

# ***trans*-Diaquatetra(nitrato-O,O')dysprosium(III) (18-Crown-6)potassium Acetonitrile Solvate: Synthesis and Crystal Structure**

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**Abstract**—A new complex  $\text{K}(\text{18-crown-6})[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot \text{CH}_3\text{CN}$  (**I**) is synthesized, and its structure is studied by X-ray diffraction analysis (space group  $P2_1/c$ ,  $a = 17.200 \text{ \AA}$ ,  $b = 13.377 \text{ \AA}$ ,  $c = 13.087 \text{ \AA}$ ,  $\beta = 94.21^\circ$ ,  $Z = 4$ , full-matrix anisotropic least squares to  $R = 0.033$  for 5283 independent reflections, CAD-4 automated diffractometer,  $\lambda\text{MoK}\alpha$  radiation). The crystal structure of the compound exists as infinite polymer chains formed by coordination bonds and composed of alternating complex anions  $[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  and cations  $[\text{K}(\text{18-crown-6})]^+$ .

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## INTRODUCTION

In this work, we describe the synthesis and X-ray diffraction results for the new crystalline complex: *trans*-diaquatetra(nitrato-O,O')dysprosium(III) (18-crown-6)potassium acetonitrile solvate,  $\text{K}(\text{18-crown-6})^+[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^- \cdot \text{CH}_3\text{CN}$  (**I**). As found in this study, the crystal structure of compound **I** exists as infinite polymer chains. No complexes containing the  $[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  fragment were obtained earlier.

## EXPERIMENTAL

**Synthesis of I.** Crystalline  $\text{Dy}(\text{NO}_3)_3$ ,  $\text{KNO}_3$ , and dibenzo-18-crown-6 crown taken in a mole ratio of 1 : 1 : 1 were mixed and dissolved in 70% aqueous ethanol. The solvents were evaporated. The precipitate that formed was dissolved in acetonitrile, and the solution was left to evaporate at room temperature. After three days, colorless single crystals of compound **I** precipitated on the bottom of the vessel.

**X-Ray diffraction analysis.** The unit cell parameters of the crystal and the three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD-4 X-ray automated diffractometer ( $\text{MoK}\alpha$  radiation, graphite monochromator). The crystals of compound **I** are monoclinic:  $[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)]^+[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^- \cdot \text{CH}_3\text{CN}$ ,  $M = 791.04$ ;  $a = 17.200(4)$ ,  $b = 13.377(4)$ ,  $c = 13.087(4) \text{ \AA}$ ,  $\beta = 94.21(2)^\circ$ ,  $V = 3003(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.750 \text{ g/cm}^3$ ,  $\mu(\text{MoK}\alpha) = 27.14 \text{ cm}^{-1}$ , space group  $P2_1/c$ .

Intensities of 5795 reflections were measured in a quadrant of the reciprocal space ( $2\theta \leq 50^\circ$ ) in the  $\omega/2\theta$  scan mode from a single crystal  $0.25 \times 0.30 \times 0.57 \text{ mm}$

in size. An absorption correction was applied to the reflection intensities by the semiempirical method [1]. After 257 systematically quenched reflections were excluded and the intensities of 255 pairs of equivalent reflections  $hk0$  and  $\bar{h}k0$  ( $R_{\text{int}} = 0.015$ ) were averaged, the working set of measured  $F^2(hkl)$  and  $\sigma(F^2)$  values contained 5283 independent reflections.

The structure of compound **I** was solved by a direct method (SHELXS-97) [2] and refined by full-matrix least squares for  $F^2$  (SHELXL-97) [2] in the anisotropic approximation for non-hydrogen atoms. Almost all reflections from the working set, including very weak reflections with  $I < 2\sigma(I)$ , except for several reflections with poorly consistent measured and calculated  $F^2$  values, were used in the refinement.

The positions of almost all hydrogen atoms in structure **I** were objectively located in the difference electron density synthesis. Then the positions of all independent hydrogen atoms for two 18-crown-6 ligands (**a** and **b**) were specified geometrically: their coordinates were calculated using the riding model [2] in the refinement procedure. The coordinates of the hydrogen atoms in two water molecules and in the  $\text{CH}_3\text{CN}$  solvate molecules were refined imposing the DFIX and SADI mild geometric constraints [2] on the short interatomic distances involving these atoms. The isotropic thermal parameters were refined for all hydrogen atoms.

The isotropic extinction coefficient was also refined for exposed crystal **I**:  $g = 0.0021(1)$  [2]. In the last cycle of the refinement, the absolute shifts of all 424 variable parameters of structure **I** were less than  $0.001\sigma$ .

The final coordinates and thermal parameters of atoms in structure **I**, the tables of bond lengths and bond

**Table 1.** Selected bond lengths and bond angles in structure **I**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Angle	ω, deg
Dy–O(11)	2.576(2)	K(a)–O(1a)	2.784(2)	O(11)DyO(21)	170.38(8)
Dy–O(12)	2.466(2)	K(a)–O(4a)	2.883(2)	O(11)DyO(w1)	67.10(7)
Dy–O(21)	2.551(2)	K(a)–O(7a)	2.799(2)	O(21)DyO(w2)	67.05(6)
Dy–O(22)	2.502(2)	K(a)–O(11)	2.974(2)	O(w1)DyO(w2)	158.45(7)
Dy–O(31)	2.420(2)	K(a)–O(13)	3.101(2)	DyO(11)K(a)	158.2(1)
Dy–O(32)	2.445(3)	K(b)–O(1b)	2.793(2)	DyO(11)N(1)	95.5(2)
Dy–O(41)	2.404(2)	K(b)–O(4b)	2.907(2)	K(a)O(11)N(1)	100.8(2)
Dy–O(42)	2.456(2)	K(b)–O(7b)	2.762(2)	DyO(21)K(b)	163.51(8)
Dy–O(w1)	2.374(2)	K(b)–O(21)	2.954(2)	DyO(21)N(2)	96.0(1)
Dy–O(w2)	2.360(2)	K(b)–O(23)	3.023(2)	K(b)O(21)N(2)	98.8(2)

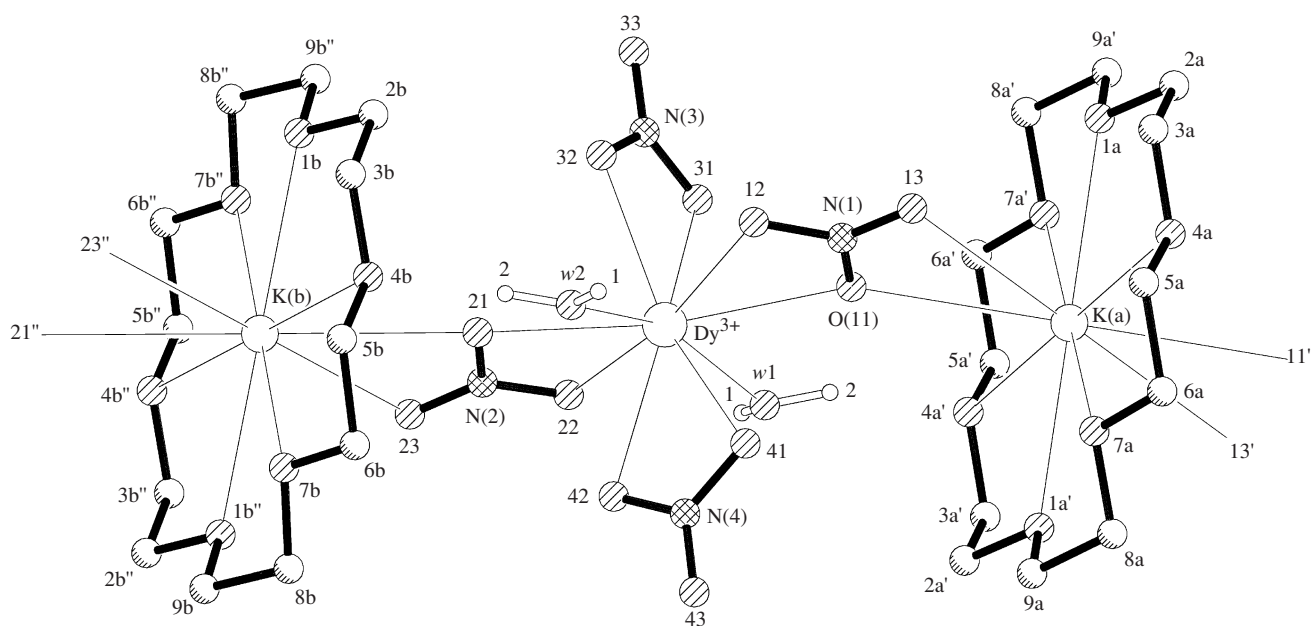
angles, and other data were deposited with the Cambridge Crystallographic Data Centre as the cif file (no. 698 426).

The final refinement parameters are  $R = 0.021$  and  $wR_2 = 0.047$  for 4165 reflections with  $I \geq 2\sigma(I)$ ;  $R = 0.033$  and  $wR_2 = 0.055$  for all independent reflections; the goodness-of-fit  $S$  is 1.02 (the definition for  $wR_2$  and  $S$  is given in [2]). In the final difference Fourier synthesis,  $-0.36 < \Delta\rho < 0.41 \text{ e \AA}^{-3}$ . The used  $f$  curves and anomalous dispersion corrections to them ( $\Delta f'$  and  $\Delta f''$ ) were borrowed from [3].

## RESULTS AND DISCUSSION

Selected bond lengths and bond angles in structure **I** are given in Table 1. In crystal **I** (figure), the alternating complex anions  $[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  and cations  $[\text{K}(\text{18-crown-6})]^+$  form infinite linear chains through interionic bonds. Structure **I** contains the symmetrically independent complex anion  $[\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  and two independent halves of two centrosymmetric cations  $[\text{K}(\text{18-crown-6})]^+$  (a and b).

In structure **I**, the coordination polyhedron of the  $\text{Dy}^{3+}$  cation is a considerably distorted octahedron with



Crystal structure of the polymer chain complex  $[\text{K}(\text{18-crown-6})\text{Dy}(\text{NO}_3)_4(\text{H}_2\text{O})_2]_n$ . The solvate  $\text{CH}_3\text{CN}$  molecule and the H atoms at the 18-crown-6 ligands are omitted for clarity. The symmetrically multiplied basis atoms are marked with stroke and two strokes.

**Table 2.** Intermolecular (interionic) hydrogen bond geometry in crystal structure I\*

H bond O—H...O	Distance, Å			Angle O—H...O, deg
	O—H	H...O	O...O	
O(w1)—H(1w1)...O(12) <sup>ii</sup>	0.90(2)	1.93(2)	2.813(3)	166(2)
O(w1)—H(2w1)...O(4a) <sup>i</sup>	0.90(2)	1.91(2)	2.763(2)	159(2)
O(w2)—H(1w2)...O(22) <sup>iii</sup>	0.90(2)	1.92(2)	2.815(3)	176(3)
O(w2)—H(2w2)...O(4b)	0.90(2)	1.89(2)	2.786(3)	171(2)

\* Symmetry transformations of atoms: <sup>i</sup>  $-x, 1-y, -z$ ; <sup>ii</sup>  $x, 1/2-y, z-1/2$ ; <sup>iii</sup>  $x, 1/2-y, z+1/2$ .

four bifurcated vertices each at two O atoms of the four NO<sub>3</sub><sup>-</sup> ligands and with two opposite vertices at the O(w1) and O(w2) atoms of the two water molecules.

The average length of the Dy—O(nitrato) coordination bonds is  $2.48 \pm 0.07$  Å. The two bonds with the bridging O(11) and O(21) atoms are noticeably longer, and two other Dy—O(w1) and Dy—O(w2) bonds are noticeably shorter than this averaged value. As a whole, the lengths of eight Dy—O bonds are appreciably less than and the Dy—O(11) and Dy—O(21) bond lengths are close to the sum of the ionic radius of the Dy<sup>3+</sup> cation (1.14 Å for the coordination number 10) [4] and the van der Waals radius of the oxygen atom, which is 1.40–1.52 Å [4, 5]. Since the ionic radius of the Dy<sup>3+</sup> cation with the coordination number ten is lacking [6], the above given value was obtained by the extrapolation of the ionic radii of Dy<sup>+</sup> with the coordination numbers seven, eight, and nine [4].

In complex anion in structure I, all NO<sub>3</sub><sup>-</sup> ligands are nearly exactly planar and have standard covalent bond lengths and bond angles. The planes of two bridging NO<sub>3</sub><sup>-</sup> ligands (with the N(1) and N(2) atoms) form a small dihedral angle of  $4.6(2)^\circ$ , and two other NO<sub>3</sub><sup>-</sup> ligands (with the central N(3) and N(4) atoms) are approximately perpendicular to each other and two bridging NO<sub>3</sub><sup>-</sup> ligands.

Two complex cations [K(18-crown-6)]<sup>+</sup> (a and b) in structure I are of the host–guest type [7]. Each of the K(a) and K(b) atoms (in the crystallographic inversion centers  $i(0, 1/2, 0)$  and  $i(1/2, 0, 0)$ , respectively) exists in the cavity of the corresponding centrosymmetric 18-crown-6 ligand (a and b). Very resembling coordination polyhedra of the K(a) and K(b) cations (coordination number 10) can be characterized as distorted hexagonal bipyramids with the base of all six O atoms of the

crown ligand and two opposite bifurcated vertices at two O atoms of two adjacent bridging NO<sub>3</sub><sup>-</sup> ligands.

In the both complex cations, the average K—O(crown) bond length is  $2.82 \pm 0.05$  Å, and the average K—O(nitrato) distance is appreciably longer ( $3.01 \pm 0.05$  Å). These average distances are somewhat shorter than or close to the sum of the ionic radius of the K<sup>+</sup> cation (1.59 Å for the coordination number 10) [4] and the above indicated van der Waals radius of the oxygen atom.

In structure I, two centrosymmetric 18-crown-6 ligands (a and b) have the corresponding resembling geometric parameters and the conformation of a distorted crown with the approximate symmetry  $D_{3d}$ . For this conformation, six O atoms of each ligand alternately deviate to opposite sides from the root-mean-square plane by  $\pm 0.214$  (a) and  $\pm 0.208$  (b) Å on the average. In the crown ligands, all torsion O—C—C—O angles are synclinal (*gauche* type) and antiperiplanar close to  $\pm 68^\circ$ , and all C—O—C angles are antiperiplanar (*trans* type) and lie in the range  $180 \pm 7^\circ$ .

For the 18-crown-6 ligands in structure I, the average O—C bond length (1.421 Å) is slightly less than the average statistical value (1.426(11) Å) for the C#—CH<sub>2</sub>—O—C# fragments [8], and the average C—O bond length (1.491 Å) is appreciably less than the average statistical value (1.524(14) Å) for the C#—CH<sub>2</sub>—CH<sub>2</sub>—C# fragments [8]. This shortening of the C—C intracyclic bonds is well known for the 18-crown-6 ligands and molecules [7, 9]. In the crown ligands of structure I, all COC bond angles (average  $112.6^\circ$ ) are larger and the OCC angles (average  $109.0^\circ$ ) are smaller than the ideal tetrahedral angle ( $109.5^\circ$ ).

In structure I, the dihedral angles between the root-mean-square planes of six O atoms of the crown ligands (a) and bonded to them bridging ligands NO<sub>3</sub><sup>-</sup> (with the N(1) and N(2) atoms are  $89.59(8)^\circ$  and  $89.18(8)^\circ$ , respectively. The angle between the root-mean-square planes of six O atoms of two 18-crown-6 ligands is small ( $3.53(9)^\circ$ ).

The bond lengths in the CH<sub>3</sub>CN solvate molecule in structure I are as follows: C—C 1.420(6) and C≡N 1.123(5) Å, and the C—C≡N angle is  $180.0(4)^\circ$ .

The crystal structure of compound I contains intermolecular (interionic) hydrogen bonds involving all hydrogen atoms of the water molecules (Table 2). All other short intermolecular (interionic) contacts are close to or slightly shorter than the sums of the van der Waals radii of the corresponding atoms.

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