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Nuclear Magnetic Resonance and X-Ray Evidence of Crystal Structure for Acetates of Calcium, Strontium, and Barium

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High-resolution ^{13}C spectra of calcium acetate hemihydrate (CAH), strontium acetate hemihydrate (SAH), and barium acetate monohydrate (BAM) have been obtained using cross-polarization (CP), high-power decoupling, and magic-angle spinning (MAS). The results indicate the existence in each case of four nonequivalent crystallographic sites for the acetate groups. These findings have been confirmed for SAH and BAM by single-crystal X-ray diffraction studies. The carboxyl chemical shifts for CAH cover a range of 9.3 ppm and the lines are remarkably sharp, so that this material is suggested as a suitable standard for checking the performance of CP/MAS spectrometers

Introduction

Metal acetates and formates exist in a variety of crystallographic forms and states of hydration. Many of these have proved to be difficult to fully characterize, since single-crystal X-ray data cannot always be readily obtained. This situation occurs when samples appear amorphous, so that suitably sized crystals cannot be produced, or when complexities of the phase diagram give rise to problems of sample handling. However, those structures which have been characterized by X-ray work show a range of bonding situations, which have been categorized (*1*, *2*) in terms of five possible extreme structures, shown in Table I. Of course, in practice, many systems show departures from the idealized scheme of Table I. Indeed, a number of examples has been reported where there are two crystallographically inequivalent (noncongruent) sites in the unit cell, with obvious connotations of variations in precise bonding type.

Acetates and formates have proved to be popular subjects of study by solid-state ^{13}C NMR (*10–19*). Most work has been carried out on static samples, and single-crystal work or bandshape studies of powders have yielded data on shielding tensor components. The simplicity of the spectra has been an attraction in such studies. Some

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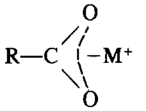
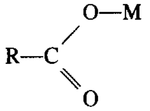
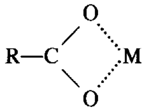
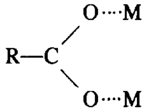
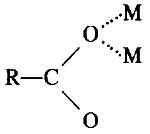
TABLE I

Metal Carboxylate Bonding Types

Type	Structure	Example	Reference
Ionic		Potassium acetate	3
Monodentate		Magnesium acetate tetrahydrate	4
Bidentate chelate		Zinc acetate dihydrate	5
Bridging bidentate		Magnesium formate dihydrate	6,7
Bridging bidendate (single oxygen)		Copper(II) formate Copper(II) formate tetrahydrate	8 9

investigations have used the magic-angle rotation technique with powders in order to establish accurate isotropic chemical shifts easily.

We have initiated a program of research on solid metal acetates and formates, primarily using ^{13}C NMR, in order to investigate the influence of metal ion, structural type, and packing on shielding. The present paper reports a study, using both solid-state NMR and single-crystal X-ray diffraction, of three group II acetates. The samples chosen were calcium acetate hemihydrate (CAH), strontium acetate hemihydrate (SAH), and barium acetate monohydrate (BAM). There are, in fact, a plethora of forms of calcium acetate, none of which were fully characterized by single-crystal X-ray work prior to our investigations. Indeed, we found it impossible to obtain suitable single crystals of our sample of calcium acetate, so that characterization as the hemihydrate was based on other evidence (see below). Our first experiments were carried out by NMR. Following preliminary measurements of proton relaxation characteristics, we used cross-polarization, high-power decoupling and magic-angle rotation (CP/HPD/MAS) to obtain high-resolution carbon-13 spectra, which proved to be of remarkably good quality. The results gave crystallographic information, which prompted us to seek single-crystal X-ray data. This was successfully obtained for SAH and BAM. We have also attempted some slow-spinning MAS experiments on CAH in order to characterize the carboxyl shielding tensor more fully.

We have made brief mention of the ^{13}C NMR spectra of CAH and BAM in several review articles and published lectures (*20–*

23). In Ref. (*20*), the material CAH was incorrectly stated to be anhydrous because of the labeling on the commercial bottle.

Experimental

Sample preparation. Our sample of CAH was obtained commercially from BDH and was labeled "dried $(CH_3 \cdot COO)_2Ca$." The material is a very fine, white powder which packed easily into the NMR rotor. The infrared and Raman spectra were recorded. Unfortunately, the literature on IR spectra of the various forms of calcium acetate appears to be confused, but the presence of a strong absorption at 1610 cm^{-1} would seem (*24*) to identify our sample as the hemihydrate. The complexity of the asymmetric C–O stretching region (1525–1570 cm^{-1} as well as 1610 cm^{-1}) would seem to point to the presence of acetate ions differing in their coordination. As confirmation of the crystalline state of our sample of CAH, the X-ray diffraction powder pattern was recorded and found to match that previously documented (*24, 25*) for the hemihydrate. Moreover, elemental analysis gave a very good match to that predicted by this formula.

Crystals of strontium acetate hemihydrate [14692-29-6] were prepared by adding aqueous acetic acid to excess strontium carbonate, stirring for several hours, filtering, and evaporating. This produced transparent, slightly wet needles, which were completely dried in a desiccator over silica gel.

It has been reported (*26*) from a partial X-ray study that material obtained in this way is monoclinic, adopting the space group $P2_1/c$ and containing two formula units per unit cell. However, our X-ray results (see below) conflict with this report (*26*) as does a more recent ESR study (*27*), which suggests a $P1$ or $P\bar{1}$ structure.

Barium acetate shows simpler solid-state behavior than the acetates of other group II metals, only the monohydrate and anhydrous material being known. Our sample of monohydrate was prepared by reaction of excess carbonate with aqueous acid, filtration, and evaporation. No X-ray data for this compound appear to be in the literature prior to our work.

NMR studies. Proton relaxation characteristics were measured at ambient temperature and a resonance frequency of 60 MHz using a conventional homebuilt pulsed spectrometer. The inversion–recovery pulse sequence was used to obtain T_{1H}, whereas the $T_{1\rho H}$ behavior was investigated using the usual spin-locking sequence with a r.f. field strength of 1 mT (≡40 kHz), which is the same as that employed for the ^{13}C cross-polarization experiments.

The ^{13}C spectra were obtained using the CP/HPD/MAS techniques with a purpose-built spectrometer operating at 22.63 MHz (90 MHz for the proton channel), which is described in Ref. (*20*). All ^{13}C spectra were obtained at ambient probe temperature (ca. 30°C). Magic-angle rotation speeds of the order of 2 kHz were employed, using the device described elsewhere (*28*). The samples were packed, with light tamping, into cylindrical glass rotors, fabricated from sections (8 mm in length) of standard 5-mm-o.d. NMR tubes, the ends being carefully ground flat. The ends of the sample tubes

TABLE II

SPECTROMETER OPERATING CONDITIONS FOR OBTAINING ^{13}C SPECTRA OF METAL ACETATES[a,b]

Metal	Contact time (ms)	Recycle delay (s)	No. of transients	No. of FID data points
Ca[c]	5	3.5	14,000	4 k
Sr	10	2.0	24,000	1 k
Ba	10	2.0	27,000	2 k

[a] Relevant to the spectra displayed in Figs. 1–3.

[b] The dwell time was 64 μs in all cases.

[c] Single contact with flip-back.

TABLE III

CARBON CHEMICAL SHIFTS AND INTENSITIES[a] FOR SOLID ALKALI METAL ACETATES

Metal	Carboxyl region, δ_C (ppm)				Methyl region, δ_C (ppm)		
Ca[b]	187.6	186.2	182.0	178.3		24.8	24.1
	(1.01)	(1.07)	(0.94)	(0.98)		(0.87)	(2.59)
Sr[c]		184.2	183.6		27.3	26.3	24.8
		(2.31)	(0.94)		(0.96)	(1.04)	(1.58)
Ba[b]	183.6	182.4	181.9	179.8	28.2	27.6	26.4
	(0.98)	(0.99)	(1.03)	(1.00)	(2.26)	(1.29)	(1.04)

[a] Given in brackets.

[b] Intensities normalized to the average of the four carboxyl peaks.

[c] Intensities normalized to the average of the peaks at $\delta_C = 27.3$ and 26.3 ppm.

are sealed with small disks cut from a PTFE sheet using a cork borer.

The spectrometer operating conditions used to obtain the carbon spectra are listed in Table II. Chemical shifts were recorded relative to an external (replacement) standard of static, liquid tetramethylsilane contained in a 10-mm-o.d. NMR tube, which replaced the MAS stator. The acquisition times used enabled shifts to be measured to an accuracy of ca. ±0.5 ppm.

TABLE IV

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR SAH

	x	y	z
Sr(1)	4050	9275	8321
Sr(2)	−553	7239	9750
C(11)	1832(8)	7794(7)	5614(4)
C(12)	1054(5)	7584(4)	6985(3)
O(11)	−225(4)	6948(3)	7266(2)
O(12)	1720(4)	8056(3)	7817(2)
C(21)	1961(6)	8792(4)	12550(3)
C(22)	2219(5)	9231(3)	11147(3)
O(21)	1685(4)	8610(3)	10376(2)
O(22)	3000(3)	10231(2)	10796(2)
C(31)	2067(9)	13645(4)	6360(4)
C(32)	2618(5)	12161(4)	6983(3)
O(31)	2401(4)	11993(3)	8181(2)
O(32)	3259(4)	11154(3)	6312(2)
C(41)	−4126(7)	5046(4)	8134(5)
C(42)	−3213(5)	5694(3)	9002(4)
O(41)	−1788(4)	4953(2)	9527(3)
O(42)	−3882(3)	6993(2)	9177(2)
Ow(1)	6299(4)	8348(3)	6377(3)

X-Ray work. Crystals of both SAH and BAM were obtained as needles, and required cleavage in the major direction in order to make them suitable for X-ray diffraction measurements. The crystal of SAH used measured approximately 0.6 × 0.2 × 0.15 mm, and that for BAM was 0.4 × 0.35 × 0.33 mm. Both crystals were mounted on a glass fiber with the longest dimension coincident with the fiber axis. In both cases, unit-cell parameters were determined, and intensity data collected, at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo*K*α radiation and an ω-2θ scan procedure (*29*).

Results

Nuclear Magnetic Resonance

In order to optimize spectrometer operating conditions for the ^{13}C CP/HPD/MAS experiments, proton spin-lattice and spin-lattice-in-the-rotating-frame relaxation times (T_{1H} and $T_{1\rho H}$, respectively) were first determined in some cases. The decay curves were single-exponential. Approximate values are: T_{1H} for CAH 1 s; T_{1H} for SAH 24

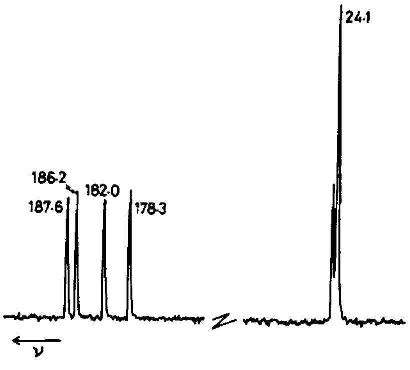


FIG. 1. Carbon-13 (22.6 MHz) spectrum of calcium acetate hemihydrate (for the spectrometer conditions see Table II).

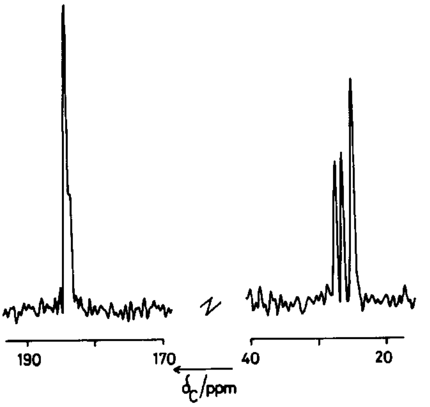


FIG. 2. Carbon-13 (22.6 MHz) spectrum of strontium acetate hemihydrate (for spectrometer conditions see Table II).

s; $T_{1\rho H}$ for CAH ms. Other measurements in our laboratory on metal acetates and formates show a very wide range of values for such relaxation times, which have no obvious correlation with the nature (e.g., state of hydration) of the sample.

The sample of CAH, which was the first to be studied, gave an excellent CP/HPD/MAS carbon spectrum (Fig. 1), clearly showing four well-resolved carboxyl peaks of equal intensity (within experimental error). This finding immediately suggested the presence of four nonequivalent sites for acetate groups in the unit cell. This is of sufficiently unusual occurrence that it was felt desirable to obtain confirmatory X-ray data, but the sample is a very fine white powder, and attempts at recrystallization tended to change the state of hydration, so a suitable crystal was not obtained. The methyl region of the ^{13}C spectrum for CAH (Fig. 1) showed a doublet of approximately 1 : 3 intensity ratio, consistent with the postulation of four overlapping lines.

The carboxyl region of the carbon spectrum (Fig. 2) of SAH was not so well-resolved as that of CAH, but showed a small splitting into two components of unequal intensity, the smaller component forming approximately one-quarter of the total. In the case of this compound (the only one in our experience with metal carboxylates) the methyl region was better resolved than the carboxyl region, and showed three peaks with intensities consistent with interpretation as a 1 : 1 : 2 distribution. These findings suggested that SAH, in common with CAH, has four nonequivalent sites for acetate groups in the unit cell. Fortunately, crystals of suitable size were available, so a full X-ray diffraction study was carried out subsequent to the NMR work (see below).

The sample of BAM showed a ^{13}C spectrum (Fig. 3) which was superficially similar to that of CAH in that four well-defined carboxyl peaks of equal intensity were observed. The methyl region showed three overlapping lines with an apparent intensity ratio of 2 : 1 : 1—clearly two sites have nearly equal chemical shifts by accident. This work was followed with a full X-ray crystallographic study, details of which are given below.

Chemical shifts and relative intensities (peak heights) for all three acetates are given in Table III. One reason for the excellence of the CAH spectrum is that the lines are very sharp. The widths of the carboxyl lines displayed in Fig. 1 are 8 Hz, while that of the methyl peak at $\delta_C = 24.8$ ppm (repre-

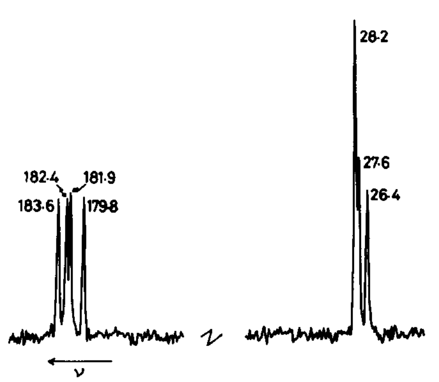


FIG. 3. Carbon-13 (22.6 MHz) spectrum of barium acetate monohydrate (for spectrometer conditions see Table II).

senting a single carbon) is 5 Hz. It appears that (unusually in our experience with our spectrometer) the dominating influence on the linewidths in the carboxyl region is missetting of the magic angle. By assuming the linewidths of carboxyl and methyl peaks due to other causes are equal, one can estimate that such residual widths are ca. 3.5 Hz, and that the angle of rotation is ca. 0.07° below the magic value. Adjustment of the angle by trial-and-error methods was not capable of improving on the result.

TABLE VI

Bond Lengths (Å) for SAH

O(12)–Sr(1)	2.472(4)	O(21)–Sr(1)	2.722(6)
O(22)–Sr(1)	2.832(5)	O(22)–Sr(1a)	2.629(5)
O(31)–Sr(1)	2.629(5)	O(32)–Sr(1)	2.691(6)
O(42)–Sr(1b)	2.499(4)	Ow(1)–Sr(1)	2.538(6)
O(11)–Sr(2)	2.663(5)	O(12)–Sr(2)	2.649(6)
O(21)–Sr(2)	2.576(5)	O(22)–Sr(2c)	2.698(5)
O(31)–Sr(2c)	2.493(4)	O(41)–Sr(2)	2.703(5)
O(41)–Sr(2d)	2.479(4)	O(42)–Sr(2)	2.645(5)
C(12)–C(11)	1.503(7)	O(11)–C(12)	1.244(5)
O(12)–C(12)	1.253(5)	C(22)–C(21)	1.509(7)
O(21)–C(22)	1.238(5)	O(22)–C(22)	1.270(5)
C(32)–C(31)	1.516(7)	O(31)–C(32)	1.260(5)
O(32)–C(32)	1.239(5)	C(42)–C(41)	1.496(6)
O(41)–C(42)	1.251(5)	O(42)–C(42)	1.271(5)
Hw(1)–Ow(1)	0.756(42)	Hw(2)–Ow(1)	0.837(40)

Note. Key to symmetry operations relating designated atoms to reference atoms at (x, y, z):
(a) $1.0 - x$, $2.0 - y$, $2.0 - z$
(b) $-1.0 + x$, y, z
(c) $-x$, $2.0 - y$, $2.0 - z$
(d) $-x$, $1.0 - y$, $2.0 - z$

Such considerations prompt us to suggest that calcium acetate hemihydrate is a good test sample for use in CP/MAS spectrometers for resolution, for magic-angle-setting, for spectrometer-tuning, and possibly for shimming. To emphasize this point we show (Fig. 4) a spectrum of CAH obtained (*30*) using a commercial spectrometer at higher magnetic field (Bruker CXP 300). This spectrum shows evidence of a splitting of the low-frequency methyl signal into three components, consistent with our interpretation above.

TABLE V

Fractional Atomic Coordinates (×10⁴) for BAM

	x	y	z
Ba(1)	6658(1)	514(1)	−960(1)
Ba(2)	4933(1)	2881(1)	4320(1)
C(11)	7793(19)	−1255(18)	3749(32)
C(12)	6577(15)	−113(15)	3764(23)
O(11)	5874(12)	169(10)	2127(14)
O(12)	6349(13)	487(10)	5302(16)
C(21)	9358(20)	−3592(16)	−739(29)
C(22)	8539(16)	−2352(17)	−1391(23)
O(21)	9104(11)	−1480(10)	−993(17)
O(22)	7291(12)	−2221(11)	−2267(18)
C(31)	3427(19)	4552(15)	−488(26)
C(32)	4634(17)	3323(16)	−568(22)
O(31)	4840(11)	2833(10)	−2213(14)
O(32)	5120(11)	2883(9)	872(15)
C(41)	8869(19)	4021(19)	4827(32)
C(42)	7644(16)	3766(14)	5062(23)
O(41)	7752(11)	2640(10)	5168(16)
O(42)	6577(12)	4647(11)	5283(19)
Ow(1)	8734(13)	821(14)	2284(18)
Ow(2)	8428(17)	1565(20)	−1562(23)

Our spinning system contains a cylindrical gas bearing which rigidly defines the

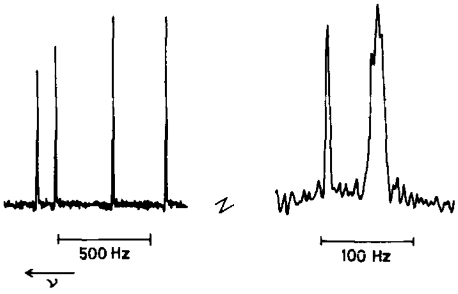


FIG. 4. Carbon-13 (75 MHz) spectrum of calcium acetate hemihydrate, obtained using a Bruker CXP 300 spectrometer. Spectrometer conditions: contact time 5 ms; recycle delay 5 s; spinning rate 3 kHz. The TOSS pulse sequence was used to suppress spinning sidebands. Twenty transients were used to acquire the spectrum, which is supplied by the courtesy of P. S. Belton, S. F. Tanner, and K. M. Wright, Food Research Institute, Norwich.

TABLE VII

BOND LENGTHS (Å) FOR BAM

O(11)–Ba(1)	2.834(14)	O(11)–Ba(1a)	2.880(14)
O(12)–Ba(1b)	2.711(14)	O(21)–Ba(1)	2.816(14)
O(22)–Ba(1)	2.926(15)	O(31)–Ba(1)	2.902(13)
O(32)–Ba(1)	2.873(13)	Ow(1)–Ba(1)	2.791(15)
Ow(2)–Ba(1)	2.744(18)		
O(11)–Ba(2)	3.083(14)	O(12)–Ba(2)	2.815(14)
O(22)–Ba(2a)	2.640(14)	O(31)–Ba(2c)	2.641(13)
O(32)–Ba(2)	2.646(13)	O(41)–Ba(2)	2.803(14)
O(42)–Ba(2)	2.927(14)	O(42)–Ba(2d)	2.725(14)
C(12)–C(11)	1.494(23)	O(11)–C(12)	1.290(19)
O(12)–C(12)	1.220(20)	C(22)–C(21)	1.512(25)
O(21)–C(22)	1.263(23)	O(22)–C(22)	1.270(21)
C(32)–C(31)	1.549(25)	O(31)–C(32)	1.261(20)
O(32)–C(32)	1.209(19)	C(42)–C(41)	1.494(22)
O(41)–C(42)	1.278(19)	O(42)–C(42)	1.254(20)

Note. Key to symmetry operations relating designated atoms to reference atoms at (x, y, z):

(a) $1.0 - x, -y, -z$
(b) $x, y, 1.0 + z$
(c) $x, y, -1.0 + z$
(d) $1.0 - x, 1.0 - y, 1.0 - z$

axis of rotation. This makes it easy to obtain stable spinning at slow speeds (<1 kHz). Such work demonstrates that the sideband intensities do not show the same

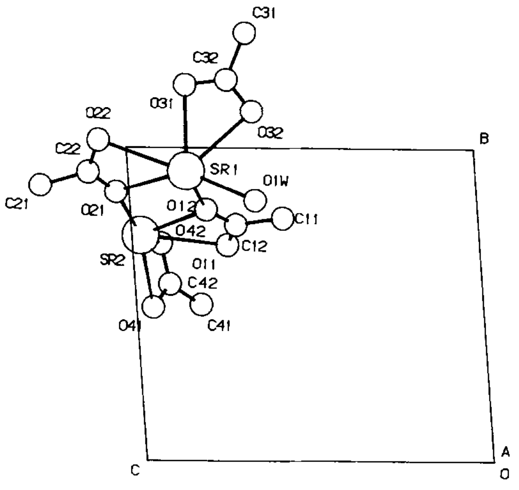


FIG. 5. Single-molecule reference diagram of SAH, obtained from X-ray diffraction experiments.

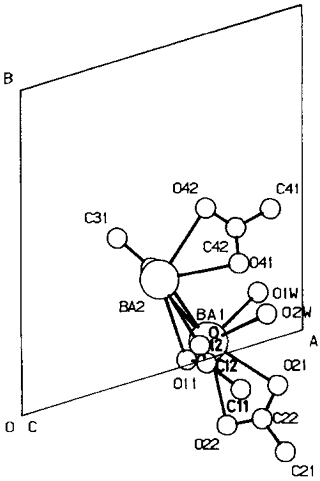


FIG. 6. Single-molecule reference diagram of BAM, obtained from X-ray diffraction experiments.

TABLE VIII

BOND ANGLES (DEG.) FOR SAH

O(21)–Sr(1) –O(12)	65.9(2)	O(22)–Sr(1) –O(12)	110.4(2)
O(22)–Sr(1) –O(21)	46.5(1)	O(31)–Sr(1) –O(12)	108.4(2)
O(31)–Sr(1) –O(21)	96.3(2)	O(31)–Sr(1) –O(22)	69.9(2)
O(32)–Sr(1) –O(12)	90.9(2)	O(32)–Sr(1) –O(21)	130.5(1)
O(32)–Sr(1) –O(22)	118.4(2)	O(32)–Sr(1) –O(31)	48.5(1)
O(42)–Sr(1) –O(12)	90.2(2)	O(42)–Sr(1) –O(21)	78.6(2)
O(42)–Sr(1) –O(22)	91.2(2)	O(42)–Sr(1) –O(31)	156.9(1)
O(42)–Sr(1) –O(32)	147.7(1)	Ow(1)–Sr(1) –O(12)	89.4(2)
Ow(1)–Sr(1) –O(21)	144.9(1)	Ow(1)–Sr(1) –O(22)	157.1(1)
Ow(1)–Sr(1) –O(31)	115.8(2)	Ow(1)–Sr(1) –O(32)	70.9(2)
Ow(1)–Sr(1) –O(42)	76.8(2)	O(12)–Sr(2) –O(11)	48.5(1)
O(21)–Sr(2) –C(12)	90.0(2)	O(21)–Sr(2) –O(11)	114.1(2)
O(21)–Sr(2) –O(12)	65.7(2)	O(41)–Sr(2) –O(11)	73.9(2)
O(41)–Sr(2) –O(12)	117.9(2)	O(41)–Sr(2) –O(21)	156.5(1)
O(42)–Sr(2) –O(11)	71.4(2)	O(42)–Sr(2) –O(12)	115.4(2)
O(42)–Sr(2) –O(21)	154.0(1)	O(42)–Sr(2) –O(41)	48.5(1)
C(12)–C(11) –H(1A)	119.4(3)	C(12)–C(11) –H(1B)	107.5(4)
C(12)–C(11) –H(1C)	101.0(4)	O(11)–C(12) –C(11)	119.4(4)
O(12)–C(12) –C(11)	118.8(4)	O(12)–C(12) –O(11)	121.8(4)
C(12)–O(11) –Sr(2)	94.7(3)	Sr(2)–O(12) –Sr(1)	117.1(2)
C(12)–O(12) –Sr(1)	147.8(2)	C(12)–O(12) –Sr(2)	95.1(3)
C(22)–C(21) –H(2A)	116.2(3)	C(22)–C(21) –H(2B)	105.8(3)
C(22)–C(21) –H(2C)	106.2(3)	O(21)–C(22) –C(21)	119.8(4)
O(22)–C(22) –C(21)	118.2(4)	O(22)–C(22) –O(21)	122.0(4)
Sr(2)–O(21) –Sr(1)	111.2(2)	C(22)–O(21) –Sr(1)	96.5(3)
C(22)–O(21) –Sr(2)	152.1(2)	C(22)–O(22) –Sr(1)	90.5(3)
C(32)–C(31) –H(3A)	119.9(3)	C(32)–C(31) –H(3B)	104.1(4)
C(32)–C(31) –H(3C)	103.9(3)	C(31)–C(32) –C(31)	118.3(4)
O(32)–C(32) –C(31)	119.7(4)	O(32)–C(32) –O(31)	122.0(4)
C(32)–O(31) –Sr(1)	95.8(3)	C(32)–O(32) –Sr(1)	93.3(3)
C(42)–C(41) –H(4A)	113.7(3)	C(42)–C(41) –H(4B)	107.4(3)
C(42)–C(41) –H(4C)	107.2(3)	O(41)–C(42) –C(41)	119.4(4)
O(42)–C(42) –C(41)	119.3(4)	O(42)–C(42) –O(41)	121.2(4)
C(42)–O(41) –Sr(2)	91.3(3)	Sr(2)–O(42) –Sr(1)	112.2(2)
C(42)–O(42) –Sr(1)	144.3(2)	C(42)–O(42) –Sr(2)	93.5(3)
Hw(1)–Ow(1)–Sr(1)	144.2(31)	Hw(2)–Ow(1)–Sr(1)	115.7(26)
Hw(2)–Ow(1)–Hw(1)	99.3(40)	–	–

pattern for the four carboxyl peaks. Thus, there are differences in magnitude (and, probably, direction) of the corresponding principal components of the shielding tensors for the four carboxyl carbons. We estimate the magnitude of such variations to be up to 20 ppm.

X-Ray Diffraction

(*a*) *Crystal data.* Compound SAH: $C_8H_{14}O_9Sr_2$, $M = 429.4$, triclinic, $a = 7.232(1)$ Å, $b = 9.927(1)$ Å, $c = 10.643(1)$ Å; $\alpha = 83.58(1)^0$, $\beta = 82.04(1)^0$, $\gamma = 73.98(1)^0$, $U = 725.1$ Å^3; space group $P\bar{1}$, $Z = 2$, $D_c = 1.97$ g cm^{-3}, $F(000) = 420$, $\lambda = 0.71069$, $\mu(\text{Mo}K\alpha) = 77.3$ cm^{-1}.

Compound BAM: $C_8H_{16}O_{10}Ba_2$, $M = 546.9$, triclinic, $a = 10.626(3)$ Å, $b = 11.462(3)$ Å, $c = 7.482(2)$ Å; $\alpha = 105.34(2)^0$, $\beta = 107.22(2)^0$, $\gamma = 70.05(2)^0$, $U = 804.5$ Å^3; space group $P\bar{1}$, $Z = 2$, $D_c = 2.26$ g cm^{-3}, $F(000) = 512$, $\lambda = 0.71069$, $\mu(\text{Mo}K\alpha) = 50.5$ cm^{-1}.

(*b*) *Data collection.* Compound SAH: 2553 data ($1.5 \leq \theta \leq 25°$) were measured of which 2173 were considered observed ($I \geq 1.5\,\sigma(I)$). A semi-empirical absorption correction using normalized and average Ψ-scan measurements (*31*) from four reflections was applied to the data; the maximum and minimum transmissions were 99.8 and 73.9%, respectively.

Compound BAM: 2834 data ($1.5 \leq \theta \leq 25°$) were measured of which 2685 were considered observed ($I \geq 1.5\,\sigma(I)$). A similar absorption correction using six reflections was applied to the data; the maximum and minimum transmissions were 99.9 and 83.3%, respectively.

(*c*) *Structure solution and refinement.* The heavy-atom method was used to solve both structures, and after refinement of all non-hydrogen atoms with isotropic temperature factors, the DIFABS (*32*) method of absorption correction was applied to the data. Following refinement of these data with anisotropic thermal parameters, difference-Fouriers revealed the positions of all methyl and water hydrogen atoms in compound SAH but only a few methyl hydrogens were visible in the case of BAM. Methyl hydrogen atoms in both structures were refined with geometric constraints and a common isotropic temperature factor for each methyl group. The hydrogen atoms for the water molecule in SAH were refined without geometric constraints but with a common temperature factor for both atoms. The final full-matrix least-squares refinement for SAH omitted three strong low-angle reflections and used a weighting

TABLE IX

Bond Angles (Deg.) for BAM

O(12)–Ba(1) –O(11)	153.3(4)	O(21)–Ba(1)–O(11)	100.2(4)
O(21)–Ba(1) –O(12)	90.2(4)	O(22)–Ba(1)–O(11)	87.7(4)
O(22)–Ba(1) –O(12)	82.1(4)	O(22)–Ba(1)–O(21)	45.5(3)
O(31)–Ba(1) –O(11)	109.4(4)	O(31)–Ba(1)–O(12)	66.3(4)
O(31)–Ba(1) –O(21)	149.6(3)	O(31)–Ba(1)–O(22)	140.0(3)
O(32)–Ba(1) –O(11)	69.6(4)	O(32)–Ba(1)–O(12)	111.6(4)
O(32)–Ba(1) –O(21)	150.2(3)	O(32)–Ba(1)–O(22)	153.0(3)
O(32)–Ba(1) –O(31)	45.3(3)	Ow(1)–Ba(1)–O(11)	72.6(5)
Ow(1)–Ba(1) –O(12)	133.8(4)	Ow(1)–Ba(1)–O(21)	66.9(5)
Ow(1)–Ba(1) –O(22)	104.3(5)	Ow(1)–Ba(1)–O(31)	115.2(5)
Ow(1)–Ba(1) –O(32)	83.3(5)	Ow(2)–Ba(1)–O(11)	138.9(4)
Ow(2)–Ba(1) –C(12)	67.4(5)	Ow(2)–Ba(1)–C(21)	76.2(6)
Ow(2)–Ba(1) –O(22)	113.8(6)	Ow(2)–Ba(1)–O(31)	77.0(6)
Ow(2)–Ba(1) –O(32)	93.2(6)	Ow(2)–Ba(1)–Ow(1)	68.4(5)
O(12)–Ba(2) –O(11)	44.2(3)	O(31)–Ba(2)–O(11)	110.2(4)
O(32)–Ba(2) –O(11)	68.8(4)	O(41)–Ba(2)–O(11)	81.9(4)
O(42)–Ba(2) –O(11)	122.0(4)	O(31)–Ba(2)–O(12)	68.4(4)
O(32)–Ba(2) –O(12)	110.1(4)	O(32)–Ba(2)–O(31)	178.0(3)
O(41)–Ba(2) –O(12)	72.6(5)	O(41)–Ba(2)–O(31)	95.9(4)
O(41)–Ba(2) –O(32)	82.2(4)	O(42)–Ba(2)–O(12)	115.6(5)
O(42)–Ba(2) –O(31)	99.0(5)	O(42)–Ba(2)–O(32)	80.3(5)
O(42)–Ba(2) –O(41)	45.2(3)		
C(12)–C(11) –H(1A)	109.4(12)	C(12)–C(11)–H(1B)	109.4(11)
C(12)–C(11) –H(1C)	109.6(12)	O(12)–C(12)–C(11)	116.3(16)
O(12)–C(12) –C(11)	118.0(16)	O(12)–C(12)–O(11)	125.6(15)
C(12)–O(11) –Ba(1)	131.9(9)	Ba(2)–O(12)–Ba(1)	112.2(5)
C(12)–O(12) –Ba(1)	148.0(10)	C(12)–O(12)–Ba(2)	99.8(10)
C(22)–C(21) –H(2A)	109.5(11)	C(22)–C(21)–H(2B)	109.5(11)
C(22)–C(21) –H(2C)	109.5(12)	O(21)–C(22)–C(21)	119.1(15)
O(22)–C(22) –C(21)	118.2(18)	O(22)–C(22)–O(21)	122.7(16)
C(22)–O(21) –Ba(1)	95.7(10)	C(22)–O(22)–Ba(1)	90.4(11)
C(32)–O(31) –H(3A)	109.7(10)	C(32)–C(31)–H(3B)	109.4(10)
C(32)–C(31) –H(3C)	109.3(10)	O(31)–C(32)–C(31)	114.1(15)
O(32)–C(32) –C(31)	116.4(15)	O(32)–C(32)–C(31)	128.7(17)
Ba(2)–O(31) –Ba(1)	111.6(4)	C(32)–O(31)–Ba(1)	91.7(10)
C(32)–O(31) –Ba(2)	154.6(10)	Ba(2)–O(32)–Ba(1)	114.5(4)
C(32)–O(32) –Ba(1)	94.2(11)	C(32)–O(32)–Ba(2)	148.4(11)
C(42)–C(41) –H(4A)	109.8(11)	C(42)–C(41)–H(4B)	110.8(12)
C(42)–C(41) –H(4C)	107.9(11)	C(41)–C(42)–C(41)	117.9(15)
O(42)–C(42) –C(41)	120.9(15)	O(42)–C(42)–O(41)	121.0(15)
C(42)–O(41) –Ba(2)	97.2(10)	C(42)–O(42)–Ba(2)	91.9(10)

scheme $\omega = 1./(\sigma^2(F_0) + g\ F_0^2)$ where $g = 0.0004$. The final R-factors were $R = \Sigma\ \Delta F / \Sigma\ F_0 = 0.024$ and $R_\omega = [\Sigma\omega\ \Delta F^2/\Sigma\omega\ F_0^2] = 0.033$. Unit weights were used for BAM, and the final R-factors were $R = 0.054$ and $R_\omega = 0.078$. All computations were made using SHELX76 (*33*) on a DEC VAX-11/750 computer.

Final atomic coordinates are given in Tables IV and V, bond lengths in Tables VI and VII, and bond angles in Tables VIII and IX for compounds SAH and BAM, respectively. Figures 5 and 6 show single-molecule reference diagrams for the two compounds. Thermal parameters and structure factor tables have been deposited with the National Auxiliary Publication Service (NAPS).[2]

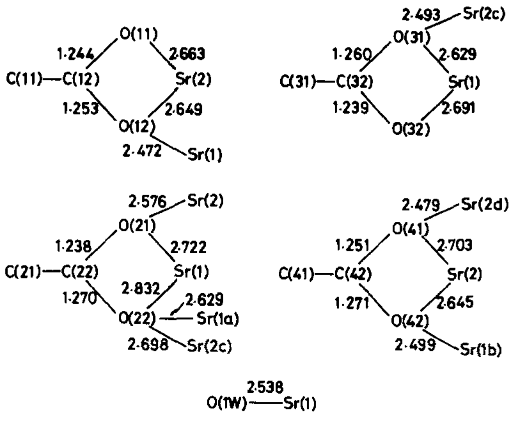


FIG. 7. The coordination of the four cyrstallographically distinct acetate sites for SAH (for all Sr–O distances ≤ 3.20 Å). Interatomic distances are given in Ångstroms. See Tab. 6 for the key to symmetry operations.

Discussion

The X-ray diffraction results show clearly that both SAH and BAM contain four nonequivalent acetate sites per unit cell, thus confirming the NMR evidence. One can, with confidence, assert from the NMR results that the same is true for CAH. Partial local environments of the acetate groups of SAH and BAM are shown in Figs. 7 and 8. It is clear that the bonding situations, though essentially ionic, do not readily correlate with the ideal cases shown in Table I. A variety of oxygen-to-metal distances in the range 2.47 to 2.84 Å are found for SAH and in the range 2.64 and 3.09 Å for BAM. In the case of SAH the coordination around acetates 1 and 3 looks similar, but differs from those of the other acetates. However, that does not seem to relate directly to the observed spectra. The ranges of carboxyl carbon shifts for CAH, SAH, and BAM differ substantially, being 9.3, 0.6, and 3.8 ppm, respectively. The range for CAH is not far short of the total spread (13.0 ppm) we have observed for a variety of metal acetates. It appears to us to

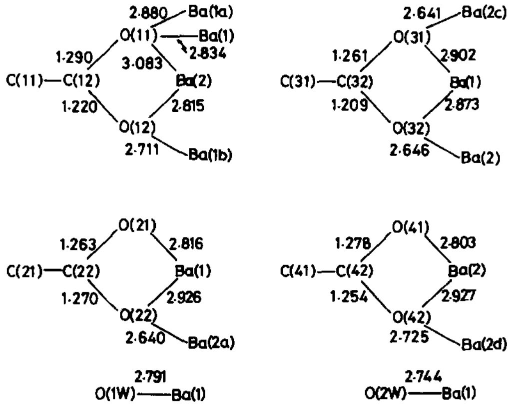


FIG. 8. The coordination of the four crystallographically distinct acetate sites for BAM (for all Ba–O distances ≤ 3.20 Å). Interatomic distances are given in Ångstroms. See Tab. 7 for the key to symmetry operations.

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[2] See NAPS document No. 04295 for 26 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or, for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for each additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

be unlikely that the effect of neighboring group magnetic susceptibilities, such as was used by Haeberlen (*34–36*) to account for proton shielding variations for calcium and lead formates, would suffice to explain variations in carbon isotropic shifts of as much as 9.3 ppm. It is therefore likely that differences in the nature of bonding between different acetate groups must be invoked.

Further understanding of the situation probably requires knowledge of the full shielding tensors. Since our work was completed NMR information on a number of metal acetates, including strontium, has been published by Ganapathy *et al.* (*37*). Unfortunately, they do not mention the state of hydration of their samples, and they use benzene as a reference, so direct comparison of their results with ours is problematic. Moreover, they did not distinguish more than one acetate site for the strontium compound, and in the case of calcium acetate, where they observed "three or more resonances in the carboxylate region," they attributed this to be existence of a mixture of compounds (presumed to be different hydrates).

Calcium acetate monohydrate has also been shown (*38*) recently to contain four nonequivalent acetate sites (and two calcium atoms) per unit cell. However, the coordination between these is different to that found in BAM, although one calcium is likewise associated with two water molecules.

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