0.52 e $Å^{-3}$. Final atomic coordinates are given in Table 1 and selected bond distances and bond angles in Table 2.

$[YL^2(H_2O)]\cdot 3H_2O$. A colourless crystal (0.12 × 0.30 × 0.50 mm) of rather poor quality was isolated from a recrystallisation of the sample from water, and examined at 120 K on a Rigaku AFC 6S four-circle diffractometer using an Oxford cryosystems low-temperature device. $C_{28}H_{36}N_5O_9Y\cdot 3H_2O$, *M* = 729.58, triclinic, *a* = 10.87(2), *b* = 11.20(2), *c* = 15.72(3) Å, α = 87.7(1), β = 74.4(1), γ = 67.7(1)°, *U* = 1614(5) $Å^3$ (by least-squares refinement of 24 reflections with $20 < 2\theta < 28°$), *Z* = 2, D_c = 1.501 g cm^{-3}, *F*(000) = 760, μ = 1.88 mm^{-1}. The intensities of 2965 independent reflections with $2\theta < 45°$ were measured by the θ–2θ scan technique; no absorption correction was applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using SHELXTL PLUS programs.[19] Phenyl groups were refined as rigid bodies, and the remaining non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were included as riding in supposed positions. Fourier difference maps revealed oxygen atoms of three crystallisation water molecules, of which O(4W) was disordered over two positions, A and B, whose occupancies were optimised to 60 and 40%. These atoms were refined in isotropic approximation, and water hydrogens were not located. The refinement converged at *R* = 0.103, *R′* = 0.131, goodness of fit 3.19 for 2300 observed reflections with $|F| > 4\sigma(F)$, 320 variables and weighting scheme $w^{-1} = \sigma^2(F) + 0.001F^2$. The final Fourier difference map contained strong residual features (−1.99 to 1.70 e $Å^{-3}$) in the vicinity of the yttrium atom (series termination was due to lack of high-angle reflections). The atomic coordinates are listed in Table 3, the relevant bond distances and angles in Table 4.

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

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Table 3 Atomic coordinates (× 10^4) for $[YL^2(H_2O)]\cdot 3H_2O$

Atom	*x*	*y*	*z*
Y	2320(1)	1789(1)	2956(1)
O(1)	−23(10)	2746(10)	2791(7)
O(2)	3048(10)	178(10)	1787(7)
O(3)	3052(11)	−1413(11)	970(7)
O(4)	2864(10)	2698(9)	1614(6)
O(5)	3600(10)	2325(10)	3710(7)
O(6)	5592(10)	2281(10)	3888(6)
O(7)	1140(10)	1936(10)	4462(6)
O(8)	1326(10)	1499(10)	5833(7)
O(1W)	1115(10)	4209(10)	3345(6)
N(1)	3751(11)	−361(11)	3651(8)
N(2)	1026(12)	167(12)	3210(8)
N(3)	−2340(13)	3129(12)	3188(8)
N(4)	5103(12)	746(11)	2119(7)
N(5)	4052(13)	2310(12)	168(8)
C(1)	3362(14)	−1388(14)	3525(10)
C(2)	1695(15)	−873(14)	3766(10)
C(3)	−524(16)	1094(14)	3624(11)
C(4)	−962(16)	2382(15)	3146(11)
C(5)	−2961(17)	4472(16)	2857(12)
C(6)	5378(15)	−896(15)	3271(10)
C(7)	5815(17)	−746(14)	2281(10)
C(8)	5332(14)	854(14)	1147(9)
C(9)	3980(16)	2035(14)	998(10)
C(10)	2864(14)	3412(14)	−98(10)
C(11)	−3801(10)	4493(12)	2245(6)
C(12)	−5318	5185	2567
C(13)	−6163	5258	2017
C(14)	−5491	4640	1146
C(15)	−3974	3949	824
C(16)	−3129	3875	1374
C(17)	1209(14)	−463(15)	2347(9)
C(18)	2587(15)	−605(18)	1632(10)
C(19)	3328(15)	56(14)	4627(9)
C(20)	1823(15)	1255(14)	5011(10)
C(21)	1827(10)	3009(10)	−332(6)
C(22)	1588	1968	55
C(23)	628	1634	−175
C(24)	−93	2341	−793
C(25)	145	3382	−1181
C(26)	1106	3716	−951
C(27)	5746(16)	1469(14)	2463(10)
C(28)	4919(17)	2035(14)	3427(11)
O(2W)	8532(18)	4265(17)	5416(10)
O(3W)	1686(21)	3665(21)	6335(12)
O(4WA)	3666(25)	4202(24)	5202(14)
O(4WB)	4419(32)	4834(30)	4789(19)

Table 4 Bond lengths (Å) and angles (°) for $[YL^2(H_2O)]\cdot 3H_2O$

Y–O(1)	2.33(1)	Y–O(2)	2.32(1)
Y–O(4)	2.36(1)	Y–O(5)	2.33(1)
Y–O(7)	2.34(1)	Y–O(1W)	2.40(1)
Y–N(1)	2.56(1)	Y–N(2)	2.74(2)
Y–N(4)	2.62(1)	O(1)–C(4)	1.26(2)
O(2)–C(18)	1.26(3)	O(4)–C(9)	1.24(1)
O(5)–C(28)	1.26(2)	O(7)–C(20)	1.28(2)
O(1)–Y–O(2)	87.3(4)	O(1)–Y–O(4)	84.8(4)
O(2)–Y–O(4)	71.7(4)	O(1)–Y–O(5)	138.7(3)
O(2)–Y–O(5)	133.0(3)	O(4)–Y–O(5)	98.6(4)
O(1)–Y–O(7)	84.3(4)	O(2)–Y–O(7)	130.8(4)
O(4)–Y–O(7)	154.2(3)	O(5)–Y–O(7)	75.1(4)
O(1)–Y–O(1W)	71.1(4)	O(2)–Y–O(1W)	141.7(4)
O(4)–Y–O(1W)	75.1(3)	O(5)–Y–O(1W)	70.2(4)
O(7)–Y–O(1W)	79.3(3)	O(1)–Y–N(1)	130.9(4)
O(2)–Y–N(1)	81.4(4)	O(4)–Y–N(1)	134.3(3)
O(5)–Y–N(1)	73.6(4)	O(7)–Y–N(1)	68.7(3)
O(1W)–Y–N(1)	136.6(4)	O(1)–Y–N(2)	63.3(4)
O(2)–Y–N(2)	63.5(4)	O(4)–Y–N(2)	124.8(4)
O(5)–Y–N(2)	135.4(4)	O(7)–Y–N(2)	69.5(4)
O(1W)–Y–N(2)	126.2(3)	N(1)–Y–N(2)	68.9(4)
O(1)–Y–N(4)	145.1(4)	O(2)–Y–N(4)	67.8(4)
O(4)–Y–N(4)	64.8(3)	O(5)–Y–N(4)	66.6(4)
O(7)–Y–N(4)	130.5(4)	O(1W)–Y–N(4)	113.6(4)
N(1)–Y–N(4)	71.1(4)	N(2)–Y–N(4)	120.0(4)

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