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The Crystal Structure of Sodium Hydrogen Oxydiacetate and Potassium Hydrogen Oxydiacetate

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In a study of the hydrogen bond system in the alkali hydrogen salts of oxydiacetic acid the crystal and molecular structures of $MHO(CH_2COO)_2$, M = Na and K, have been determined from X-ray intensity data. Both compounds are monoclinic, space group $P2_1/c$. There are four formula units in the cell with $a = 6{\cdot}990$ (1), $b = 9{\cdot}610$ (1), $c = 8{\cdot}434$ (2) Å, $\beta = 103{\cdot}34$ (1)° for $NaHO(CH_2COO)_2$ and $a = 7{\cdot}102$ (2), $b = 10{\cdot}451$ (1), $c = 8{\cdot}558$ (2) Å, $\beta = 101{\cdot}44$ (2)° for $KHO(CH_2COO)_2$. The structure of the sodium compound was refined to $R = 0{\cdot}074$ from intensities collected by the photographic Weissenberg technique. The intensities for the potassium compound were obtained with a linear single-crystal diffractometer and this structure was refined to $R = 0{\cdot}036$. The two compounds are isostructural, and contain infinite chains of oxydiacetate ions linked by a short hydrogen bond. The chains are cross-linked by the alkali metal ions. The hydrogen bond is probably asymmetric with hydrogen–oxygen distances 1·01 (5) and 1·47 (5) Å in the sodium and 1·05 (3) and 1·44 (3) Å in the potassium compound. The oxygen–oxygen distances are 2·462 (3) and 2·480 (2) Å, respectively.

Introduction

A study of the tris(oxydiacetato)lanthanoidate(III) complexes in the solid state has previously been reported by one of the present authors (Albertsson, 1968, 1970). As X-ray diffraction methods were used, the heavy lanthanoid ions prevented an accurate determination of the geometry of the oxydiacetate ion. To overcome this difficulty an investigation of the well crystallized alkali hydrogen oxydiacetates was commenced. The isostructural sodium and potassium compounds (below denoted NaHOXY and KHOXY) are described in this communication, and a following paper will deal with rubidium hydrogen oxydiacetate. Especially in the potassium and rubidium compounds the interaction between the ligand and the large central ion was expected to be fairly weak. The structural data thus obtained for the ligand could then be compared with the corresponding data for solid complexes with stronger metal–ligand interactions, *e.g.* the rare earth oxydiacetates (Albertsson, 1972).

The alkali hydrogen oxydiacetates are acid salts formed by a simple symmetric dicarboxylic acid. A series of such compounds has been thoroughly studied by Speakman and coworkers (Macdonald & Speakman, 1972). Its members embody infinite chains of dicarboxylate residues linked end-to-end by short hydrogen bonds across elements of twofold crystallographic symmetry (2, *m*, or $\bar{1}$). The general features of NaHOXY and KHOXY turned out to be the same but in these two compounds there is no symmetry element between the oxydiacetate ions. We therefore considered it worth while to make a thorough study of the alkali hydrogen oxydiacetates in order to make further contributions to the question of the symmetry of short hydrogen bonds, and the nature of their potential-energy wells.

Experimental

Crystals of NaHOXY and KHOXY were prepared by slow evaporation at room temperature of aqueous solutions of equimolar amounts of oxydiacetic acid and the appropriate alkali hydroxide. In both cases the crystals obtained were colourless and predominantly of prismatic shape. The composition of the crystals was checked by elemental analysis and by titration with sodium hydroxide. Oscillation and Weissenberg photographs showed that both crystallize in the Laue class $2/m$ with systematic absences $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$. The space group is thus $P2_1/c$ (No. 14). The lattice constants were determined by least-squares refinement based on powder data obtained at 25 °C with a Guinier–Hägg camera of radius 5·00 cm. Cu $K\alpha_1$ radiation was used with aluminium ($a=4{\cdot}04934$ Å) as internal standard.

Crystal data

1. Sodium hydrogen oxydiacetate, $NaC_4H_5O_5$ (NaHOXY); F.W. 156·1. Monoclinic; space group $P2_1/c$; $a=6{\cdot}990$ (1),* $b=9{\cdot}610$ (1), $c=8{\cdot}434$ (2) Å, $\beta=103{\cdot}34$ (1)°, $V=551{\cdot}2$ Å^3; $Z=4$; $D_m=1{\cdot}89$ g cm^{-3}, $D_x=1{\cdot}883$.

2. Potassium hydrogen oxydiacetate, $KC_4H_5O_5$ (KHOXY); F.W. 172·2. Monoclinic; space group $P2_1/c$; $a=7{\cdot}102$ (2), $b=10{\cdot}451$ (1), $c=8{\cdot}558$ (2) Å, $\beta=101{\cdot}44$ (2)°, $V=622{\cdot}5$ Å^3; $Z=4$; $D_m=1{\cdot}86$ g cm^{-3}, $D_x=1{\cdot}837$.

The densities were determined from the loss of weight in benzene.

A crystal (tabular **a**) of NaHOXY, with dimensions 0·04 × 0·30 × 0·20 mm, was mounted along **b** and integrated equi-inclination Weissenberg photographs were taken with Ni-filtered Cu radiation. The multiple-film technique was used. The intensities were estimated visually and 864 independent reflexions in the layers $h0l$–$h8l$ were measured, corresponding to about 70% of the possible number in the recorded reciprocal region.

The X-ray intensities of KHOXY were collected at 25·0 ± 0·2 °C with a PAILRED linear single-crystal

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* Estimated standard deviations referring to the least significant digits are given in parentheses.

Table 1. *Atomic coordinates with standard deviations* (× 10^4)

	NaHOXY			KHOXY		
	x	y	z	x	y	z
M^+	2734 (2)	163 (1)	824 (2)	2683 (1)	82 (1)	1020 (1)
O(1)	1828 (3)	2563 (2)	390 (3)	1755 (2)	2615 (1)	530 (2)
O(2)	−739 (3)	1034 (3)	1480 (3)	−712 (2)	1138 (2)	1666 (2)
O(3)	−2167 (3)	2920 (3)	2268 (3)	−2271 (2)	2828 (1)	2377 (2)
O(4)	4680 (3)	1440 (3)	−801 (3)	4522 (2)	1602 (1)	−758 (2)
O(5)	5369 (3)	3491 (2)	−1792 (3)	5373 (2)	3504 (1)	−1567 (2)
C(1)	387 (4)	3303 (4)	984 (4)	298 (3)	3254 (2)	1141 (3)
C(2)	−914 (4)	2303 (4)	1623 (3)	−966 (3)	2294 (2)	1768 (3)
C(3)	3084 (4)	3500 (3)	−174 (4)	3006 (3)	3485 (2)	−20 (3)
C(4)	4469 (4)	2698 (4)	−973 (3)	4386 (3)	2762 (2)	−823 (3)
H(1)	−3700 (72)	2024 (53)	2655 (59)	−3615 (48)	1997 (32)	2924 (41)
H(2)	−491 (73)	3816 (54)	51 (60)	−672 (49)	3818 (32)	247 (42)
H(3)	957 (71)	3859 (56)	1899 (59)	883 (47)	3829 (34)	2020 (41)
H(4)	2333 (76)	4210 (55)	−1006 (58)	2264 (47)	4113 (37)	−758 (42)
H(5)	3883 (74)	4063 (53)	801 (57)	3709 (45)	3989 (35)	929 (42)

Table 2. *Anisotropic thermal parameters with standard deviations* (× 10^4)

The form of the temperature factor is $\exp(-\beta_{11}h^2-\ldots-2\beta_{12}hk-\ldots)$. The root-mean-square components R_i (× 10^3 Å) of thermal displacement along the ellipsoid axes are also listed.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Na^+	135 (3)	62 (2)	108 (2)	12 (2)	44 (2)	−1 (1)	179	156	197
O(1)	117 (4)	58 (3)	124 (3)	0 (2)	81 (3)	0 (2)	165	117	221
O(2)	142 (5)	62 (4)	110 (3)	8 (3)	54 (3)	4 (2)	177	153	204
O(3)	114 (4)	86 (3)	115 (3)	1 (3)	73 (3)	5 (2)	200	120	213
O(4)	123 (5)	58 (4)	109 (3)	11 (2)	60 (3)	3 (2)	165	138	205
O(5)	126 (4)	68 (3)	108 (3)	2 (2)	79 (3)	5 (2)	178	118	214
C(1)	100 (6)	67 (4)	91 (4)	4 (3)	58 (4)	−2 (3)	178	114	190
C(2)	86 (5)	70 (5)	64 (3)	4 (3)	26 (3)	6 (3)	152	131	183
C(3)	103 (6)	53 (4)	98 (4)	3 (3)	54 (4)	0 (3)	158	128	192
C(4)	92 (5)	67 (6)	61 (4)	2 (3)	33 (3)	−2 (3)	157	124	177
K^+	114 (1)	44 (1)	98 (1)	9 (1)	49 (1)	3 (1)	158	139	199
O(1)	120 (3)	51 (1)	138 (3)	9 (2)	84 (3)	1 (2)	170	122	237
O(2)	140 (4)	58 (2)	134 (3)	1 (2)	65 (3)	−8 (2)	180	157	229
O(3)	125 (3)	65 (2)	131 (3)	−3 (2)	79 (3)	−15 (2)	186	129	236
O(4)	147 (4)	58 (2)	139 (3)	16 (2)	85 (3)	11 (2)	175	142	244
O(5)	126 (3)	62 (1)	124 (3)	4 (2)	72 (3)	10 (2)	183	136	227
C(1)	104 (4)	56 (2)	112 (4)	6 (2)	65 (3)	−7 (2)	179	117	213
C(2)	94 (4)	55 (2)	73 (3)	2 (2)	32 (3)	−5 (2)	168	134	177
C(3)	114 (4)	58 (2)	104 (4)	1 (2)	62 (3)	3 (2)	178	130	208
C(4)	83 (4)	53 (2)	76 (3)	6 (2)	25 (3)	2 (2)	164	136	174

diffractometer. A crystal, prismatic **b**, with dimensions $0\cdot14 \times 0\cdot12 \times 0\cdot30$ mm, was mounted along **b** and 1749 independent reflexions with $\theta \leq 30°$ (layers $h0l$–$h10l$) were measured with the ω-scan technique. The intensities of 693 reflexions were judged to be insignificantly different from the background as they had $I < 3\sigma_C(I)$. I is the net intensity obtained in a scan and $\sigma_C(I)$ is based on counting statistics. These reflexions were given zero weight in the subsequent refinement. The Mo $K\alpha$ radiation used was monochromated by reflexion from the (002) plane of a graphite crystal. The take-off angle was 6°. The pulse-height discrimination levels were set for a 95% window centred on the Mo $K\alpha$ peak. Coincidence losses were negligible. The stabilities of the crystal and the electronics were checked by measuring the intensities of three standard reflexions for each layer, and variations of less than 2% were observed over each 24 h period.

The intensities were corrected for absorption, polarization and Lorentz effects. For the PAILRED data the approximate polarization factor was calculated according to Arndt & Willis (1966). The linear absorption coefficient is $22\cdot1$ cm^{-1} for NaHOXY and $8\cdot1$ cm^{-1} for KHOXY. The ranges of the transmission factors were $0\cdot73$–$0\cdot83$ and $0\cdot82$–$0\cdot92$, respectively.

Table 3. *Observed and calculated structure factors for* KHOXY

In each group the running index l, $|F_o| \times 10$, and $|F_c| \times 10$ are given. An asterisk denotes a reflexion with zero weight.

[illegible]

Table 3 (*cont.*)

[illegible]

Table 4. *Observed and calculated structure factors for* NaHOXY

In each group the running index l, $|F_o| \times 10$ and $|F_c| \times 10$ are given.

[illegible]

Structure determination and refinement

The potassium parameters in KHOXY were deduced from Harker sections in the three-dimensional vector map. The oxygen and carbon atoms were located in a difference map based on these parameters. The preliminary atomic coordinates, individual isotropic thermal parameters, and one scale factor for each recorded layer were improved by full-matrix least-squares refinements. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(|F_o|)$, where $\sigma^2(|F_o|) = \sigma_C^2(|F_o|^2)/4|F_o|^2$. In spite of the exclusion of the usual term $k^2|F_o|^2$ in the weight function the average value of $w(|F_o| - |F_c|)^2$ in different $|F_o|$ and $\sin\theta$ intervals was fairly constant. The refinement converged to $R = 0\cdot10$. R is defined by $R = \sum||F_o| - |F_c||/\sum F_o|$.

The hydrogen atoms were located in a difference map obtained from reflexions with $\sin\theta/\lambda < 0\cdot5$ Å^{-1}. They were included in the refinement with the fixed thermal parameter $B = 5\cdot0$ Å^2. R decreased to $0\cdot088$. A difference synthesis calculated at this point indicated anisotropic thermal vibrations of all non-hydrogen atoms. Inclusion of the corresponding parameters in the least-squares refinement together with an overall scale factor, resulted in a final R of $0\cdot036$. 106 parameters were varied compared to 66 when isotropic thermal parameters were used. The shifts in the parameters were less than 10% of the estimated standard deviations in the last cycle of refinement. A final difference map was featureless.

The structure of NaHOXY was solved by the method of symbolic addition (Karle & Karle, 1966). NaHOXY and KHOXY were found to be isostructural, which was expected since they belong to the same space group and have comparable cell dimensions. The parameters of NaHOXY were improved by the same calculations as for KHOXY but the weight function used in the least-squares refinement was chosen according to Cruickshank as $w=1/(2{\cdot}0+|F_o|+0{\cdot}016|F_o|^2)$ The final value of R was 0·074.

The atomic coordinates with their estimated standard deviations are listed in Table 1. The thermal parameters and the root-mean-square components of thermal displacement along the principal axes of the ellipsoids of vibration are given in Table 2. The observed and calculated structure factors are listed in Tables 3 and 4.

The scattering factors were taken from *International Tables for X-ray Crystallography* (1968) (Na$^+$ and K$^+$), from Hanson, Herman, Lea & Skillman (1964) (O and C), and from Stewart, Davidson & Simpson (1965) (H).

The calculations were performed on the UNIVAC 1108 computer in Lund. A short account of the program system used is given by Oskarsson (1973).

Description and discussion of the structure

NaHOXY and KHOXY are composed of oxydiacetate residues linked end-to-end by short hydrogen bonds to form infinite zigzag chains parallel to (201) as shown in Fig. 1. The chains are crosslinked by the alkali metal ions. The structure thus closely resembles the structures of the alkali hydrogen salts of oxalic, malonic, succinic, and glutaric acid (Pedersen, 1968; Sime, Speakman & Parthasarathy, 1970; McAdam, Currie & Speakman, 1971; Macdonald & Speakman, 1972), and of hydrazinium hydrogen oxalate (Ahmed, Liminga & Olovsson, 1968).

The oxydiacetate ion is shown in Fig. 2. Its interatomic distances and angles in NaHOXY and KHOXY are given in Table 5. The highest possible symmetry for this ligand is *mm* but in these solid compounds there are no symmetry relationships between its atoms. In spite of this the dimensions of the two halves of the molecule are almost the same in both compounds. The non-hydrogen atoms of each acetic acid residue are nearly coplanar. The deviations of relevant atoms from the least-squares planes through the ligand-halves are given in Table 6. In NaHOXY and KHOXY the angles between these halves are 7·4 and 5·1°, respectively. The ligand is thus almost planar in both compounds as was earlier found in the lanthanoid oxydiacetates (Albertsson, 1970). A comparison of the geometry of the oxydiacetate ion in various compounds is postponed to a following paper when more results have been published.

Table 5. *Selected interatomic distances and angles for the ligand in* NaHOXY *and* KHOXY

	NaHOXY	KHOXY
(*a*) Distances		
O(1)–C(1)	1·415 (4) Å	1·416 (3) Å
O(1)–C(3)	1·414 (4)	1·415 (3)
C(1)–C(2)	1·506 (4)	1·514 (3)
C(3)–C(4)	1·513 (4)	1·507 (3)
C(2)–O(2)	1·235 (4)	1·226 (3)
C(2)–O(3)	1·277 (4)	1·279 (3)
C(4)–O(4)	1·223 (4)	1·217 (3)
C(4)–O(5)	1·286 (4)	1·294 (3)
O(1)–O(2)	2·643 (3)	2·660 (2)
O(1)–O(4)	2·659 (3)	2·656 (2)
C(1)–H(2)	1·01 (5)	1·09 (3)
C(1)–H(3)	0·95 (5)	0·99 (3)
C(3)–H(4)	1·03 (5)	0·99 (4)
C(3)–H(5)	1·03 (5)	1·01 (3)
(*b*) Angles		
C(1)–O(1)–C(3)	110·3 (2)°	111·8 (2)°
O(1)–C(1)–C(2)	110·1 (3)	110·2 (2)
O(1)–C(3)–C(4)	109·7 (3)	109·7 (2)
C(1)–C(2)–O(2)	120·9 (3)	121·5 (2)
C(1)–C(2)–O(3)	112·7 (3)	112·5 (2)
O(2)–C(2)–O(3)	126·4 (3)	126·0 (2)
C(3)–C(4)–O(4)	121·5 (3)	122·1 (2)
C(3)–C(4)–O(5)	112·3 (3)	112·9 (2)
O(4)–C(4)–O(5)	126·1 (3)	125·0 (2)
H(2)–C(1)–H(3)	115 (4)	108 (3)
H(4)–C(3)–H(5)	107 (4)	106 (3)

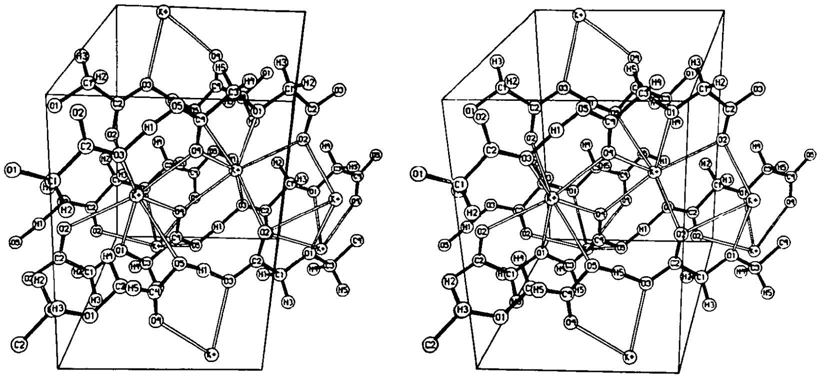

Fig. 1. A stereoscopic pair of drawings showing the content of a unit cell of KHO(CH$_2$COO)$_2$. The *c* axis points towards the reader, *a* to the right, and *b* upwards. Figs. 1–3 are drawn with the plot program *ORTEP* written by Johnson (1965).

Table 6. *Deviations from the least-squares planes through the ligand halves for* NaHOXY *and* KHOXY

Atoms defining plane: (I) O(1), C(1), C(2), O(2), O(3); (II) O(1), C(3), C(4), O(4), O(5).

	I		II	
	NaHOXY	KHOXY	NaHOXY	KHOXY
O(1)	−0·031 Å	−0·015 Å	0·094 Å	0·070 Å
O(2)	0·014	0·006		
O(3)	−0·023	−0·011		
O(4)			−0·036	−0·025
O(5)			0·072	0·056
C(1)	0·039	0·019		
C(2)	0·000	0·001		
C(3)			−0·117	−0·085
C(4)			−0·014	−0·016

The results obtained for the hydrogen bonds connecting the oxydiacetate groups in NaHOXY and KHOXY are given in Table 7. Both bonds are short, 2·462 (3) and 2·480 (2) Å, respectively, and slightly bent. In both compounds the acceptor and donor C–O–H angles are equal within the limits of error, with a mean value of 115°. In contrast to the situation in the similar malonate, succinate, and glutarate compounds (Macdonald & Speakman, 1972) the best X-ray position of the hydrogen atom is nearer one of the hydrogen bonded carboxylate oxygen atoms than the other, indicating asymmetric hydrogen bonds in spite of the short O···O distances. Moore & Power (1971) reinvestigated potassium hydrogen oxalate by neutron diffraction and established an asymmetric hydrogen bond in this case also. The hydrogen–oxygen distances were 1·054 (5) and 1·467 (5) Å with an oxygen–oxygen distance of 2·518 (3) Å. A neutron diffraction study of KHOXY has been made to obtain more accurate parameters for the hydrogen atoms so that a better description of the symmetry of the hydrogen bond can be made. The result (Albertsson & Grenthe, 1973) confirms the description given above.

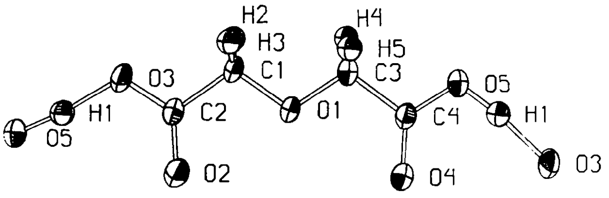

Fig. 2. The oxydiacetate ion and the hydrogen bond. The thermal ellipsoids for the non-hydrogen atoms in KHOXY are scaled to include 50% probability.

Table 7. *The hydrogen bond*

The superscripts in Tables 7 and 8 indicate transformations applied to the coordinates given in Table 1: (i) $1+x,\frac{1}{2}-y,-\frac{1}{2}+z$; (ii) $\bar{x},\bar{y},\bar{z}$, (iii) $\bar{x},-\frac{1}{2}+y,\frac{1}{2}-z$; (iv) $1-x,\bar{y},\bar{z}$; (v) $x,\frac{1}{2}-y,\frac{1}{2}+z$.

	NaHOXY	KHOXY
$O(3^i)\cdots O(5)$	2·462 (3) Å	2·480 (2) Å
$O(5)$——$H(1^i)$	1·01 (5)	1·05 (3)
$O(3)\cdots H(1)$	1·47 (5)	1·44 (3)
$\angle O(5)$–$H(1)\cdots O(3^i)$	165 (5)°	172 (3)°
$\angle C(4)$–$O(5)$——$H(1^i)$	114 (3)	113 (2)
$\angle C(2)$–$O(3)\cdots H(1)$	115 (2)	117 (1)

In the structure of KHOXY the potassium ion is surrounded by seven oxygen atoms which form a pentagonal bipyramid. The various K^+–O distances range from 2·70 to 2·92 Å (Table 8), in agreement with those given by Pedersen (1968) for potassium hydrogen oxalate. Each pyramid is linked to two others by edge-sharing, and in this way infinite chains are formed parallel to **a** as shown in Fig. 3. This description also applied to NaHOXY, although in this case three of the Na^+–O bonds are considerably longer than the other four (Table 8). The distances range from 2·38 to 2·77 Å

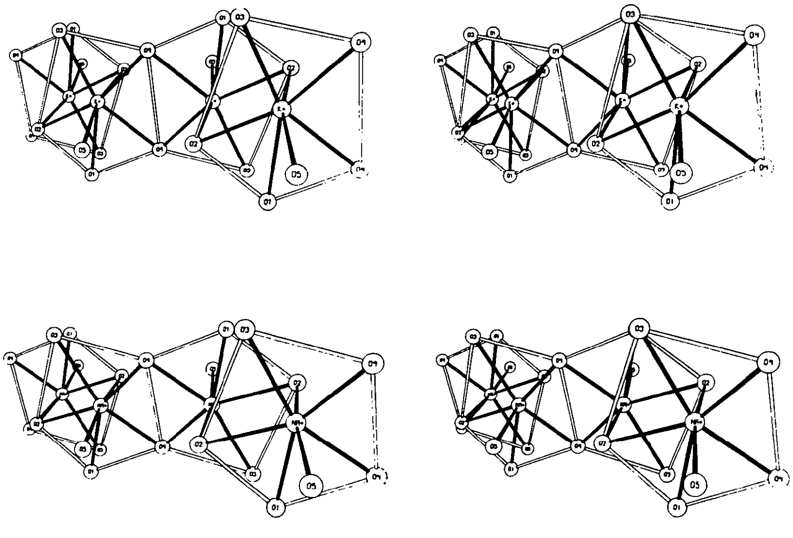

Fig. 3. Stereoscopic pairs of drawings showing the chains of pentagonal bipyramids around the potassium and sodium ions, respectively.

and are comparable with those given by Glen, Silverton & Hoard (1962). All oxygen atoms in the ligand are coordinated to the alkali metal ions. Three of the coordination sites are used by a chelated ligand and the rest by carboxylate oxygen atoms of four adjoining ligands (Fig. 1).

Table 8. *Coordination distances in* NaHOXY *and* KHOXY

	NaHOXY	KHOXY
M$^+$-O(1)	2·398 (3) Å	2·740 (2) Å
M$^+$-O(2)	2·742 (3)	2·805 (2)
M$^+$-O(4)	2·468 (3)	2·708 (2)
M$^+$-O(3^{iii})	2·773 (3)	2·770 (2)
M$^+$-O(4^{iv})	2·378 (3)	2·695 (2)
M$^+$-O(2^{ii})	2·407 (3)	2·756 (2)
M$^+$-O(5^{v})	2·720 (3)	2·921 (2)

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Guanidinium 5,5-Diethylbarbiturate Dihydrate

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$[CH_6N_3]^+[C_8H_{11}N_2O_3]^-.2H_2O$: M.W. 274·3: triclinic, $P\bar{1}$: $a=12·984(5)$, $b=7·134(3)$, $c=9·110(4)$Å, $\alpha=92·92(2)$, $\beta=104·00(2)$, $\gamma=114·73(2)$°:25°C: $D_{\text{meas}}=1·26$, $D_{\text{calc}}=1·25$ g cm^{-3} for Z=2. The two covalent and two hydrogen bonds at the barbiturate deprotonated nitrogen atom are tetrahedrally disposed. The crystal structure has features in common with that of calcium barbital trihydrate.

Introduction

The salt (Fig. 1) was prepared by addition of one equivalent of 5,5-diethylbarbituric acid (hereafter called barbital) to a fresh solution of guanidine in ethanol. The ethanol was evaporated and the dihydrate was recrystallized from water.

The lattice parameters* and intensity data were measured on a computer-controlled four-circle diffractometer using graphite monochromated Mo$K\alpha$ radiation ($\lambda=0·7107$ Å). The crystal was a transparent prism (0·25 × 0·35 × 0·40 mm) mounted with **c** along the diffractometer φ axis. Intensities were scanned in the $\theta/2\theta$ mode at 1° in 2θ per 60 s, with 10 s background counts at the scan limits. Of the 2757 non-symmetry-related reflections with $2\theta \le 50°$, 868 were found to have an integrated intensity less than 2σ. These were assigned an intensity of $\sigma(I)$. No corrections were made for X-ray absorption.

The phase problem was solved by direct methods, using the symbolic addition procedure. The atomic par-

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* The transformation matrix $(0,-1,0/0,0,1/-1,-1,0)$ gives the reduced cell with parameters 7·134, 9·110, 11·914 Å, 73·29, 81·79, 87·71°. The reduced cell was not used in this crystal structure determination.