

of the  $\text{Cu}^{\text{II}}$  ions attain a five-coordinate geometry while the remaining  $(n - 2)$   $\text{Cu}^{\text{II}}$  ions retain a distorted octahedral geometry.

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## Structure of an Erbium Coordination Compound with L-Proline, $\{\text{[Er(Pro)}_2(\text{H}_2\text{O})_5\text{]Cl}_3\}_n$

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**Abstract.** *catena*-Poly[ $\{\text{pentaqua(L-proline-O)-erbio-}\mu\text{-}(\text{L-proline-O:O}')\}$  trichloride],  $\{\text{[Er(C}_5\text{H}_9\text{NO}_2)_2(\text{H}_2\text{O})_5\text{]Cl}_3\}_n$ ,  $M_r = 594.0$ , monoclinic,  $P2_1$ ,  $a = 8.294$  (1),  $b = 10.981$  (3),  $c = 11.934$  (3) Å,  $\beta = 107.04$  (2)°,  $V = 1039.2$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.90$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 45.2$  cm<sup>-1</sup>,  $F(000) = 586$ ,  $T = 298$  K,  $R = 0.0244$  for 1711 unique reflections [ $I > 3\sigma(I_o)$ ]. The crystal consists of one-dimensional chains of infinite length in which one L-proline ligand bridges two neighboring Er ions, the other L-proline ligand being monodentate.

**Introduction.** Rare-earth elements are now used extensively in agriculture, medicine and biochemical research. It is therefore important to understand their biological effects. The structures and properties of some rare-earth amino acid coordination compounds have been investigated (Gao, Tang, Song, Fu & Liu, 1990; Jin, Yang, Yang, Wu & Xu, 1989; Legendiewicz, Huskowska, Argay & Waskowska, 1984; Li & Pan, 1985; Mathur & Srivastava, 1970). In this paper, the crystal structure of an erbium trichloride L-proline coordination compound is reported.

**Experimental.** The title compound was prepared by the reaction of equimolar amounts of erbium tri-

chloride with L-proline in an aqueous solution at pH ≈ 4 for 8 h. The resulting solution was concentrated in a thermostat bath at 323 K until most of the water had evaporated. The concentrated solution was dried in a vacuum desiccator over phosphorus pentoxide for several weeks and colorless crystals were obtained. A prism-shaped crystal of dimensions 0.38 × 0.44 × 0.12 mm was selected for crystal-structure determination. Intensity data were collected at room temperature using a Nicolet R3/m diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Cell parameters were obtained by a least-squares method using 25 reflections with  $5.14 < 2\theta < 21.76^\circ$ . Data were collected with  $3.00 < 2\theta < 48.00^\circ$  using the  $\omega$ - $2\theta$  scan method, and were corrected for Lorentz, polarization and absorption effects (transmission coefficients: min. 0.481, max. 0.933). The range for  $h$  was 0 to 10, for  $k$  0 to 14 and for  $l$  -15 to 15. The intensity variation of one standard reflection (423) was  $\pm 2\%$  about the mean value. The main computer program used was *SHELXTL* (Sheldrick, 1983). Of the 1907 reflections measured, 1845 were independent, of which 1711 were observed [ $I > 3\sigma(I_o)$ ] and were used in the refinements. The structure was solved by Patterson techniques. Full-matrix least-squares refinement on  $F$  of positional and anisotropic thermal parameters. H atoms were placed in calculated positions and assigned isotropic thermal parameters ( $U = 0.08$  Å<sup>2</sup>) and 225 least-

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$B_{\text{eq}}$
Er	989 (1)	5000	5870 (1)	16 (1)
Cl(1)	6671 (2)	4925 (3)	8136 (2)	36 (1)
Cl(2)	4612 (2)	1911 (2)	5099 (2)	31 (1)
Cl(3)	5741 (3)	3731 (2)	2523 (2)	41 (1)
O(1)	-1722 (7)	5299 (5)	4473 (5)	39 (2)
O(2)	381 (6)	3344 (5)	4610 (4)	21 (2)
O(3)	1476 (7)	6552 (5)	4637 (5)	34 (2)
O(4)	1110 (9)	2583 (8)	8244 (7)	60 (3)
O(5)	3550 (7)	4598 (5)	5374 (5)	26 (2)
O(6)	2434 (7)	3488 (5)	7096 (5)	35 (2)
O(7)	-294 (6)	6694 (5)	6469 (4)	21 (2)
O(8)	-849 (8)	4111 (6)	6780 (6)	41 (2)
O(9)	3056 (7)	6023 (5)	7315 (5)	34 (2)
N(1)	2123 (8)	2663 (6)	2234 (6)	27 (2)
N(2)	5243 (9)	2231 (7)	7836 (6)	31 (2)
C(1)	643 (9)	2788 (6)	3772 (6)	16 (2)
C(2)	1378 (10)	3511 (7)	2933 (7)	25 (3)
C(3)	1061 (12)	2689 (13)	1008 (8)	53 (4)
C(4)	300 (16)	3911 (12)	841 (9)	59 (4)
C(5)	7 (13)	4202 (9)	2013 (9)	44 (4)
C(6)	2338 (10)	2724 (7)	7845 (7)	27 (3)
C(7)	3784 (10)	1864 (8)	8294 (7)	32 (3)
C(8)	6765 (11)	1600 (10)	8577 (9)	47 (4)
C(9)	6372 (14)	1344 (17)	9716 (10)	80 (6)
C(10)	4651 (13)	1836 (12)	9604 (8)	51 (4)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Er—O(1)	2.398 (5)	Er—O(2)	2.319 (5)
Er—O(3)	2.362 (6)	Er—O(5)	2.406 (6)
Er—O(6)	2.303 (6)	Er—O(7)	2.356 (5)
Er—O(8)	2.330 (8)	Er—O(9)	2.332 (5)
O(2)—C(1)	1.243 (9)	O(4)—C(6)	1.254 (13)
O(6)—C(6)	1.246 (11)	O(7)—C(1 <sup>i</sup> )	1.250 (8)
N(1)—C(2)	1.499 (11)	N(1)—C(3)	1.471 (10)
N(2)—C(7)	1.521 (12)	N(2)—C(8)	1.484 (11)
C(1)—C(2)	1.537 (12)	C(1)—O(7 <sup>ii</sup> )	1.251 (8)
C(2)—C(5)	1.530 (11)	C(3)—C(4)	1.471 (19)
C(4)—C(5)	1.523 (17)	C(6)—C(7)	1.497 (11)
C(7)—C(10)	1.518 (12)	C(8)—C(9)	1.515 (18)
C(9)—C(10)	1.495 (17)		
O(1)—Er—O(2)	71.0 (2)	O(1)—Er—O(3)	76.4 (2)
O(2)—Er—O(3)	101.9 (2)	O(1)—Er—O(5)	124.7 (2)
O(2)—Er—O(5)	74.7 (2)	O(3)—Er—O(5)	69.8 (2)
O(1)—Er—O(6)	138.4 (2)	O(2)—Er—O(6)	79.7 (2)
O(3)—Er—O(6)	139.8 (2)	O(5)—Er—O(6)	72.0 (2)
O(1)—Er—O(7)	71.8 (2)	O(2)—Er—O(7)	141.6 (2)
O(3)—Er—O(7)	78.1 (2)	O(5)—Er—O(7)	136.8 (2)
O(6)—Er—O(7)	125.0 (2)	O(1)—Er—O(8)	76.9 (2)
O(2)—Er—O(8)	85.8 (2)	O(3)—Er—O(8)	147.9 (2)
O(5)—Er—O(8)	141.6 (2)	O(6)—Er—O(8)	72.0 (2)
O(7)—Er—O(8)	76.9 (2)	O(1)—Er—O(9)	141.7 (2)
O(2)—Er—O(9)	146.1 (2)	O(3)—Er—O(9)	83.7 (2)
O(5)—Er—O(9)	76.1 (2)	O(6)—Er—O(9)	75.2 (2)
O(7)—Er—O(9)	72.2 (2)	O(8)—Er—O(9)	107.3 (2)
Er—O(2)—C(1)	148.2 (5)	Er—O(6)—C(6)	144.1 (6)
Er—O(7)—C(1 <sup>i</sup> )	141.6 (5)	C(2)—N(1)—C(3)	108.5 (7)
C(7)—N(2)—C(8)	106.8 (7)	O(2)—C(1)—C(2)	117.8 (6)
O(2)—C(1)—O(7 <sup>ii</sup> )	125.0 (7)	C(2)—C(1)—O(7 <sup>ii</sup> )	117.1 (7)
N(1)—C(2)—C(1)	110.4 (6)	N(1)—C(2)—C(5)	104.5 (6)
C(1)—C(2)—C(5)	111.7 (7)	N(1)—C(3)—C(4)	105.1 (9)
C(3)—C(4)—C(5)	104.2 (9)	C(2)—C(5)—C(4)	105.7 (9)
O(4)—C(6)—O(6)	125.9 (8)	O(4)—C(6)—C(7)	116.2 (8)
O(6)—C(6)—C(7)	117.9 (8)	N(2)—C(7)—C(6)	110.0 (7)
N(2)—C(7)—C(10)	100.9 (7)	C(6)—C(7)—C(10)	118.0 (8)
N(2)—C(8)—C(9)	104.6 (9)	C(8)—C(9)—C(10)	107.7 (9)
C(7)—C(10)—C(9)	104.5 (9)		

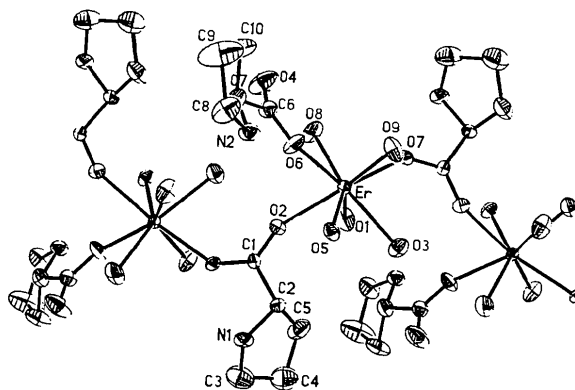
Symmetry codes: (i)  $-x, \frac{1}{2} + y, 1 - z$ ; (ii)  $-x, -\frac{1}{2} + y, 1 - z$ .

squares parameters were refined. Final  $R = 0.0244$ ,  $wR = 0.0297$ , max.  $\Delta/\sigma = 0.003$ ,  $w = [\sigma^2(F)]^{-1}$ . Max., min.  $\Delta\rho$  values in final difference synthesis 0.97,  $-1.71 \text{ e \AA}^{-3}$ . The absolute structure was not established experimentally. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1.\* The important bond distances and angles are listed in Table 2. Fig. 1 shows a section of the polymeric chains present in the crystal.

The complex consists of Er ions, chloride ions, proline molecules and water molecules. It is interesting to note that the two crystallographically distinct proline ligands are not structurally equivalent. One acts as a bidentate bridging ligand, contributing both of its carboxylate O atoms to coordinate with two neighboring Er ions to form a one-dimensional chain of infinite length. The second proline ligand is monodentate, contributing only one carboxylate O atom to coordinate with an Er ion, while the second O atom forms a strong hydrogen bond [O(9)⋯O(3) 2.616  $\text{\AA}$ ] with a coordinated water molecule. In the bridging proline ligand, the bond lengths C(1)—O(7<sup>ii</sup>) and C(1)—O(2) are 1.251 (8) and 1.243 (9)  $\text{\AA}$ , respectively, and in the monodentate proline C(6)—O(4) and C(6)—O(6) are 1.254 (13) and 1.246 (11)  $\text{\AA}$ , respectively. This suggests that the carboxyl groups present in the two different proline ligands have an average structure and do not have distinct C=O and C—O bonds. Each Er ion is both linked to three proline O atoms forming Er—O bonds with an

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55787 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1025]

Fig. 1. Configuration of  $\{[\text{Er}(\text{Pro})_2(\text{H}_2\text{O})_5]^{3+}\}_n$ . H atoms have been omitted for clarity.

average length of 2.326 Å, and bonded to five water O atoms with an average Er—O(water) bond length of 2.366 Å. The coordination number of the Er ion is eight and its coordination polyhedron can be described as a distorted triangular dodecahedron. In the crystal, the proline amino groups remain protonated and unbonded to the metal ions, but are associated with O atoms of the same proline to form intraligand hydrogen bonds [N(1)⋯O(7) 2.684 Å, N(2)⋯O(6) 2.627 Å]. The distances between Cl anions and Er cations are longer than 4.639 Å and the average of the shortest distances between Cl anions and N atoms of the amino groups is 3.165 Å, indicating that the Cl anions do not coordinate with

the Er cations but are attracted electrostatically to the amino groups.

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## Structure of Dipotassium (Nitrilo- $\kappa$ N-triacetato- $\kappa^3$ O,O'',O''')oxoperoxo-vanadate(V)—Water (1/2)

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**Abstract.**  $K_2[V(C_6H_6NO_6)O(O_2)] \cdot 2H_2O$ ,  $M_r = 401.28$ , orthorhombic,  $Pnam$ ,  $a = 7.597$  (5),  $b = 12.951$  (3),  $c = 13.131$  (5) Å,  $V = 1291.9$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.06$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 14.4$  cm<sup>-1</sup>,  $F(000) = 808$ ,  $T = 295$  K,  $R = 0.019$  for 1820 unique reflections. Vanadium is surrounded by a seven-membered coordinating pentagonal bipyramid formed by a tetradentate nitrilotriacetate ligand, a bidentate peroxy group and a vanadyl oxygen. The bipyramid is symmetrical relative to the mirror plane passing through the V atom, the apical O atoms, the equatorial N atom and the midpoint between the peroxy O atoms. The nitrilotriacetate ligand forms three glycinate rings with the V atom, one of which coincides with the mirror plane, the two others being symmetrical relative to the plane. The compound is remarkably stable towards decomposition.

**Introduction.** This work continues our structural study of peroxovanadates (Lapshin, Smolin, Shepelev, Gyepesova & Schwendt, 1989; Lapshin, Smolin, Shepelev, Schwendt & Gyepesova, 1990a,b), in which all peroxovanadates were unstable. This has been noted by other authors (Stomberg, 1984a; Volnov, 1987). The interesting feature of the present compound is its long-term stability in air at room temperature. Since peroxy complexes are thermodynamically unstable it is important to study the stabilizing effect of certain ligands and to correlate this with the structure.

**Experimental.** A single red crystal with approximate dimensions 0.40 × 0.45 × 0.50 mm was mounted on an automatic three-circle normal-beam single-crystal X-ray diffractometer with graphite-monochromated Mo  $K\alpha$  radiation;  $\omega$ - $2\theta$  scan method. Lattice parameters were determined from the setting of 22 reflec-

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