Acta Cryst. (1999). C55, 324-326

Dicalcium triacetate nitrate dihydrate

Brian G. Cooksey, Lorraine T. Gibson, Alan R. Kennedy, David Littlejohn, Lesley Stewart and Norman H. Tennent

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

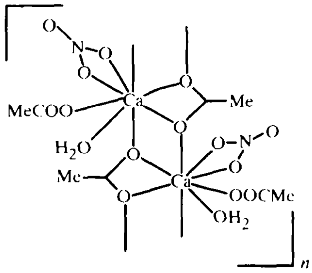
(*Received 12 August 1998; accepted 5 October 1998*)

Abstract

The structure of tri-μ-acetato-diaqua-μ-nitrato-dicalcium, $[Ca_2(CH_3COO)_3(NO_3)(H_2O)_2]_n$, is shown to consist of infinite O-bridged double-stranded calcium chains crosslinked both by bridging anions and by hydrogen bonding to form a three-dimensional polymer. Both the independent Ca centres are eight-coordinate.

Comment

The deterioration of porous museum artefacts as a result of salt efflorescence is a widespread problem. Typically, soluble-salt contaminants in a porous material (such as stone and ceramics) are transported to the surface of an artefact by fluctuations in the relative humidity of the storage or display environment. Investigation of thecotrichite, a common efflorescence salt with an extremely fibrous habit, has shown it to have the stoichiometry $Ca_3(CH_3COO)_3(NO_3)_2Cl{\cdot}7H_2O$ (Gibson *et al.*, 1997). We wished to investigate the thermodynamic stability of thecotrichite and to this end prepared a series of calcium double salts which may be present in the thecotrichite system. One of these, $Ca_2(CH_3COO)_3(NO_3){\cdot}2H_2O$, (I), gave crystals suitable for single-crystal diffraction analysis and its structure is described herein. The only previously described crystal structure of a Group 2 metal acetate nitrate double salt is $Sr_2(CH_3COO)_2(NO_3)_2{\cdot}3H_2O$ (Lengauer & Glester, 1997).



(I)

The crystal structure of (I) consists of double-stranded Ca chains propagating along the *b* direction. These are linked by bridging O atoms from both nitrate and acetate anions to form a three-dimensional polymeric array. This structural type is related to that seen in $Ca(CH_3COO)_2{\cdot}H_2O$ and $Ca(CH_3COO)_2(CH_3COOH){\cdot}H_2O$ (Klop *et al.*, 1984; Klop & Spek, 1984). There is also an extensive network of hydrogen bonds (Table 3) extending both along the chains and between them.

The two independent Ca centres both attain eight-coordination through bonding to two O atoms of a chelated nitrate, two O atoms of a chelated acetate, three O atoms from three separate bridging acetates and one water molecule. The acetate ligand containing the O2 and O3 atoms binds in a bridging mode only, but all of the other anions are involved in both chelating and bridging interactions. The calcium-to-acetate bond distances [range 2.329 (2)–2.574 (2) Å] are within the range found for other calcium acetate salts (Helems *et al.*, 1988; van der Sluis *et al.*, 1987; and references cited above). Three of the calcium-to-nitrate Ca—O distances also lie in the expected range, but the fourth [Ca2—O8 2.744 (4) Å] is elongated by approximately 0.15 Å. The water ligands and the methyl group at C4 are affected by disorder. These groups were each modelled over two sites with equal occupancy for each component.

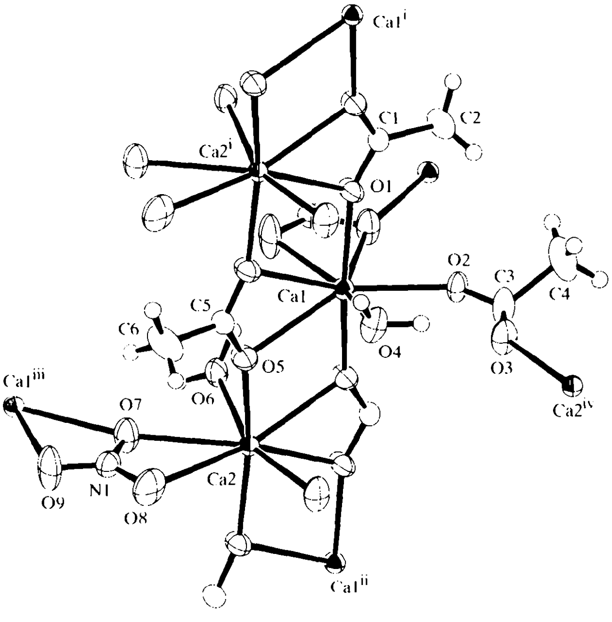


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I) showing the double-stranded calcium chain propagating along the *b* direction. Non-H atoms are shown as 50% probability ellipsoids and H atoms as small spheres of arbitrary radii. Only one component of each pair of disordered atoms is shown. [Symmetry codes: (i) $x, 1+y, z$; (ii) $x, -1+y, z$; (iii) $\frac{3}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}+z$; (iv) $1-x, \frac{1}{2}+y, -z$.]

Experimental

Calcium acetate (3.16 g, 0.02 mol) and calcium nitrate hydrate (3.64 g, 0.02 mol) were dissolved in warm distilled water

ISSN 0108-2701 © 1999

(22 ml). Cooling to room temperature overnight gave (I) as colourless needles.

Crystal data

$[Ca_2(C_2H_3O_2)_3(NO_3)(H_2O)_2]$
$M_r = 355.33$
Orthorhombic
Pnma
$a = 17.882$ (5) Å
$b = 6.8049$ (9) Å
$c = 11.712$ (6) Å
$V = 1425.2$ (8) Å^3
$Z = 4$
$D_x = 1.656$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 18 reflections
$\theta = 10.45$–18.27°
$\mu = 0.852$ mm^{-1}
$T = 295$ (2) K
Acicular
0.40 × 0.10 × 0.08 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.801$, $T_{max} = 0.942$
1772 measured reflections
1772 independent reflections

1113 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.106$
$S = 1.023$
1772 reflections
128 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.0079P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0039 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ca1	0.65158 (4)	3/4	−0.02145 (5)	0.02159 (19)
Ca2	0.65523 (4)	1/4	−0.20017 (5)	0.02066 (19)
O1	0.65918 (10)	1.0907 (2)	−0.00611 (14)	0.0339 (4)
O2	0.59956 (13)	3/4	0.1680 (2)	0.0314 (6)
O3	0.47574 (14)	3/4	0.1655 (2)	0.0429 (7)
O4†	0.52272 (18)	0.8247 (6)	−0.0607 (3)	0.0426 (11)
O5	0.64907 (10)	0.5901 (2)	−0.22059 (14)	0.0341 (5)
O6†	0.78649 (18)	0.3096 (5)	−0.1649 (3)	0.0348 (10)
O7	0.73624 (15)	1/4	−0.3844 (2)	0.0434 (7)
O8	0.62093 (16)	1/4	−0.4285 (3)	0.0558 (9)
O9	0.70715 (17)	1/4	−0.5604 (2)	0.0589 (10)
N1	0.68643 (17)	1/4	−0.4597 (3)	0.0323 (7)
C1	0.65995 (18)	5/4	0.0473 (3)	0.0228 (7)
C2	0.6622 (3)	5/4	0.1752 (3)	0.0449 (11)
C3	0.5372 (2)	3/4	0.2122 (3)	0.0444 (11)
C4†	0.5347 (3)	0.8783 (13)	0.3268 (5)	0.073 (2)
C5	0.6427 (2)	3/4	−0.2719 (3)	0.0279 (8)
C6	0.6289 (4)	3/4	−0.3989 (3)	0.0676 (16)

† Site occupancy = 0.50.

Table 2. *Selected bond distances* (Å)

Ca1—O1	2.329 (2)	Ca2—O5	2.329 (2)
Ca1—O4	2.404 (3)	Ca2—O3^{ii}	2.377 (3)
Ca1—O2	2.406 (3)	Ca2—O6	2.418 (3)
Ca1—O9^{i}	2.567 (3)	Ca2—O1^{iii}	2.519 (2)
Ca1—O7^{i}	2.569 (3)	Ca2—O7	2.599 (3)
Ca1—O5	2.574 (2)	Ca2—O8	2.744 (4)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (ii) $1-x, 1-y, -z$; (iii) $x, \frac{3}{2}-y, z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4*E*···O3	1.00	1.86	2.825 (4)	162
O6—H6*E*···O2^{i}	0.93	1.99	2.855 (5)	154
O4—H4*D*···O3^{ii}	0.82	2.34	3.143 (4)	166
O6—H6*D*···O9^{iii}	1.00	2.24	3.239 (5)	178

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $1 - x, 2 - y, -z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

The water ligands and one methyl group are disordered, each over two crystallographically related positions with equal occupancy. In addition, the H atoms of the other methyl groups are also disordered. An alternative solution in space group $Pna2_1$ was considered, but rejected as the quality of the solution (R and wR) was poorer than that reported and the disordered components were still present. The H atoms of the water ligands were placed as found. Methyl H atoms were placed in calculated positions with the group orientation assigned by refining a rotational parameter about the C—Me bonds. U_{iso}(H) was set to $1.2U_{eq}$(O) for water and to $1.5U_{eq}$(C) for methyl groups.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

The authors acknowledge NERC for funding LTG.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1288). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Gibson, L. T., Cooksey, B. G., Littlejohn, D. & Tennent, N. H. (1997). *Anal. Chim. Acta*, **337**, 151–164, 253–264.
Helems, R., Cole, L. B. & Holt, E. M. (1988). *Inorg. Chim. Acta*, **152**, 9–15.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Klop, E. A., Schouten, A., van der Sluis, P. & Spek, A. L. (1984). *Acta Cryst.* **C40**, 51–53.
Klop, E. A. & Spek, A. L. (1984). *Acta Cryst.* **C40**, 1817–1819.
Lengauer, C. L. & Giester, G. (1997). *Acta Cryst.* **C53**, 870–872.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sluis, P. van der, Schouten, A. & Spek, A. L. (1987). *Acta Cryst.* C**43**, 1922–1924.

Acta Cryst. (1999). C**55**, 326–328

(1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato-*O,O′*)(1,4,7,10,13-pentaoxapentadecane-κ^5O)sodium

Louis J. Farrugia[a] and Ian M. Watson[b]

[a]*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, and* [b]*Institute of Photonics, University of Strathclyde, Wolfson Centre, 106 Rottenrow, Glasgow G4 0NW, Scotland. E-mail: louis@chem.gla.ac.uk*

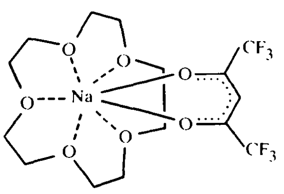
(*Received 27 August 1998; accepted 8 October 1998*)

Abstract

The title compound, $[Na(C_5HF_6O_2)(C_{10}H_{20}O_5)]$, contains a seven-coordinate Na^+ ion with an irregular coordination geometry. It is bonded to the five crown ether and the two β-diketonate O atoms. The structure contains no unusual features, the conformation of the crown ether being very similar to those in compounds described previously. There are no particularly short intermolecular contacts and the title compound behaves as a discrete molecule, which probably accounts for its relatively high volatility.

Comment

The title compound, (I), sublimes without decomposition at 390 K and a pressure of *ca* 5 Pa, and is thus potentially useful as a precursor for chemical vapour deposition of NaF films. It is also air stable, in contrast to the sodium fluoroalkoxides used in most reported work in this area (Lingg *et al.*, 1992; Samuels *et al.*, 1993, 1994). Furthermore, (I) is of interest as an analogue of the various structurally characterized volatile group 2 metal compounds containing 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa) and polyether ligands (Motevalli *et al.*, 1996).



(I)

To date, more than 60 structures containing 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) coordinated to an Na^+ ion have been described. The Na^+ ion is invariably bonded to all five O atoms of the crown ether, and in the vast majority of cases increases its coordination number by either one or two by binding to other (usually hard) donor atoms. In rare cases, as in hexakis(phenylthiolato)tantalum (Koo *et al.*, 1990) or the tetrachloronickel salts (Ruhlandt-Senge & Muller, 1990), the Na^+ ion remains five-coordinate.

In complex (I), the Na^+ ion is seven-coordinate. The Na—O(crown ether) distances are in the range 2.446 (2)–2.549 (3) Å [mean 2.493 (3) Å] and are substantially longer than the Na—O(diketonate) distances of 2.371 (2) and 2.381 (2) Å. The Na^+ ion is displaced by 0.9894 (13) Å from the mean plane described by the crown-ether O atoms. The distances from the mean plane are: O11 −0.0221 (14), O12 0.2972 (14), O13 −0.4832 (15), O14 0.4420 (14) and O15 −0.2339 (14) Å. Thus, the Na^+ ion is on the same side of the mean plane as two of the crown-ether O atoms (O12 and O14). The literature compounds most closely related to (I) are (15-crown-5)(4-ethoxybutan-2-one-4-olato-*O,O′*)sodium (Cambillau *et al.*, 1982) and (15-crown-5)[diphenylethyl(diphenylmethyl)cyanoacetonato]sodium (Coleman *et al.*, 1991), both of which contain a six-membered Na—O=C(*R*)C(*R*)C(*R*)=O β-diketonate ring system. For these compounds, the mean Na—O(crown ether) and mean Na—O(ketonate) distances are 2.491/2.309 and 2.478/2.320 Å, respectively.

The coordination geometry of the Na^+ ion could be crudely described as a very distorted pentagonal bipyramid, with atoms O1 and O13 in axial positions, but with the remaining five O atoms being far from coplanar. The conformation of the crown ether is similar to that described by Buchanan *et al.* (1994), with all

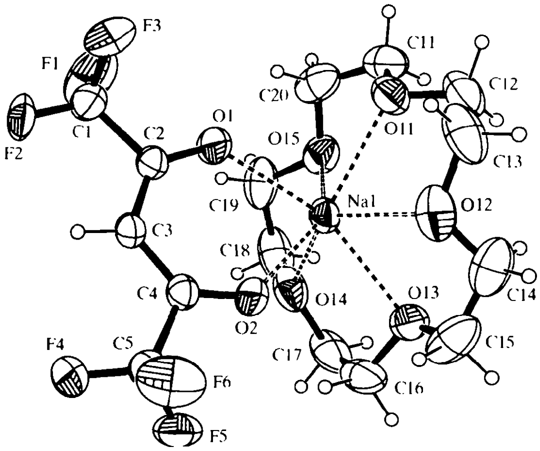


Fig. 1. View of (I) (30% probability displacement ellipsoids). Only the F atoms of the major component of disorder are shown.