Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Bis($\mu$-acetato-$\kappa^3O,O'$:$O'$)bis[bis(acetato-$\kappa^2O,O'$)diaquadysprosium(III)] tetrahydrate

**Ricardo Baggio,[a]* Juan Carlos Muñoz[b] and Mireille Perec[c]**

[a]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, [b]Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile, and [c]Departamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Buenos Aires, Argentina
Correspondence e-mail: baggio@cnea.gov.ar

Received 16 July 2002
Accepted 19 August 2002
Online 21 September 2002

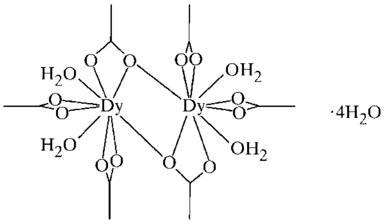
The title compound, $[Dy_2(C_2H_3O_2)_6(H_2O)_4]\cdot 4H_2O$, crystallizes in the form of dimeric units related by an inversion centre. Each cation is nine-coordinate, binding to two water molecules and three acetate groups, two of which are bidentate and the third tridentate. This last acetate group acts as a bridge between neighbouring metal atoms, leading to an intradimer Dy$\cdots$Dy separation of 4.170 (1) Å.

## Comment

The structures of hydrated rare earth acetates are well known, mainly because they can be easily obtained as well shaped crystals by evaporation of aqueous solutions (Gmelin Handbook, 1984). In these crystals, the acetate groups bridge two rare earth cations in a variety of coordination modes, resulting in dimeric and/or polymeric forms (Ouchi *et al.*, 1988). In addition, water ligands are incorporated in the first coordination sphere of the rare earth cations, leading to coordination numbers in hydrated rare earth acetates of 9 or 10.

Rare earth acetates are used as starting materials in a wide range of applications in materials science, including superconductors, magnetic materials and catalysts (Parker & Williams, 1996; Segal, 1989; Wang *et al.*, 1994). We report here the crystal structure of the title dysprosium acetate, $[Dy_2(CH_3COO)_6(H_2O)_4]\cdot 4H_2O$, (I), for which geometric data could not be found. A search of the October 2001 release of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) showed that (I) is isostructural with the reported dimeric acetates of lanthanides of medium-to-small atomic radius, namely Gd [(II); Favas *et al.*, 1980], Eu [(III); Yansheng *et al.*, 1988], Ho [(IV); Bats *et al.*, 1979] and Er [(V); Sawase *et al.*, 1984], as well as with the as yet unreported Tb analogue [(VI); Baggio *et al.*, 2002].

The molecular diagram of (I) (Fig. 1) shows dimeric units related by an inversion centre [at (1,0,1) in the reported coordinates]. The two Dy$^{III}$ metal ions are linked by two bridging tridentate carboxylate groups; one of the carboxylate O atoms in the acetate anion is bound to two Dy atoms, whereas the second O atom is bound to only one. As a result, atoms O2*B* and O2*B*′ bind in a $\mu_2$-bridging manner to both metal centres, forming a monoatomic bridge. Due to the inversion centre, the Dy—O2*B*—Dy′—O2*B*′ loop is perfectly planar.



(I)

The two $DyO_9$ coordination polyhedra are best described as distorted TCTP. The Dy—O$_{aqua}$ distances are 2.342 (3) and 2.357 (3) Å, the shortest in the polyhedra, whereas the Dy—O$_{carboxylate}$ distances display a rather broad range, from 2.365 (3) to 2.558 (3) Å. The resulting intradimer Dy$\cdots$Dy separation is 4.170 (1) Å, and the next shortest distance between Dy centres is 6.213 (1) Å.

Interactions between dimers are through medium-to-weak hydrogen bonds (Table 2), in which all the water H atoms are involved, including an O1*W*—H1*WA*$\cdots$O1*C*$(2-x, -y, 2-z)$ intradimer interaction. The resulting packing is a sequence of broad two-dimensional structures parallel to the crystal-

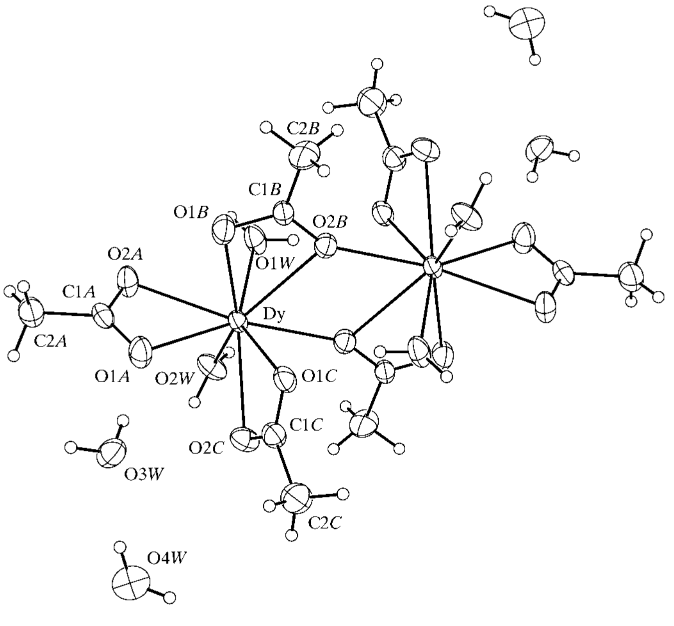


**Figure 1**
A view of the dimeric unit of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S010827010201510X

lographic (001) plane, alternately composed of the dimeric entities (at $z \sim 0$ and $z \sim 1$ in Fig. 2) and of the hydrate water molecules (at $z \sim \frac{1}{2}$). A transverse-cut view of this spatial set-up is shown in Fig. 2, where the hydrogen-bond interactions can be clearly seen; further details are given in the caption.

It should be noted that the size of the lanthanide cation seems to have a negligible effect on the geometric parameters of the dimeric entities; the least-squares fit (Sheldrick, 1991) of the $LnO_9$ coordination polyhedra in (I) with those in compounds (II)–(VI) gave the following maximum deviations: Gd 0.042 (4), Eu 0.038 (4), Ho 0.023 (2), Er 0.053 (5) and Tb 0.022 (2) Å. This family of lanthanide dimers, with essentially the same structure, should be of interest for comparative studies of their different electronic and magnetic properties, in particular superexchange between the lanthanide atoms, which may occur through the bridging O atoms.

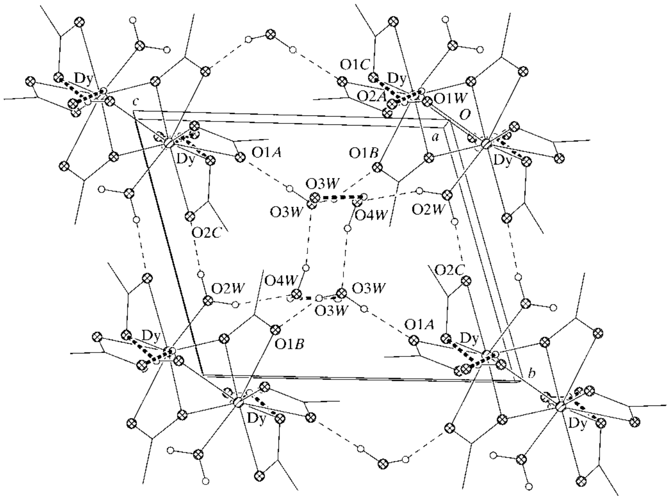


**Figure 2**
A schematic packing view of (I), showing the hydrogen-bonding interactions. H atoms attached to C atoms have been omitted for clarity. The first five hydrogen bonds in Table 2 (which connect the structure in the plane of the paper) have been drawn as simple broken lines; the remaining three (almost vertical in the figure) have been represented by heavy dashed lines.

## Experimental

Dysprosium carbonate (0.20 g) was dissolved in a water–acetic acid solution (25 ml; 1:1 *v*/*v*) and boiled under reflux for 1 h. After one week, colourless crystals of (I) suitable for X-ray diffraction were isolated and dried in air. Analysis calculated for $C_{12}H_{34}Dy_2O_{20}$: C 17.50, H 4.15%; found: C 17.45, H 4.15%. IR spectroscopic analysis, (KBr, cm$^{-1}$): 1540 (*vs*), 1455 (*vs*), 1417 (*vs*), 1385 (*vs*), 1315 (*m*), 1050 (*m*), 1025 (*m*), 965 (*m*), 944 (*m*), 680 (*s*, *br*), 610 (*w*), 475 (*w*). The thermogravimetric analysis diagram shows a weight loss of 16% in the temperature range 356.7–419.5 K, which corresponds to the simultaneous loss of all the crystallization and coordination water molecules (calculated 15.5%).

### *Crystal data*

$[Dy_2(C_2H_3O_2)_6(H_2O)_4]\cdot 4H_2O$
$M_r = 823.39$
Triclinic, $P\overline{1}$
$a = 8.872$ (1) Å
$b = 9.249$ (1) Å
$c = 10.456$ (1) Å
$\alpha = 91.71$ (1)°
$\beta = 114.11$ (1)°
$\gamma = 117.88$ (1)°
$V = 665.8$ (2) Å$^3$

$Z = 1$
$D_x = 2.054$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 112 reflections
$\theta = 3.7$–24.1°
$\mu = 5.65$ mm$^{-1}$
$T = 293$ (2) K
Block, colourless
0.34 × 0.28 × 0.20 mm

### *Data collection*

Bruker SMART diffractometer with APEX CCD detector
$\varphi$ and $\omega$ scans
Absorption correction: refined on $\Delta F$ (*SADABS* in *SAINT–NT*; Bruker, 2000)
$T_{\min} = 0.17$, $T_{\max} = 0.31$
3864 measured reflections

2797 independent reflections
2746 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 27.9°$
$h = -11 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 13$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.095$
$S = 1.06$
2797 reflections
182 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0883P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.49$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.05$ e Å$^{-3}$

**Table 1**
Selected interatomic distances (Å).

| | | | |
|---|---|---|---|
| Dy—O1*W* | 2.357 (3) | Dy—O2*A* | 2.458 (3) |
| Dy—O2*W* | 2.342 (3) | Dy—O2*B*$^{\rm i}$ | 2.365 (3) |
| Dy—O1*A* | 2.387 (3) | Dy—O2*B* | 2.558 (3) |
| Dy—O1*B* | 2.444 (3) | Dy—O2*C* | 2.453 (4) |
| Dy—O1*C* | 2.425 (3) | | |

Symmetry code: (i) $2 - x, -y, 2 - z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2*W*—H2*WA*···O2*C*$^{\rm i}$ | 0.83 (5) | 1.88 (5) | 2.715 (5) | 174 (6) |
| O2*W*—H2*WB*···O4*W*$^{\rm i}$ | 0.83 (5) | 1.93 (3) | 2.726 (6) | 161 (6) |
| O3*W*—H3*WA*···O1*A* | 0.83 (5) | 1.95 (3) | 2.773 (4) | 171 (6) |
| O3*W*—H3*WB*···O1*B*$^{\rm ii}$ | 0.83 (5) | 1.91 (3) | 2.723 (4) | 165 (7) |
| O4*W*—H4*WB*···O3*W* | 0.83 (5) | 1.98 (3) | 2.797 (5) | 168 (8) |
| O1*W*—H1*WA*···O1*C*$^{\rm iii}$ | 0.83 (5) | 2.00 (5) | 2.751 (4) | 150 (6) |
| O1*W*—H1*WB*···O2*A*$^{\rm iv}$ | 0.83 (5) | 1.96 (6) | 2.699 (4) | 148 (7) |
| O4*W*—H4*WA*···O3*W*$^{\rm v}$ | 0.83 (5) | 2.19 (3) | 2.893 (5) | 143 (3) |

Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $2 - x, -y, 2 - z$; (iv) $1 - x, -y, 2 - z$; (v) $2 - x, 1 - y, 1 - z$.

H atoms attached to C atoms were added in their expected positions and not refined, but they were allowed to ride. Terminal methyl H atoms in the acetate groups were additionally allowed to rotate. H atoms pertaining to the water molecules were found in difference Fourier maps and were included subject to mild restraints so as to avoid undesirable drifting, with final values of O—H = 0.83 (5) Å and H···H = 1.66 × O—H. A scheme of riding isotropic displacement parameters was used, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}$ of the parent atom.

Data collection: *SMART–NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT–NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

This work was supported by the Universidad de Buenos Aires and by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina). We acknowledge Fundación Andes (grant No. C13575) and CONICYT–FONDAP (grant No. 11980002) for the purchase of a CCD detector, and the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system. MP is a member of CONICET and JCM is a grateful recipient of a Deutscher Akademischer Austauschdienst scholarship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1129). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Baggio, R., Barja, B., Garland, M. T., Aramendia, P. F., Peña, O. & Perec, M. (2002). *Inorg. Chim. Acta.* Submitted.

Bats, J. W., Kalus, R. & Fuess, H. (1979). *Acta Cryst.* B**35**, 1225–1227.

Bruker (2000). *SAINT–NT*. Version 6.02a. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SMART–NT*. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.

Favas, M. C., Kepert, D. L., Skelton, B. W. & White, A. H. (1980). *J. Chem. Soc.* pp. 454–458.

Gmelin (1984). *Gmelin Handbook of Inorganic Chemistry: Sc, Y, La–Lu, Carboxylates*, Part D5. Weinheim: Verlag Chemie.

Ouchi, A., Suzuki, Y., Ohki, Y. & Koizumi, Y. (1988). *Coord. Chem. Rev.* **92**, 29–43.

Parker, D. & Williams, J. A. G. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3613–3746.

Sawase, H., Koizumi, Y., Suzuki, Y., Shimoi, M. & Ouchi, A. (1984). *Bull. Chem. Soc. Jpn*, **57**, 2730.

Segal, D. (1989). *Chemical Synthesis of Advanced Ceramic Materials*. Cambridge University Press.

Sheldrick, G. M. (1991). *SHELXTL/PC*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Wang, S., Pang, Z., Smith, K. D. L. & Wagner, M. J. (1994). *J. Chem. Soc. Dalton Trans.* pp. 955–964.

Yansheng, Y., Lubin, L. & Mak, T. C. W. (1988). *Chin. J. Struct. Chem.* (*Jiegou Huaxue*), **7**, 1.