

presence of additional centres of symmetry apart from the space group symmetries. No short intermolecular distances were observed.

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Structures of Partially Deuterated Sodium Hydrogen Succinate at 295 and 120 K and Rubidium Hydrogen Succinate at 120 K

BY NICOLINE KALSBECK

Department of Chemistry, The H.C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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Abstract. $\text{Na}^+ \cdot \text{C}_4(\text{H,D})\text{H}_4\text{O}_4^-$, $M_r = 140.07$ (undeuterated), monoclinic, $C2/c$, $Z = 4$, $F(000) = 288$; at $T = 295$ K: $a = 9.217$ (1), $b = 9.998$ (1), $c = 7.365$ (1) Å, $\beta = 117.07$ (1)°, $V = 604.3$ (3) Å³, $D_x = 1.539$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 17.667$ cm⁻¹, $R = 0.036$ for 572 observed reflections; at $T = 120$ K: $a = 8.844$ (2), $b = 10.284$ (3), $c = 7.349$ (2) Å, $\beta = 117.33$ (2)°, $V = 593.8$ (6) Å³, $D_x = 1.567$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.886$ cm⁻¹, $R = 0.028$ for 1891 observed reflections. $\text{Rb}^+ \cdot \text{C}_4\text{H}_5\text{O}_4^-$, $M_r = 202.55$, monoclinic, $C2/c$, $a = 16.927$ (3), $b = 6.1050$ (6), $c = 6.3343$ (9) Å, $\beta = 109.17$ (1)°, $V = 618.3$ (3) Å³, $Z = 4$, $D_x = 2.176$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 77.299$ cm⁻¹, $F(000) = 392$, $T = 120$ K, $R = 0.031$ for 1692 observed reflections. No significant discrepancies are observed in the crystal structure of partially deuterated sodium hydrogen succinate at 295 and 120 K. In this salt the hydrogen succinate ions are linked by short crystallographically symmetric hydrogen bonds across an inversion centre and in rubidium hydrogen succinate across a twofold axis forming infinite chains in the structure. The length of the short hydrogen bond is 2.4272 (9) Å at 295 K

and 2.4295 (5) Å at 120 K in partially deuterated sodium hydrogen succinate and 2.4406 (15) Å in rubidium hydrogen succinate. In both salts the H atom in the short hydrogen bond is best described by two equally populated sites on each side of the centre of the hydrogen bond. The Na⁺ ion is coordinated by six O atoms with four short (2.37–2.40 Å) and two long (2.58 Å) Na—O distances forming an irregular octahedron. The coordination polyhedron for the Rb⁺ ion is a square antiprism formed by eight O atoms with Rb—O distances in the range 2.92–3.02 Å.

Introduction. The crystal structure determinations of partially deuterated sodium hydrogen succinate (1) and rubidium hydrogen succinate (2) were performed as a continuation of earlier studies of acid salts of malonic acid and succinic acid with special interest in the hydrogen bonding (Kalsbeek & Larsen, 1991; Kalsbeek, 1991, 1992). Acid salts of carboxylic acids and dicarboxylic acids have been extensively investigated, both structurally (Speakman, 1972) and spectroscopically (Hadži, 1965).

In many acid salts of dicarboxylic acids the anions are linked in infinite chains by short crystallographically symmetric hydrogen bonds (Currie & Speakman, 1970; Chapuis, Zalkin & Templeton, 1975; Soriano-Garcia, Toscano, Villena, Rodríguez & Campero-Celis, 1988; McAdam, Currie & Speakman, 1971; McAdam & Speakman, 1971; Küppers, 1982; Kalsbeek & Larsen, 1991; Kalsbeek, 1991). It has been debated whether the H atom in the short hydrogen bond is located on the crystallographic symmetry element or whether there is statistical or dynamical disorder of the H atom. The later two are not distinguishable in an X-ray experiment. The structures of methylammonium hydrogen succinate monohydrate and dimethylammonium hydrogen succinate (Kalsbeek & Larsen, 1991), diethylammonium hydrogen succinate (Kalsbeek, 1991) and lithium hydrogen succinate (Küppers, 1982) showed that the H atom in the short hydrogen bond is best described by two equally populated sites on each side of the symmetry element.

In order to investigate the isotope effect on the short hydrogen bond an attempt was made to crystallize sodium hydrogen succinate from H₂O and D₂O. The isotope effect for short O—H—O hydrogen bonds has been reviewed by Rundle (1964) and discussed for several hydrogen oxalate salts and a hydrogen maleate salt by Tellgren & Olovsson (1971), Thomas (1972, 1973) and Hussain, Schlemper & Fair (1980).

The unit-cell dimensions for partially deuterated sodium hydrogen succinate changed very uncharacteristically when the temperature was decreased from 295 to 120 K. The following differences in cell dimensions were observed: -0.373 (*a* axis), 0.286 (*b* axis), -0.016 Å (*c* axis) and 0.26° (β). The significant increase in length in the direction of the *b* axis on cooling is quite remarkable; usually decreases, as in the direction of the *a* axis, are observed. This observation led to the assumption that there might be a phase transition between the two temperatures, and consequently data for compound (1) were collected at 295 and 120 K.

Experimental. Equimolar amounts of succinic acid and NaOH were dissolved in H₂O and D₂O respectively. Crystallization of sodium hydrogen succinate from H₂O failed while colourless crystals suitable for the diffraction studies were obtained from D₂O by slow evaporation. The crystals were not fully deuterated. From a neutron-diffraction study of compound (1) (N. Kalsbeek, unpublished results) the degree of deuteration was determined to *ca* 15%. In order to obtain virtually full deuteration the solution must be kept isolated from the air. The investigation of the isotope effect on the short hydrogen bond in compound (1) was not permitted as crystals from H₂O

Table 1. *Crystal data and summary of results from data reduction and structure refinements*

	Compound (1) (295 K)	Compound (1) (120 K)	Compound (2)
Crystal size (mm)	0.14 × 0.10 × 0.60	0.25 × 0.25 × 0.45	0.04 × 0.18 × 0.18
Intensity data collection			
Maximum $\sin\theta/\lambda$ (Å ⁻¹)	0.6288	0.9938	0.9939
Range of <i>h</i>	-11-11	0-17	0-33
Range of <i>k</i>	-12-12	0-20	-12-12
Range of <i>l</i>	-9-9	-14-12	-12-11
Number of measured reflections	5183	2650	5514
Structure refinement			
Number of unique reflections	638	2458	2543
Number of reflections used in refinement	572	1891	1692
Criterion for significance	$I/\sigma(I) > 2$	$I/\sigma(I) > 2$	$I/\sigma(I) > 2$
Number of variables	54	54	54
Weights w^{-1}	$\sigma_a^2(F) + 0.0004 F ^2$	$\sigma_a^2(F) + 0.0004 F ^2$	$\sigma_a^2(F) + 0.0004 F ^2$
<i>R</i>	0.036	0.028	0.031
<i>wR</i>	0.056	0.040	0.036
<i>S</i>	1.544	1.408	0.840
Maximum shift/e.s.d.	0.001	0.001	0.001
Maximum, minimum in $\Delta\rho$ (e Å ⁻³)	0.194, -0.345	0.368, -0.317	0.587, -2.115

were not obtained. The colourless crystals of rubidium hydrogen succinate were obtained by slow evaporation of a solution containing equimolar amounts of succinic acid and Rb₂CO₃.

The data collections were performed at 295 and 120 K (1) and 120 K (2) using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu *K* α radiation (295 K) and Mo *K* α radiation (120 K). ω -2 θ scans were applied. Unit-cell dimensions were determined from a least-squares refinement of 22 reflections with $38.1 < \theta < 46.8^\circ$ in (1) (295 K), $16.0 < \theta < 25.8^\circ$ in (1) (120 K) and $18.7 < \theta < 22.1^\circ$ in (2). Experimental conditions and results from refinements are summarized in Table 1. For compound (1) at 295 K and compound (2) correction for absorption was performed; maximum and minimum transmission factors were 0.8646, 0.5392 in (1) and 0.4945, 0.1002 in (2). To reduce the effects of extinction, which were severe for rubidium hydrogen succinate, it was necessary to dip the crystal in liquid nitrogen about 20 times. Still the remeasurement of three standard reflections (200, 020, 002) every 10000 s showed an increase of 4.9% in intensity during exposure time which resulted in a linear correction. Maximum and minimum correction factors were 0.99995 and 0.97643. Remeasurement of the same three standard reflections for partially deuterated sodium hydrogen succinate showed that correction for decay was not necessary at any of the temperatures. The symmetry equivalent reflections were averaged giving $R_{\text{int}} = 0.029$ in (1) at 295 K, $R_{\text{int}} = 0.010$ in (1) at 120 K and $R_{\text{int}} = 0.036$ in (2).

The structure of compound (1) was, at both temperatures, solved by direct methods with the program *SHELXS86* (Sheldrick, 1990) which provided coordinates for all non-H atoms. The structure

of compound (2) was solved by calculating the Patterson function from which the Rb^+ ion was located. The H atoms in compound (1) and the remaining atoms in compound (2) were located from $\Delta\rho$ maps. Both structures were refined using the full-matrix least-squares method minimizing $\sum w(|F_o| - |F_c|)^2$. The positional and isotropic displacement parameters for the H atoms were included in the refinement.

Refinement for compound (1) was attempted in the non-centrosymmetric space group Cc and in the centrosymmetric $C2/c$. Values of R , wR and S in Cc are comparable to those found in $C2/c$ (even slightly smaller) but some of the displacement parameters for the H atoms became non-positive definite and no convergence was obtained.

Two refinement models were examined for the position of the H atom in the short hydrogen bond in a similar way as earlier by Kalsbeek & Larsen (1991). In agreement with their observations the displacement parameter was much larger [$B = 9(1) \text{ \AA}^2$ for compound (1) at 295 K, $4.9(5) \text{ \AA}^2$ for compound (1) at 120 K and $6(2) \text{ \AA}^2$ for compound (2)] when the H atom was placed in the special position, than when it was in a general position corresponding to two half-populated sites on each side of the centre of the hydrogen bond [$B = 5.0(8) \text{ \AA}^2$ for compound (1) at 295 K, $2.6(5) \text{ \AA}^2$ for compound (1) at 120 K and $2(1) \text{ \AA}^2$ for compound (2)]. The separation between the two half-populated H atoms is $0.80(4) \text{ \AA}$ for compound (1) at 295 K, $0.67(3) \text{ \AA}$ for compound (1) at 120 K and $0.71(8) \text{ \AA}$ for compound (2).

All calculations except the structure determinations for compound (1) were performed with the Enraf-Nonius *SDP* program system (Enraf-Nonius, 1985). Scattering-factor values for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and used as contained in the program system.

Discussion. The final positional and equivalent isotropic displacement parameters are given in Table 2.* Both compounds crystallize in the monoclinic space group $C2/c$ but they are not isostructural.

As is found in most acid salts of succinate acid both anion and cation in the two investigated salts are found on crystallographic symmetry elements; the hydrogen succinate ion on an inversion centre and the alkali metal ion on the twofold axis. Table 3

* Lists of observed and calculated structure factors, anisotropic displacement parameters (U values) and bond lengths and angles in the coordination polyhedra for the alkali metal ions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54974 (56 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0263]

Table 2. *Final positional and equivalent isotropic displacement parameters* (\AA^2)

H atoms were refined isotropically. $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$. $U(295 \text{ K})/U(120 \text{ K})$ is the ratio of the equivalent isotropic displacement parameters at the two temperatures for compound (1).

Compound (1) (295 K)						$U(295 \text{ K})/$
Occu-		x	y	z	U_{eq}	$U(120 \text{ K})$
pancy						
Na	0.5	0.00000	0.42697 (6)	0.75000	0.0272 (1)	2.937
O(1)	1.0	0.20321 (11)	0.26242 (10)	0.81795 (9)	0.0605 (3)	3.001
O(2)	1.0	0.36787 (9)	0.09248 (7)	0.85821 (11)	0.0327 (3)	3.019
C(1)	1.0	0.26812 (11)	0.17582 (11)	0.74945 (12)	0.0306 (3)	2.997
C(2)	1.0	0.21704 (13)	0.18615 (12)	0.52344 (12)	0.0361 (3)	3.039
H(1)	0.5	0.212 (5)	0.247 (4)	0.944 (5)	0.063 (10)	1.909
H(2)	1.0	0.102 (2)	0.181 (2)	0.456 (2)	0.056 (5)	2.074
H(3)	1.0	0.263 (2)	0.115 (1)	0.485 (2)	0.042 (4)	2.333
Compound (1) (120 K)						
Na	0.5	0.00000	0.42873 (3)	0.75000	0.00926 (5)	
O(1)	1.0	0.20671 (5)	0.26562 (4)	0.81892 (5)	0.02016 (8)	
O(2)	1.0	0.36504 (4)	0.08953 (3)	0.85843 (5)	0.01083 (6)	
C(1)	1.0	0.26872 (5)	0.17590 (4)	0.74959 (6)	0.01021 (6)	
C(2)	1.0	0.21785 (6)	0.18603 (5)	0.52352 (6)	0.01188 (8)	
H(1)	0.5	0.225 (4)	0.248 (3)	0.949 (4)	0.033 (6)	
H(2)	1.0	0.093 (1)	0.182 (1)	0.449 (2)	0.027 (3)	
H(3)	1.0	0.268 (1)	0.116 (1)	0.485 (1)	0.018 (3)	
Compound (2)						
Rb	0.5	0.00000	0.79539 (4)	0.75000	0.01192 (4)	
O(1)	1.0	0.56690 (7)	0.84322 (22)	0.90146 (22)	0.0143 (3)	
O(2)	1.0	0.62051 (8)	0.62995 (23)	0.69526 (22)	0.0155 (3)	
C(1)	1.0	0.62922 (9)	0.75082 (25)	0.85710 (26)	0.0113 (3)	
C(2)	1.0	0.71401 (9)	0.80525 (28)	1.02423 (26)	0.0141 (3)	
H(1)	0.5	0.522 (4)	0.812 (7)	0.783 (13)	0.023 (16)	
H(2)	1.0	0.720 (1)	0.959 (4)	1.028 (5)	0.006 (5)	
H(3)	1.0	0.712 (2)	0.769 (5)	1.172 (5)	0.024 (8)	

is a more complete list of symmetry elements found in hydrogen succinate salts than the one previously given by Kalsbeek & Larsen (1991). Lithium, partially deuterated sodium, potassium and rubidium hydrogen succinate all crystallize in $C2/c$ but none of these salts are isostructural. All four salts contain the alkali metal ion on the twofold axis and the hydrogen succinate ion on an inversion centre (Table 3). In the structure of compound (1) the short hydrogen bond is across an inversion centre in contrast to the other three salts crystallizing in $C2/c$ where the short hydrogen bond is found across the crystallographic twofold axis.

In Fig. 1 the hydrogen succinate ions in the two salts are represented illustrating the atom-numbering scheme and their stereochemistry. The conformation of the hydrogen succinate ion is illustrated by the torsion angle $\text{O}(1)-\text{C}(1)-\text{C}(2)-\text{C}(2')$ given in Table 3 and by Fig. 1. The hydrogen succinate ion found in compound (1) is in the *cis* conformation as observed in one of the hydrogen succinate ions in ethylammonium hydrogen succinate (Kalsbeek, 1991) while it is in the *trans* conformation in compound (2). From Table 3 the *trans* conformation is the most common in hydrogen succinate ions.

Values of the ratio of the equivalent isotropic displacement parameters at 295 and 120 K for compound (1) are listed in Table 2. The value of this ratio is very close to 3 for the five non-H atoms in the structure, indicating that the Debye temperature

Table 3. *Hydrogen succinate salts*

Cation	Space group	Z	Site symmetry			Torsion angle (°)	O(1)···O(1') (Å)	Reference
			Anion	Cation	Short hydrogen bond			
CH ₃ NH ₃ ⁺	<i>P2₁/m</i>	2	$\bar{1}$	<i>m</i>	$\bar{1}$	179	2.4448 (5)	Kalsbeek & Larsen (1991)
(CH ₃) ₂ NH ₂ ⁺	<i>Cmcm</i>	4	<i>2/m</i>	<i>m2m</i>	<i>2/m</i>	180	2.4395 (7)	Kalsbeek & Larsen (1991)
C ₂ H ₅ NH ₃ ⁺ †	<i>P1</i>	4	$\bar{1}$	<i>1</i>	$\bar{1}$	178 ⁱ	2.456 (4) ⁱⁱⁱ	
			$\bar{1}$	<i>1</i>	$\bar{1}$	19 ⁱⁱ	2.483 (4) ^{iv}	Kalsbeek (1991)
(C ₂ H ₅) ₂ NH ₂ ⁺	<i>Pban</i>	4	$\bar{2}$	<i>2</i>	$\bar{2}$	163	2.4370 (7)	Kalsbeek (1991)
Cs ⁺	<i>P2₁/m</i>	2	$\bar{1}$	<i>m</i>	$\bar{1}$	177	2.41 (4)	McAdam & Speakman (1971)
Li ⁺	<i>C2/c</i>	4	$\bar{1}$	<i>2</i>	$\bar{2}$	178	2.478 (1)	Küppers (1982)
K ⁺	<i>C2/c</i>	4	$\bar{1}$	<i>2</i>	$\bar{2}$	180	2.446 (4)	McAdam, Currie & Speakman (1971)
Na ⁺ (295 K)	<i>C2/c</i>	4	$\bar{1}$	<i>2</i>	$\bar{1}$	68	2.4272 (9)	
(120 K)	—	—	—	—	—	62	2.4295 (5)	
Rb ⁺	<i>C2/c</i>	4	$\bar{1}$	<i>2</i>	$\bar{2}$	179	2.4406 (15)	

† Two independent hydrogen succinate ions and two short hydrogen bonds are found in this salt. Torsion angles: (i) O(11)—C(11)—C(12)—C(13), (ii) O(21)—C(21)—C(22)—C(23); short hydrogen bonds: (iii) O(11)···O(23), (iv) O(13)···O(21').

for this compound is below 120 K. From Fig. 1 the displacement parameters of all the non-H atoms in compound (1) at both temperatures are significantly elongated in the same direction. The elongated direction is perpendicular to the chains of anions linked by the very short hydrogen bonds. As was observed for the differences in cell dimensions for compound (1) on cooling, the smallest changes are in the direction of the very strong hydrogen bond.

Partially deuterated sodium hydrogen succinate is isostructural at 295 and 120 K and so the suspected phase transition has not occurred.

Bond lengths and angles are given in Table 4. For both compounds at both temperatures the geometry of the carboxy groups is between those found in a true carboxylic acid group and a true carboxylate group. This is also found in other acid salts where the anions are linked by short crystallographically symmetric hydrogen bonds, for example, Kalsbeek & Larsen (1991) and Kalsbeek (1991). The average values of the C—O distances in the carboxy groups in compound (1) at 120 K (1.2641 Å) and in compound (2) (1.2689 Å) are almost equal and close to the values usually found in carboxy groups, while the value found in compound (1) at 295 K is significantly shorter (1.2543 Å). It is striking that the two C—C distances found in the hydrogen succinate ion in compound (1) at 120 K differ by about four times as much as those found in compound (1) at 295 K and compound (2).

The packing in the two structures is illustrated by the stereo drawings given in Fig. 2. The hydrogen succinate ions in both compounds are linked by short crystallographically symmetric hydrogen bonds forming infinite chains in the structure. In compound (1) the chains are parallel to the *c* axis while they are in the *ac* plane in compound (2). The strong interaction caused by the very short hydrogen bonds in the direction of the *c* axis in compound (1) is reflected in the insignificant change (−0.016 Å) in the length of this axis on cooling. From Fig. 2 the Na⁺ ions in compound (1) are found alternating

Table 4. *Bond lengths (Å), bond angles (°) and hydrogen-bond geometry (Å, °)*

Hydrogen succinate anions	Compound (1)			Compound (2)				
	(295 K)	(120 K)						
C(1)—O(1)	1.2794 (15)	1.2917 (7)		1.3056 (22)				
C(1)—O(2)	1.2292 (11)	1.2365 (5)		1.2321 (11)				
C(1)—C(2)	1.5132 (12)	1.5124 (6)		1.5144 (19)				
C(2)—C(2')	1.5196 (17)	1.5346 (7)		1.5096 (25)				
O(1)—C(1)—O(2)	123.17 (9)	123.31 (4)		123.61 (13)				
O(1)—C(1)—C(2)	114.85 (8)	114.72 (4)		113.70 (14)				
O(2)—C(1)—C(2)	121.95 (10)	121.96 (4)		122.69 (15)				
C(1)—C(2)—C(2')	110.54 (8)	110.64 (3)		113.74 (14)				
Cations	Compound (1)			Compound (2)				
	(295 K)	(120 K)						
Na—O(1)	2.3690 (11)	2.3584 (5)		Rb—O(1 ⁱⁱ)	2.9179 (15)			
Na—O(1 ⁱⁱ)	2.3690 (11)	2.3584 (5)		Rb—O(1 ⁱⁱⁱ)	2.9179 (15)			
Na—O(2 ⁱⁱⁱ)	2.3957 (10)	2.3807 (4)		Rb—O(1 ^{iv})	3.0182 (13)			
Na—O(2 ^{iv})	2.3957 (10)	2.3807 (4)		Rb—O(1 ^v)	3.0182 (13)			
Na—O(2 ^v)	2.5785 (7)	2.5666 (3)		Rb—O(2 ^{vi})	2.9231 (11)			
Na—O(2 ^{vi})	2.5785 (7)	2.5666 (3)		Rb—O(2 ^{vii})	2.9231 (11)			
Average	2.4477	2.4352		Rb—O(2 ^{viii})	2.9862 (14)			
				Rb—O(2 ^{ix})	2.9862 (14)			
				Average	2.9614			
				D—H···A	D···A	D—H	H···A	D—H···A
Compound (1) (295 K)	O(1)—H(1)···O(1')	2.4272 (9)	0.90 (4)	1.57 (4)	158 (4)			
Compound (1) (120 K)	O(1)—H(1)···O(1')	2.4295 (5)	0.91 (3)	1.53 (3)	167 (3)			
Compound (2)	O(1)—H(1)···O(1')	2.4406 (15)	0.90 (6)	1.58 (6)	159 (5)			

Symmetry codes: Compound (1) (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x, y, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$. Compound (2) (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ix) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (x) $-x + 1, y, -z + \frac{1}{2}$.

with the chains of anions in the direction of the *a* axis. Cooling reduces thermal vibration of the atoms and apparently this favours the electrostatic interaction between anions and cations resulting in a reduction of the *a* axis. For the structure to accommodate this reduction the *b* axis is elongated.

From the two different refinement models for the position of the H atom in the short hydrogen bond discussed above it is concluded that this H atom in both salts and at both temperatures is best described by two half-populated H atoms on each side of the centre of the hydrogen bond. From Table 4 the length of the short hydrogen bond in compound (1)

is 2.4272 (9) Å at 295 K and 2.4295 (5) Å at 120 K, and in compound (2) 2.4406 (15) Å. The alkali metal ions are located between the chains of anions.

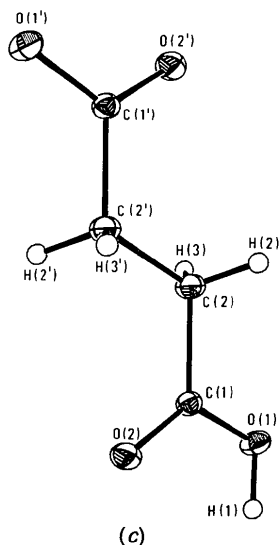
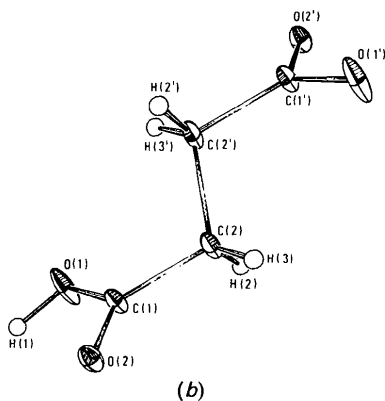
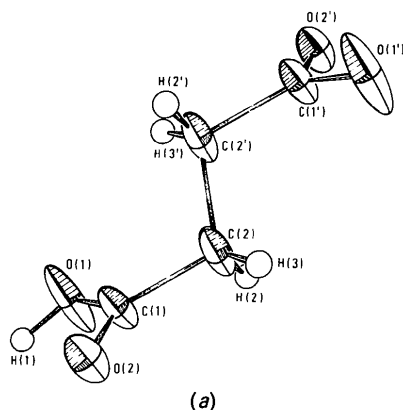


Fig. 1. ORTEP (Johnson, 1965) drawings of the hydrogen succinate ion found in (a) compound (1) (295 K), (b) compound (1) (120 K) and (c) compound (2) illustrating the atom-numbering schemes. The thermal ellipsoids enclose 50% probability and the H atoms are drawn as spheres with a fixed radius. Compound (1) (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; compound (2) (i) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + 2$.

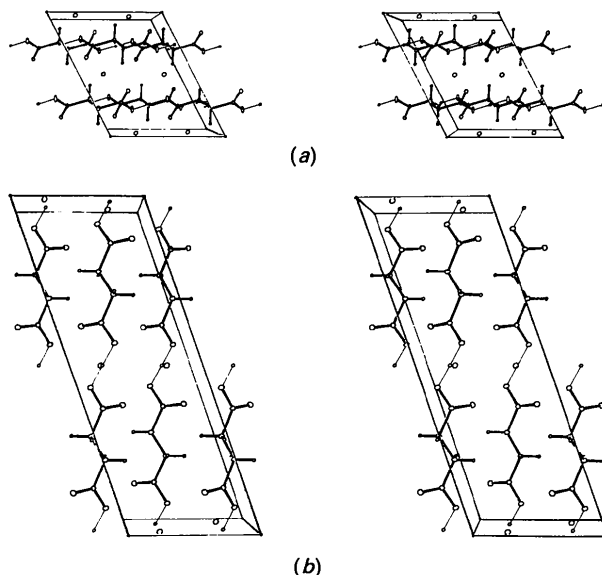


Fig. 2. Stereo drawings of (a) compound (1) and (b) compound (2). Both compounds are seen along the *b* axis. The *a* axis is vertical and the *c* axis horizontal.

Na⁺ in compound (1) is coordinated by six O atoms from the anions. From Table 4 the resulting octahedron is distorted with four short (2.37–2.40 Å) and two long (2.58 Å) Na—O distances. The average Na—O distance is 2.45 Å at 295 K and 2.44 Å at 120 K. The next two O atoms are found at a distance of 3.64 Å. The coordination polyhedron for Rb⁺ in compound (2) is a square antiprism formed by eight O atoms with Rb—O distances in the range 2.92–3.02 Å (average Rb—O is 2.96 Å). The next O atoms are at distances of 3.56 (two atoms) and 3.99 Å (two atoms).

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Structure of a Polymeric Cadmium Complex Containing Triply Bridging Monophenylphosphinate Ligands

BY JING-LONG DU, STEVEN J. RETTIG, ROBERT C. THOMPSON AND JAMES TROTTER

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

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Abstract. Poly-aqua- μ -chloro- μ -monophenylphosphinato-cadmium(II), [Cd(C₆H₅O₂P)(Cl)(H₂O)]_x, M_r = 306.96, triclinic, $P\bar{1}$, a = 12.855 (2), b = 13.501 (2), c = 5.8864 (6) Å, α = 102.60 (1), β = 103.24 (1), γ = 110.235 (9)°, V = 882.3 (2) Å³, Z = 4, D_x = 2.311 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 29.1 cm⁻¹, $F(000)$ = 592, T = 294 K, R = 0.024 (wR = 0.029) for 9816 reflections with $I \geq 3\sigma(I)$. The crystal structure contains three independent cadmium ions, all of which have distorted octahedral coordinations. One Cd forms chains along c with double phosphinate bridges; the other two Cd ions form Cd(H₂O)₂Cl₂O₂ units linked to each other along c by double Cl...H—O hydrogen bonds and to the phosphinate chains by O—Cd—O and Cl—Cd—Cl bridges and by (phosphinate)O...H—O hydrogen bonds, thus resulting in (1 $\bar{1}$ 0) polymeric sheets. The sheets are linked by van der Waals interactions between interleaving phenyl groups which are oriented perpendicular to the polymeric sheets. The phosphinate groups exhibit a triply bridging mode of coordination, not previously observed for organophosphinate complexes, in which one oxygen binds to two different metals and the second oxygen binds to a third metal.

Introduction. The potential of organophosphinate ligands to bind to metals in a variety of different ways has been realized for some time (Gillman, 1974; Gillman & Eichelberger, 1976); however, relatively few different bonding modes have, in fact, been identified by single-crystal X-ray diffraction. While there are some examples of monodentate phos-

phinate bonding (Betz & Bino, 1988; Du, Rettig, Thompson & Trotter, 1991), the most common mode is that of bidentate bridging in which each O atom of a phosphinate ligand binds to a different metal ion (Betz, Bino, Du, Lo & Thompson, 1990). The title compound provides the first example of an organophosphinate complex in which the phosphinate ligand exhibits a triply bridging mode of coordination whereby one O atom binds to two different metals and the second O atom binds to a third metal. A similar mode of phosphinate bonding has recently been reported for the inorganic phosphinate complex [CoCl(H₂O)(H₂PO₂)]_x (Marcos, Ibáñez, Amorós & Le Bail, 1991).

Experimental. Cadmium dichloride dihydrate (1.14 g) and monophenylphosphinic acid (0.71 g) were dissolved in 100 mL of distilled water in an open beaker. The beaker was loosely covered and its contents allowed to evaporate slowly. Crystals in the form of colourless prisms formed over a period of two weeks. The crystals were collected by filtration and air-dried. Analysis gives C 23.6 (calc. 23.5%), H 2.51 (calc. 2.63%). Colorless prism, 0.17 × 0.25 × 0.25 mm, Rigaku AFC6S diffractometer, lattice parameters from 25 reflections with θ = 29.9–32.5°. Intensities for $\theta < 45^\circ$, hkl : 0 to 25, -26 to 26, -11 to 11, ω - 2θ scan, ω scan width (1.10 + 0.35tan θ)° at 32° min⁻¹ (up to eight rescans), stationary backgrounds at each end of the scan counted 50% of the scan time, three standard reflections showed only small random fluctuations in intensity, Lp and absorption corrections (empirical, based on azimu-