*Acta Cryst.* (1979). B**35**, 1341–1345

# Packing Patterns in Lanthanide–edta Complexes: Crystal and Molecular Structures of Sodium Triaqua(ethylenediaminetetraacetato)dysprosate(III) Pentahydrate and Caesium Diaqua(ethylenediaminetetraacetato)ytterbate(III) Trihydrate

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(*Received* 11 *December* 1978; *accepted* 20 *February* 1979)

## Abstract

$Na^+[Dy(C_{10}H_{12}N_2O_8)(H_2O)_3]^-.5H_2O$, $Na^+$ $C_{10}H_{18}$-$DyN_2O_{11}^-.5H_2O$, crystallizes in space group *Fdd*2 with $a$ = 19·34 (1), $b$ = 35·40 (2), $c$ = 12·116 (6) Å, $Z$ = 16. $Cs^+[Yb(C_{10}H_{12}N_2O_8)(H_2O)_2]^-.3H_2O$, $Cs^+$ $C_{10}H_{16}N_2O_{10}Yb^-.3H_2O$ crystallizes in space group $P2_1/c$ with $a$ = 12·935 (6), $b$ = 8·997 (5), $c$ = 17·22 (1) Å, $\beta$ = 106·7 (2)°, $Z$ = 4. The structures were refined to a final $R$ of 0·045 and 0·050 respectively. The decrease in ionic radius from $Dy^{3+}$ to $Yb^{3+}$ results in a change in coordination number of the $Ln^{3+}$ ion from nine to eight with concomitant loss of a water molecule.

## Introduction

Previous work on the structures of edta salts of the lanthanides, having general formula $MLnA.8H_2O$ ($M$ = monovalent cation, Ln = lanthanide), has shown that several of these compounds are isomorphous, crystallizing in the space group *Fdd*2 with $Z$ = 16, and that this isomorphism is remarkably indifferent to the choice of monovalent cation: $Na^+$, $K^+$, $NH_4^+$. Furthermore, consideration of relative atomic sizes suggested that in the sequence $La^{3+}$ to $Lu^{3+}$ there should be a transition from nine-coordinated $Ln(OH_2)_3A^-$ to eight-coordinated $Ln(OH_2)_2A^-$, with a prediction that Tb would be eight-coordinated (Hoard, Lee & Lind, 1965). However, the structure of $NaTbA.8H_2O$ shows Tb to be nine-coordinated (Lee, 1967). It was therefore decided to investigate the structures of both the Dy and Yb salts to determine their coordinations and packing patterns.

## Experimental

Crystals of the Dy complex were prepared by refluxing 10 mmol of dysprosium oxide and 25 mmol of $H_4$ edta in 50 ml water, for 15 h, periodically adding small sodium hydroxide pellets until the oxide dissolved and the pH reached 5·5. Cooling and evaporation yielded the desired product. The Yb complex was prepared in an analogous manner.

The lattice constants were obtained by least squares from the settings of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda$ = 0·7107 Å). During data collection three reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details are listed in Table 1. The data were corrected for Lorentz–polarization effects but not for absorption.

## Solution and refinement of the structures

$Na[Dy(edta)(H_2O)_3].5H_2O$ (I) was solved by locating the Dy atom in a Patterson map; subsequent weighted difference syntheses yielded the positions of all the remaining non-hydrogen atoms. The final full-matrix least-squares refinement was carried out with Dy anisotropic and the remaining non-hydrogen atoms isotropic. At no stage of the refinement could H atoms be located in difference maps and they were therefore omitted. $Cs[Yb(edta)(H_2O)_2].3H_2O$ (II) was solved in a similar manner except that in the final stages methylenic H atoms did appear in difference maps. The latter were therefore included in the final model with constrained refinement (C—H = 1·08 Å) and a single temperature factor. The water H atoms could not be located and were omitted. Details of the final refinement are given in Table 1. Tables 2 and 3 show the final atomic coordinates and temperature factors for (I) and (II) respectively.†

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† Lists of hydrogen atomic coordinates for (II) and structure factors for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34227 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/061341-05$01.00

Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of* (I) *and* (II)

| Crystal data | (I) | (II) |
|---|---|---|
| Molecular formula | $Na^+[Dy(edta)(H_2O)_3]^-.5H_2O$ | $Cs^+[Yb(edta)(H_2O)_2]^-.3H_2O$ |
| $M_r$ | 617·8 | 684·2 |
| Space group | *Fdd*2 | $P2_1/c$ |
| $a$ | 19·34 (1) Å | 12·935 (6) Å |
| $b$ | 35·40 (2) | 8·997 (5) |
| $c$ | 12·116 (6) | 17·22 (1) |
| $\beta$ | | 106·7 (2)° |
| $D_m$ | 1·96 Mg $m^{-3}$ | 2·35 Mg $m^{-3}$ |
| $D_c$ | 1·98 for $Z = 16$ | 2·37 for $Z = 4$ |
| $\mu$(Mo $K\alpha$) | 3·51 $mm^{-1}$ | 6·47 $mm^{-1}$ |
| $F(000)$ | 4912 | 1300 |
| Data collection | | |
| Crystal dimensions | 0·2 × 0·3 × 0·5 mm | 0·25 × 0·2 × 0·2 mm |
| Scan mode | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| Scan width | 1·2° $\theta$ | 1·2° $\theta$ |
| Scan speed | 0·03° $\theta\,s^{-1}$ | 0·04° $\theta\,s^{-1}$ |
| Range scanned ($2\theta$) | 6–44° | 6–50° |
| Stability of standard reflections | 1·7% | 0·65% |
| Number of reflections collected | 1423 | 3614 |
| Number of observed reflections | 1192 with $I(\mathrm{rel}) > 3\sigma I(\mathrm{rel})$ | 3354 with $I(\mathrm{rel}) > 2\sigma I(\mathrm{rel})$ |
| Number of variables | 125 | 120 |
| $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ | 0·045 | 0·050 |
| $R_w = \Sigma\, w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma\, w^{1/2}\|F_o\|$ | 0·043 | 0·058 |
| Weighting scheme $w$ | $(\sigma^2 F)^{-1}$ | $(\sigma^2 F + 2 \times 10^{-3} F)^{-1}$ |
| $U$ (methylene H) | – | 0·018 Å$^2$ |

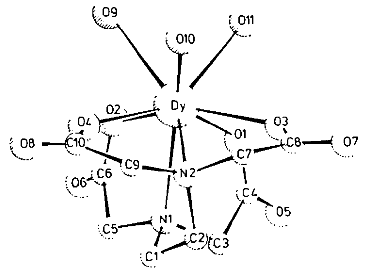

Fig. 1. Perspective view of $Dy^{3+}$ complex anion with atomic nomenclature.

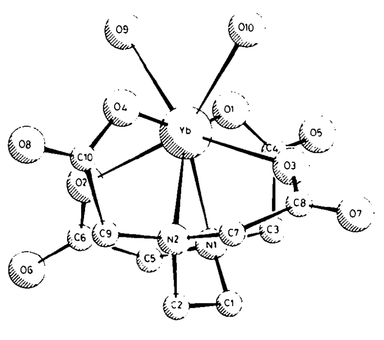

Fig. 2. Perspective view of $Yb^{3+}$ complex anion with atomic nomenclature.

## Description of the structure and discussion

The molecular structures with atomic nomenclature of the two compounds appear in Figs. 1 and 2. In (I), the structure around the central ion consists of a girdle of four O atoms (one each from the four acetate groups) on either side of which are bonded three waters and two N atoms effectively *trans* to each other. The coordination geometry can best be described by a quasi-mirror passing through $Dy^{3+}$ and the two N atoms. In this approximation C(1) and C(2) of the puckered ethylenediamine ring are omitted. In the $Yb^{3+}$ complex, the eight-coordinated square antiprismatic geometry (Fig. 3) shows effectively twofold symmetry about an axis bisecting the angle N(1)—Yb—N(2). A certain amount of puckering in the five chelate rings of the edta moiety is evident in both compounds, but bond lengths and angles (Table 4) were comparable with those found in similar metal-ion–edta crystal studies (Weakliem & Hoard, 1959; Lind, Hamor, Hamor & Hoard, 1964). Thus in $Li[Fe(edta)(H_2O)]$, the 114·2° encountered at a methylene C atom and the 115·6° at a carboxylate C atom represent examples of maximum angular strain in the chelate rings for this compound; analogous deviations from ideal tetrahedral and $sp^2$ geometry in the present study are respectively 111·9 and 115·5° in (I) and 114·1 and 115·2° in (II).

Assuming that the nature of the cation does not radically influence coordination to the central Ln ion, the decreasing atomic radius of the latter is manifested in the expulsion of a water molecule from the inner coordination sphere on changing from $Dy^{3+}$ to $Yb^{3+}$. Hoard, Lee & Lind (1965) report that, for $[La(edta)(H_2O)_3]^-$, the displacement of $La^{3+}$ from the mean plane of the four complexed O atoms of edta is 0·60 Å on the side away from the N atoms. In (I), this distance is 0·48 Å, a decrease of 0·12 Å, and illustrates the enhanced ability of edta to envelop more effectively the smaller cation. In (II) this trend is continued to such an extent as to cause the rejection of one water molecule with consequent change in coordination number.

Bell (1977) discusses the largely electrostatic interaction between Ln ion and ligand which causes increasing stability as the size of $Ln^{3+}$ decreases. Thus the average of the four $Ln^{3+}$—O lengths is 2·507 in $[La(edta)(3H_2O)]^-$, 2·319 in (I) and 2·262 Å in (II). The average $Ln^{3+}$—N and $Ln^{3+}$—$OH_2$ lengths in the three structures show similar shortening, having average values of 2·755, 2·628 and 2·533 Å respectively for the former type of bond, and 2·580, 2·462 and 2·369 Å for the latter.

Table 2. *Fractional atomic coordinates* (×10⁴) *and temperature factors* (Å² ×10³) *for* (I)

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Dy | 823 (0) | 1553 (0) | 0 | * |
| $Na^+$ | 1372 (5) | 1321 (3) | 3203 (9) | 54 (3) |
| O(1) | 963 (7) | 1822 (4) | 1862 (12) | 28 (4) |
| O(2) | −290 (8) | 1677 (4) | 790 (13) | 41 (4) |
| O(3) | 2029 (8) | 1682 (4) | 380 (12) | 38 (4) |
| O(4) | 173 (8) | 1640 (4) | −1555 (13) | 33 (4) |
| O(5) | 1054 (9) | 2307 (5) | 3001 (15) | 53 (5) |
| O(6) | −1008 (9) | 2089 (5) | 1575 (15) | 63 (5) |
| O(7) | 3103 (7) | 1766 (4) | −211 (13) | 40 (4) |
| O(8) | 68 (8) | 1703 (4) | −3391 (13) | 39 (5) |
| O(9) | 22 (7) | 980 (3) | −92 (13) | 33 (3) |
| O(10) | 1341 (9) | 1104 (4) | −1168 (13) | 36 (5) |
| O(11) | 1301 (8) | 1065 (4) | 1260 (12) | 29 (4) |
| N(1) | 558 (8) | 2283 (4) | 150 (18) | 35 (5) |
| N(2) | 1468 (8) | 1939 (5) | −1523 (14) | 25 (5) |
| C(1) | 753 (12) | 2477 (8) | −899 (22) | 36 (7) |
| C(2) | 1459 (11) | 2352 (6) | −1252 (19) | 34 (6) |
| C(3) | 929 (13) | 2453 (8) | 1072 (22) | 37 (8) |
| C(4) | 974 (12) | 2163 (7) | 2042 (21) | 41 (7) |
| C(5) | −217 (11) | 2337 (6) | 318 (18) | 36 (6) |
| C(6) | −501 (12) | 2016 (6) | 936 (20) | 38 (6) |
| C(7) | 2216 (12) | 1807 (6) | −1547 (20) | 37 (6) |
| C(8) | 2458 (11) | 1768 (6) | −404 (17) | 27 (5) |
| C(9) | 1151 (11) | 1854 (6) | −2622 (22) | 36 (6) |
| C(10) | 411 (10) | 1727 (5) | −2515 (24) | 32 (5) |
| *W*(1) | 634 (8) | 390 (4) | 1089 (13) | 47 (5) |
| *W*(2) | 1472 (11) | 985 (6) | 5643 (19) | 85 (7) |
| *W*(3) | 1212 (12) | 1783 (7) | 4603 (20) | 102 (8) |
| *W*(4) | 194 (14) | 1121 (8) | 3460 (24) | 132 (10) |
| *W*(5) | 2594 (17) | 2154 (9) | 5720 (29) | 193 (14) |

* Anisotropic parameters in the form

$$T = \exp[-2\pi^2(\varepsilon_i\varepsilon_j h_i h_j a_i^* a_j^* U_{ij})]$$

| (Å² ×10³) | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Dy | 13 (0) | 32 (1) | 23 (1) | 1 (1) | −2 (1) | −1 (1) |

Table 3. *Fractional atomic coordinates* (×10⁴) *and temperature factors* (Å² ×10³) *for* (II)

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Yb | 3758 (0) | 964 (0) | 1549 (0) | * |
| $Cs^+$ | 6039 (0) | 2308 (1) | 5008 (0) | * |
| O(1) | 4122 (5) | 77 (7) | 2834 (4) | 26 (1) |
| O(2) | 2651 (5) | −873 (6) | 922 (4) | 23 (1) |
| O(3) | 3611 (5) | 3310 (7) | 1957 (4) | 23 (1) |
| O(4) | 4007 (5) | 1225 (7) | 299 (4) | 24 (1) |
| O(5) | 3965 (5) | 503 (8) | 4068 (4) | 33 (2) |
| O(6) | 1133 (6) | −2197 (8) | 693 (4) | 35 (2) |
| O(7) | 3173 (7) | 5687 (6) | 1651 (5) | 46 (2) |
| O(8) | 3227 (5) | 698 (7) | −1008 (4) | 30 (2) |
| O(9) | 5051 (5) | −906 (6) | 1577 (4) | 22 (1) |
| O(10) | 5516 (5) | 2011 (7) | 1972 (4) | 31 (2) |
| N(1) | 2098 (6) | 860 (7) | 2041 (4) | 20 (2) |
| N(2) | 2198 (6) | 2302 (8) | 561 (4) | 20 (2) |
| C(1) | 1308 (7) | 2003 (11) | 1651 (5) | 27 (2) |
| C(2) | 1142 (8) | 2070 (11) | 746 (6) | 29 (2) |
| C(3) | 2458 (7) | 1116 (10) | 2935 (6) | 25 (2) |
| C(4) | 3614 (6) | 503 (10) | 3331 (5) | 20 (2) |
| C(5) | 1632 (8) | −665 (11) | 1879 (6) | 29 (2) |
| C(6) | 1798 (7) | −1295 (10) | 1084 (6) | 24 (2) |
| C(7) | 2516 (8) | 3892 (10) | 634 (6) | 30 (2) |
| C(8) | 3125 (7) | 4366 (10) | 1487 (5) | 23 (2) |
| C(9) | 2118 (6) | 1726 (10) | −262 (5) | 21 (2) |
| C(10) | 3187 (7) | 1185 (9) | −338 (5) | 19 (2) |
| *W*(1) | −1403 (6) | 3180 (9) | 809 (5) | 44 (2) |
| *W*(2) | −76 (7) | 608 (10) | 3591 (6) | 55 (2) |
| *W*(3) | 8682 (8) | 822 (10) | 1954 (7) | 65 (3) |

* Anisotropic thermal parameters

| (Å² ×10³) | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Yb | 21 (0) | 12 (0) | 10 (0) | 1 (0) | 2 (0) | 0 |
| $Cs^+$ | 34 (0) | 25 (0) | 31 (0) | 10 (0) | 8 (0) | 2 (0) |

## Packing patterns and close contacts

(I) crystallizes in the space group *Fdd*2. O···O contacts in the range 2·474 to 2·985 Å (Table 5) are shown by dotted lines in the left half of the [001] projection shown in Fig. 4 and represent probable H-bonding. Stronger indications of formal H-bonds were not possible due to the uncertainty of the H atom positions on any of the water molecules. As regards $Na^+$···O close contacts, the environment of the $Na^+$ atom can best be described in terms of its position at the centre of a highly distorted octahedron, depicted by broken lines in the right half of Fig. 4. The $Na^+$···O distance varies from 2·40 to 2·54 Å, and agrees favourably with similar results obtained by Fallon & Gatehouse (1976), who measured distorted octahedral $Na^+$···O distances varying between 2·356 and 2·481

Table 4. *Bond lengths* (Å) *and selected angles* (°), *with e.s.d.'s in parentheses for the complex anions*

| | $[Dy(edta)(H_2O)_3]^-$ | $[Yb(edta)(H_2O)_2]^-$ |
|---|---|---|
| O(1)–*M* | 2·464 (14) | 2·269 (6) |
| O(2)–*M* | 2·396 (15) | 2·249 (6) |
| O(3)–*M* | 2·420 (14) | 2·250 (6) |
| O(4)–*M* | 2·285 (15) | 2·278 (6) |
| O(9)–*M* | 2·553 (12) | 2·363 (6) |
| O(10)–*M* | 2·351 (16) | 2·374 (6) |
| O(11)–*M* | 2·483 (14) | |
| N(1)–*M* | 2·642 (16) | 2·527 (7) |
| N(2)–*M* | 2·614 (17) | 2·538 (7) |
| C(1)–N(1) | 1·493 (31) | 1·469 (11) |
| C(1)–C(2) | 1·498 (30) | 1·511 (12) |
| C(2)–N(2) | 1·496 (25) | 1·503 (11) |
| C(3)–N(1) | 1·458 (31) | 1·492 (11) |
| C(3)–C(4) | 1·561 (35) | 1·556 (11) |
| C(4)–O(5) | 1·277 (25) | 1·219 (11) |
| C(4)–O(1) | 1·229 (25) | 1·278 (10) |
| C(5)–N(1) | 1·523 (25) | 1·493 (11) |
| C(5)–C(6) | 1·466 (29) | 1·553 (13) |
| C(6)–O(6) | 1·276 (26) | 1·233 (11) |
| C(6)–O(2) | 1·280 (24) | 1·271 (11) |
| C(7)–N(2) | 1·520 (26) | 1·484 (11) |
| C(7)–C(8) | 1·469 (30) | 1·513 (13) |
| C(8)–O(7) | 1·269 (23) | 1·220 (11) |
| C(8)–O(3) | 1·298 (22) | 1·289 (11) |
| C(9)–N(2) | 1·496 (30) | 1·484 (10) |
| C(9)–C(10) | 1·505 (27) | 1·507 (11) |
| C(10)–O(8) | 1·254 (28) | 1·248 (11) |
| C(10)–O(4) | 1·289 (28) | 1·289 (10) |
| | | |
| O(1)–*M*–O(4) | 139·7 (5) | 155·6 (2) |
| O(2)–*M*–O(3) | 139·0 (5) | 137·7 (2) |
| O(1)–*M*–O(11) | 70·4 (5) | |
| O(2)–*M*–O(9) | 67·6 (5) | 80·6 (2) |
| O(4)–*M*–O(10) | 80·2 (5) | 82·3 (2) |
| N(1)–*M*–O(9) | 131·5 (4) | 129·2 (2) |
| N(2)–*M*–O(10) | 74·1 (5) | 121·6 (2) |
| O(9)–*M*–O(10) | 72·3 (5) | 70·5 (2) |
| O(9)–*M*–O(11) | 72·6 (5) | |
| O(10)–*M*–O(11) | 75·0 (4) | |
| N(1)–*M*–N(2) | 68·2 (5) | 69·7 (2) |
| C(1)–N(1)–*M* | 110·0 (14) | 111·5 (5) |
| C(2)–C(1)–N(1) | 109·8 (19) | 111·9 (7) |
| C(1)–C(2)–N(2) | 111·1 (19) | 110·8 (7) |
| C(2)–N(2)–*M* | 110·5 (13) | 112·8 (5) |
| C(3)–N(1)–*M* | 111·2 (14) | 107·3 (5) |
| C(4)–C(3)–N(1) | 109·5 (20) | 111·9 (7) |
| C(3)–C(4)–O(5) | 115·5 (21) | 118·6 (7) |
| C(3)–C(4)–O(1) | 120·7 (22) | 115·3 (7) |
| C(4)–O(1)–*M* | 123·0 (15) | 122·9 (5) |
| C(5)–N(1)–*M* | 108·8 (11) | 107·9 (5) |
| C(6)–C(5)–N(1) | 109·9 (18) | 110·4 (7) |
| C(5)–C(6)–O(6) | 116·2 (21) | 118·0 (8) |
| C(5)–C(6)–O(2) | 122·3 (21) | 115·7 (8) |
| C(6)–O(2)–*M* | 120·9 (14) | 125·9 (6) |
| C(7)–N(2)–*M* | 107·8 (12) | 104·7 (5) |
| C(8)–C(7)–N(2) | 108·3 (18) | 114·1 (8) |
| C(7)–C(8)–O(7) | 119·2 (19) | 118·5 (8) |
| C(7)–C(8)–O(3) | 120·5 (18) | 115·2 (8) |
| C(8)–O(3)–*M* | 121·4 (12) | 124·4 (5) |
| C(9)–N(2)–*M* | 109·1 (11) | 107·4 (5) |
| C(10)–C(9)–N(2) | 111·9 (21) | 112·4 (7) |
| C(9)–C(10)–O(8) | 116·8 (24) | 118·5 (7) |
| C(9)–C(10)–O(4) | 119·2 (23) | 117·9 (7) |
| C(10)–O(4)–*M* | 125·5 (13) | 119·7 (5) |

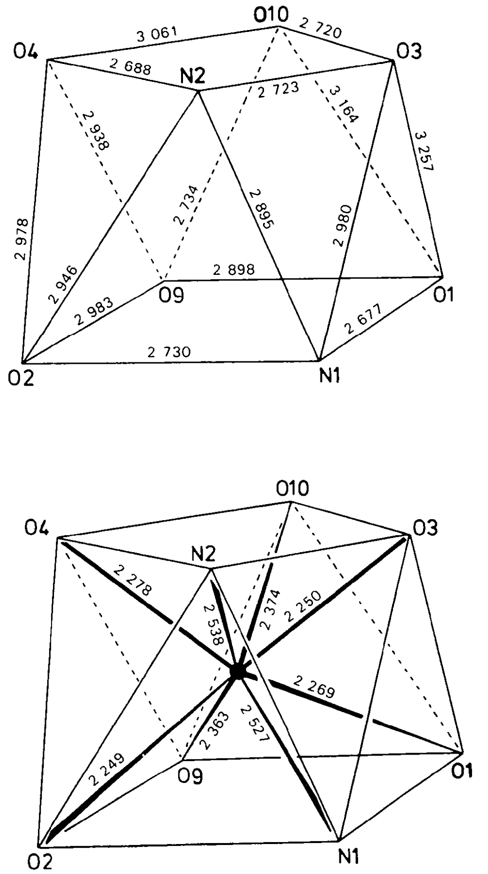

Fig. 3. Square anti-prismatic geometry about the $Yb^{3+}$ ion.

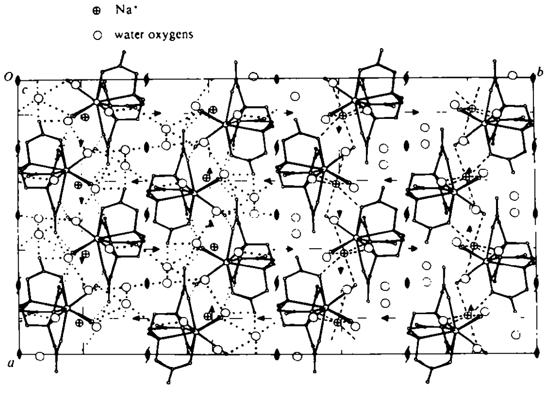

Fig. 4. [001] projection of $Dy^{3+}$ structure. Probable H-bonds are shown by dotted lines in the left half of the figure. The broken lines in the right half show $Na^+\cdots O$ close contacts.

Å in sodium $\mu$-triethylenetetraaminehexaacetato-di[oxovanadate(IV)] decahydrate, and Cameron, Mannan & Rahman (1976) where the $Na^+\cdots O$ distance ranged between 2·35 and 2·56 Å in sodium acetate trihydrate.

Table 5. *Intramolecular and intermolecular hydrogen bonding in* (I)

E.s.d.'s are in parentheses.

Symmetry code

(i) $\frac{1}{2}+x,\ y,\ \frac{1}{2}+z;$

(ii) $\frac{1}{4}+x,\ \frac{1}{4}-y,\ \frac{1}{4}+z;$

(iii) $\frac{1}{4}+x,\ \frac{1}{4}-y,\ -\frac{3}{4}+z;$

(iv) $\frac{1}{4}-x,\ \frac{1}{4}+y,\ \frac{1}{4}+z;$

(v) $\frac{1}{2}-x,\ \frac{1}{2}-y,\ z.$

| | | | |
|---|---|---|---|
| $O(11)\cdots O(1)$ | 2·85 (2) | $O(10)\cdots O(9)$ | 2·90 (2) |
| $O(9)\cdots O(2)$ | 2·76 (2) | $O(9)\cdots O(11)$ | 2·98 (2) |
| $O(11)\cdots O(3)$ | 2·81 (2) | $O(10)\cdots O(11)$ | 2·95 (2) |
| $O(10)\cdots O(4)$ | 2·99 (2) | $O(9)\cdots O(4)$ | 2·95 (2) |
| $W(5)\cdots O(6^{\rm i})$ | 2·90 (4) | $W(1)\cdots O(9)$ | 2·79 (2) |
| $W(2)\cdots O(6^{\rm ii})$ | 2·78 (3) | $W(1)\cdots O(11)$ | 2·72 (2) |
| $O(7)\cdots O(2^{\rm iii})$ | 2·76 (3) | $O(5)\cdots W(1^{\rm iv})$ | 2·69 (2) |
| $O(7)\cdots O(10^{\rm ii})$ | 2·69 (2) | $W(2)\cdots W(4^{\rm ii})$ | 2·77 (3) |
| $O(3)\cdots O(9^{\rm ii})$ | 2·70 (2) | $W(5)\cdots W(4^{\rm ii})$ | 2·77 (4) |
| $O(11)\cdots O(4^{\rm ii})$ | 2·78 (2) | $W(5)\cdots W(1^{\rm ii})$ | 2·79 (4) |
| $W(3)\cdots O(5)$ | 2·70 (3) | $W(5)\cdots W(5^{\rm v})$ | 2·47 (5) |
| $O(10)\cdots O(8^{\rm ii})$ | 2·63 (2) | | |

Table 6. *Intramolecular and intermolecular hydrogen bonding in* (II)

E.s.d.'s are in parentheses.

Symmetry code

(i) $1-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z;$

(ii) $1-x,\ -y,\ -z;$

(iii) $-x,\ -y,\ -z;$

(iv) $-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z;$

(v) $1+x,\ y,\ z.$

| | | | |
|---|---|---|---|
| $O(9)\cdots O(1)$ | 2·90 (1) | $O(9)\cdots O(4)$ | 2·94 (1) |
| $O(10)\cdots O(1)$ | 3·16 (1) | $O(10)\cdots O(4)$ | 3·06 (1) |
| $O(9)\cdots O(2)$ | 2·98 (1) | $O(10)\cdots O(9)$ | 2·73 (1) |
| $O(10)\cdots O(3)$ | 2·72 (1) | | |
| $O(10)\cdots O(1^{\rm i})$ | 2·80 (1) | $O(9)\cdots O(8^{\rm ii})$ | 2·69 (1) |
| $O(3)\cdots O(9^{\rm i})$ | 2·71 (1) | $W(3)\cdots O(8^{\rm ii})$ | 2·88 (1) |
| $W(1)\cdots O(6^{\rm iii})$ | 2·85 (1) | $W(3)\cdots W(1^{\rm v})$ | 2·88 (1) |
| $O(6)\cdots W(2^{\rm iv})$ | 2·87 (1) | $W(2)\cdots W(1^{\rm iv})$ | 2·89 (1) |
| $O(7)\cdots O(10^{\rm i})$ | 2·76 (1) | $W(3)\cdots W(2^{\rm v})$ | 2·82 (1) |

The packing of (II) is shown by the four unit cells as a [010] projection (Fig. 5). The channels of water molecules in the *bc* plane are extensively H-bonded (Table 6), the O···O close contacts being in the range 2·686 to 3·164 Å. Gupta & Mahata (1976) found that in caesium hydrogen acetylenedicarboxylate monohydrate, $Cs^+$ was ninefold coordinated to surrounding O atoms, the $Cs^+\cdots O$ distances ranging from 3·31 to 3·40 Å. In the present study, $Cs^+$ is irregularly surrounded, the six $Cs^+\cdots O$ close contacts having values <3·40 Å.

In (II), the change in the crystal packing from *Fdd*2 to $P2_1/c$ is probably influenced by at least three factors, which are not necessarily independent:

(i) the loss of a water molecule concomitant with the decreasing size of the central ion as the coordination number of the $Ln^{3+}$ changes from nine to eight results in a different geometry of the complex Yb anion;

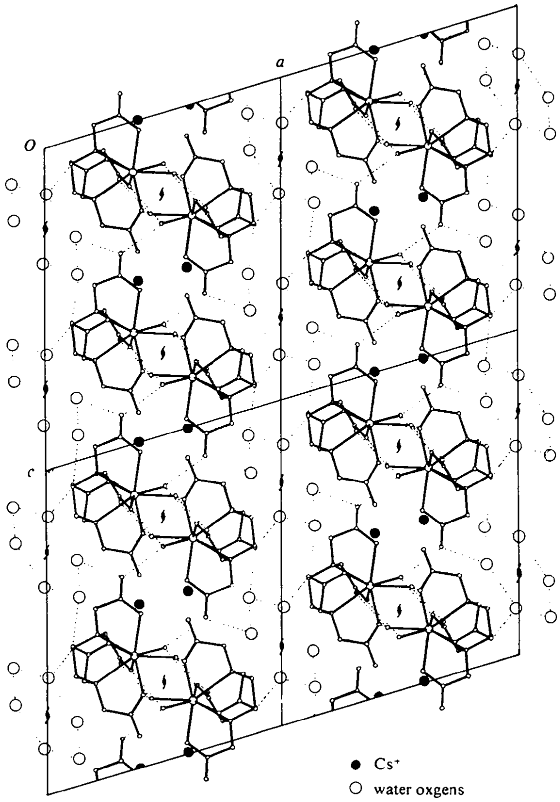

Fig. 5. [010] projection of $Yb^{3+}$ structure. Probable H-bonds are shown by dotted lines.

(ii) the different number of waters of crystallization;

(iii) the large size of the $Cs^+$ cation.

In order to separate these factors we are undertaking a study of the $K^+$ salt of the $Yb^{3+}$ complex.

All calculations were carried out on a Univac 1106 computer at the University of Cape Town.

We thank the Council for Scientific and Industrial Research (Pretoria) for the diffractometer data collection and the CSIR and the University of Cape Town for research grants.

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