Mo2—O1	1.70 (2)	Mo4—O9^{ii}	1.72 (2)
Mo2—O4^{iv}	1.73 (2)	Mo4—O6	1.933 (14)
Mo2—O3^{v}	1.959 (15)	Mo4—O8^{ii}	1.93 (2)
Mo2—O6^{ii}	2.00 (2)	Mo4—O3^{viii}	2.23 (2)
Mo2—O6^{vi}	2.29 (2)	Mo4—O7	2.438 (15)
Mo2—O9	2.30 (2)	N—C	1.46 (3)
Mo3—O10^{vii}	1.668 (14)		

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

The powder diffraction pattern was indexed in a monoclinic system using the Ito method from CSD software (Akselrud et al., 1993). The systematic absences among hkl and h0l reflections lead to the possible space groups Cc and C2/c. The centrosymmetric space group C2/c was chosen and confirmed later during the crystal structure determination. The cell dimensions together with the 7.3% weight loss at 583 K for the reaction

$$(NH_3CH_3)_x MoO_{3+\frac{x}{2}} \xrightarrow{(t^\circ, O_2)} MoO_3$$
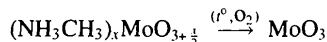
allowed us to determine the exact composition as $(NH_3CH_3)_2[Mo_7O_{22}]$. Only two molybdates were known with the same composition: $Cs_2Mo_7O_{22}$ (Gatehouse & Miskin, 1975) and $Tl_2Mo_7O_{22}$ (Tolédano, Touboul & Paulette, 1976). Their symmetry appears to be the same and their cell dimensions are very similar to those of the methylammonium compound. This fact allowed us to use the atomic coordinates from the Tl compound as a starting model in the Rietveld refinement. The positions of the remaining atoms were located from the difference Fourier map after least-squares profile fitting of the known atomic parameters. The N atom in the methyl-ammonium cation differs from the C atom by having much shorter contacts with neighboring O atoms due to hydrogen bonding (N···O 2.8 versus C···O 3.2 Å). The final Rietveld refinement (Fig. 3) was performed using GSAS (Larson & Von Dreele, 1990). Individual isotropic atomic displacement parameters were refined only for Mo atoms and a single parameter was used for the O atoms and atoms of the methyl-ammonium cation. A surface roughness absorption correction (Suortti, 1972) was applied.

Data collection: DMS software from Scintag. Cell refinement: CSD (Akselrud et al., 1993). Data reduction: CSD. Program(s) used to refine structure: CSD, GSAS (Larson & Von Dreele, 1990). Molecular graphics: POLIEDRI (Pilati, 1990), INSIGHTII (Biosym Technologies, 1995). Software used to prepare material for publication: CSD, GSAS.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1181). Services for accessing these data are described at the back of the journal.

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Potassium Diaqua(ethylenediaminetetraacetato)ytterbate(III) Pentahydrate

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Abstract

The Yb atom in the title compound, $K[Yb(C_{10}H_{12}N_2O_8)(H_2O)_2].5H_2O$, is eight-coordinate through two N and four O atoms in edta, and two water O atoms, where edta denotes ethylenediaminetetraacetate. The geometry around the Yb atom is influenced by the size and electrostatic properties of the countercations.

Comment

The crystal structures of several lanthanide–edta (Ln–edta) complexes (where edta denotes ethylenediamine-tetraacetate) have been reported and it has been suggested that the coordination numbers of the complexes depend on the changing ionic radii; a ten-coordinate complex for La (Lind, Lee & Hoard, 1965), nine-coordinate complexes for La (Hoard, Lee & Lind, 1965; Nakamura, Kurisaki, Wakita & Yamaguchi, 1995), Nd

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(Matković-Čalogović, 1988; Nakamura *et al.*, 1995), Pr, Sm, Gd (Templeton, Templeton, Zalkin & Ruben, 1982), Eu (Nakamura *et al.*, 1995), Dy (Nassimbeni, Wright, van Niekerk & McCallum, 1979) and Ho (Templeton, Templeton & Zalkin, 1985), and an eight-coordinate complex for Yb (Nassimbeni *et al.*, 1979). It is expected that the molecular structures and coordination numbers in the complex anions are probably influenced by the countercations because electrostatic interaction has assumed the primary role in the bonding. In this work, we have investigated the stereochemical effects of the countercations and obtained more information on Yb–edta complexes.

(1)
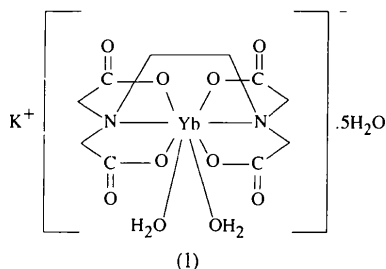
As shown in Fig. 1, the structure of the title compound, (1), is similar to that of the corresponding complex with Cs^+, (2) (Nassimbeni *et al.*, 1979). The Yb atom in (1) is surrounded by two N and four O atoms in edta, and two water O atoms (O9 and O10). In the Yb complex, the bond distances around the Yb atom for the K^+ salt are somewhat different from those of the Cs^+ salt. Specifically, the Yb—O distances of the carboxylate in (1) are somewhat longer (0.011 Å) than those in (2), while the Yb—N and Yb—O(water) distances in (1) are somewhat shorter (0.026 and 0.019 Å) than those in (2). In addition to the slight differences in bond distances, there are some significant differences in bond angles. The bond angles related to the O9 and O10 water atoms are significantly
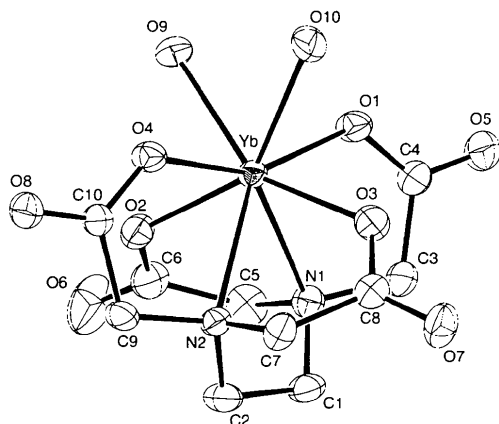
different, *e.g.* N1—Yb—O9 121.35 (10)° [129.2 (2)° for (2)], O2—Yb—O9 72.16 (9)° [80.6 (2)°], O3—Yb—O9 148.77 (9)° [141.7 (2)°], *etc.* These will depend on the interactions between K^+ and O9 [2.837 (3) Å] or O10 [2.919 (3) Å].

Accordingly, it seems that the geometry around the lanthanide atom will be influenced by the size and electrostatic properties of the countercations.

Although most of the nine-coordinate Ln–edta complexes have similar chemical formulae and crystallize in the same orthorhombic space group $Fdd2$, the K^+ salt, (1), is the pentahydrate in space group $P\bar{1}$ and the Cs^+ salt, (2), is the trihydrate in space group $P2_1/c$. Furthermore, K^+ is surrounded by seven $K^+ \cdots O$ close contacts having values of 2.612 (3)–3.082 (4) Å (average 2.858 Å), while Cs^+ is surrounded by six close contacts having values < 3.40 Å (Nassimbeni *et al.*, 1979). The differences in the crystal water molecules and the crystal systems for the lanthanide complexes also seem to be influenced by the countercations.
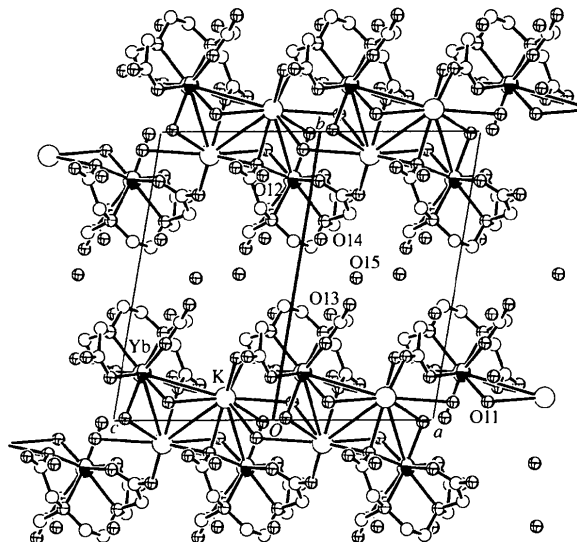

Fig. 2. A packing diagram of the title compound.

Experimental

An aqueous solution (0.005 mol dm^{-3}) of ethylenediaminetetraacetic acid (H_4edta) neutralized by K_2CO_3 was added to an aqueous solution of $Yb(CH_3COO)_3.4H_2O$ (1:1 molar ratio) and stirred for 2 h at room temperature. Colourless single crystals were obtained by allowing the concentrated solution to stand in a refrigerator for a week.

Crystal data

$K[Yb(C_{10}H_{12}N_2O_8)(H_2O)_2].$-$5H_2O$	Mo $K\alpha$ radiation
	$\lambda = 0.7107$ Å
$M_r = 626.46$	Cell parameters from 25
Triclinic	reflections
$P\bar{1}$	$\theta = 14.9–15.0°$

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title anion with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

$a = 9.097\,(2)$ Å
$b = 13.940\,(2)$ Å
$c = 8.933\,(3)$ Å
$\alpha = 98.89\,(2)°$
$\beta = 114.81\,(2)°$
$\gamma = 83.16\,(2)°$
$V = 1014.0\,(5)$ Å^3
$Z = 2$
$D_x = 2.052$ Mg m^{-3}
D_m not measured

$\mu = 4.89$ mm^{-1}
$T = 296$ K
Stick
$0.25 \times 0.25 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-7S diffractometer
ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{min} = 0.326$, $T_{max} = 0.376$
4957 measured reflections
4664 independent reflections

4385 reflections with
  $I > 3\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.49°$
$h = 0 \rightarrow 11$
$k = -17 \rightarrow 18$
$l = -11 \rightarrow 10$
3 standard reflections
  every 150 reflections
  intensity decay: 4.87%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.038$
$S = 1.007$
4384 reflections
262 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)$
  $+ 0.00053|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.0471$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -2.46$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Yb—O1	2.279 (2)	Yb—O9	2.337 (2)
Yb—O2	2.256 (2)	Yb—O10	2.350 (2)
Yb—O3	2.249 (2)	Yb—N1	2.506 (3)
Yb—O4	2.304 (2)	Yb—N2	2.531 (3)
O1—Yb—O2	103.78 (9)	O3—Yb—O9	148.77 (9)
O1—Yb—O3	86.20 (9)	O3—Yb—O10	74.90 (9)
O1—Yb—O4	155.86 (9)	O3—Yb—N1	77.34 (10)
O1—Yb—O9	79.81 (9)	O3—Yb—N2	69.32 (9)
O1—Yb—O10	81.35 (9)	O4—Yb—O9	83.07 (9)
O1—Yb—N1	67.69 (9)	O4—Yb—O10	77.95 (9)
O1—Yb—N2	135.71 (8)	O4—Yb—N1	136.36 (9)
O2—Yb—O3	138.74 (9)	O4—Yb—N2	67.51 (8)
O2—Yb—O4	86.85 (9)	O9—Yb—O10	75.47 (9)
O2—Yb—O9	72.16 (9)	O9—Yb—N1	121.35 (10)
O2—Yb—O10	145.61 (9)	O9—Yb—N2	137.71 (9)
O2—Yb—N1	70.26 (9)	O10—Yb—N1	139.37 (9)
O2—Yb—N2	76.39 (9)	O10—Yb—N2	123.58 (9)
O3—Yb—O4	100.15 (9)	N1—Yb—N2	71.15 (9)

The non-H atoms were refined anisotropically. H atoms were included but not refined. All H atoms, except for those of the water molecules, were calculated and fixed at their positions relative to their parent C atoms, with C—H = 0.95 Å. The water H atoms were found by the difference Fourier technique.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *TEXSAN*. Program(s) used to refine structure: *TEXSAN*.

Molecular graphics: *ORTEP*II (Johnson, 1976) and *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Tetracaesium Bis(diethylenetriamine-N,N,N',N'',N''-pentacetato)didysprosate(III) Tridecahydrate

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Abstract

The structure of the title compound, Cs$_4$[Dy$_2$(C$_{14}$H$_{18}$-N$_3$O$_{10}$)$_2$].13H$_2$O, is unlike that of any previously reported Ln–DTPA complex (where DTPA is diethyl-

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