

O(3)—C(4)	1.275 (4)	C(9)—C(16)	1.484 (6)
O(4)···Cl	3.032 (2)	C(10)—C(15 <sup>iv</sup> )	1.505 (5)
O(4)—C(7)	1.281 (4)	C(10)—C(17)	1.48 (1)
C(2)—C(3)	1.523 (8)	C(10)—C(20 <sup>v</sup> )	1.485 (7)
Cl—Zr—O(2 <sup>ii</sup> )	161.0 (2)	O(2)—C(2)—C(3)	115.0 (4)
Cl—Zr—O(4)	81.5 (1)	C(5 <sup>i</sup> )—C(2 <sup>ii</sup> )—C(3 <sup>ii</sup> )	123.6 (3)
Cl—Zr—O(1 <sup>i</sup> )	123.0 (1)	C(11)—C(3)—C(11 <sup>iii</sup> )	106.8 (4)
Cl—Zr—O(3)	86.6 (1)	C(12 <sup>i</sup> )—C(3 <sup>ii</sup> )—C(11 <sup>iii</sup> )	109.8 (3)
O(1 <sup>i</sup> )—Zr—O(2 <sup>ii</sup> )	76.0 (2)	O(3)—C(4)—C(8)	123.1 (3)
O(1 <sup>i</sup> )—Zr—O(4)	74.0 (2)	O(3)—C(4)—C(9)	114.5 (3)
O(3)—Zr—O(2 <sup>ii</sup> )	78.6 (2)	C(8)—C(4)—C(9)	122.4 (3)
O(3)—Zr—O(4 <sup>iii</sup> )	151.7 (2)	C(2 <sup>ii</sup> )—C(5 <sup>i</sup> )—C(1 <sup>i</sup> )	123.7 (4)
O(3)—Zr—O(4)	76.3 (2)	C(19)—C(6)—C(19 <sup>iii</sup> )	99.9 (6)
O(3)—Zr—O(1 <sup>i</sup> )	133.2 (2)	C(19)—C(6)—C(18)	128.1 (5)
O(3)—Zr—O(3 <sup>iii</sup> )	77.4 (2)	O(4)—C(7)—C(8)	122.6 (3)
O(4)—Zr—O(2 <sup>ii</sup> )	106.1 (2)	O(4)—C(7)—C(10)	114.8 (3)
O(4)—Zr—O(4 <sup>iii</sup> )	126.5 (2)	C(8)—C(7)—C(10)	122.6 (3)
C(1)—O(1 <sup>i</sup> )—Zr	137.7 (3)	C(7)—C(8)—C(4)	123.3 (3)
C(2)—O(2 <sup>ii</sup> )—Zr	138.7 (3)	C(16)—C(9)—C(13)	108.5 (4)
C(4)—O(3)—Zr	135.0 (2)	C(16)—C(9)—C(14)	111.0 (3)
C(7)—O(4)—Zr	134.4 (2)	C(13)—C(9)—C(14)	108.1 (5)
O(1)—C(1)—C(5)	122.5 (4)	C(17)—C(10)—C(20 <sup>v</sup> )	110.1 (6)
O(1)—C(1)—C(6)	116.2 (4)	C(17)—C(10)—C(15 <sup>iv</sup> )	103.5 (5)
C(5)—C(1)—C(6)	121.4 (4)	C(20 <sup>v</sup> )—C(10)—C(15 <sup>iv</sup> )	112.8 (4)
O(2 <sup>ii</sup> )—C(2 <sup>ii</sup> )—C(5 <sup>i</sup> )	121.4 (5)		

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

The refinement was performed in the centrosymmetric space group  $P2_1/m$ . The Zr<sup>4+</sup> ions were found from the Patterson map and a Fourier calculation was used to locate the Cl<sup>-</sup> positions. The coordinates of the other non-H atoms were obtained from difference Fourier syntheses. Initially, atom C(18) was placed on the 2(e) site and had a very high anisotropic displacement parameter along the *b* axis [ $U_{22} = 0.73(13) \text{ \AA}^2$ ]. By setting it on the 4(*f*) site, the  $U_{22}$  coefficient was reduced to  $0.25(3) \text{ \AA}^2$ . A tetrahedral geometry was imposed on the H atoms of the methyl radicals using *SHELX76 AFIX* (Sheldrick, 1976).

Data collection: *DIF4* (Stoe & Cie, 1988*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELX76*. Program(s) used to refine structure: *SHELX76*. Molecular graphics: *SCHAKAL92* (Keller, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- France, P. W., Drexhage, M. G., Parker, J. M., Moore, M. W., Carter, S. F. & Wright, J. V. (1990). *Fluoride Glass Optical Fibres*, pp. 12, 65–66, 132, 186. Glasgow: Blackie.
- Fujiura, K., Nishida, Y., Sato, H., Sugawara, H., Kobayashi, K., Terunuma, Y. & Takahashi, S. (1993). *J. Non-Cryst. Solids*, **161**, 14–17.
- Jardin, M., Guéry, J. & Jacoboni, C. (1995). *J. Non-Cryst. Solids*. In the press.
- Keller, E. (1992). *SCHAKAL92. Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
- Nishida, Y., Fujiura, K., Sato, H., Sugawara, H., Kobayashi, K. & Takahashi, S. (1992). *Jpn. J. Appl. Phys.* **31**, L1692–L1694.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sievers, R. E., Eisentraut, K. J., Springer, C. S. & Meek, D. W. (1967). *Adv. Chem. Ser.* **71**, 141–154.
- Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1988*b*). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- VonDreele, R. B., Stezowski, J. J. & Fay, R. C. (1971). *J. Am. Chem. Soc.* **93**, 2887–2892.

*Acta Cryst.* (1995). **C51**, 2232–2235

## Inclusion Complex of *N,N'*-(1,1'-Dimethylene-3,3'-biisoquinoline 2,2'-dioxide)-4,13-diaza-18-crown-6 with Sodium Bromide

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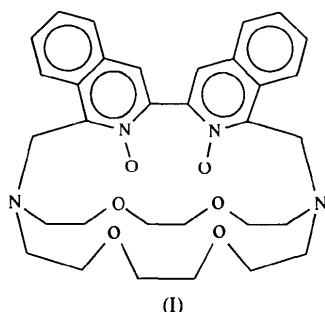
## Abstract

In the title compound, {25,28,33,36-tetraoxa-1,22,39,40-tetraazahexacyclo[20.8.8.1<sup>3,11</sup>.1<sup>12,20</sup>.0<sup>4,9</sup>.0<sup>14,19</sup>]tetraconta-3(40),4,6,8,10,12(39),13,15,17,19-decaene 39,40-dioxide-O,O',O'',O''',O''''}sodium bromide monohydrate, [Na(C<sub>32</sub>H<sub>38</sub>N<sub>4</sub>O<sub>6</sub>)]Br·H<sub>2</sub>O, the Na<sup>+</sup> cation is located in the geometrical centre of the ligand molecule and is octahedrally coordinated by the six O atoms [Na<sup>+</sup>—O distances vary from 2.391(1) to 2.673(1) Å] in a distorted octahedral arrangement. The water molecules are located in channels formed by cryptate cations and Br<sup>-</sup> anions along the [111] direction of the unit cell.

## Comment

Macrocyclic and macrobicyclic ligands containing heterocyclic *N*-oxide groups are able to bind lanthanide cations and form photoactive cryptates that display strong luminescence and, thus, are of interest both as new luminescent materials and potential labels for time-resolved photoimmunoassays (Alpha, Lehn & Mathis, 1987; Alpha, Balzani, Lehn, Perathoner & Sabbatini, 1987; Lehn, 1987; Sabbatini, Perathoner, Balzani, Alpha & Lehn, 1987). The syntheses of the title ligand, (I), and its lithium and europium(III) cryptates were reported by Lehn, Pietraszkiwicz & Karpiuk (1990). In order to study the details of the cryptate structures and the ligand conformation in the complex, these cryptates were crystallized and their X-ray analyses were undertaken. The present paper reports on the 'Li<sup>+</sup> cryptate'. However, in accordance with some concern regarding the quality of

the cation as mentioned by Lehn *et al.* (1990), during the refinement it became clear that instead of  $\text{Li}^+$  the  $\text{Na}^+$  cryptate was formed and this structure is reported herein. A view of the cryptate is presented in Fig. 1.



The coordination polyhedron around the  $\text{Na}^+$  cation (Fig. 2a) can be described as a distorted octahedron formed by the six O atoms of the macrocyclic ligand. The  $\text{Na}^+$ —O distances vary from 2.391 (1) Å, observed for  $\text{Na}$ —O31, to 2.674 (1) Å, for  $\text{Na}$ —O13. The four N atoms are in the second coordination sphere and the  $\text{Na}^+$ ...N distances vary from 2.820 (2) Å ( $\text{Na}$ ...N1) to 3.230 (2) Å ( $\text{Na}$ ...N41).

A comparison of the values of the bond distances and valence angles with those observed in other structures found in the literature that contain the 1,10-diaza-18-crown-6 moiety shows no significant differences. The energetically preferred and, consequently, the most common conformations about the C—C and C—O bonds in crown ethers and aza-crown ethers are *gauche* (*g*) and *anti* (*a*), respectively [*gauche* is equivalent to synclinal in the notation of Klyne & Prelog (1960), *i.e.* close to  $60^\circ$  ( $g^+$ ) or  $-60^\circ$  ( $g^-$ ); *anti* is equivalent to antiperipla-

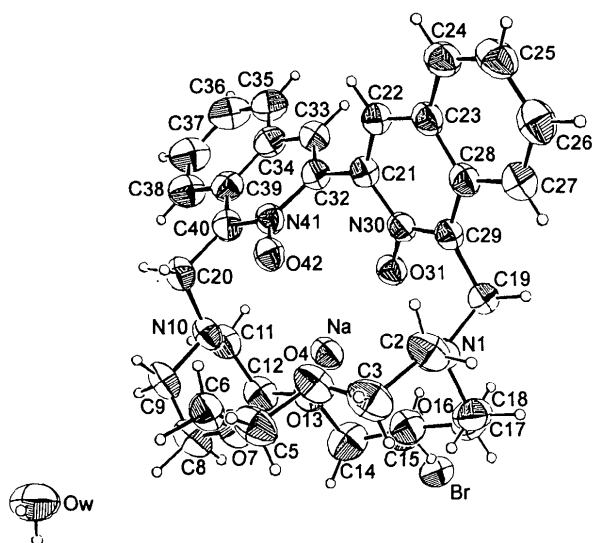


Fig. 1. View of the complex with 50% probability ellipsoids (ORTEPII; Johnson, 1976).

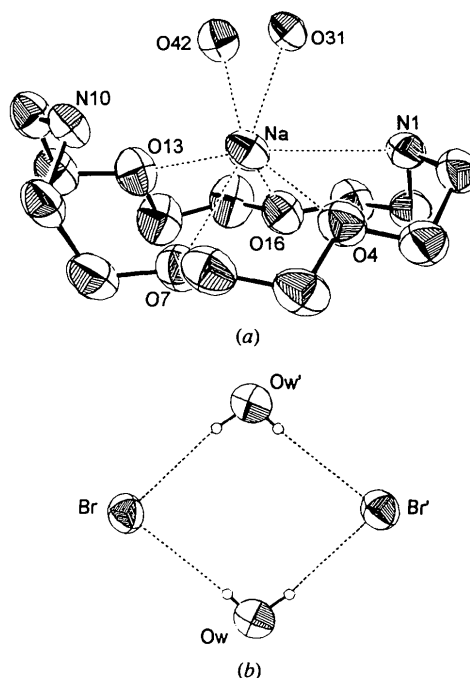


Fig. 2. (a) Coordination of the  $\text{Na}^+$  cation. (b) 'Square' formed by the two centrosymmetrically related  $\text{Br}^-$  ions and two water molecules (ORTEPII; Johnson, 1976).

nar, *i.e.* close to  $180^\circ$ ). The torsion angles around the C—N bonds observed in known structures containing a 1,10-diaza-18-crown-6 fragment [found by examination of 102 entries in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983)] are almost equally distributed between *gauche* and *anti* conformations. The sequence of torsion angles in the macrocyclic ring is  $g^-g^-aag^+ag^+g^+g^-g^-aag^+aag^-a$  and there is only one exception from the 'ideal' conformation: C6—O7—C8—C9 which adopts the  $g^+$  conformation [ $70.3(2)^\circ$ ] instead of the expected *anti* conformation.

The crystal comprises complex cryptate cations and  $\text{Br}^-$  anions forming channels along the [111] crystallographic direction. The  $\text{Br}^-$  ions are part of the wall of the channel, which is filled with water molecules hydrogen bonded to the  $\text{Br}^-$  anions; each water molecule forms two hydrogen bonds to two centre-of-symmetry-related  $\text{Br}^-$  ions [the  $\text{OW}\cdots\text{Br}$  distances are 3.393 (2) Å (*via* H1W) and 3.389 (2) Å (*via* H2W) to the  $\text{Br}^-$  ions in the symmetry equivalent positions  $x,y,z$  and  $-x,-y,-z$ , respectively].  $\text{Br}^-$  anions are also involved in two hydrogen bonds to the two centre-of-symmetry-related water molecules and, thus, form a parallelogram of two  $\text{Br}^-$  ions and two water molecules (Fig. 2b) with the  $\text{OW}\cdots\text{OW}'$  diagonal parallel to the [111] direction. Fig. 3 shows a view along the channel and the arrangement of the water molecules. There are no intermolecular contacts shorter than the sum of van der Waals radii in the structure.

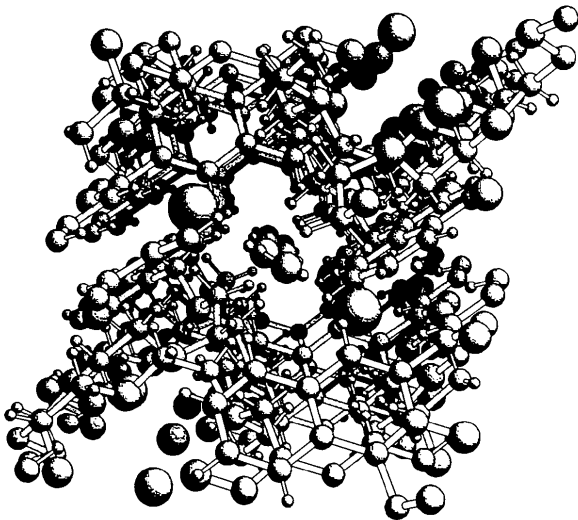


Fig. 3. View down the channel showing the arrangement of the water molecules (ATOMS; Dowty, 1994).

## Experimental

The title compound was obtained by the method of Lehn, Pietraszkiewicz & Karpiuk (1990). The density  $D_m$  was measured by flotation in a trichloromethane–dichloromethane mixture.

### Crystal data

[Na(C<sub>32</sub>H<sub>38</sub>N<sub>4</sub>O<sub>6</sub>)]Br·H<sub>2</sub>O

$M_r = 695.58$

Triclinic

$P1$

$a = 10.625 (1) \text{ \AA}$

$b = 12.598 (2) \text{ \AA}$

$c = 13.551 (1) \text{ \AA}$

$\alpha = 101.85 (1)^\circ$

$\beta = 112.30 (1)^\circ$

$\gamma = 90.66 (1)^\circ$

$V = 1634.4 (3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.413 \text{ Mg m}^{-3}$

$D_m = 1.417 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8\text{--}40^\circ$

$\mu = 2.284 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prismatic

$0.49 \times 0.42 \times 0.21 \text{ mm}$

Pale yellow

### Data collection

Enraf–Nonius CAD-4 four-circle diffractometer

$\omega$ – $2\theta$  scans

Absorption correction: none

7032 measured reflections

6713 independent reflections

6368 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0121$

$\theta_{\text{max}} = 74.89^\circ$

$h = -13 \rightarrow 13$

$k = -15 \rightarrow 0$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 60 min

intensity decay: 1.5%

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.0361$

$\Delta\rho_{\text{max}} = 0.359 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.434 \text{ e \AA}^{-3}$

$wR(F^2) = 0.1068$

$S = 1.052$

6597 reflections

567 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.7746P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.009$

Extinction correction:

*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:

0.0024 (2)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
Na	0.13973 (6)	0.26590 (5)	0.65748 (5)	0.04810 (15)
Br	0.22789 (2)	−0.090647 (15)	0.04731 (2)	0.06435 (6)
N1	−0.01061 (13)	0.19104 (10)	0.76654 (11)	0.0457 (3)
C2	−0.1567 (2)	0.1743 (2)	0.6952 (2)	0.0587 (5)
C3	−0.1842 (2)	0.1206 (2)	0.5774 (2)	0.0657 (5)
O4	−0.11104 (13)	0.18119 (11)	0.53731 (10)	0.0605 (3)
C5	−0.1334 (2)	0.1365 (2)	0.4253 (2)	0.0639 (5)
C6	−0.0355 (2)	0.1948 (2)	0.3967 (2)	0.0643 (5)
O7	0.09577 (13)	0.17593 (11)	0.45922 (10)	0.0609 (3)
C8	0.1995 (2)	0.1949 (2)	0.4190 (2)	0.0678 (5)
C9	0.2323 (2)	0.3122 (2)	0.42751 (14)	0.0583 (5)
N10	0.27687 (13)	0.38202 (11)	0.53774 (10)	0.0453 (3)
C11	0.4245 (2)	0.3902 (2)	0.60045 (15)	0.0541 (4)
C12	0.4767 (2)	0.2866 (2)	0.6317 (2)	0.0585 (5)
O13	0.40192 (12)	0.24972 (11)	0.68795 (11)	0.0595 (3)
C14	0.4472 (2)	0.1524 (2)	0.7223 (2)	0.0739 (6)
C15	0.3945 (2)	0.1374 (2)	0.8055 (2)	0.0729 (6)
O16	0.24876 (12)	0.12181 (10)	0.75857 (10)	0.0562 (3)
C17	0.1980 (2)	0.0961 (2)	0.8346 (2)	0.0637 (5)
C18	0.0444 (2)	0.08772 (14)	0.7871 (2)	0.0609 (4)
C19	0.0106 (2)	0.26632 (12)	0.87200 (13)	0.0447 (3)
C20	0.2335 (2)	0.49193 (14)	0.53080 (13)	0.0484 (4)
C21	0.0560 (2)	0.53628 (11)	0.81372 (11)	0.0412 (3)
C22	−0.0466 (2)	0.59108 (12)	0.82853 (12)	0.0434 (3)
C23	−0.1429 (2)	0.54202 (12)	0.85843 (11)	0.0422 (3)
C24	−0.2522 (2)	0.59704 (14)	0.87259 (14)	0.0519 (4)
C25	−0.3444 (2)	0.5462 (2)	0.8992 (2)	0.0593 (5)
C26	−0.3320 (2)	0.4384 (2)	0.9126 (2)	0.0584 (4)
C27	−0.2276 (2)	0.38315 (14)	0.89919 (13)	0.0496 (4)
C28	−0.12949 (15)	0.43358 (12)	0.87154 (11)	0.0401 (3)
C29	−0.01782 (15)	0.37940 (11)	0.85817 (11)	0.0390 (3)
N30	0.07325 (12)	0.43211 (9)	0.83365 (9)	0.0382 (3)
O31	0.18236 (10)	0.38877 (8)	0.82913 (8)	0.0444 (2)
C32	0.1567 (2)	0.58155 (12)	0.77925 (12)	0.0428 (3)
C33	0.2410 (2)	0.67363 (13)	0.83646 (13)	0.0488 (4)
C34	0.3349 (2)	0.71312 (13)	0.79846 (14)	0.0495 (4)
C35	0.4247 (2)	0.80897 (15)	0.8578 (2)	0.0604 (5)
C36	0.5168 (2)	0.8437 (2)	0.8208 (2)	0.0705 (6)
C37	0.5225 (2)	0.7858 (2)	0.7242 (2)	0.0729 (6)
C38	0.4370 (2)	0.6931 (2)	0.6640 (2)	0.0634 (5)
C39	0.3394 (2)	0.65379 (13)	0.69943 (14)	0.0477 (4)
C40	0.24698 (15)	0.55870 (12)	0.63963 (12)	0.0436 (3)
N41	0.15725 (12)	0.52633 (10)	0.67876 (10)	0.0405 (3)
O42	0.06496 (10)	0.44439 (9)	0.62261 (8)	0.0444 (2)
OW	0.1041 (2)	0.14364 (13)	0.1288 (2)	0.0892 (6)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Na—O31	2.3910 (12)	O4—C5	1.432 (2)
Na—O42	2.4704 (13)	C5—C6	1.476 (3)
Na—O16	2.5257 (14)	C6—O7	1.383 (2)
Na—O7	2.5506 (14)	O7—C8	1.439 (3)
Na—O4	2.6111 (14)	C8—C9	1.486 (3)
Na—O13	2.6735 (14)	C9—N10	1.464 (2)
Na...N1	2.820 (2)	N10—C11	1.463 (2)
Na...N10	3.101 (2)	C11—C12	1.503 (3)
Na...N30	3.137 (2)	C12—O13	1.423 (2)
Na...N41	3.230 (2)	O13—C14	1.425 (3)

N1—C2	1.469 (2)	C14—C15	1.478 (4)
N1—C18	1.468 (2)	C15—O16	1.427 (2)
C2—C3	1.512 (3)	O16—C17	1.419 (3)
C3—O4	1.400 (3)	C17—C18	1.503 (3)
C18—N1—C2	111.52 (14)	C9—N10—C11	113.64 (14)
N1—C2—C3	113.2 (2)	N10—C11—C12	114.37 (15)
C2—C3—O4	109.8 (2)	C11—C12—O13	108.84 (14)
C3—O4—C5	113.26 (15)	C12—O13—C14	112.35 (15)
O4—C5—C6	108.9 (2)	O13—C14—C15	108.7 (2)
C5—C6—O7	109.0 (2)	C14—C15—O16	110.2 (2)
C6—O7—C8	116.3 (2)	C15—O16—C17	110.6 (2)
O7—C8—C9	113.1 (2)	O16—C17—C18	110.0 (2)
C8—C9—N10	115.4 (2)	C17—C18—N1	113.22 (15)
C18—N1—C2—C3	-72.1 (2)	C9—N10—C11—C12	-68.2 (2)
N1—C2—C3—O4	-55.4 (2)	N10—C11—C12—O13	-54.3 (2)
C2—C3—O4—C5	-179.1 (2)	C11—C12—O13—C14	-178.94 (15)
C3—O4—C5—C6	-170.7 (2)	C12—O13—C14—C15	163.8 (2)
O4—C5—C6—O7	63.8 (2)	O13—C14—C15—O16	63.8 (2)
C5—C6—O7—C8	160.2 (2)	C14—C15—O16—C17	173.9 (2)
C6—O7—C8—C9	70.3 (2)	C15—O16—C17—C18	176.0 (2)
O7—C8—C9—N10	57.1 (2)	C2—N1—C18—C17	165.3 (2)
C8—C9—N10—C11	88.6 (2)	O16—C17—C18—N1	-63.9 (2)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985). Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*; *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976); *ATOMS* (Dowty, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- Alpha, B., Balzani, V., Lehn, J.-M., Perathoner, S. & Sabbatini, N. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 1266–1267.
- Alpha, B., Lehn, J.-M. & Mathis, G. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 266–267.
- B. A. Frenz & Associates Inc. (1985). *SDP. Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- Dowty, E. (1994). *ATOMS. A Computer Program for Displaying Atomic Structures*. IBM-PC version 2.3 32-bit. Shape Software, Kingsport, USA.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–568.
- Lehn, J.-M. (1987). *Supramolecular Photochemistry*, edited by V. Balzani, pp. 29–42. Dordrecht: Reidel.
- Lehn, J.-M., Pietraszkiewicz, M. & Karpiuk, J. (1990). *Helv. Chim. Acta*, **73**, 106–111.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Sabbatini, N., Perathoner, S., Balzani V., Alpha, B. & Lehn, J.-M. (1987). *Supramolecular Photochemistry*, edited by V. Balzani, pp. 29–42. Dordrecht: Reidel.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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## *trans*-Bis(1,10-phenanthroline)-*trans*-bis(2,4,6-trinitrophenolato-*O,O'*)calcium(II)

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## Abstract

In the title compound,  $[\text{Ca}(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ , the  $\text{Ca}^{2+}$  ion exhibits eightfold coordination with four O atoms, two from each 2,4,6-trinitrophenolate (picrate) molecule, and four N atoms from two phenanthroline molecules, forming a twisted square antiprism. The N atoms of the phenanthroline molecule are polarized by the cation so that the Ca—N distances are comparable to the Ca—O(NO) distances.

## Comment

The structure determination of the title compound, (I), was undertaken as part of studies of the coordination chemistry of alkali and alkaline earth cations. (I) was synthesized from acetone medium using 2,4,6-trinitrophenolate (picrate) as the anion and 1,10-phenanthroline (phen) as a coordinating ligand (Vijayvergiya, 1984; Kanters, Stouten, Vijayvergiya & Poonia, 1987). This compound is stable in the solid phase (stability constant in acetone  $7.143 \times 10^{-3}$ , m.p. 583 K; Vijayvergiya, 1984), as has been observed for other Ca compounds (Singh, Reinhardt & Poonia, 1980, 1984; Poonia, Chandra, Padmanabhan & Yadav, 1990). The cation is eightfold coordinated by four O atoms of two picrate molecules and four N atoms of two phenanthroline molecules to form a twisted square-antiprismatic environment (Fig. 1).