20–300 K, with an average μ_{eff} per radical of 1·743 (8) BM.* Below 20 K the moment increases slightly, reaching a maximum value of 1·805 BM at 6 K, the lowest temperature investigated. The equation of the least-squares straight line for the 20–300 K data is $1/\chi = 1·3003$ (17) $T + 1·43$ (18) or in standard Curie–Weiss form $\chi = 0·7691$ (11)/[$T + 1·10$ (14)]. Thus the results closely approach those expected for a single free spin on each nitroxyl radical.

In view of the relatively large separation between radical centers, it is not surprising that the magnetic data from 20–300 K show no evidence for interaction between the free spins of the nitroxyl radicals. The small increase in μ_{eff} below 20 K could be indicative of the onset of some sort of magnetic ordering, but a more thorough magnetic study would be needed to establish this point. The layered packing illustrated in Fig. 1 could very well give rise to one- or two-dimensional magnetic ordering at low temperatures.

This is the second instance in which the tmpCN radical has combined with a transition-metal complex to yield a material of well-defined stoichiometry containing no direct metal–nitroxyl interaction. With $Cu(F_6acac)_2$, in the presence of small amounts of water,

a product with a linear chain structure was obtained (Dickman & Doedens, 1983). The nitroxyl O atom of the tmpCN ligand was hydrogen bonded to a coordinated water molecule and very weakly bound to copper through its nitrile N atom. When water was rigorously excluded, no new product could be isolated. Thus, no complex of tmpCN containing a metal–nitroxyl covalent bond has yet been prepared.

---

* 1 BM (Bohr magneton) $\equiv 0·927 \times 10^{-23}$ Am^2; 1 e.m.u. $\equiv 4\pi \times 10^{-6}$ SI unit.

References

ANDERSON, O. P. & KUECHLER, T. C. (1980). *Inorg. Chem.* **19**, 1417–1422.
BOEYENS, J. C. A. & KRUGER, G. J. (1970). *Acta Cryst.* B**26**, 668–672.
CORFIELD, P. W.R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
DICKMAN, M. H. (1983). PhD Thesis, Univ. of California, Irvine.
DICKMAN, M. H. & DOEDENS, R. J. (1983). *Inorg. Chem.* **22**, 1591–1594.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
PORTER, L. C., DICKMAN, M. H. & DOEDENS, R. J. (1983). *Inorg. Chem.* **22**, 1962–1964.
SIEDLE, A. R., KISTENMACHER, T. J., METZGER, R. M., KUO, C.-K., VAN DUYNE, R. P. & CAPE, T. (1980). *Inorg. Chem.* **19**, 2048–2051.
SIEDLE, A. R., NEWMARK, R. A. & PIGNOLET, L. H. (1983). *Inorg. Chem.* **22**, 2281–2286.
STROUSE, C. E. (1981). Personal communication.
TURLEY, J. W. & BOER, F. P. (1972). *Acta Cryst.* B**28**, 1641–1644.

Structure of Calcium Hydrogen Triacetate Monohydrate, CaH(C$_2$H$_3$O$_2$)$_3$.H$_2$O

BY E. A. KLOP AND A. L. SPEK*

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, Universiteit van Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

Abstract. $M_r = 236·24$, triclinic, $P\bar{1}$, $a = 6·858$ (1), $b = 12·281$ (2), $c = 12·520$ (3) Å, $\alpha = 83·86$ (2), $\beta = 91·62$ (2), $\gamma = 87·09$ (2)°, $U = 1046·5$ (3) Å^3, $Z = 4$, $D_x = 1·499$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 5·9 cm^{-1}, $T = 295$ K, $F(000) = 496$, $R = 0·046$ for 2551 observed reflections with $I > 2·5\sigma(I)$. The structure consists of infinite multiple O-bridged double-stranded Ca chains running in the **a** direction that are cross linked in the **b** and **c** directions *via* hydrogen bonds.

---

* To whom correspondence should be addressed.

Introduction. The acid salt CaH(OAc)$_3$.H$_2$O was crystallized in an attempt to prepare the neutral salt Ca(OAc)$_2$.H$_2$O. Its existence has been reported previously by Walter-Levy & Perrier (1958) who studied the ternary system CaO–Ac$_2$O–H$_2$O at 298 K. Acid salts of monocarboxylic acids are not rare; for a review see Speakman (1972). The structure of the neutral salt Ca(OAc)$_2$.H$_2$O has been published previously (Klop, Schouten, van der Sluis & Spek, 1984). The study of the crystal structures of the calcium acetates is considered to be relevant for the understanding of the incongruently saturating behaviour of the double salt CaCu-(OAc)$_4$.6H$_2$O (Klop, Duisenberg & Spek, 1983).

Experimental. Colourless transparent crystals of the title compound were grown from a solution of $Ca(OAc)_2$ in diluted acetic acid and are unstable in air. D_m not determined. A suitable specimen ($0.12 \times 0.35 \times 0.65$ mm) was cut from a needle in a drop of paraffin to prevent decay due to loss of water and was sealed in a Lindemann-glass capillary. Enraf–Nonius CAD-4F diffractometer. Cell parameters calculated by least squares from the setting angles of 11 reflections with $12.8 < \theta < 16.7°$. Unique data set (h 0:8, k -14:14, l -14:14) with $\theta \le 25°$ obtained using the $\omega/2\theta$-scan mode with Zr-filtered Mo $K\alpha$ radiation; total of 3994 reflections scanned; fluctuations of 2% and a decay of 17% during 44 h of X-ray exposure time monitored by one reference reflection ($\overline{335}$) and the data corrected accordingly; intensity data corrected for Lorentz, polarization and absorption effects (Walker & Stuart, 1983); min. and max. absorption correction 0.727 and 1.378; unique set of 3168 reflections obtained of which 2551 with $I > 2.5\sigma(I)$ used in the calculations. Structure solved by Patterson and Fourier methods and refined on F by blocked full-matrix least-squares procedures. H atoms introduced at calculated positions and refined on their carrier atoms, except for those involved in hydrogen bonding which were located from a difference electron density map. The methyl-group protons of $C(12)$ were refined with a disorder model (two mutually staggered conformations with population ratio 56:44). Anisotropic thermal parameters for all nonhydrogen atoms. Empirical extinction correction: $F^{corr}_{calc} = F[1 - 2.99 \times 10^{-7}F^2/\sin(\theta)]$. Convergence reached $R = 0.046$, $wR = 0.058$, $w^{-1} = [\sigma^2(F) + 0.001F^2]/1.236$, $S = 0.97$, $(\Delta/\sigma)_{max} = 0.2$; min. and max. residual electron density -0.048, 0.56 e Å^{-3}. Scattering factors from Cromer & Mann (1968). Anomalous-dispersion corrections from Cromer & Liberman (1970). Calculations carried out on the CYBER175 of the University of Utrecht with programs of the *SHELX*76 (Sheldrick, 1976) and *EUCLID* (Spek, 1982) packages.

Discussion. Table 1 lists the final atomic parameters.* Table 2 gives details of the geometry. Fig. 1 illustrates part of the infinite O-bridged Ca chain, including the asymmetric part of the unit cell with composition $Ca_2H_2(OAc)_6.2H_2O$, along with the adopted numbering scheme. Two such chains link through O bridges into a double-stranded multiple O-bridged Ca chain running in the **a** direction, resembling that found in $Ca(OAc)_2.H_2O$ (Klop, Schouten, van der Sluis & Spek, 1984). The chains are connected in the **b** and **c** directions through

---

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

H atoms not involved in H bonding are omitted. For non-H atoms
$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq} or U_{iso}(Å^2)
Ca(1)	-0.0071 (1)	0.0530 (1)	0.1500 (1)	0.0193 (2)
Ca(2)	0.4796 (1)	0.2161 (1)	0.1861 (1)	0.0207 (2)
O(1)	-0.1823 (4)	0.2366 (2)	0.1748 (2)	0.0320 (9)
O(2)	0.1351 (4)	0.2376 (2)	0.1808 (2)	0.0298 (9)
O(3)	0.0076 (4)	-0.1129 (2)	0.0379 (2)	0.0289 (9)
O(4)	0.0054 (4)	-0.1485 (2)	0.2123 (2)	0.0305 (9)
O(5)	0.4336 (5)	0.5241 (2)	0.1444 (2)	0.049 (1)
O(6)	0.4752 (5)	0.3849 (2)	0.2704 (2)	0.035 (1)
O(7)	0.3354 (4)	0.0395 (2)	0.1493 (2)	0.0323 (9)
O(8)	0.6504 (4)	0.0401 (2)	0.1427 (2)	0.0317 (9)
O(9)	0.5004 (5)	0.1541 (2)	0.3746 (2)	0.041 (1)
O(10)	0.5191 (7)	0.2987 (3)	0.4645 (3)	0.068 (2)
O(11)	-0.0150 (7)	-0.1635 (3)	0.4793 (3)	0.066 (2)
O(12)	-0.0107 (6)	-0.2950 (3)	0.3718 (3)	0.060 (1)
O(13)	-0.0048 (6)	0.0371 (3)	0.3405 (2)	0.050 (1)
O(14)	0.4443 (5)	0.3459 (2)	0.0310 (2)	0.041 (1)
C(1)	-0.0289 (6)	0.2882 (3)	0.1717 (3)	0.023 (1)
C(2)	-0.0432 (7)	0.4119 (3)	0.1561 (4)	0.037 (1)
C(3)	0.0066 (5)	-0.1811 (3)	0.1203 (3)	0.023 (1)
C(4)	0.0066 (8)	-0.3013 (3)	0.1082 (4)	0.044 (2)
C(5)	0.4642 (6)	0.4870 (3)	0.2394 (3)	0.033 (1)
C(6)	0.489 (1)	0.5649 (4)	0.3231 (5)	0.071 (2)
C(7)	0.4976 (6)	-0.0104 (3)	0.1408 (3)	0.022 (1)
C(8)	0.5071 (7)	-0.1311 (3)	0.1284 (4)	0.043 (2)
C(9)	0.5140 (7)	0.1920 (4)	0.4581 (4)	0.042 (2)
C(10)	0.529 (1)	0.1267 (5)	0.5670 (4)	0.067 (2)
C(11)	-0.0132 (8)	-0.2590 (4)	0.4659 (4)	0.049 (2)
C(12)	-0.014 (1)	-0.3471 (5)	0.5580 (4)	0.072 (3)
H(1)	0.51 (1)	0.331 (5)	0.400 (6)	0.10 (2)
H(2)	0.003 (8)	-0.237 (5)	0.307 (5)	0.09 (2)
H(113)	-0.005 (8)	-0.006 (4)	0.370 (4)	0.05 (1)
H(213)	-0.008 (6)	0.092 (4)	0.390 (4)	0.05 (1)
H(114)	0.441 (9)	0.421 (5)	0.063 (5)	0.11 (2)
H(214)	0.48 (1)	0.361 (6)	-0.022 (5)	0.11 (2)

Table 2. *Relevant data on the geometry of* $CaH(C_2H_3O_2)_3.H_2O$

(a) Bond distances

Ca(1)–O(1)	2.553 (3)	O(3)–C(3)	1.258 (4)
Ca(1)–O(2)	2.575 (3)	O(4)–C(3)	1.259 (4)
Ca(1)–O(3)	2.594 (3)	O(5)–C(5)	1.236 (5)
Ca(1)–O(3^i)	2.388 (3)	O(6)–C(5)	1.270 (4)
Ca(1)–O(4)	2.510 (3)	O(7)–C(7)	1.255 (5)
Ca(1)–O(7)	2.347 (3)	O(8)–C(7)	1.245 (5)
Ca(1)–O(8^{ii})	2.362 (3)	O(9)–C(9)	1.192 (6)
Ca(1)–O(13)	2.372 (3)	O(10)–C(9)	1.324 (6)
Ca(2)–O(1^{iii})	2.352 (3)	O(11)–C(11)	1.202 (6)
Ca(2)–O(2)	2.362 (3)	O(12)–C(11)	1.302 (6)
Ca(2)–O(6)	2.424 (3)	C(1)–C(2)	1.509 (5)
Ca(2)–O(7)	2.510 (3)	C(3)–C(4)	1.500 (5)
Ca(2)–O(8)	2.524 (3)	C(5)–C(6)	1.504 (7)
Ca(2)–O(9)	2.399 (3)	C(7)–C(8)	1.505 (5)
Ca(2)–O(14)	2.375 (3)	C(9)–C(10)	1.504 (7)
O(1)–C(1)	1.255 (5)	C(11)–C(12)	1.495 (7)
O(2)–C(1)	1.253 (5)		

(b) O-bridged Ca···Ca distances (Å)

Ca(1)–Ca(1^i)	4.107 (2)	Ca(1)–Ca(2)	4.018 (1)
Ca(1)–Ca(2^{ii})	4.022 (1)		

(c) Bond angles (°)

O(1)–C(1)–O(2)	120.4 (3)	O(8)–C(7)–C(8)	120.1 (4)
O(1)–C(1)–C(2)	119.5 (4)	O(9)–C(9)–O(10)	122.7 (5)
O(2)–C(1)–C(2)	120.1 (4)	O(9)–C(9)–C(10)	125.1 (5)
O(3)–C(3)–O(4)	120.1 (3)	O(10)–C(9)–C(10)	112.1 (4)
O(3)–C(3)–C(4)	119.6 (4)	O(11)–C(11)–O(12)	123.8 (5)
O(4)–C(3)–C(4)	120.3 (4)	O(11)–C(11)–C(12)	121.9 (5)
O(5)–C(5)–O(6)	122.8 (3)	O(12)–C(11)–C(12)	114.3 (4)
O(5)–C(5)–C(6)	119.4 (4)	C(9)–O(10)–H(1)	107 (4)
O(6)–C(5)–C(6)	117.8 (4)	C(11)–O(12)–H(2)	116 (3)
O(7)–C(7)–O(8)	119.9 (3)	H(113)–O(13)–H(213)	103 (6)
O(7)–C(7)–C(8)	120.0 (4)	H(114)–O(14)–H(214)	101 (6)

Table 2 (cont.)

(d) Hydrogen bonds (Å and °)

	O···O	O–H	H···O	∠O–H···O	∠H···O–X	X
O(10)–H(1)···O(6)	2·548 (5)	0·86 (7)	1·69 (7)	176 (7)	125 (2)	C(5)
O(12)–H(2)···O(4)	2·550 (4)	1·03 (6)	1·52 (6)	175 (5)	116 (2)	C(3)
O(13)–H(113)···O(11)	2·864 (5)	0·61 (5)	2·25 (5)	179 (7)	135 (1)	C(11)
O(13)–H(213)···O(11^{iv})	2·876 (5)	0·97 (4)	1·94 (5)	162 (4)	131 (1)	C(11^{iv})
O(14)–H(114)···O(5)	2·732 (4)	1·04 (6)	1·71 (6)	166 (6)	111 (2)	C(5)
O(14)–H(214)···O(5^v)	2·750 (4)	0·73 (7)	2·09 (7)	152 (7)	145 (2)	C(5^v)

Symmetry code: (i) $-x, -y, -z$; (ii) $x - 1, y, z$; (iii) $x + 1, y, z$; (iv) $-x, -y, 1 - z$; (v) $1 - x, 1 - y, -z$.

Fig. 1. Part of one strand of the infinite double-stranded Ca chain running in the a direction, including the asymmetric unit Ca$_2$H$_2$(OAc)$_6$.2H$_2$O, along with the adopted numbering scheme. Triple lines are used to indicate the Ca coordination whereas double lines represent hydrogen bridges. For the symmetry code see Table 2.

Fig. 2. Projection of the unit-cell down a illustrating the cross linking between the Ca chains via a hydrogen-bond network in the bc plane. Ca atoms are indicated by dotted spheres and O atoms by black spheres.

hydrogen bonds as shown in Fig. 2. Ca(1) is coordinated by eight O atoms belonging to five OAc groups and one water molecule. Its coordination can be described as distorted dodecahedral (O···O edges 2·18 to 3·42 Å). Ca(2) is coordinated by seven O atoms of five OAc groups and one water molecule thus forming a pentagonal bipyramid. Both coordination numbers are also found in the structure of Ca(OAc)$_2$.H$_2$O and are common for Ca coordination (Einspahr & Bugg, 1981).

Three of the four OAc ions act both as bidentate chelating and as O-bridging ligands. One OAc ion and one AcOH molecule act as monodentate ligands and are involved in the hydrogen-bond network along with the second AcOH molecule that is not coordinated to Ca. The geometry of the OAc groups is as usual for ionized and protonated species.

The crystals were grown and kindly supplied by Mr P. van der Sluis.

References

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.
EINSPAHR, H. & BUGG, C. E. (1981). Acta Cryst. B37, 1044–1052.
KLOP, E. A., DUISENBERG, A. J. M. & SPEK, A. L. (1983). Acta Cryst. C39, 1342–1344.
KLOP, E. A., SCHOUTEN, A., VAN DER SLUIS, P. & SPEK, A. L. (1984). Acta Cryst. C40, 51–53.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
SPEAKMAN, J. C. (1972). Struct. Bonding (Berlin), 12, 141–199.
SPEK, A. L. (1982). Computational Crystallography, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
WALKER, N. & STUART, D. (1983). Acta Cryst. A39, 158–166.
WALTER-LEVY, L. & PERRIER, J. (1958). C. R. Acad. Sci. 256, 1553–1556.