orbital at the 2-nitro-1,3-indandionato ligand. If the optical electronegativity of Fe^{II} is chosen to be 1·95 then an optical electronegativity of 1·2 is found for the nitronate ligand. This is a reasonable result considering that a nitronato ligand is expected to be more oxidizing than a pyridine N-oxide ligand, for which a value of 0·8 has been reported (Beyers, Chou, Lever & Parish, 1969).

The four shortest hydrogen bonds are shown in Fig. 2. The aqua ligand $H_2O(81)$ (Fig. 1) makes hydrogen bonds to both of the crystal water molecules; O(81)···O(83): 2·698 (5), O(81)···O(84): 2·667 (5) Å. The carbonyl oxygen O(13) is acceptor for hydrogen bonds from the aqua ligand $H_2O(82)$ and the crystal water $H_2O(83)$; O(13)···O(82): 2·790 (4), O(13)···O(83): 2·784 (4) Å.

References

BEYERS, W., CHOU, B. F. C., LEVER, A. B. P. & PARISH, R. V. (1969). *J. Am. Chem. Soc.* **91**, 1329–1333.
FEIGEL, F. & ANGER, V. (1972). *Spot Tests in Inorganic Analysis*, pp. 263–274. Amsterdam: Elsevier.
GÜTLICH, P., LINK, R. & TRAUTWEIN, A. (1978). *Mössbauer Spectroscopy and Transition Metal Chemistry*, p. 280. Berlin: Springer Verlag.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
SELENIUS, C.-O. & LUNDGREN, J.-O. (1980). *Acta Cryst.* **B36**, 3172–3175.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SIMONSEN, O. (1988). Unpublished.
SIMONSEN, O. & JACOBSEN, J. P. (1977). *Acta Cryst.* **B33**, 3045–3049.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
STROUSE, J., LAYTEN, S. W. & STROUSE, C. E. (1977). *J. Am. Chem. Soc.* **99**(1), 562–572.
TAYLOR, D. (1978). *Aust. J. Chem.* **31**, 713–721.
WANAG, G. (1936). *Chem. Ber.* **69**, 1066–1074.

Structure of [DyCl₃(triethylene glycol)].18-crown-6*

By Robin D. Rogers† and Russell D. Etzenhouser

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA

Abstract. Trichloro(triethylene glycol)dysprosium-1,4,-7,10,13,16-hexaoxacyclooctadecane (1/1), [DyCl₃(C₆H₁₄O₄)].C₁₂H₂₄O₆, $M_r = 683·4$, monoclinic, $C2/c$, $a = 18·666$ (9), $b = 9·769$ (5), $c = 14·931$ (6) Å, $\beta = 108·67$ (5)°, $V = 2579$ Å³, $Z = 4$, $D_x = 1·76$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0·71073$ Å, $\mu = 30·9$ cm⁻¹, $F(000) = 1372$, $T = 123$ K, final $R = 0·035$ for 2108 observed $[F_o \geq 5\sigma(F_o)]$ reflections. The Dy ion is seven-coordinate in a distorted pentagonal bipyramidal geometry. The Dy atom and equatorial Cl [Dy–Cl = 2·621 (2) Å] reside on a crystallographic twofold axis. The axial chlorines [Dy–Cl = 2·607 (1) Å] are bent away from the equatorial Cl position [Cl_{ax}–Dy–Cl_{ax} = 162·65 (7)°]. The alcoholic O atoms [Dy–O = 2·316 (4) Å] donate hydrogen bonds to a crown ether molecule (which resides around a center of inversion) forming polymeric hydrogen-bonded chains. The unique etheric Dy–O separation is 2·455 (4) Å.

Introduction. The reaction of pure triethylene glycol (EO3) with hydrated lanthanide chlorides produces two different types of coordination complexes (Rogers, Voss & Etzenhouser, 1988): nine-coordinate heptahydrates for the early- and mid-lanthanides, $[M(OH_2)_5$-(EO3)]Cl₃.2H₂O (M = Nd, Eu, Gd, Dy and Y have been structurally characterized), and seven-coordinate anhydrous complexes of the smaller lanthanides, $[MCl_3(EO3)].CH_3CN$ (M = Ho, Lu), $[MCl_3(EO3)].$-OHMe [M = Eu, Yb, Lu (Rogers & Etzenhouser, 1988)], and [LuCl₃(EO3)]. The seven-coordinate species were also isolated for Dy and Y, but only as 18-crown-6 adducts, $[MCl_3(EO3)].18$-crown-6. These latter complexes were found to be slightly hygroscopic and disordered in the solid state. Recently, we isolated a new very deliquescent form of the Dy^{III} complex of this type, which we have found to be the ordered form of [DyCl₃(EO3)].18-crown-6. In order to better compare the seven-coordinate geometry of this complex (the earliest lanthanide we have managed to isolate with this low coordination number) with the previously determined seven-coordinate late-lanthanide/EO3 com-

$$[DyCl_3(C_6H_{14}O_4)].C_{12}H_{24}O_6$$

plexes, we have carried out a detailed structural investigation.

Experimental. The isolation of the title complex has been reported (Rogers, Voss & Etzenhouser, 1988). A colorless single-crystal fragment grown from aceto-nitrile:methanol (3:1). D_m not determined. Crystal $0.20 \times 0.33 \times 0.23$ mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 20°$). Corrections for Lorentz–polarization effect and for absorption (empirical), range of relative transmission factors 68/100%. $\theta_{max} = 25°$; h -21 to 21, k 0 to 11, l 0 to 17 ($h + k \neq 2n$ not collected). 2503 reflections measured, 2108 independent observed reflections $[F_o \geq 5\sigma(F_o)]$. Structure solved via Patterson function and subsequent difference Fourier techniques. Crown ether and glycol carbon H atoms placed 0.95 Å from the bonded C atom with a fixed isotropic thermal parameter $B = 5.5$ Å^2 and allowed to ride with the C—H distance fixed. The alcoholic H atom located from a difference Fourier map and included with fixed contributions ($B = 5.5$ Å^2). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX*76 (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights $= [\sigma(F_o)^2]^{-1}$, 146 parameters varied. $R = 0.035$, $wR = 0.035$, $S = 2.5$. Δ/σ in final least-squares refinement cycle < 0.01, $\Delta\rho < 2.0$ e Å^{-3} near Dy in final difference map.*

Discussion. Fractional coordinates and U_{eq} values are given in Table 1, distances and angles in Table 2, and an *ORTEP* illustration (Johnson, 1976) of the formula unit, atom-labeling scheme, and hydrogen bonding in Fig. 1. The Dy ion, which is seven-coordinate in a distorted pentagonal bipyramidal geometry, resides on a crystallographic twofold axis with equatorial chlorine Cl(1). Alcoholic oxygen O(1) donates a hydrogen bond to the 18-crown-6 molecule which resides around a center of inversion {H(1)[O(1)]···O(3) = 1.64 Å, O(1)—H(1)···O(3) = 173°, O(1)···O(3) = 2.626 (5) Å}. The hydrogen bonding results in polymeric chains.

In the previously determined complexes of this type, $[MCl_3(EO3)].18$-crown-6 [$M = $ Dy, Y (Rogers, Voss & Etzenhouser, 1988)], the overall geometries are identical with the exception of disorder in the glycol ligand. The Dy—Cl distances, however, are quite different, a consequence of very different packing environments found for the two complexes. In the previously

---

Table 1. *Final fractional coordinates for* |DyCl$_3$-(EO3)|.18-crown-6

	x	y	z	U_{eq}*
Dy	0.0000	0.77038 (4)	0.7500	0.012
Cl(1)	0.0000	0.5021 (2)	0.7500	0.023
Cl(2)	0.06646 (8)	0.8106 (2)	0.6230 (1)	0.028
O(1)	0.1138 (2)	0.7341 (4)	0.8685 (3)	0.018
O(2)	0.0691 (2)	0.9809 (4)	0.8146 (2)	0.014
O(3)	0.1762 (2)	0.5018 (4)	0.9422 (3)	0.018
O(4)	0.2891 (2)	0.5897 (4)	0.8731 (3)	0.018
O(5)	0.3423 (2)	0.8652 (4)	0.9026 (3)	0.018
C(1)	0.1675 (3)	0.8426 (6)	0.9080 (4)	0.019
C(2)	0.1219 (3)	0.9689 (6)	0.9075 (4)	0.019
C(3)	0.0247 (3)	1.1050 (5)	0.8018 (4)	0.015
C(4)	0.2082 (3)	0.4120 (6)	0.8910 (4)	0.022
C(5)	0.2336 (3)	0.4931 (6)	0.8215 (4)	0.021
C(6)	0.3220 (3)	0.6580 (6)	0.8127 (4)	0.023
C(7)	0.3796 (3)	0.7607 (6)	0.8697 (4)	0.021
C(8)	0.3953 (3)	0.9659 (6)	0.9529 (4)	0.021
C(9)	0.3538 (3)	1.0679 (6)	0.9935 (4)	0.021

$* U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

Table 2. *Bond distances* (Å) *and angles* (°) *for* $[DyCl_3(EO3)].18$-crown-6

Dy—Cl(1)	2.621 (2)	Dy—Cl(2)	2.607 (1)
Dy—O(1)	2.316 (4)	Dy—O(2)	2.455 (4)
O(1)—C(1)	1.447 (6)	O(2)—C(2)	1.427 (6)
O(2)—C(3)	1.447 (6)	O(3)—C(4)	1.416 (6)
O(3)—C(9^{ii})	1.430 (8)	O(4)—C(5)	1.431 (6)
O(4)—C(6)	1.411 (6)	O(5)—C(7)	1.410 (6)
O(5)—C(8)	1.426 (6)	C(1)—C(2)	1.497 (7)
C(3)—C(3^i)	1.53 (1)	C(4)—C(5)	1.498 (7)
C(6)—C(7)	1.517 (7)	C(8)—C(9)	1.504 (7)
Cl(1)—Dy—Cl(2)	98.68 (3)	Cl(1)—Dy—O(1)	81.20 (9)
Cl(1)—Dy—O(2)	146.89 (8)	Cl(2)—Dy—O(1)	92.6 (1)
Cl(2)—Dy—O(2)	81.18 (9)	Cl(2)—Dy—Cl(2^i)	162.65 (7)
Cl(2)—Dy—O(1^i)	90.1 (1)	Cl(2)—Dy—O(2^i)	84.3 (1)
O(1)—Dy—O(2)	65.8 (1)	O(1)—Dy—O(1^i)	162.4 (2)
O(1)—Dy—O(2^i)	131.8 (1)	O(2)—Dy—O(2^i)	66.2 (2)
Dy—O(1)—C(1)	123.0 (3)	Dy—O(2)—C(2)	115.2 (3)
Dy—O(2)—C(3)	116.3 (3)	C(2)—O(2)—C(3)	112.6 (4)
C(4)—O(3)—C(9^{ii})	113.0 (4)	C(5)—O(4)—C(6)	110.8 (4)
C(7)—O(5)—C(8)	110.2 (4)	O(1)—C(1)—C(2)	106.5 (4)
O(2)—C(2)—C(1)	106.6 (4)	O(2)—C(3)—C(3^i)	105.6 (4)
O(3)—C(4)—C(5)	109.1 (5)	O(4)—C(5)—C(4)	108.1 (4)
O(4)—C(6)—C(7)	109.2 (5)	O(5)—C(7)—C(6)	109.5 (4)
O(5)—C(8)—C(9)	108.0 (4)	O(3^{ii})—C(9)—C(8)	108.5 (5)

Symmetry codes: (i) $-x, y, 1.5-z$; (ii) $0.5-x, 1.5-y, 2-z$.

Fig. 1. Polymeric chains of the formula unit, [DyCl$_3$(EO3)].18-crown-6. 50% probability ellipsoids for thermal motion. H atoms arbitrarily reduced.

determined disordered form of [DyCl₃(EO3)].18-crown-6 (also determined at 123 K) the Dy—Cl(1) equatorial distance is shorter at 2·605 (2) Å than the Dy—Cl(2) axial separation of 2·626 (2) Å. Indeed, that is true of all of the previously structurally characterized complexes containing the [MCl₃(EO3)] unit, though some variation in the magnitude of the difference is observed for various hydrogen-bonding environments. In the title complex this situation is reversed. The axial distance [Dy—Cl(2) = 2·607 (2) Å] is shorter than the equatorial Dy—Cl(1) separation of 2·621 (2) Å. Since there are no hydrogen bonds to the Cl atoms it is probable that packing effects are responsible for these differences. An analysis of non-bonding contacts around each Cl position in both complexes does in fact reveal interesting differences. The non-bonding contacts between Cl(1) and Cl(2) and the other atoms in the metal coordination sphere are similar for both complexes; however, non-bonded contacts between these atoms and other symmetry-related formula units are different. In the disordered complex the closest non-bonded contacts of the latter type for equatorial Cl(1) are six Cl···C ⁱcrown ether C(8), C(9)] separations ranging from 3·616 (7) to 3·760 (7) Å. The closest equatorial Cl contacts of this type in the title complex are much longer and there are only four under 4 Å: two Cl(1)···C(9) (crown) contacts at 3·987 (5) Å and two Cl(1)···C(3) (glycol) contacts of 3·954 (6) Å. The equatorial Cl in the disordered complex, Cl(2), has only three such contacts under 4 Å, two to glycol carbon atoms: Cl(2)···C(2) = 3·86 (1), Cl(2)···C(3)ⁱ = 3·88 (2) Å and one to the crown ether: Cl(2)···C(5) = 3·957 (7) Å. The Cl(2) contacts in this category in the title complex under 4 Å range from 3·538 (6) to 3·977 (6) Å. There are five such contacts, all to atoms in the crown ether. For both complexes, the shortest Dy—Cl separation occurs for the Cl having five or six Cl···crown ether contacts under 4 Å regardless of its position in an axial or equatorial coordination site. The longest observed Dy—Cl separation occurs when there are only a few (four or less) contacts under 4 Å and when these are quite long (>3·8 Å).

The Dy—O separations are slightly different in the two determinations of [DyCl₃(EO3)].18-crown-6. The Dy—O alcoholic distance is just over 3σ shorter in the title complex [2·316 (4) versus 2·331 (4) Å] and the Dy—O etheric separation is just over 3σ longer than observed previously [2·455 (4) versus 2·442 (5) Å]. The glycol ligand itself in the title complex is normal with O—C—C—O torsion angles alternating $\pm g$ [C(1)—C(2) = −50·0; C(3)—C(3ⁱ) = 59·1°] and the C—C—O—C angles anti [C(2)—O(2) = −175·7; C(3)—O(2) = 176·7°]. The average bonding parameters are C—O = 1·440 (9), C—C = 1·51 (2) Å, C—O—C = 112·6 (4) and C—C—O = 106·2 (4)°.

The 18-crown-6 molecule displays its full D_{3d} symmetry and accepts one hydrogen bond on each side of the macrocycle. The average bonding parameters are C—O = 1·421 (9), C—C = 1·506 (8) Å, C—O—C = 111 (1) and C—C—O = 108·7 (6)°.

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72, 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

ROGERS, R. D. & ETZENHOUSER, R. D. (1988). Acta Cryst. C44, 1400–1402.

ROGERS, R. D., VOSS, E. J. & ETZENHOUSER, R. D. (1988). Inorg. Chem. 27, 533–542.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

The Structure of Tetraguanidinium Pentamolybdodiphenylphosphonate*

BY DAN-GÖRAN LYXELL AND ROLF STRANDBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Abstract. [C(NH₂)₃]₄[(C₆H₅P)₂Mo₅O₂₁], $M_r = 1272·2$, tetragonal, $P4_1$, $a = 15·682$ (2), $c = 31·267$ (5) Å, $V = 7690$ (2) Å³, $Z = 8$, $D_x = 2·20$ Mg m⁻³, Mo Kᾱ, $\lambda = 0·71069$ Å, $\mu = 1·735$ mm⁻¹, $F(000) = 4976$, $T = 298$ K, $R = 0·035$, based on 9345 unique observed reflexions. The structure contains $(C_6H_5P)_2Mo_5O_{21}^{4-}$

* Multicomponent Polyanions. 42.