Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.078$

$wR(F^2) = 0.279$

$S = 1.077$

1770 reflections

214 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.1520P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.421$ e Å^{-3}

$\Delta\rho_{min} = -1.190$ e Å^{-3}

Extinction correction: none

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sr—O6	2.574 (7)	C1—C2	1.440 (12)
Sr—O7	2.586 (6)	C2—C3	1.369 (13)
Sr—O8	2.583 (6)	C3—C4	1.361 (13)
Sr—N3	2.777 (7)	C4—C5	1.417 (13)
C1—C6	1.422 (13)	C5—C6	1.363 (13)
O6—Sr—O7	95.7 (2)	O6—Sr—N3	63.0 (2)
O6—Sr—O8	101.4 (2)	O7—Sr—N3	63.7 (2)
O7—Sr—O8	107.2 (2)	O8—Sr—N3	63.6 (2)
C11—N3—C7—C8	165.3 (8)	N3—C9—C10—O7	−54.6 (13)
C9—N3—C7—C8	−72.9 (11)	C9—N3—C11—C12	169.5 (8)
N3—C7—C8—O6	−51.3 (13)	C7—N3—C11—C12	−69.8 (10)
C11—N3—C9—C10	−78.7 (10)	N3—C11—C12—O8	−52.6 (11)
C7—N3—C9—C10	160.2 (9)		

The poor quality of the available crystals limited the resolution of the data to 22.5°, which led in turn to the low data/parameter ratio of 8.27. The structure was solved by direct methods using *SHELXTL/PC* (Sheldrick, 1995) and refined using full-matrix least-squares methods. Refinement was carried out on F^2 for all reflections, except for 241 with very negative F^2. All H atoms were fixed, except for the three hydroxyl group H atoms, which were located in a difference Fourier map. The H atoms were not refined and all non-H atoms were treated anisotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1079). Services for accessing these data are described at the back of the journal.

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(2,5,8,11,14-Pentaoxapentadecane-κ^5O)-bis(2,4,6-trinitrophenolato-O^1,O^2)-calcium(II)

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Abstract

In the title complex, $[Ca(C_6H_2N_3O_7)_2(C_{10}H_{22}O_5)]$, the tetraglyme ligand coordinates with Ca^{2+} through all five O atoms to form an equatorial arrangement around the cation. Both the picrate counter-anions chelate through their phenolic O atom and one of the O atoms of an *o*-nitro group. The anions are on opposite sides of the plane formed by the tetraglyme ligand. The Ca^{2+} coordination number is nine. The geometry around the cation is of the monocapped square antiprism type.

Comment

The structures of complexes of the *s*-block metal ions, $[M(anion)_x(ligand)_y(solvent)_z]$, where the ligand is an electrically neutral molecule with O- and N-donor atoms, appear to depend strongly on whether or not a polar or polarizable hydrogen(s) is present on the ligand. A ligand such as the glyme molecule, which lacks polarizable H atoms, interacts with the cation resulting in the formation of ion-paired complexes only (Poonia & Bajaj, 1979), whereas ligands carrying polarizable hydrogen(s), such as glycols, diamines and ethanolamines, coordinate with the cation and also bond to the counter-anion. This latter case usually leads to a decrease in the cation–anion interaction, maybe to the extent that the cation and one or more counter-anions no longer remain within a bonding distance of each other (Bajaj & Poonia, 1987; Poonia & Bajaj, 1979; Fenton, 1987). The title compound, (I), has been investigated in order to gain a deeper insight into systems lacking polar or polarizable H atoms.

(I)
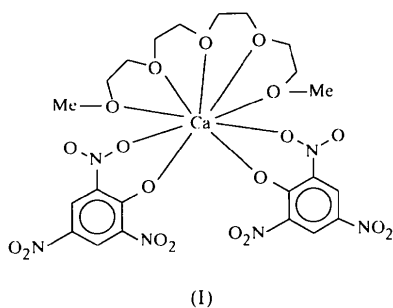
The Ca²⁺ ion is nine-coordinate, with the geometry being of the monocapped square antiprism type. Tetraglyme coordinates through all five O atoms. Both picrate anions coordinate through their phenolic O atom and one of the O atoms of an o-nitro group. The distances between Ca²⁺ and the tetraglyme O atoms vary between 2.451 (4) and 2.604 (4) Å (Table 1). The Ca—O(phenoxide) distances are 2.388 (4) and 2.458 (4) Å, and the Ca—O(nitro) distances are 2.527 (4) and 2.597 (5) Å. The Ca—O(ether) distances are comparable to the average distances of 2.468 (3) and 2.453 (5) Å observed in the cases of [Ca(tetraglyme)(NCS)₂]·H₂O and [Ca(triglyme)(NCS)₂]·H₂O, respectively (Wei et al., 1987), except for Ca—O15, which is slightly longer [2.604 (4) Å].

The torsion angles in the polyether chain have the sequence ag⁻a gg⁻a aga ag⁻a, which is different than that seen in tetraglyme complexes of the thiocyanates of Ca²⁺, Sr²⁺ and Ba²⁺ (Wei et al., 1987), where this sequence was ag⁻a ag⁺a ag⁻a ag⁻a in all three complexes. In the present complex, the torsion angle C15—O16—C16—C17 is −98.0 (7)°, which is more nearly in a gauche conformation than the anti conformation found in the thiocyanate complexes. This kink places one 1,4-dioxa unit perpendicular to the other three. Thus, the conformation of the polyether becomes helical rather than extended. This helical arrangement is observed with longer polyethers (Vögtle & Weber, 1979; Dale, 1980), while ligands with five heteroatoms fold in an equatorial plane. It seems that the participation of a bigger coordinating anion also forces a change in conformation. Four O atoms (O16–O19) are coplanar (±0.1 Å), whereas the fifth O atom (O15) is 1.8 (4) Å out of the plane. The Ca²⁺ ion is only 0.48 (1) Å out of the plane of these four O atoms. The O···O distances range from 2.679 (4) to 2.763 (4) Å, which is comparable to what has been found in [Ca(tetraglyme)(NCS)₂], but the opening of the horseshoe is considerably larger (O15···O19 4.159 Å) compared with 3.502 (8) Å in the above-mentioned complex. This longer O···O distance is obviously due to non-planarity of the O15 atom.

Comparing the results of the present structure with that of [Ca(tetraethyleneglycol)(picrate)(H₂O)](picrate) (Singh et al., 1980, 1984), it can be seen that in the latter complex only one picrate chelates with the cation. The tetraethylene glycol chelates through all its O atoms, while the eighth coordination site is occupied by a water molecule. The second picrate molecule does not interact with the cation and is extensively hydrogen bonded to the hydroxyl groups of the tetraethylene glycol. This hydrogen bonding decreases the nucleophilic character of the picrate anion. In the case of the title compound, since the ligand lacks polarizable hydrogen(s), lack of hydrogen bonding forces the anion to interact directly with the cation. A similar absence of hydrogen bonding has been
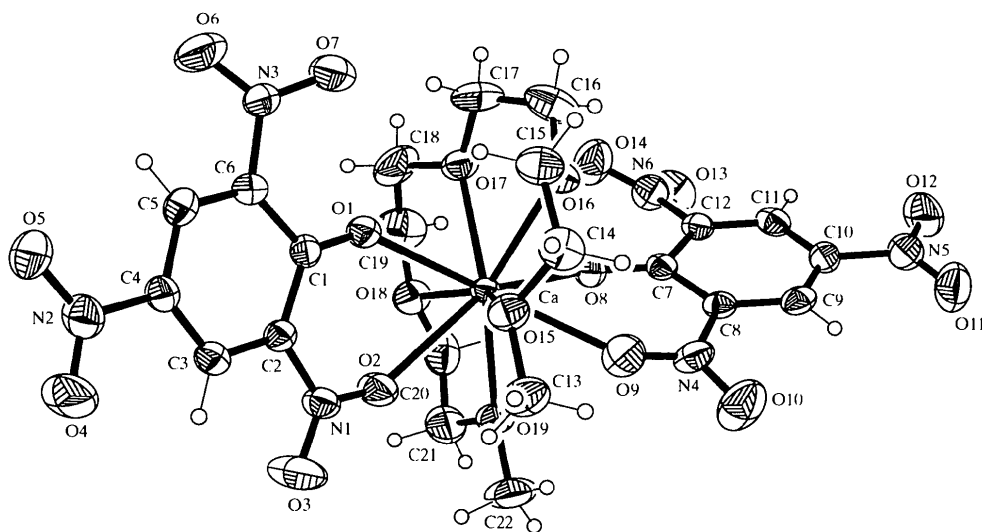

Fig. 1. Drawing (SHELXTL/PC; Sheldrick, 1995) of the final model of (I), showing non-H atoms with displacement ellipsoids drawn at 30% probability.

observed in the case of [M(tetraglyme)(NCS)$_2$]·H$_2$O and [M(triglyme)(NCS)$_2$]·H$_2$O (M = Ca^{2+}, Sr^{2+}, Ba^{2+}; Wei *et al.*, 1987), and in all these cases, a 1:1 ion-paired complex is observed.

Experimental

The synthesis of the title compound was carried out by adding tetraglyme dropwise to a warm solution of calcium picrate in alcohol (1:1 ratio). A crystalline product was obtained which was recrystallized from absolute ethanol by slow evaporation. Yellow crystals (m.p. 453–457 K) were obtained after 3 d.

Crystal data

[Ca(C$_6$H$_2$N$_3$O$_7$)$_2$(C$_{10}$H$_{22}$O$_5$)]	Mo $K\alpha$ radiation
M_r = 718.57	λ = 0.71073 Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
a = 8.736 (2) Å	θ = 20–25°
b = 9.655 (2) Å	μ = 0.305 mm^{-1}
c = 18.773 (4) Å	T = 293 (2) K
α = 99.79 (3)°	Needle
β = 95.90 (3)°	0.3 × 0.2 × 0.2 mm
γ = 102.93 (3)°	Yellow
V = 1504.4 (5) Å^3	
Z = 2	
D_x = 1.586 Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	R_{int} = 0.044
2θ–θ scans	θ_{max} = 22.5°
Absorption correction:	h = 0 → 8
ψ scan (North *et al.*,	k = −12 → 10
1968)	l = −20 → 20
T_{min} = 0.737, T_{max} = 0.941	3 standard reflections
4296 measured reflections	every 97 reflections
3835 independent reflections	intensity decay: none
2586 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.061	$\Delta\rho_{max}$ = 0.450 e Å^{-3}
$wR(F^2)$ = 0.187	$\Delta\rho_{min}$ = −0.329 e Å^{-3}
S = 1.047	Extinction correction: none
3452 reflections	Scattering factors from
433 parameters	*International Tables for*
H atoms not refined	*Crystallography* (Vol. C)
w = 1/[$\sigma^2(F_o^2)$ + (0.0975P)^2	
+ 0.3048P]	
where P = (F_o^2 + 2F_c^2)/3	

Table 1. *Selected geometric parameters (Å, °)*

Ca—O8	2.388 (4)	Ca—O19	2.516 (4)
Ca—O17	2.451 (4)	Ca—O2	2.527 (4)
Ca—O1	2.458 (4)	Ca—O9	2.597 (5)
Ca—O18	2.474 (4)	Ca—O15	2.604 (4)
Ca—O16	2.485 (4)		
O8—Ca—O17	74.37 (13)	O18—Ca—O2	82.2 (2)
O8—Ca—O1	147.25 (13)	O16—Ca—O2	133.01 (14)

O17—Ca—O1	73.41 (12)	O19—Ca—O2	66.57 (13)
O8—Ca—O18	81.74 (14)	O8—Ca—O9	64.06 (14)
O17—Ca—O18	65.90 (15)	O17—Ca—O9	129.22 (14)
O1—Ca—O18	90.41 (13)	O1—Ca—O9	137.52 (14)
O8—Ca—O16	79.88 (13)	O18—Ca—O9	130.2 (2)
O17—Ca—O16	66.74 (14)	O16—Ca—O9	78.0 (2)
O1—Ca—O16	82.23 (13)	O19—Ca—O9	71.8 (2)
O18—Ca—O16	132.20 (14)	O2—Ca—O9	104.72 (15)
O8—Ca—O19	77.91 (13)	O8—Ca—O15	122.58 (14)
O17—Ca—O19	127.1 (2)	O17—Ca—O15	124.22 (14)
O1—Ca—O19	127.59 (13)	O1—Ca—O15	72.89 (12)
O18—Ca—O19	66.23 (15)	O18—Ca—O15	154.54 (14)
O16—Ca—O19	148.13 (15)	O16—Ca—O15	65.73 (13)
O8—Ca—O2	144.43 (13)	O19—Ca—O15	108.65 (14)
O17—Ca—O2	126.02 (14)	O2—Ca—O15	73.28 (15)
O1—Ca—O2	64.10 (12)	O9—Ca—O15	64.74 (14)
C13—O15—C14—C15	179.9 (5)	C17—O17—C18—C19	167.2 (7)
C16—O16—C15—C14	−171.2 (6)	C20—O18—C19—C18	−159.1 (7)
O15—C14—C15—O16	−61.2 (7)	O17—C18—C19—O18	49.5 (10)
C15—O16—C16—C17	−98.0 (7)	C19—O18—C20—C21	−174.4 (6)
C18—O17—C17—C16	−174.0 (6)	C22—O19—C21—C20	−172.6 (5)
O16—C16—C17—O17	−50.8 (9)	O18—C20—C21—O19	−60.0 (7)

The poor quality of the crystal limited the resolution of the data to 22.5°. Refinement on F^2 included all reflections, except for 383 with very negative F^2. All the H atoms were fixed but not refined. All non-H atoms were treated anisotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XPREP* in *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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