Neutron Diffraction Study of Sodium Hydrogen Oxalate Monohydrate, NaHC₂O₄.H₂O, at 120 K*

By Robert G. Delaplane, Roland Tellgren and Ivar Olovsson

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Abstract. $M_r = 130.03$, triclinic, $P\bar{1}$, $a = 6.4235$ (7), $b = 6.6580$ (8), $c = 5.6941$ (10) Å, $\alpha = 85.048$ (9), $\beta = 110.100$ (13), $\gamma = 104.963$ (14)°, $V = 220.94$ (9) Å³, $Z = 2$, $D_x = 1.954$ g cm⁻³, neutron radiation, $\lambda = 1.210$ Å, $\mu_{obs} = 1.13$ cm⁻¹, $T = 120$ K, $R = 0.036$ for 1122 reflections. The crystal structure agrees well with that determined previously at 295 K. The three $O \cdots O$ hydrogen-bond lengths contract by 0.005 (2), 0.012 (2) and 0.018 (2) Å respectively with cooling. The thermal parameters of the oxalate group at both temperatures are compared using a rigid-body model.

Introduction. The present investigation was undertaken in order to obtain accurate positional and thermal parameters of the nuclei in NaHC₂O₄.H₂O at 120 K for subsequent deformation electron density studies (Delaplane, Tellgren & Olovsson, 1984). At lower temperature, smearing effects due to thermal motion of the atoms in the crystal are reduced which sharpens the features in electron density maps. The crystal structure and electron density study at 295 K using combined X-ray and neutron diffraction techniques have been reported previously (Tellgren & Olovsson, 1971; Tellgren, Thomas & Olovsson, 1977).

Experimental. Crystals grown from aqueous solution by slow evaporation at 295 K. Cell-dimension determination: crystal 0.12 mm diameter; Enraf–Nonius CAD-4 diffractometer cooled with nitrogen gas stream to 120 ± 1 K; measured angles of Mo $K\alpha_1$ peaks of 32 reflections (2 $\theta > 60°$) used as input for least-squares fit of lattice parameters. Neutron data collection: crystal volume 38 mm³; Hilger & Watts diffractometer, R2 reactor at Studsvik, Sweden; Displex CS-1003 refrigerator, cryostat described by Gustafsson & Tellgren (1984); flux at sample 1.3×10^6 n cm⁻² s⁻¹; temperature 120 ± 0.5 K calibrated with KH₂PO₄ phase transition at 122.8 K; ω–2θ scan mode; 1198 unique reflections measured up to $\sin\theta/\lambda = 0.693$ Å⁻¹ ($-8 \leq h \leq 8$, $-8 \leq k \leq 0$, $-7 \leq l \leq 7$). Data reduction: background correction with profile analysis (Lehmann

& Larsen, 1974); variances estimated from counting statistics and fluctuations of three standard reflections remeasured every 8 h, I and $\sigma(I)$ rescaled for 4.0% intensity decrease (McCandlish, Stout & Andrews, 1975); Lorentz and absorption correction, transmission ranged from 0.641 to 0.885. Least-squares refinement of scale factor, positional and anisotropic thermal parameters for all atoms; $\sum w(F_o^2 - F_c^2)^2$ minimized with $w^{-1} = \sigma^2(F_o^2) + (0.015)^2 F_o^4$; scattering amplitudes from Koester & Steyerl (1977); final cycles included anisotropic extinction correction, type I with Lorentzian mosaic-spread distribution (Becker & Coppens, 1975) with anisotropy of Thornley & Nelmes (1974); values of $g_{ij} \times 10^8$: 1.5 (2), 8.7 (7), 5.4 (7), -3.4 (3), -2.6 (4), 2.8 (5); 39 reflections with extinction correction ≥ 1.5; $R(F^2) = 0.053$, $wR(F^2) = 0.076$, $S = 3.38$ for 1122 reflections with $F_o^2 > 3\sigma(F_o^2)$. All shifts in final cycle $< 0.01 \sigma$; max. peak in $\Delta\rho$ map $< 3.8\%$ of maximum in ρ map. Computer programs of Lundgren (1982).

Discussion. Atomic parameters are listed in Table 1.† The crystal structure of NaHC₂O₄.H₂O (henceforth NAHOX) is illustrated in Fig. 1. Hydrogen oxalate ions are linked lengthwise by $O(2)-H \cdots O(4)$ hydrogen bonds to form infinite chains along the c axis which are in turn cross-linked by two hydrogen bonds *via* the water molecules and electrostatic Na⁺$\cdots$O interactions. The oxalate group is nonplanar with a dihedral twist of 12.90 (5)° about C(1)–C(2). Details of the structure at 295 K have been given previously (Tellgren & Olovsson, 1971; Tellgren, Thomas & Olovsson, 1977). Interatomic distances and angles are given in Table 2 together with those determined by neutron diffraction techniques at 295 K. Agreement in a comparison of corresponding covalent bond lengths and angles is good. Typically, the covalent bonds appear to become shorter with increasing temperature due to the apparent shifts of librating atoms towards the center of libration which reflects the limitation of an ellipsoid model to describe accurately the thermal motion. The largest

---

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39547 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

effect due to reducing the temperature to 120 K is a contraction of the hydrogen bonds and the $Na^+\cdots O$ interactions. Differences in the $O\cdots O$ distances are 0·005 (2), 0·012 (2) and 0·018 (2) Å in order of increasing hydrogen-bond length. Corresponding $H\cdots O$ differences are 0·006 (3), 0·013 (3) and 0·022 (3) Å. Contractions of the $Na^+\cdots O$ distances range from 0·004 (3) to 0·030 (3) Å. These changes are reflected in a comparison of the cell parameters at the two temperatures. The shortest hydrogen bond [O(2)–H···O(4)] and two of the shortest $Na^+\cdots O$ contacts which decrease very little have large components in the direction of the c axis which diminishes by only 0·0041 (13) Å. The largest difference of 0·0797 (11) Å is noted for the a axis; the O(W)–H(2)···O(3) hydrogen bond and two of the longer $Na^+\cdots O$ contacts have large components in this direction.

The anisotropic thermal parameters for the non-H atoms in the $HC_2O_4^-$ ion are physically reasonable according to the criteria of the 'rigid-bond test' (Hirshfeld, 1976), which examines the components of vibrational motion for each pair of bonded atoms in the bond direction. Differences less than 0·001 Å² for bonds comprising non-hydrogen atoms suggest an adequate description of the vibrations. A comparison of the mean-square amplitudes of vibration along mutual

Table 1. *Atomic coordinates* ($\times 10^4$) *and the r.m.s. components* ($R_i \times 10^3$ *in* Å) *along the principal axes of thermal vibration*

|	x	y	z	R_1	R_2	R_3
Na	2517 (2)	271 (2)	2400 (2)	86 (4)	99 (3)	121 (3)
C(1)	2582 (1)	5394 (1)	3529 (1)	71 (4)	82 (2)	103 (2)
C(2)	2764 (1)	6398 (1)	5977 (1)	74 (2)	78 (3)	99 (2)
O(1)	2456 (1)	3550 (1)	3418 (2)	72 (4)	103 (3)	132 (1)
O(2)	2629 (1)	6727 (1)	1709 (2)	81 (3)	88 (3)	139 (1)
O(3)	3342 (1)	8334 (1)	6117 (1)	74 (4)	90 (2)	113 (2)
O(4)	2338 (1)	5145 (1)	7621 (2)	78 (3)	90 (3)	135 (1)
O(W)	1457 (1)	826 (1)	8141 (2)	92 (4)	97 (3)	125 (1)
H	2536 (3)	6049 (3)	93 (3)	124 (4)	141 (3)	176 (2)
H(1)	1903 (3)	2245 (3)	7623 (4)	121 (4)	172 (4)	187 (2)
H(2)	2099 (3)	−12 (3)	7407 (4)	120 (7)	167 (3)	196 (2)
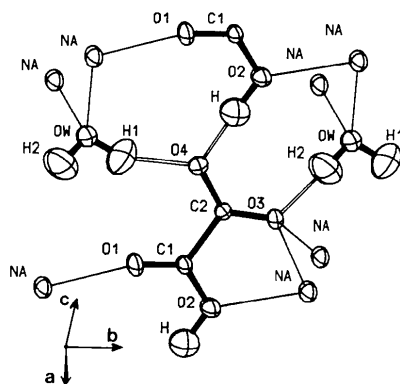
Fig. 1. An illustration of the structure of $NaHC_2O_4.H_2O$. Thermal ellipsoids are plotted at 90% probability.

Table 2. *Covalent bond lengths* (Å) *and angles* (°)

	NaHC$_2$O$_4$.H$_2$O				α-H$_2$C$_2$O$_4$.2H$_2$O
	120 K^a		295 K^b		100 K^c
C(1)–C(2)	1·553 (1)	[1·558]*	1·552 (1)	[1·559]	1·544 (1)
C(1)–O(1)	1·215 (1)	[1·217]	1·210 (1)	[1·215]	1·222 (1)
C(1)–O(2)	1·308 (1)	[1·310]	1·307 (1)	[1·314]	1·287 (1)
C(2)–O(3)	1·247 (1)	[1·249]	1·245 (1)	[1·250]	
C(2)–O(4)	1·253 (1)	[1·255]	1·249 (1)	[1·255]	
O(2)–H	1·036 (2)	[1·039]	1·036 (1)	[1·040]	1·071 (1)
O(W)–H(1)	0·965 (2)		0·963 (2)		0·969 (1)
O(W)–H(2)	0·966 (3)		0·962 (2)		0·967 (1)
O(2)–H···O(4)	2·566 (2)		2·571 (1)		
O(W)·H(1)···O(4)	2·794 (1)		2·806 (1)		
O(W)–H(2)···O(3)	2·806 (1)		2·824 (1)		
H···O(4)	1·531 (2)		1·537 (1)		
H(1)···O(4)	1·878 (2)		1·892 (2)		
H(2)···O(3)	1·840 (3)		1·862 (2)		
Na–O(W)	2·307 (2)		2·311 (1)		
–O(1)	2·320 (2)		2·327 (1)		
–O(3)	2·352 (1)		2·363 (1)		
–O(W)'	2·383 (1)		2·408 (1)		
–O(2)	2·449 (2)		2·462 (1)		
O(3)'	2·443 (1)		2·473 (1)		
O(1)–C(1)–O(2)	125·44 (9)		125·23 (6)		126·98 (3)
C(2)·C(1)–O(1)	121·19 (7)		121·36 (5)		120·43 (3)
C(2)–C(1)–O(2)	113·36 (7)		113·40 (5)		112·59 (3)
O(3)·C(2)–O(4)	127·19 (7)		127·25 (6)		
C(1)–C(2)–O(3)	117·41 (6)		117·33 (5)		
C(1)–C(2)–O(4)	115·40 (7)		115·41 (5)		
C(2)–O(2)–H	112·85 (12)		112·76 (9)		113·3 (1)
H(1)–O(W)–H(2)	107·60 (22)		107·77 (14)		106·1 (2)
Dihedral twist(°) about C(1)–C(2)	12·90 (4)		12·92 (4)		
O(2)–H···O(4)	176·75 (18)		176·17 (13)		
O(W)–H(1)···O(4)	157·32 (24)		157·69 (14)		
O(W)–H(2)···O(3)	177·86 (20)		177·75 (14)		

Notes: (*a*) this investigation; (*b*) Tellgren, Thomas & Olovsson (1977); (*c*) Feld & Lehmann (1979).

* Values in square brackets have been corrected for rigid-body motion.

bond directions for each of the five pairs of covalently bonded C and O atoms indicates a maximum difference of 0·0006 (5) Å² for the C(2)–O(4) bond and an r.m.s. difference of 0·0003 Å². Amplitude differences are larger for O(2)–H, O(W)–H(1) and O(W)–H(2) with corresponding values of 0·0095 (9), 0·0054 (10) and 0·0059 (11) Å² reflecting larger m.s. amplitudes for the H atoms. These values agree with those expected for vibrational amplitudes derived from spectroscopy (Coppens & Sabine, 1969; Eriksson & Hermansson, 1983).

The r.m.s. amplitudes of the thermal ellipsoids along the principal axes of vibration are included in Table 1. The thermal motion of the $HC_2O_4^-$ ion is anisotropic with the largest r.m.s. displacement for each atom approximately normal to the mean plane of the ion. The rigid-body analysis of Schomaker & Trueblood (1968) was used to fit the **T**, **L** and **S** tensors to the observed thermal parameters for the C and O atoms of the oxalate group. In order to analyze the effects of cooling, the same procedure was applied to the parameters previously derived at 295 K (Tellgren, Thomas & Olovsson, 1977). The r.m.s. deviation of the observed U_{ij} from those calculated from the rigid-body model

Table 3. *Principal components of translation* (**T**) *and libration* (**L**) *tensors with orientation to the inertial axes of the* $HC_2O_4^-$ *group* [I_1: *approximately perpendicular to mean plane;* I_3 *approximately parallel to* $C(1)-C(2); I_2 = I_3 \times I_1$]

		I_1	I_2	I_3
120 K				
T_1	0·092 Å	12·5°	79·6°	83·2°
T_2	0·084	86·6	72·6	162·2
T_3	0·071	78·0	159·5	106·4
L_1	3·9°	81·4	9·9	85·0
L_2	1·8	30·2	95·0	119·8
L_3	1·7	61·3	98·6	30·3
295 K				
T_1	0·131 Å	26·5	95·1	64·1
T_2	0·117	66·3	54·2	134·8
T_3	0·107	78·8	143·7	124·0
L_1	5·3°	124·5	42·2	68·9
L_2	4·2	85·7	112·9	23·4
L_3	2·6	145·1	123·2	99·5

was 0·0002 and 0·0004 Å² at 120 and 295 K, respectively; corresponding values for $\sigma(U_{ij})$ were 0·0003 and 0·0006 Å². The tensor components of **T** and **L** with respect to the principal inertia axes **I** with an origin at the center of mass are given in Table 3. Values for the **S** components were small indicating little correlation of translational and librational motion. At both temperatures the anisotropy of **T** is characterized by maximum values in directions near the major inertial axis I_1 which is approximately perpendicular to the mean plane through the oxalate group. At 120 K the largest libration occurs about an axis deviating 9·9° from I_2 which lies approximately in the plane, whereas at 298 K, this libration axis does not lie near any of the inertial axes.

Agreement between corresponding covalent bond distances improved after applying a rigid-body correction, r.m.s. difference 0·002 Å. An exception is a minor overcorrection of C(1)–O(2) at 295 K. The rigid-body motion of the oxalate group at 295 K resembles that found for the same group at room temperature in $NH_4HC_2O_4.\frac{1}{2}H_2O$ (Küppers, 1973) and the oxalic acid molecule in both α- and β-$D_2C_2O_4.D_2O$ (Coppens & Sabine, 1969). Minor differences are due to modifications induced by the particular hydrogen-bond system in each case and the usual systematic errors such as differing extinction effects which are inherent in the determination of thermal parameters.

As the major inertial axis I_1 of the $HC_2O_4^-$ ion in NAHOX deviates about 20° from the *a* axis, the observed anisotropic behavior of both **T** and **L** for the oxalate group explains an important part of the large contraction of the *a* axis with cooling. No rigid-body analysis was attempted for H_2O owing to the small number of observed parameters; however, both Na^+ and H_2O also have large components of m.s. amplitudes in the *a* direction. Williams (1972) has shown that thermal expansion is proportional to the m.s. amplitude of

vibration in a given direction. The average ratio $U_{ii}^{295}/U_{ii}^{120}$ is 2·2 for the C and O atoms which indicates that the m.s. amplitudes of vibration are proportional to the temperature within the harmonic approximation (Cyvin, 1968); the temperature ratio here is 2·46. The lower average ratio for H of 1·6 is expected due to the increased contribution of high-frequency modes to the H amplitudes.

The geometries of the $HC_2O_4^-$ ion in several different solids have been summarized by Thomas & Renne (1975) and Küppers (1973). In general the C_2O_4 group may be planar or twisted, and the C–O lengths of the carboxylate group are not equal depending on the difference between the acceptor roles of the O atoms. In NAHOX at 120 K, C(2)–O(4) is 0·005 (1) Å longer than C(2)–O(3) as O(4) accepts the strongest hydrogen bond [H···O(4) distance 1·531 (2) Å], and the two C–C–O angles differ by 2·0 (1)°.

A recent neutron diffraction investigation of the structure of α-$H_2C_2O_4.2H_2O$ (henceforth α-POX) at 100 K permits a detailed comparison of the geometry of the hydrogen oxalate ion and the oxalic acid molecule (Feld & Lehmann, 1979). Corresponding bond lengths and angles are included in Table 2. The original atom-numbering system has been changed to correspond to that used for NAHOX. Assuming that modifications due to a temperature difference of 20 K are small, several significant differences in the identical moieties of both groups are evident which are due to the combined effects of protonation and differences in crystalline environment. In α-POX the acid molecule is a donor in a moderately strong hydrogen bond to a water molecule [O–H···O distance 2·489 (1) Å] which is shorter than the corresponding hydrogen bond in NAHOX [O(2)–H···O(4) distance 2·566 (2) Å]. In $HC_2O_4^-$ the O(2)–H distance is shorter by 0·035 (2) Å and the H···O acceptor distance 0·114 (3) Å longer than the corresponding values in α-POX. The O–H lengths for both species agree with those expected for the corresponding H···O distances according to the empirical correlation given by Olovsson & Jönsson (1976). As is common for dibasic acids, the second proton is held more tightly after ionization of the first. In addition the protonation of $HC_2O_4^-$ leads to changes throughout the C_2O_4 skeleton: shortening of the C(1)–O(2) bond by 0·021 (2) Å, lengthening of C(1)=O(1) by 0·007 (2) Å and shortening of C(1)–C(2) by 0·020 (2) Å, which indicates a greater π delocalization of the electron density distribution in the acid molecule. Typically, the mean values of the two C–O distances at each end of the C_2O_4 group are similar: in $HC_2O_4^-$, 1·262 and 1·250 Å, respectively; in $H_2C_2O_4$, 1·255 Å at both ends.

The crystalline environment in α-POX is also consistent with a weaker C(1)=O(1) bond with more ionic character. In NAHOX, O(1) has only one ionic interaction with the Na^+ ion whereas in α-POX,

O(1) accepts two weak hydrogen bonds [H···O distances: 1·418 (1) and 1·877 (2) Å] from the water molecule.

That the C—C bond in C_2O_4 groups possesses some π character has been demonstrated experimentally and theoretically as peaks of deformation density in sections through the midpoint of the bond which are elongated normal to the C_2O_4 plane (Tellgren, Thomas & Olovsson, 1977; Stevens & Coppens, 1980, and references therein). However, in general the C_2O_4 group has an abnormally long sp^2–sp^2 single C—C bond which is lengthened stepwise as the acid molecule loses both protons (Küppers, 1973).

References

BECKER, P. & COPPENS, P. (1975). Acta Cryst. A31, 417–425.
COPPENS, P. & SABINE, T. M. (1969). Acta Cryst. B25, 2442–2451.
CYVIN, S. J. (1968). Molecular Vibrations and Mean Square Amplitudes, p. 78. Trondheim: Universitetsforlaget.
DELAPLANE, R. G., TELLGREN, R. & OLOVSSON, I. (1984). To be published.
ERIKSSON, A. & HERMANSSON, K. (1983). Acta Cryst. B39, 703–711.
FELD, R. & LEHMANN, M. S. (1979). Unpublished results.
GUSTAFSSON, T. & TELLGREN, R. (1984). To be published.
HIRSHFELD, F. L. (1976). Acta Cryst. A32, 239–244.
KOESTER, L. & STEYERL, A. (1977). Neutron Physics, p. 36. Berlin: Springer-Verlag.
KÜPPERS, H. (1973). Acta Cryst. B29, 318–327.
LEHMANN, M. S. & LARSEN, F. K. (1974). Acta Cryst. A30, 580–584.
LUNDGREN, J.-O. (1982). Crystallographic Computer Programs. Report UUIC-B13-04-05. Institute of Chemistry, Univ. of Uppsala.
McCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). Acta Cryst. A31, 245–249.
OLOVSSON, I. & JÖNSSON, P.-G. (1976). In The Hydrogen Bond – Recent Developments in Theory and Experiments, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY. Amsterdam: North-Holland.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63–76.
STEVENS, E. D. & COPPENS, P. (1980). Acta Cryst. B36, 1864–1876.
TELLGREN, R. & OLOVSSON, I. (1971). J. Chem. Phys. 54, 127–134.
TELLGREN, R., THOMAS, J. O. & OLOVSSON, I. (1977). Acta Cryst. B33, 3500–3504.
TEULON, P., DELAPLANE, R. G., OLOVSSON, I. & ROZIERE, J. (1984). To be published.
THOMAS, J. O. & RENNE, N. (1975). Acta Cryst. B31, 2161–2163.
THORNLEY, F. R. & NELMES, R. J. (1974). Acta Cryst. A30, 748–757.
WILLIAMS, D. E. (1972). Acta Cryst. A28, 84–88.

Structure of Potassium Tetrakis(isothiocyanato)cobaltate(II) Monohydrate Nitromethane Solvate, $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$, at 120 K by Neutron Diffraction

BY J. S. WOOD

Chemistry Department, University of Massachusetts, Amherst, MA 01003, USA

AND R. K. MCMULLAN

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Abstract. $M_r = 509·6$, monoclinic, $I2$ (conventional $C2$), $a = 11·098$ (2), $b = 5·227$ (1), $c = 16·496$ (3) Å, $\beta = 100·06$ (1)°, $V = 942·2$ (3) Å³, $Z = 2$, $D_x = 1·796$, $D_m = 1·78$ g cm⁻³, $\lambda = 1·0470$ (1) Å, $\mu = 0·771$ cm⁻¹, $T = 120$ K. Final $R(F^2) = 0·038$ for 2011 observed reflections. The structure is built from chains of approximately tetrahedral $[Co(NCS)_4]^{2-}$ anions parallel to b and interconnected by O–H···S hydrogen bonds of length 3·377 (2) Å. The potassium ions are linked by the nitromethane and water molecules to give double chains also parallel to b. Average bond distances in the anion are Co–N 1·964 (2), N–C 1·173 (1) and C–S 1·627 (2) Å.

Introduction. As part of a program of study of the charge-density distributions in small coordination complexes, we have undertaken an analysis of the $[Co(NCS)_4]^{2-}$ anion because of its well established electronic properties and the fact that detailed charge-density studies of the free thiocyanate ion have been carried out (Bats, Coppens & Kvick, 1977; Bats & Coppens, 1977). The structure of $[Co(NCS)_4]^{2-}$ has been determined in combination with several different cations: $Hg[Co(NCS)_4]$ (Jeffrey & Rose, 1968), $K_2[Co(NCS)_4].3H_2O$ (Drew & Hamid bin Othman, 1975), $Na_2[Co(NCS)_4].8H_2O$ (Mereiter & Preisinger, 1982) and $[N(CH_3)_4]_2[Co(NCS)_4]$ (Hoffman & Wood,