Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(nitrato-κ^2O,O')(1,4,7,10,13-pentaoxacyclopentadecane)calcium(II)

Michael D. Brown, William Levason and Michael Webster*

School of Chemistry, University of Southampton, Southampton SO17 1BJ, England

Correspondence e-mail:
m.webster@soton.ac.uk

Received 29 March 2005
Accepted 22 April 2005
Online 7 May 2005

The crystal structure of the title compound, $[Ca(NO_3)_2(C_{10}H_{20}O_5)]$, at 120 K contains discrete molecules with nine-coordinate Ca atoms. There are two molecules in the asymmetric unit, related by a pseudo-inversion centre. The crown bonds through five O atoms [Ca—O = 2.464 (2)–2.567 (2) Å] and the nitrates are bidentate [Ca—O = 2.444 (2)–2.588 (2) Å]. The structure is a polymorph of a previously reported room-temperature form.

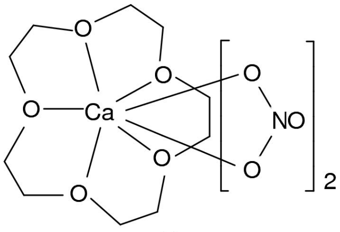
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.040
wR factor = 0.089
Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A room-temperature crystal structure of the title compound, (I), has been reported in the space group *Pbca* (No. 61) (Junk & Steed, 1999). There appears to be a typographical error in the cell dimensions reported in the paper (*a* and *c* have been interchanged) when compared with the values in the deposited CIF.



(I)

Our orthorhombic cell parameters were similar to the published values with, as expected, slightly smaller values due to the lower temperature (cell volume *ca* 2.7% smaller). However, the observed absences were not consistent with space group *Pbca*, but rather with space group $Pca2_1$ (No. 29) or *Pbcm* (No. 57) (both referred to standard settings). No solution emerged in the centrosymmetric space group *Pbcm*, but a solution did result from a direct methods calculation in $Pca2_1$, with two similar molecules in the asymmetric unit. The Flack (1983) parameter indicates an inversion twin.

There is a pseudo-centre of symmetry relating the two molecules and the solution in the space group *Pbca* was explored, even though well over half of the reflections were 'observed' in the *h*0*l* zone with *l* odd (in the appropriate orientation). Although a solution with one molecule in the asymmetric unit could be obtained, refinement failed to reduce *R*1 below 0.18 and the displacement ellipsoids were very elongated.

The conclusion is that, at 120 K, the crystal structure is correctly described in the non-centrosymmetric space group $Pca2_1$ and represents a polymorph of the room-temperature structure.

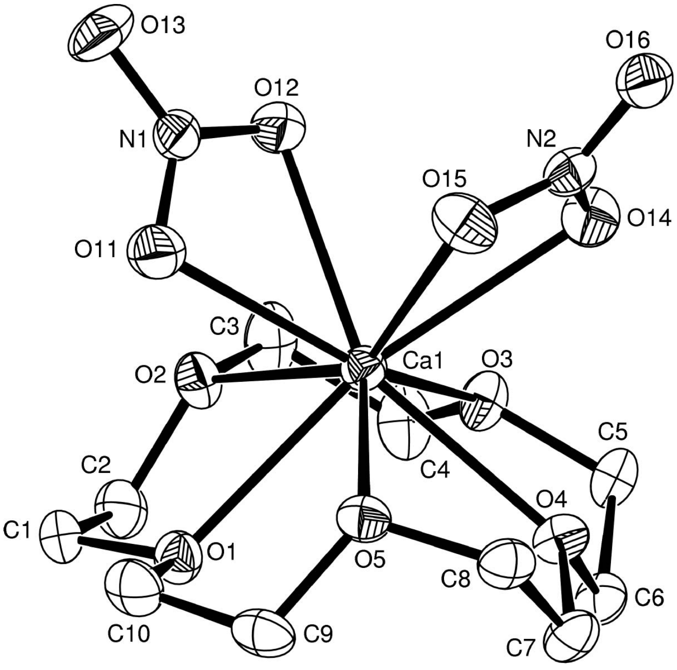


Figure 1
One of the two molecules in the asymmetric unit of $[Ca(NO_3)_2$(15-crown-5)], showing the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The other molecule is very similar.

On transforming the data to the *Pbca* orientation, the systematic absences correspond to the non-standard space group setting $Pb2_1a$ (No. 29), which is a maximal non-isomorphic subgroup of *Pbca.* Whether this polymorph is stable at room temperature or a structural change occurs on cooling is not clear; however, the relationship between the two structures perhaps favours the latter.

The geometry agrees well with the earlier room-temperature structure (Junk & Steed, 1999). The Ca atoms are nine-coordinate with two bidentate nitrate groups (Fig. 1 and Table 1). The Ca—O bonds to the crown ligands [2.464 (2)–2.567 (2) Å] can be compared with the literature values [2.474 (3)–2.581 (4) Å; Junk & Steed, 1999]. The nitrates are bonded fairly symmetrically [differences in Ca—O within each ligand range from 0.006 (3) to 0.144 (3) Å] and, as noted before (Valle *et al.*, 1986), the terminal N—O bond is shorter than the bridging bonds by *ca* 0.04 Å; values for one typical ligand are included in Table 1. There is also a distortion of the angles at nitrogen, the O—N—O angle involved in the four-membered ring being several degrees smaller than the ideal value of 120°.

Experimental

Crystals were isolated during the attempted crystal growth of a calcium azide/15-crown-5 complex. The nitrate was present in the mixture in small amounts from the synthesis $[Ca(NO_3)_2$(15-crown-5) and CsN_3 in methanol] and led to the isolated product.

Crystal data

$[Ca(NO_3)_2(C_{10}H_{20}O_5)]$
$M_r = 384.36$
Orthorhombic, $Pca2_1$
$a = 15.1940$ (15) Å
$b = 15.908$ (3) Å
$c = 13.227$ (2) Å
$V = 3197.1$ (8) Å^3
$Z = 8$
$D_x = 1.597$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3946 reflections
$\theta = 2.9$–27.5°
$\mu = 0.45$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.22 × 0.17 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.814$, $T_{max} = 0.986$
24234 measured reflections
6509 independent reflections

5672 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 27.5°$
$h = -18 \rightarrow 19$
$k = -20 \rightarrow 18$
$l = -17 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.089$
$S = 1.03$
6509 reflections
435 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.774P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Absolute structure: Flack (1983), 2675 Friedel pairs
Flack parameter = 0.48 (3)

Table 1
Selected geometric parameters (Å, °).

Ca1—O1	2.514 (2)	Ca2—O8	2.464 (2)
Ca1—O2	2.561 (2)	Ca2—O9	2.502 (2)
Ca1—O3	2.4759 (19)	Ca2—O10	2.514 (2)
Ca1—O4	2.476 (2)	Ca2—O17	2.453 (2)
Ca1—O5	2.523 (2)	Ca2—O18	2.502 (2)
Ca1—O11	2.454 (2)	Ca2—O20	2.448 (2)
Ca1—O12	2.460 (2)	Ca2—O21	2.548 (2)
Ca1—O14	2.588 (2)	N1—O11	1.268 (3)
Ca1—O15	2.444 (2)	N1—O12	1.263 (3)
Ca2—O6	2.539 (2)	N1—O13	1.226 (3)
Ca2—O7	2.567 (2)		
O4—Ca1—O3	66.82 (6)	O10—Ca2—O6	64.58 (7)
O4—Ca1—O5	66.15 (6)	O8—Ca2—O7	64.85 (7)
O1—Ca1—O5	64.39 (7)	O6—Ca2—O7	64.10 (7)
O3—Ca1—O2	65.25 (6)	O17—Ca2—O18	51.94 (7)
O1—Ca1—O2	64.45 (7)	O20—Ca2—O21	50.99 (7)
O11—Ca1—O12	52.36 (7)	O13—N1—O12	121.1 (3)
O15—Ca1—O14	50.61 (7)	O13—N1—O11	121.1 (3)
O8—Ca2—O9	66.28 (6)	O12—N1—O11	117.8 (2)
O9—Ca2—O10	65.58 (6)		

H atoms were placed in calculated positions (C—H = 0.99 Å) with a common refined U_{iso}.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97.*

We thank the EPSRC for financial support (MDB).

m1016 Michael D. Brown *et al.* • $[Ca(NO_3)_2(C_{10}H_{20}O_5)]$ *Acta Cryst.* (2005). E**61**, m1015–m1017

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

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

Junk, P. C. & Steed, J. W. (1999). *J. Chem. Soc. Dalton Trans.* pp. 407–414.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Valle, G., Casotto, G., Zanonato, P. L. & Zarli, B. (1986). *Polyhedron*, **5**, 2093–2096.

Acta Cryst. (2005). E**61**, m1015–m1017 Michael D. Brown *et al.* • [$Ca(NO_3)_2(C_{10}H_{20}O_5)$] **m1017**