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The Hydrogen-Bond System in a Water-Rich Crystalline Hydrate: A Neutron Diffraction Study of Trisodium Tris(oxydiacetato)cerate(III) Nonahydrate

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To obtain information on the hydrogen-bond system in solid $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 9\text{H}_2\text{O}$ the structure of this triclinic (space group $P\bar{1}$) compound has been studied by single-crystal neutron diffractometry. The structure was refined to $R=0.063$. The unit cell has $a=10.3597$ (7), $b=11.6189$ (12), $c=12.7957$ (9) Å, $\alpha=113.001$ (4), $\beta=90.227$ (4), $\gamma=92.065$ (7)°, $Z=2$. The positions of the heavy atoms agree with the earlier X-ray study. The structure is built up of layers, parallel to the ab plane, containing tris(oxydiacetato)cerate(III) ions connected by partly hydrated Na^+ ions. The layers are held together in the c direction by van der Waals and hydrogen bonds, the latter *via* water molecules. Pairs of identical non-coordinated water molecules are located in a disordered state within the layers. Hydrogen bonds transfer the disorder to a second non-coordinated water molecule in the structure. One of the water molecules, coordinated to Na^+ , is located in such a large cavity that it can occupy two sites, one of which is energetically slightly less favourable than the other. Because of crystal-packing considerations all the hydrogen bonds are bent and rather weak.

Introduction

When salts of oxoanions are precipitated from water, the ability of the water molecule to form hydrogen bonds normally causes 'water of crystallization' to be incorporated in the solid phase. The effect is often further increased by the O lone-pair orbitals which make water an excellent ligand for many cations. The building blocks of such crystalline hydrates are thus hydrated ions, and the crystal packing may be determined by hydrogen bonds donated and accepted by the water molecules.

In a structural study of nine-coordinate, mononuclear lanthanoid complexes with the tridentate ligands oxydiacetate (or diglycolate) and pyridine-2,6-dicarboxylate (dipicolinate) several water-rich crystalline hydrates were encountered (Albertsson, 1972). Four dipicolinate structures were investigated: triclinic $\text{Na}_3[\text{ML}_3] \cdot 15\text{H}_2\text{O}$, $M=\text{Ce}-\text{Dy}$, monoclinic $\text{Na}_3[\text{ML}_3] \cdot 13\text{H}_2\text{O}$, $M=\text{Ho}-\text{Yb}$, orthorhombic $\text{Na}_3[\text{ML}_3] \cdot 14\text{H}_2\text{O}$, $M=\text{Yb}-\text{Lu}$, and

hexagonal $\text{Na}_3[\text{ML}_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, $M=\text{Ho}-\text{Lu}$, $L^{2-}=\text{C}_7\text{H}_3\text{NO}_4^{2-}$. In the triclinic, monoclinic, and hexagonal compounds several of the water molecules appeared to be dynamically disordered. In the oxydiacetate compounds $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $M=\text{Ce}-\text{Lu}$, the water content is fairly low, and the molecules are confined to one set of equivalent positions in the structure. As X-ray diffraction was used in all cases, only some of the crystal-packing considerations could be revealed. Both the outer and the inner, *i.e.* coordinated, carboxylate O atoms of the mononuclear complexes can act as acceptors of hydrogen bonds, donated by the water molecules. Without knowledge of the locations of the water H atoms it is impossible to establish the hydrogen-bond schemes.

In a study of Ce compounds with very low magnetic heat capacities (Doran, Erich & Wolf, 1972; Albertsson, Chen & Wolf, 1975) large crystals of a new triclinic phase of trisodium tris(oxydiacetato)cerate(III) nonahydrate (TCDG) were obtained. The X-ray structure has been reported (Elding, 1976). The crystal data

are given in Table 1. Of the nine independent water O atoms in the asymmetric unit, two appeared to be statistically distributed over two positions each, but no indication of dynamic disorder was found. This fact and the large crystals of TCDG make it possible to employ neutron diffraction to locate the H atoms. A difficulty is the large number of atoms in the asymmetric unit and the triclinic symmetry, which give many independent parameters and reflexions, but TCDG still provides our best opportunity to study a hydrogen-bond system in this type of compound.

Table 1. *Crystal data of TCDG*,
 $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 9\text{H}_2\text{O}$

Numbers in parentheses represent estimated standard deviations in the last significant digits.

F.W. 767.6	Space group $P\bar{1}$
$a = 10.3597$ (7) Å	$\alpha = 113.001$ (4)°
$b = 11.6189$ (12)	$\beta = 90.227$ (4)
$c = 12.7957$ (9)	$\gamma = 92.065$ (7)
$V = 1416.6$ (1) Å ³	$D_m = 1.78$ g cm ⁻³
$Z = 2$	$D_x = 1.80$

Experimental

Large (~500 mm³) single crystals of TCDG were ground by hand, with carborundum, to a suitable size and shape. The crystal chosen for the experiment was a parallelepiped bounded by the planes {100}, {01 $\bar{1}$ }, and {011} and was 4.25 × 4.65 × 6.80 mm. The inten-

sities of 4876 reflexions within the half sphere $\sin \theta/\lambda \leq 0.584 \text{ \AA}^{-1}$ were recorded at room temperature with the Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy reactor R2, Studsvik. The ω -2 θ step scan technique was used. The neutron wavelength was 1.210 Å, and the flux at the crystal was about $10^6 \text{ s}^{-1} \text{ cm}^{-2}$. Roughly 10 min were spent measuring each reflexion. Three standard reflexions (800, $\bar{6}21$, and $0\bar{6}0$) were recorded at regular intervals to check the crystal and electronic stabilities. The variation in their intensities was negligible in spite of the long duration of the experiment which, owing to reactor stops, extended over three months.

The intensities were corrected for Lorentz, absorption and secondary extinction effects, the last being applied at the refinement stage. The value for the linear absorption coefficient was determined to be 1.84 cm^{-1} , corresponding to an incoherent scattering cross-section for H of 43 b. The transmission factor varied within the range 0.438–0.512.

Of the 4876 reflexions, 1646 had $I < 2\sigma_c(I)$ and were given zero weight in the subsequent refinement [the standard deviations $\sigma_c(I)$ were estimated from counting statistics]. As 700 parameters were varied, we had a ratio as small as 4.6 between the independent measurements and parameters. The large proportion of weak reflexions can be attributed to the large number of H atoms (30 out of 70) in the structure, giving a high incoherent background, and thus high standard devia-

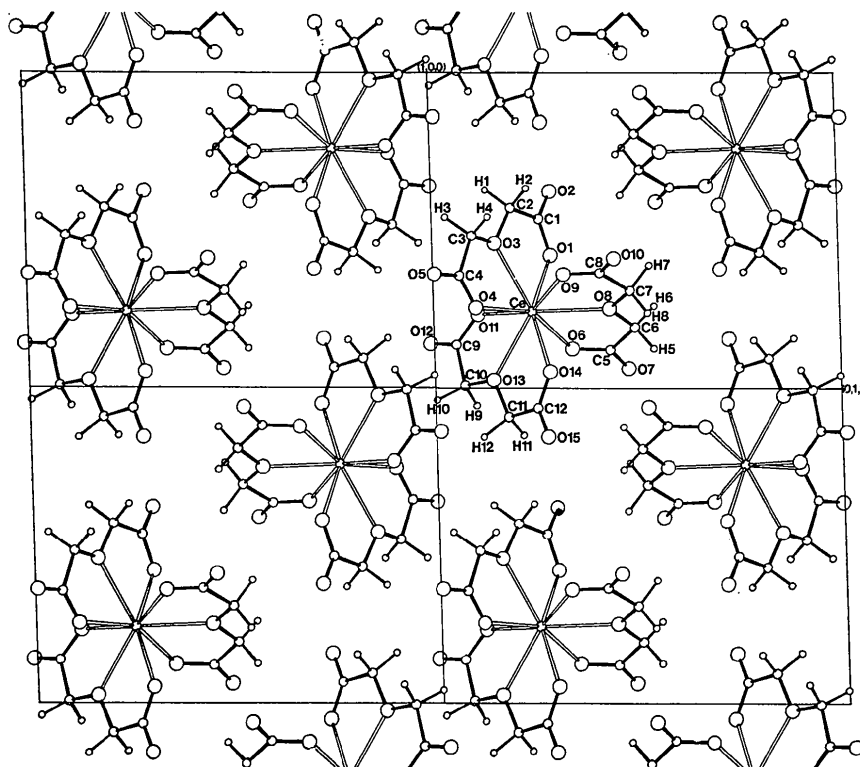


Fig. 1. The layer containing the tris(oxydiacetato)cerate(III) ions projected on the plane (01 $\bar{1}$).

tions, leading to errors in the bond lengths and angles somewhat larger than would otherwise have been the case.

Refinement

Preliminary values of the coordinates, and the isotropic temperature factors for non-H atoms were obtained from the earlier X-ray investigation (Elding, 1976). A least-squares refinement of these parameters with the neutron data gave 0.40 for $R = \sum |F_o| - |F_c| / \sum |F_o|$. The subsequent difference synthesis revealed the positions of all H atoms. H normally has a rather large vibratory motion even in solids and to obtain a good fit between the model of TCDG, with many H atoms, and experiment, we must use an anisotropic thermal model. The asymmetric unit of TCDG contains 70 atoms of which seven are statistically disordered. Thus, we had to refine more than 693 parameters, a task that could not be carried out simultaneously. Instead, the positional and thermal parameters of about 12 atoms at a time were varied in two cycles of full-matrix least-squares refinement together with the overall scale factor, while the parameters for the rest of the atoms were kept fixed. The order of the atoms varied in the refinement was: (i) H atoms attached to C, (ii) H atoms in water molecules, (iii) water O atoms, (iv) C atoms and (v) Ce, Na and the rest of the O atoms. After one pass through this series R had decreased to 0.16. A second pass was made in the same way, but this time including a correction for secondary extinction. This resulted in an R of 0.083. A third pass produced the value 0.067. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with weights $w = [\sigma_o^2 / (2F_o)^2 + (cF_c)^2]^{-1}$, where c is an adjustable constant.

At this stage, a difference synthesis revealed a peak about 1.5 Å from the position of OW(7) and two nearby troughs. This could indicate that, like W(4), W(7) was disordered. OW(7), H(71), and H(72) were thus divided between the old (A) and new (B) positions and refined with one occupancy factor. This resulted in an occupancy of 0.73 for the old positions (0.27 for the new) and a drop in R to 0.063. The final difference map in the X-ray investigation also revealed a peak (1.7 e Å⁻³) at the same position as found for OW(7B) in this study.

Correction for extinction was made according to

Table 2. Atomic coordinates with estimated standard deviations ($\times 10^4$)

For statistically disordered atoms the occupancy of the position is given.

	x	y	z
Ce	2413 (4)	2383 (4)	2458 (3)
Na(1)	-1258 (6)	6064 (7)	2155 (5)
Na(2)	2637 (6)	6945 (6)	1853 (6)
Na(3)	4010 (6)	8611 (6)	4337 (6)
O(1)	4164 (3)	2011 (4)	3569 (3)
O(2)	6183 (4)	1607 (4)	3886 (4)
O(3)	4585 (3)	1662 (4)	1457 (3)

Table 2 (cont.)

	x	y	z	Occupancy
O(4)	2568 (3)	1953 (4)	372 (3)	
O(5)	3664 (4)	1712 (5)	-1180 (4)	
O(6)	1195 (4)	2375 (4)	4128 (3)	
O(7)	559 (5)	3183 (5)	5918 (4)	
O(8)	2511 (4)	4377 (4)	4298 (3)	
O(9)	3628 (4)	4260 (4)	2454 (4)	
O(10)	4165 (4)	6296 (4)	3131 (4)	
O(11)	2279 (3)	68 (4)	1827 (4)	
O(12)	1328 (4)	-1827 (4)	1151 (4)	
O(13)	230 (3)	1178 (4)	1631 (4)	
O(14)	536 (3)	3573 (4)	2298 (4)	
O(15)	-1521 (4)	3839 (4)	1951 (4)	
OW(1)	-974 (4)	6684 (5)	590 (5)	
OW(2)	940 (4)	5466 (4)	1560 (4)	
OW(3)	-3567 (5)	6202 (7)	1925 (6)	
OW(4A)	-1951 (12)	8397 (12)	2997 (10)	0.47 (3)
OW(4B)	-2263 (14)	9516 (18)	3120 (14)	0.53 (3)
OW(5)	4117 (3)	8729 (4)	2506 (4)	
OW(6)	1754 (4)	8083 (4)	3736 (4)	
OW(7A)	3135 (10)	6054 (11)	-72 (10)	0.74 (4)
OW(7B)	3855 (25)	5370 (36)	591 (30)	0.26 (4)
OW(8)	6262 (4)	9139 (5)	4855 (4)	
OW(9)	212 (4)	10079 (4)	3977 (4)	
C(1)	5328 (3)	1769 (3)	3280 (3)	
C(2)	5693 (3)	1710 (4)	2123 (3)	
C(3)	4848 (3)	1750 (4)	411 (3)	
C(4)	3584 (3)	1802 (3)	-182 (3)	
C(5)	1162 (4)	3235 (4)	5115 (3)	
C(6)	1908 (5)	4453 (4)	5304 (4)	
C(7)	3098 (4)	5513 (4)	4356 (3)	
C(8)	3685 (3)	5343 (3)	3214 (3)	
C(9)	1313 (3)	-688 (3)	1432 (3)	
C(10)	32 (3)	-134 (3)	1349 (3)	
C(11)	-931 (3)	1821 (3)	1754 (3)	
C(12)	-626 (3)	3189 (3)	2017 (3)	
H(11)	-1529 (7)	7172 (9)	336 (8)	
H(12)	-138 (7)	7155 (8)	736 (7)	
H(21)	934 (10)	4848 (9)	742 (8)	
H(22)	899 (8)	4889 (9)	1915 (8)	
H(31)	-3647 (10)	6846 (12)	1683 (11)	
H(32)	-4333 (10)	6121 (12)	2304 (10)	
H(41A)	-2437 (27)	8490 (25)	2375 (24)	0.47 (3)
H(42A)	-1269 (16)	8999 (16)	3262 (14)	0.47 (3)
H(41B)	-2566 (12)	9057 (11)	2477 (12)	0.53 (3)
H(42B)	-2772 (13)	10263 (15)	3343 (13)	0.53 (3)
H(51)	3561 (7)	9274 (8)	2284 (8)	
H(52)	4879 (7)	8649 (9)	2063 (8)	
H(61)	1311 (8)	8805 (9)	3736 (8)	
H(62)	1069 (8)	7641 (8)	3913 (9)	
H(71A)	2578 (18)	6332 (16)	-522 (16)	0.74 (4)
H(72A)	3390 (23)	5335 (21)	-581 (26)	0.74 (4)
H(71B)	3929 (49)	4836 (62)	981 (38)	0.26 (4)
H(72B)	3731 (48)	4991 (55)	-392 (54)	0.26 (4)
H(81)	6361 (8)	8709 (10)	5329 (9)	
H(82)	6934 (8)	8860 (10)	4267 (8)	
H(91)	-20 (19)	10133 (18)	4732 (14)	0.50
H(92)	506 (9)	10921 (8)	4057 (7)	
H(93)	-667 (19)	9897 (18)	3615 (17)	0.50
H(1C)	6258 (10)	869 (11)	1708 (9)	
H(2C)	6333 (10)	2519 (12)	2218 (9)	
H(3C)	5431 (8)	989 (13)	-142 (9)	
H(4C)	5464 (8)	2565 (12)	523 (10)	
H(5C)	1238 (21)	5185 (13)	5552 (15)	
H(6C)	2561 (25)	4661 (20)	5973 (9)	
H(7C)	3907 (21)	5792 (17)	4995 (11)	
H(8C)	2410 (24)	6212 (11)	4573 (15)	
H(9C)	-626 (7)	-293 (10)	1935 (9)	
H(10C)	-423 (8)	-608 (9)	489 (8)	
H(11C)	-1533 (9)	1739 (11)	2428 (10)	
H(12C)	-1568 (9)	1404 (10)	979 (10)	

Table 3. *Thermal parameters with standard deviations* ($\times 10^4$)

The form of the temperature factor is $\exp(-\beta_{11}h^2 - 2\beta_{12}hk \dots)$. The root-mean-square components R_i ($\times 10^3$ 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
Ce	36 (3)	18 (3)	9 (3)	-1 (3)	3 (3)	2 (2)	76	111	143
Na(1)	62 (6)	88 (7)	21 (5)	8 (5)	5 (4)	14 (5)	119	183	235
Na(2)	66 (6)	39 (6)	48 (6)	-8 (5)	-2 (5)	11 (5)	143	192	197
Na(3)	56 (6)	47 (6)	38 (5)	-5 (5)	7 (5)	14 (5)	149	173	185
O(1)	42 (3)	75 (4)	27 (3)	0 (3)	-10 (3)	27 (3)	105	162	209
O(2)	52 (4)	74 (5)	35 (3)	8 (3)	-11 (3)	16 (3)	134	180	218
O(3)	22 (3)	65 (4)	27 (3)	5 (3)	4 (2)	21 (3)	106	131	195
O(4)	30 (3)	75 (5)	27 (3)	5 (3)	2 (2)	24 (3)	127	128	209
O(5)	55 (4)	118 (6)	25 (3)	31 (4)	12 (3)	31 (4)	112	157	271
O(6)	76 (4)	42 (4)	24 (3)	-18 (3)	16 (3)	3 (3)	116	138	236
O(7)	130 (6)	94 (6)	44 (4)	-41 (5)	25 (4)	25 (4)	130	204	316
O(8)	85 (4)	33 (4)	23 (3)	-17 (3)	10 (3)	5 (3)	122	127	234
O(9)	79 (4)	47 (4)	47 (4)	-21 (3)	15 (3)	22 (3)	117	181	238
O(10)	74 (4)	39 (4)	59 (4)	2 (3)	27 (3)	25 (3)	128	166	240
O(11)	32 (3)	32 (3)	64 (4)	-2 (3)	-12 (3)	16 (3)	122	136	222
O(12)	70 (4)	26 (4)	75 (4)	2 (3)	12 (3)	17 (3)	118	185	244
O(13)	24 (3)	30 (3)	49 (3)	-7 (3)	-8 (3)	12 (3)	100	142	194
O(14)	36 (3)	37 (4)	63 (4)	-1 (3)	-6 (3)	24 (3)	137	139	214
O(15)	42 (3)	47 (4)	73 (4)	17 (3)	-3 (3)	17 (3)	124	181	237
OW(1)	46 (4)	78 (5)	84 (4)	-5 (3)	-22 (3)	52 (4)	132	178	260
OW(2)	67 (4)	54 (4)	40 (3)	-9 (3)	2 (3)	14 (3)	163	171	208
OW(3)	74 (5)	152 (8)	124 (6)	32 (5)	50 (5)	61 (6)	165	284	318
OW(4A)	48 (12)	71 (14)	22 (9)	1 (10)	-3 (8)	8 (8)	122	164	216
OW(4B)	59 (13)	100 (20)	56 (11)	35 (12)	22 (10)	30 (12)	140	205	258
OW(5)	38 (3)	63 (4)	49 (3)	3 (3)	3 (3)	36 (3)	141	146	205
OW(6)	54 (4)	61 (4)	58 (4)	8 (3)	9 (3)	26 (3)	165	184	205
OW(7A)	109 (11)	107 (13)	62 (9)	18 (9)	13 (7)	19 (8)	197	246	268
OW(7B)	135 (28)	166 (41)	87 (37)	57 (25)	5 (22)	28 (30)	228	252	353
OW(8)	63 (4)	74 (5)	48 (3)	1 (4)	6 (3)	30 (4)	167	190	208
OW(9)	61 (4)	53 (4)	49 (3)	-25 (3)	-2 (3)	21 (3)	127	185	220
C(1)	34 (3)	44 (3)	30 (2)	5 (2)	-10 (2)	15 (2)	107	158	168
C(2)	20 (2)	81 (4)	33 (3)	-1 (3)	-6 (2)	29 (3)	95	141	217
C(3)	39 (3)	88 (4)	26 (3)	8 (3)	1 (2)	30 (3)	113	144	226
C(4)	42 (3)	54 (3)	31 (3)	11 (3)	8 (2)	21 (3)	131	147	183
C(5)	79 (4)	45 (3)	29 (3)	-16 (3)	22 (3)	11 (3)	105	151	240
C(6)	153 (6)	56 (4)	36 (3)	-43 (4)	32 (4)	3 (3)	134	149	332
C(7)	122 (5)	33 (3)	37 (3)	-29 (3)	33 (3)	-1 (3)	117	133	299
C(8)	55 (3)	19 (3)	46 (3)	-3 (2)	10 (3)	15 (2)	93	160	195
C(9)	44 (3)	23 (3)	33 (3)	2 (2)	-6 (2)	10 (2)	114	140	169
C(10)	42 (3)	26 (3)	34 (3)	1 (2)	-3 (3)	11 (2)	123	146	162
C(11)	23 (3)	49 (3)	45 (3)	4 (2)	-1 (2)	17 (3)	111	169	181
C(12)	32 (3)	40 (3)	33 (3)	12 (2)	-4 (2)	13 (2)	110	151	170
H(11)	76 (7)	95 (9)	84 (8)	14 (7)	-19 (6)	53 (7)	150	234	260
H(12)	62 (7)	79 (8)	64 (7)	-4 (6)	-9 (6)	34 (6)	177	200	225
H(21)	129 (11)	75 (9)	56 (7)	3 (8)	8 (7)	5 (7)	177	248	268
H(22)	93 (8)	78 (9)	84 (8)	9 (7)	-1 (7)	49 (7)	178	226	249
H(31)	120 (11)	120 (13)	127 (12)	25 (10)	53 (10)	57 (10)	208	255	332
H(32)	100 (10)	154 (14)	114 (11)	0 (9)	42 (9)	74 (11)	176	286	313
H(41A)	123 (27)	21 (22)	82 (24)	-12 (20)	9 (21)	19 (21)	98	237	270
H(42A)	112 (16)	86 (17)	68 (13)	-22 (14)	10 (13)	48 (13)	147	235	267
H(41B)	70 (11)	28 (10)	66 (11)	-18 (9)	4 (9)	-2 (9)	107	196	253
H(42B)	81 (13)	107 (17)	69 (12)	32 (12)	8 (11)	41 (12)	183	213	265
H(51)	64 (7)	67 (8)	88 (8)	20 (6)	12 (6)	40 (7)	160	201	251
H(52)	59 (6)	93 (9)	69 (7)	26 (6)	37 (6)	39 (7)	128	214	258
H(61)	80 (8)	81 (9)	80 (8)	16 (7)	4 (7)	26 (7)	193	227	245
H(62)	81 (8)	73 (8)	93 (9)	3 (7)	23 (7)	37 (7)	185	206	269
H(71A)	119 (15)	172 (21)	116 (15)	2 (14)	-30 (14)	85 (16)	204	279	331
H(72A)	172 (27)	83 (21)	107 (20)	52 (17)	13 (16)	30 (16)	187	282	324
H(71B)	212 (60)	160 (64)	60 (31)	-25 (46)	1 (33)	25 (36)	205	298	360
H(72B)	52 (42)	107 (56)	70 (57)	-17 (39)	17 (36)	-43 (37)	141	159	375
H(81)	82 (8)	105 (11)	87 (8)	0 (7)	-20 (7)	44 (8)	189	240	263
H(82)	90 (8)	99 (10)	69 (7)	28 (7)	30 (7)	18 (7)	165	256	262
H(91)	79 (13)	85 (19)	64 (18)	11 (13)	-36 (16)	24 (14)	136	219	271
H(92)	138 (10)	62 (8)	42 (6)	-4 (7)	4 (6)	20 (6)	170	189	275
H(93)	116 (20)	111 (21)	73 (16)	32 (19)	12 (16)	63 (16)	163	230	286
H(1C)	143 (10)	114 (12)	78 (9)	63 (9)	19 (8)	49 (8)	186	225	322
H(2C)	118 (11)	121 (14)	73 (8)	-60 (10)	-23 (8)	45 (9)	179	215	324
H(3C)	69 (8)	189 (16)	61 (8)	78 (10)	27 (7)	38 (9)	123	215	361

Table 3 (cont.)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
H(4C)	61 (7)	190 (16)	119 (11)	-37 (9)	-16 (7)	115 (12)	156	201	362
H(5C)	372 (31)	83 (13)	149 (17)	30 (17)	194 (21)	18 (12)	150	239	539
H(6C)	520 (41)	272 (30)	25 (7)	-293 (32)	-14 (14)	26 (12)	130	210	653
H(7C)	401 (13)	186 (21)	47 (9)	-195 (24)	-26 (14)	25 (11)	171	217	549
H(8C)	411 (42)	50 (10)	153 (17)	53 (16)	200 (24)	36 (11)	151	189	549
H(9C)	37 (6)	114 (12)	101 (10)	-13 (7)	7 (7)	61 (9)	126	229	279
H(10C)	74 (8)	68 (9)	69 (8)	-2 (7)	-22 (7)	19 (7)	171	202	250
H(11C)	93 (9)	107 (13)	103 (10)	1 (8)	47 (8)	63 (10)	142	247	301
H(12C)	81 (8)	77 (10)	90 (9)	0 (7)	-23 (7)	11 (8)	184	215	291

Zachariasen (1967), first with an isotropic and then an anisotropic model (Coppens & Hamilton, 1970). A type I model was arbitrarily chosen. Mosaic spread parameters of 2.86, 2.39, and 2.22'' were obtained. The extinction corrections multiplying F_o were mostly in the range 1.00–1.30. 22 values were higher than 1.50, the highest being 2.21 for 21 $\bar{1}$. After the final cycle of

refinement the value of R was 0.063 and the value of R_w 0.047 $\{R_w = [\sum w(|F_o| - |F_c|)^2 / w|F_o|^2]^{1/2}\}$. The unusual result that R_w is less than R is due to the large number of weak reflexions which were given zero weight in the refinement. In a case where such reflexions are included the result will be $R_w > R$. The final value of c in the weighting function was 0.005 as this value gave the

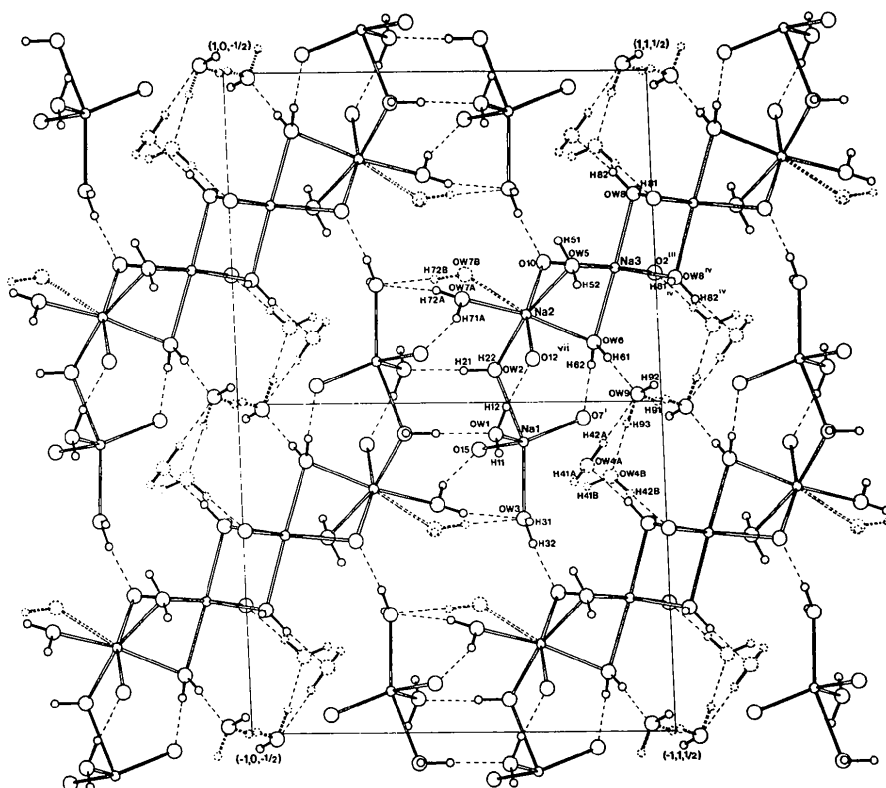


Fig. 2. The layer containing the sodium chains and the water molecules projected on the plane (01 $\bar{1}$).

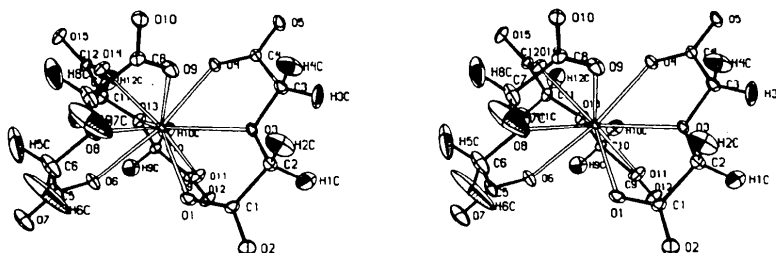


Fig. 3. A stereoscopic pair of drawings of the cerium coordination polyhedron. The thermal ellipsoids are scaled to include 30% probability.

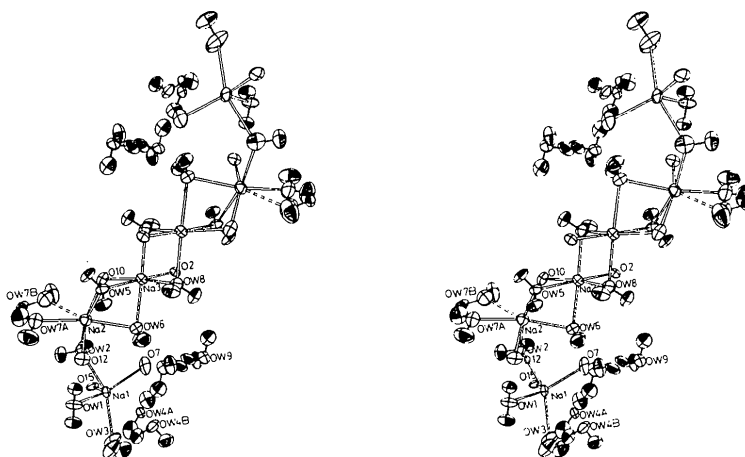


Fig. 4. A stereoscopic pair of drawings of the sodium chain including the water molecules $W(4)$ and $W(9)$. The thermal ellipsoids are scaled to include 50% probability.

best constancy of $w(|F_o| - |F_c|)^2$ in different $|F_o|$ intervals.

The coherent scattering amplitudes were taken from Bacon (1972). The final positional and thermal parameters are given in Tables 2 and 3 respectively.* Because of the mode of refinement and the number of weak reflexions in the data set, no discussion of the thermal parameters is given. All calculations were made on the Univac 1108 computer in Lund.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31896 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

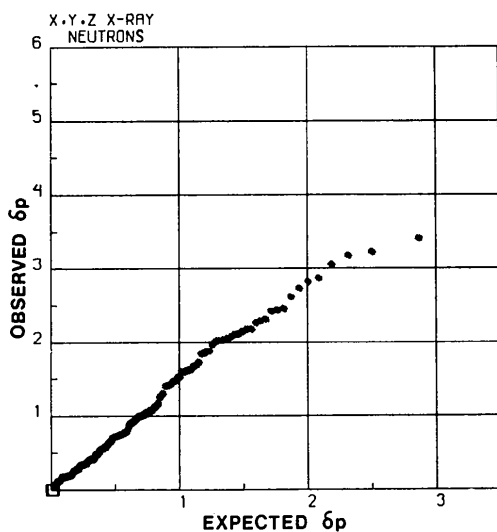


Fig. 5. A half-normal probability plot of the positional coordinates of the non-hydrogen atoms from the X-ray and neutron investigation. Slope: 1.52, intercept: -0.04 .

The heavy-atom structure

The structure can be described as built up of parallel layers containing tris(oxydiacetato)cerate(III) ions interspaced with layers containing finite chains of six connected O polyhedra around Na^+ ions. Figs. 1 and 2 show projections of the Ce and Na layers, respectively, on $(01\bar{1})$. The Na chains are parallel to $[111]$. Stereoscopic pairs of drawings of the Ce complex and Na chain are shown in Figs. 3 and 4.

The positions of the non-H atoms are in general agreement with those found in the X-ray study. Their coordinates are compared in a half-normal probability plot (Fig. 5) (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972). The points in the plot fall approximately on a straight line with slope 1.52 and intercept -0.04 . The estimated standard deviations are slightly smaller in the neutron diffraction study. The plot thus indicates that the estimated errors in the positional coordinates are not unduly incorrect in either investigation.

The agreement of the positions of the non-H atoms between the two investigations has the consequence that all geometrical features that are based on the coordinates of the heavy atoms only are essentially the same in the two cases. Selected interatomic distances and angles with estimated standard deviations for the ligands and the coordination polyhedron around Ce are given in Table 4. Nine carboxylate and ether O atoms, located 2.45–2.61 Å from Ce, form a distorted tricapped trigonal prism (Fig. 3). The non-H atoms of the oxydiacetate ligands are nearly coplanar. The deviations from the least-squares planes through the ligands and the ligand-halves are given in Table 5. The angle between the two ligand-halves is about three times as large in ligand 2 (9.6°) as in 1 and 3 (3.4 and 3.5° respectively). Such values for this angle were also found in Na (7.4°) and K hydrogen oxydiacetate (5.1°) (Albertsson, Grenthe & Herbertsson, 1973).

The C—H lengths (Table 4*b–d*) vary between 1.04 and 1.12 Å with a mean of 1.09 Å. The H—C—H angles

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations for the tris(oxydiacetato)cerate(III) complex

(a) The coordination polyhedron

Ce—O(1)	2.452 (5)	O(4)—O(11)	3.391 (6)
Ce—O(4)	2.524 (6)	O(4)—O(3)	2.608 (5)
Ce—O(6)	2.488 (6)	O(4)—O(13)	3.207 (5)
Ce—O(9)	2.480 (6)	O(6)—O(14)	3.238 (6)
Ce—O(11)	2.486 (6)	O(6)—O(11)	3.346 (6)
Ce—O(14)	2.480 (5)	O(6)—O(8)	3.587 (6)
Ce—O(3)	2.593 (5)	O(6)—O(13)	3.089 (6)
Ce—O(8)	2.577 (6)	O(9)—O(14)	3.259 (6)
Ce—O(13)	2.606 (5)	O(9)—O(8)	2.589 (6)
O(1)—O(6)	3.166 (5)	O(9)—O(3)	2.990 (6)
O(1)—O(11)	3.097 (6)	O(11)—O(13)	2.585 (5)
O(1)—O(9)	3.490 (6)	O(11)—O(3)	3.120 (5)
O(1)—O(3)	2.612 (5)	O(3)—O(8)	4.401 (6)
O(1)—O(8)	3.116 (6)	O(3)—O(13)	4.544 (4)
O(4)—O(9)	3.109 (6)	O(8)—O(13)	4.520 (6)
O(4)—O(14)	3.279 (5)		

(b) Ligand 1

O(3)—C(2)	1.413 (5)	C(2)—O(3)—C(3)	114.5 (3)
O(3)—C(3)	1.409 (5)	O(1)—C(1)—O(1)	125.1 (4)
O(1)—O(2)	2.229 (5)	O(1)—C(1)—C(2)	116.9 (3)
O(4)—O(5)	2.217 (6)	O(2)—C(1)—C(2)	118.0 (3)
C(1)—O(1)	1.271 (5)	O(4)—C(4)—O(5)	125.6 (4)
C(1)—O(2)	1.242 (5)	O(4)—C(4)—C(3)	118.1 (3)
C(4)—O(4)	1.250 (5)	O(5)—C(4)—C(3)	116.4 (3)
C(4)—O(5)	1.243 (5)	O(3)—C(2)—C(1)	111.2 (3)
C(1)—C(2)	1.506 (5)	O(3)—C(3)—C(4)	109.7 (3)
C(3)—C(4)	1.526 (5)		
C(2)—H(1C)	1.10 (1)		
C(2)—H(2C)	1.10 (1)	H(1C)—C(2)—H(2C)	106.7 (9)
C(3)—H(3C)	1.10 (1)		
C(3)—H(4C)	1.08 (1)	H(3C)—C(3)—H(4C)	101.7 (9)

(c) Ligand 2

O(8)—C(6)	1.406 (6)	C(6)—O(8)—C(7)	114.2 (4)
O(8)—C(7)	1.408 (6)	O(6)—C(5)—O(7)	126.0 (5)
O(6)—O(7)	2.222 (7)	O(6)—C(5)—C(6)	116.8 (4)
O(9)—O(10)	2.227 (6)	O(7)—C(5)—C(6)	117.2 (4)
C(5)—O(6)	1.270 (5)	O(9)—C(8)—O(10)	126.5 (4)
C(5)—O(7)	1.225 (6)	O(9)—C(8)—C(7)	117.0 (3)
C(8)—O(9)	1.254 (6)	O(10)—C(8)—C(7)	116.5 (4)
C(8)—O(10)	1.240 (5)	O(8)—C(6)—C(5)	110.3 (4)
C(5)—C(6)	1.520 (6)	O(8)—C(7)—C(8)	110.1 (3)
C(7)—C(8)	1.528 (5)		
C(6)—H(5C)	1.07 (2)		
C(6)—H(6C)	1.04 (2)	H(5C)—C(6)—H(6C)	107 (2)
C(7)—H(7C)	1.12 (2)		
C(8)—H(8C)	1.05 (2)	H(7C)—C(7)—H(8C)	111 (1)

(d) Ligand 3

O(13)—C(10)	1.429 (5)	C(10)—O(13)—C(11)	113.7 (3)
O(13)—C(11)	1.414 (5)	O(11)—C(9)—O(12)	125.0 (4)
O(11)—O(12)	2.217 (6)	O(11)—C(9)—C(10)	117.4 (3)
O(14)—O(15)	2.232 (5)	O(12)—C(9)—C(10)	117.6 (3)
C(9)—O(11)	1.270 (5)	O(14)—C(12)—O(15)	125.7 (4)
C(9)—O(12)	1.229 (5)	O(14)—C(12)—C(11)	116.4 (3)
C(12)—O(14)	1.269 (5)	O(15)—C(12)—C(11)	118.0 (3)
C(12)—O(15)	1.240 (5)	O(13)—C(10)—C(9)	109.2 (3)
C(9)—C(10)	1.517 (5)	O(13)—C(11)—C(12)	109.9 (3)
C(11)—C(12)	1.511 (5)		
C(10)—H(9C)	1.08 (1)		
C(10)—H(10C)	1.11 (1)	H(9C)—C(10)—H(10C)	106.3 (8)
C(11)—H(11C)	1.10 (1)		
C(11)—H(12C)	1.12 (1)	H(11C)—C(11)—H(12C)	103.4 (8)

Table 5. Deviations (Å) from the least-squares planes through (I) the ligand and (II, III) the ligand-halves

(a) Ligand 1

	I	II	III
C(1)	−0.004	−0.008	
C(2)	−0.066	−0.106	
O(1)	−0.076	−0.037	
O(2)	0.081	0.064	
O(3)	0.106	0.086	0.069
O(4)	0.022		−0.030
O(5)	0.025		0.052
C(3)	−0.090		−0.085
C(4)	0.002		−0.006

Angle between the two ligand-halves: 4.1°.

(b) Ligand 2

	I	II	III
C(5)	0.013	−0.011	
C(6)	−0.093	−0.008	
O(6)	0.081	−0.000	
O(7)	0.060	0.010	
O(8)	−0.094	0.009	0.030
O(9)	−0.093		−0.011
O(10)	0.148		0.024
C(7)	−0.031		−0.035
C(8)	0.010		−0.007

Angle between the two ligand-halves: 9.6°.

(c) Ligand 3

	I	II	III
C(9)	0.014	0.006	
C(10)	0.003	−0.047	
O(11)	−0.050	−0.020	
O(12)	0.038	0.024	
O(13)	0.073	0.037	0.092
O(14)	0.003		−0.039
O(15)	0.069		0.070
C(11)	−0.142		−0.110
C(12)	−0.008		−0.014

Angle between the two ligand-halves: 3.6°.

are in the range 102–111°. The mean is 106°. Thus, the geometry of the methylene groups does not deviate much from what would be expected.

As shown in Fig. 4 the Na chain consists of Na(1), Na(2), Na(3), Na(3^{iv}), Na(2^{iv}), and Na(1^{iv})*. Bond and contact distances in the chain are given in Table 6. The distorted trigonal bipyramid around Na(1) and the octahedron around Na(2) share the corner OW(2) while the octahedra around Na(2) and Na(3) share the triangular face OW(5) OW(6) O(10). The two symmetry-related halves of the chain are joined by the edge OW(8)—OW(8^{iv}) which belongs both to the octahedron around Na(3) and the octahedron around Na(3^{iv}).

The geometry of the water molecules

In general, one expects that the water molecule in crystalline hydrates has a geometry which is very little changed from the geometry of an isolated water molecule. This should be especially true when the water

* For superscripts, see Table 9.

Table 6. Coordination and contact distances (Å) with estimated standard deviations in the sodium chain

For superscripts, see Table 9.

Na(1)—O(7 ⁱ)	2.371 (8)	Na(2)—OW(7A)	2.336 (14)
Na(1)—O(15)	2.500 (9)	Na(2)—OW(7B)	2.329 (35)
Na(1)—OW(1)	2.395 (9)	Na(3)—O(2 ⁱⁱⁱ)	2.393 (8)
Na(1)—OW(2)	2.441 (8)	Na(3)—O(10)	2.536 (8)
Na(1)—OW(3)	2.429 (8)	Na(3)—OW(5)	2.403 (8)
Na(1)—OW(4A)	2.625 (15)	Na(3)—OW(6)	2.438 (7)
Na(1)—OW(4B)	2.392 (21)	Na(3)—OW(8)	2.414 (7)
Na(2)—O(10)	2.604 (8)	Na(3)—OW(8 ^{iv})	2.434 (8)
Na(2)—O(12 ^{vii})	2.411 (8)	Na(1)—Na(2)	4.183 (9)
Na(2)—OW(2)	2.336 (8)	Na(2)—Na(3)	3.292 (10)
Na(2)—OW(5)	2.399 (8)	Na(3)—Na(3 ^{iv})	3.566 (13)
Na(2)—OW(6)	2.451 (8)		
O(7 ⁱ)—O(15)	3.572 (7)	O(12 ^{vii})—OW(5)	3.275 (6)
O(7 ⁱ)—OW(1)	4.429 (7)	O(12 ^{vii})—OW(6)	3.379 (7)
O(7 ⁱ)—OW(2)	3.398 (7)	O(12 ^{vii})—OW(7A)	3.059 (12)
O(7 ⁱ)—OW(3)	4.009 (8)	O(12 ^{vii})—OW(7B)	4.097 (34)
O(7 ⁱ)—OW(4A)	3.090 (14)	OW(2)—OW(6)	3.300 (6)
O(15)—OW(1)	4.033 (7)	OW(2)—OW(7A)	3.322 (12)
O(15)—OW(2)	3.276 (6)	OW(2)—OW(7B)	3.258 (28)
O(15)—OW(3)	3.539 (8)	OW(5)—OW(6)	3.139 (6)
OW(1)—OW(2)	3.005 (16)	OW(5)—OW(7A)	3.648 (12)
OW(1)—OW(3)	3.336 (7)	OW(5)—OW(7B)	3.709 (38)
OW(1)—OW(4A)	3.138 (13)	O(2 ⁱⁱⁱ)—O(10)	3.667 (6)
OW(2)—OW(4A)	4.454 (13)	O(2 ⁱⁱⁱ)—OW(6)	3.605 (6)
OW(3)—OW(4A)	2.852 (14)	O(2 ⁱⁱⁱ)—OW(8)	3.276 (6)
O(10)—OW(2)	3.785 (6)	O(2 ⁱⁱⁱ)—OW(8 ^{iv})	3.544 (7)
O(10)—OW(5)	3.227 (6)	OW(10)—OW(8)	3.775 (6)
O(10)—OW(6)	3.206 (6)	OW(5)—OW(8)	3.599 (6)
O(10)—OW(7A)	4.130 (13)	OW(5)—OW(8 ^{iv})	3.352 (6)
O(10)—OW(7B)	3.010 (36)	OW(6)—OW(8 ^{iv})	3.582 (6)
O(12 ^{vii})—OW(2)	3.395 (6)	OW(8)—OW(8 ^{iv})	3.283 (9)

molecule is only weakly bonded, e.g. to Na⁺ ions, carboxylate O atoms, and other water molecules as in TCDG (Hamilton & Ibers, 1968). The isolated molecule at room temperature has the mean values O—H = 0.9743 Å and H—O—H = 104.52° (Kuchitsu, 1971). In their survey of the water-molecule geometry in crystalline hydrates, determined by neutron diffraction, Ferraris & Franchini-Angela (1972) found the average value 0.956 Å for the O—H length with $\frac{2}{3}$ of the distances within 0.932 to 0.980 Å, and the average value 107.8° for the H—O—H angle with $\frac{2}{3}$ of the angles within 105 to 111°, i.e. a shorter length and a larger angle than in the free molecule. However, these values are uncorrected for vibratory motion. Pedersen (1975) has estimated that the observed value of the O—H distance is about 0.04 Å shorter, and the observed H—O—H angle is about 2° larger, than the mean. Compared with the values reported by Ferraris & Franchini-Angela

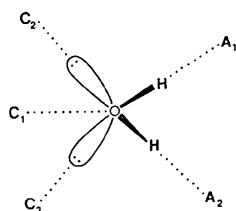


Fig. 6. The environment of a water molecule related to the configuration of the lone-pair orbitals.

Table 7. Bond distances (Å) and angles (°) in the water molecules

OW(1)—H(11)	0.96 (1)		
OW(1)—H(12)	0.99 (1)	H(11)—OW(1)—H(12)	104 (1)
OW(2)—H(21)	1.01 (1)		
OW(2)—H(22)	0.94 (1)	H(21)—OW(2)—H(22)	99 (1)
OW(3)—H(31)	0.92 (1)		
OW(3)—H(32)	0.95 (1)	H(31)—OW(3)—H(32)	109 (1)
OW(4A)—H(41A)	0.98 (3)		
OW(4A)—H(42A)	0.94 (2)	H(41A)—OW(4A)—H(42A)	111 (2)
OW(4B)—H(41B)	0.84 (2)		
OW(4B)—H(42B)	0.98 (2)	H(41B)—OW(4B)—H(42B)	104 (2)
OW(5)—H(51)	0.99 (1)		
OW(5)—H(52)	0.96 (1)	H(51)—OW(5)—H(52)	105 (1)
OW(6)—H(61)	0.97 (1)		
OW(6)—H(62)	0.94 (1)	H(61)—OW(6)—H(62)	101 (1)
OW(7A)—H(71A)	0.96 (2)		
OW(7A)—H(72A)	0.89 (3)	H(71A)—OW(7A)—H(72A)	102 (2)
OW(7B)—H(71B)	0.94 (7)		
OW(7B)—H(72B)	1.16 (7)	H(71B)—OW(7B)—H(72B)	122 (6)
OW(8)—H(81)	0.93 (1)		
OW(8)—H(82)	0.99 (1)	H(81)—OW(8)—H(82)	108 (1)
OW(9)—H(91)	0.98 (2)		
OW(9)—H(92)	0.98 (1)	H(91)—OW(9)—H(92)	107 (1)
OW(9)—H(93)	1.00 (2)	H(92)—OW(9)—H(93)	109 (1)

(1972) this implies that, on average, the corrected O—H distance is stretched 0.02 Å and the corrected H—O—H angle enlarged 1.5° when a water molecule is bonded.

As shown in Table 7, the observed (uncorrected) O—H lengths in TCDG vary between 0.84 and 1.01 Å with the average 0.957 Å, excluding the bonds in *W(7B)*, 1.16 and 0.94 Å. The angles H—O—H are in the interval 99–111° with the average 105.4°, again excluding *W(7B)* where the angle is 122°. Most observed geometries of the water molecules in TCDG are thus near the expected one. The average O—H length is the average found by Ferraris & Franchini-Angela (1972), but five of the eleven bond angles are smaller than 105° and none is larger than 111°. The average is 2.4° smaller than the value found by Ferraris & Franchini-Angela (1972). Compared to the estimation by Pedersen (1975) this implies that, on average, the corrected bond angles should be reduced by about 1° when the water molecules are incorporated in TCDG. The only feasible conclusion is that, as expected, the water molecules might be less affected by the bonding in TCDG than by the bonding in many other crystalline hydrates. The greatest deviations from the expected geometry are found in the statistically distributed water molecules, especially in *W(7B)*. As the occupancy factor of this

Table 8. Classification of water molecules in crystalline hydrates with reference to TCDG

For definitions, see Fig. 6.

Type	C ₁	C ₂	C ₃	Water molecules in TCDG
1C	M ⁺	—	—	<i>W(7)</i>
1D	M ²⁺	—	—	—
1F	H	—	—	<i>W(4A)</i>
2A	—	M ⁺	M ⁺	<i>W(2), W(5), W(6), W(8)</i>
2B	—	M ²⁺	M ²⁺	—
2E	—	H	H	<i>W(4B), W(9)</i>
2G	—	M ⁺	H	<i>W(1), W(3), [W(4A)]</i>
2H	—	M ²⁺	H	—

water molecule is only 0.27 the disorder of $W(7)$ might be an artifact but since $OW(7B)$ was revealed both in the X-ray and neutron study, we have included it in this model of TCDG. The disordered water molecules $W(4)$, $W(7)$, and $W(9)$ will be discussed below.

The hydrogen-bond system

When discussing the bonds in which the water molecules participate we use the classification originally proposed by Chidambaram, Sequeira & Sikka (1964) and later extended by Hamilton & Ibers (1968) and Ferraris & Franchini-Angela (1972) (see also Hansson, 1973). A water molecule normally interacts with its environment in the way depicted by Fig. 6. A_1 and A_2

are the hydrogen-bond acceptors and C_1 , C_2 , and C_3 are cations interacting with the molecule on the lone-pair side. A water molecule in a crystalline hydrate can belong to one of three classes according to the number of contacts C_i . Each of these classes is then subdivided on the basis of the chemical nature of the C_i 's. As we only have Na^+ ions and water H atoms as the cations C_i and at most two contacts are found on the lone-pair side of a water molecule in TCDG, our classification is confined to the following types: 1C, 1F, 2A, 2E, and 2G. In Table 8 the water molecules of TCDG are divided amongst these classes.

In an often-encountered situation the water molecule is in an approximately tetrahedral environment of A_1 , A_2 , C_2 , and C_3 , with C_2 and C_3 apparently directed

Table 9. *The environments of the water molecules in TCDG*

For definitions of A_i , C_i and 'type' see Fig. 6 and Table 8. The superscripts (i)–(xi) indicate the following equivalent sites in the structure: (i) $-x, 1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $-x, 1-y, -z$; (vi) $-x, 2-y, 1-z$; (vii) $x, 1+y, z$; (viii) $x-1, y, z$; (ix) $1-x, 1-y, -z$; (x) $x-1, 1+y, z$; (xi) $1+x, y, z$.

Water molecule	Type	Acceptor atoms and contacting cations				Angles ($^\circ$)					
		A_1	A_2	$C_2(C_1)$	C_3	A_1-O-A_2	$A_1-O-C_2(C_1)$	A_1-O-C_3	$A_2-O-C_2(C_1)$	A_2-O-C_3	C_2-O-C_3
$W(1)$	2G	O(4 ^v)	O(12 ^{viii})	Na(1)	H(21 ^v)	102.1 (2)	132.7 (3)	97.3 (4)	103.7 (3)	116.1 (4)	105.7 (4)
$W(2)$	2A	OW(1 ^v)	O(14)	Na(1)	Na(2)	79.9 (2)	111.9 (2)	115.0 (3)	86.7 (2)	132.6 (3)	122.2 (3)
$W(3)$	2G	O(5 ^v)	O(10 ^{viii})	Na(1)	H(72A ^v)	105.5 (2)	101.7 (3)	107.9 (9)	139.1 (3)	115.0 (8)	84.1 (8)
$W(3)$	2G	O(5 ^v)	O(10 ^{viii})	Na(1)	H(72B ^v)	105.5 (2)	101.7 (3)	91.2 (18)	139.1 (3)	111.9 (16)	97.3 (15)
$W(4A)$	1F	O(5 ^v)	OW(9)	H(82 ^{viii})	—	128.7 (5)	102.6 (6)	—	100.3 (6)	—	—
[$W(4A)$]	2G	O(5 ^v)	OW(9)	H(82 ^{viii})	Na(1)	128.7 (5)	102.6 (6)	98.5 (4)	100.3 (6)	111.2 (5)	116.4 (7)]
$W(4B)$	2E	O(5 ^v)	O(2 ^s)	H(82 ^{viii})	H(93)	94.7 (5)	104.0 (7)	141.2 (11)	91.3 (6)	112.3 (11)	102.8 (11)
$W(5)$	2A	O(11 ^{viii})	O(5 ^{ix})	Na(2)	Na(3)	112.3 (2)	88.7 (2)	120.8 (2)	111.3 (3)	124.3 (2)	86.5 (3)
$W(6)$	2A	OW(9)	O(7 ⁱ)	Na(2)	Na(3)	86.8 (2)	117.0 (3)	116.3 (3)	111.2 (3)	143.2 (3)	84.7 (3)
$W(7A)$	1C	OW(3 ^v)	O(15 ^v)	Na(2)	—	75.4 (3)	144.8 (5)	—	125.2 (4)	—	—
$W(7B)$	1C	OW(3 ^v)	O(9)	Na(2)	—	123.3 (13)	132.8 (12)	—	83.2 (10)	—	—
$W(8)$	2A	O(1 ⁱⁱⁱ)	OW(4A ^{xi})	Na(3)	Na(3 ^{iv})	127.1 (3)	85.4 (2)	113.6 (2)	116.0 (3)	112.1 (3)	94.7 (3)
$W(8)$	2A	O(1 ⁱⁱⁱ)	OW(4B ^{xi})	Na(3)	Na(3 ^{iv})	151.7 (4)	85.4 (2)	113.6 (2)	113.3 (4)	87.0 (4)	94.7 (3)
$W(9A)$	2E	O(6 ^{vii})	OW(9 ^{vi})	H(61)	H(42A)	114.4 (3)	119.3 (3)	136.3 (5)	85.1 (4)	93.2 (5)	95.1 (6)
$W(9B)$	2E	O(6 ^{vii})	OW(4B)	H(61)	H(91 ^{vi})	114.3 (4)	119.3 (3)	117.0 (7)	119.1 (5)	99.9 (7)	80.3 (7)

Table 10. *The O—H...O hydrogen-bond geometries in TCDG*

For superscripts, see Table 9.

	O...O	O—H	H...O	\angle O—H...O
OW(4B)—H(41B)...O(5 ^v)	2.71 (2) Å	0.84 (2) Å	1.90 (1) Å	164 (2) $^\circ$
OW(9)—H(91)...OW(9 ^{vi})	2.73 (1)	0.98 (2)	1.78 (2)	166 (2)
OW(2)—H(22)...O(14)	2.73 (1)	0.94 (1)	1.81 (1)	165 (1)
OW(9)—H(93)...OW(4B)	2.74 (2)	1.00 (2)	1.75 (3)	173 (2)
OW(9)—H(92)...O(6 ^{vii})	2.76 (1)	0.98 (1)	1.78 (1)	174 (1)
OW(6)—H(61)...OW(9)	2.78 (1)	0.97 (1)	1.83 (1)	166 (1)
OW(3)—H(32)...O(10 ^{viii})	2.80 (1)	0.95 (1)	1.86 (1)	169 (1)
OW(5)—H(52)...O(5 ^{ix})	2.80 (1)	0.96 (1)	1.85 (1)	173 (1)
OW(4B)—H(42B)...O(2 ^s)	2.81 (2)	0.98 (2)	1.84 (2)	173 (2)
OW(1)—H(12)...O(12 ^{viii})	2.81 (1)	0.99 (1)	1.83 (1)	173 (1)
OW(7A)—H(72A)...OW(3 ^v)	2.82 (1)	0.89 (3)	1.95 (3)	165 (3)
OW(5)—H(51)...O(11 ^{viii})	2.84 (1)	0.99 (1)	1.86 (1)	169 (1)
OW(8)—H(81)...O(1 ⁱⁱⁱ)	2.85 (1)	0.93 (1)	1.97 (1)	157 (1)
OW(4A)—H(42A)...OW(9)	2.86 (1)	0.94 (2)	1.93 (2)	170 (2)
OW(4A)—H(41A)...O(5 ^v)	2.88 (1)	0.98 (3)	1.92 (3)	164 (2)
OW(6)—H(62)...O(7 ⁱ)	2.89 (1)	0.94 (1)	1.96 (1)	169 (1)
OW(8)—H(82)...OW(4A ^{xi})	2.89 (1)	0.99 (1)	1.91 (2)	171 (1)
OW(8)—H(82)...OW(4B ^{xi})	2.86 (2)	0.99 (1)	2.07 (2)	136 (1)
OW(1)—H(11)...O(4 ^v)	2.91 (1)	0.96 (1)	1.95 (1)	173 (1)
OW(2)—H(21)...OW(1 ^v)	2.91 (1)	1.01 (1)	1.93 (1)	162 (1)
OW(3)—H(31)...O(5 ^v)	2.94 (1)	0.92 (1)	2.02 (1)	175 (1)
OW(7A)—H(71A)...O(15 ^v)	2.97 (1)	0.96 (2)	2.07 (2)	156 (2)
OW(7B)—H(72B)...OW(3 ^v)	3.02 (4)	1.16 (7)	1.91 (6)	159 (5)
OW(7B)—H(71B)...O(9)	3.13 (4)	0.94 (7)	2.25 (5)	155 (5)

towards the electron maxima of the lone pairs. Also, when only one contact, C_1 , is established, it sometimes takes place in a tetrahedral, lone-pair direction instead of the direction of the twofold axis of the water molecule (the bisector of the lone-pair orbitals). It should, however, be stressed that for bonds that are mainly electrostatic in character, the cations C_i are expected to be directed, not necessarily towards the electron-rich areas of the lone pairs, but towards the minima in the electrostatic potential function. This is also true for hydrogen bonds: as the H atom of a bond receives a net positive charge and there appears to be no electron accumulation at the centre of the bonds, we have to look upon them as mainly electrostatic in character (Kvick, 1974; Almlöf, Kvick & Thomas, 1973; Bonaccorsi, Pullman, Scrocco & Tomasi, 1972). Even when lone pairs are well defined, as is the case for the water molecule, the electrostatic potential minima may have an extended form. Deviations of C_2 and C_3 from the lone-pair directions are thus to be expected in such complicated structures as TCDG.

The environments of all water molecules in TCDG are listed in Table 9 and the geometries of their hydrogen bonds to the acceptor O atoms in Table 10. The immediate conclusion drawn from all the angles listed in Table 9 is that none of the water molecules in TCDG is in a tetrahedral environment; only occasional coincidences seem to occur between the electron maxima

of the lone pair and the minima of the electrostatic potential. This conclusion can be restated in the form that the main operative force when hydrogen bonds are formed in TCDG is not the lone-pair geometry of the water molecules (or the acceptor carboxylate O atoms) but the crystal packing considerations of the bulky tris(oxydiacetate) complexes.

$W(2)$, $W(5)$, $W(6)$, and $W(8)$ are shared between two Na^+ ions and all belong to class 2A in Table 8, *i.e.* they are only donating hydrogen bonds. They have their H atoms approximately in planes perpendicular to the lines between the two coordinated Na^+ ions. Their bond angles are approximately bisected by the plane through the two Na^+ ions and their O atom. In this way the repulsion between the Na^+ ions and the water H atoms is minimized. $W(2)$ donates one hydrogen bond to $W(1')$ of an adjoining chain and one to O(14) in the layer of Ce complexes below the actual Na layer. $W(5)$ is bonded to O(11^{vii}) and O(5^{ix}) in the complex layer above. $W(6)$ forms the intrinsic hydrogen bond $\text{OW}(6)\text{-H}(62)\cdots\text{O}(7')$ which together with $\text{OW}(1)\text{-H}(12)\cdots\text{O}(12^{\text{vii}})$ further connects the Na(1) and Na(2) polyhedra in the Na chain. $W(6)$ also donates a bond to the non-coordinated $W(9)$. Finally, $W(8)$ participates in a bond to O(1ⁱⁱⁱ) in the complex layer below and in a bond where the non-coordinated $W(4^{\text{xi}})$ acts as acceptor.

$W(1)$, $W(3)$, and $W(7)$ are each bonded only to one

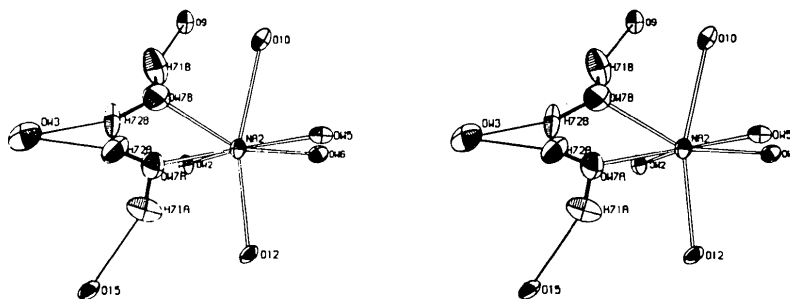


Fig. 7. A stereoscopic pair of drawings of the coordination around the statistically distributed water molecule $W(7)$. The thermal ellipsoids are scaled to include 30% probability.

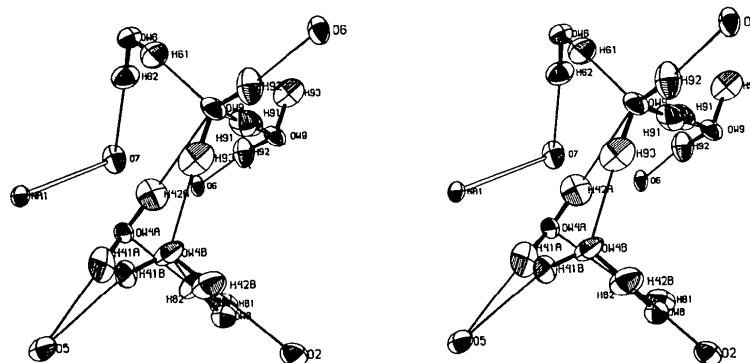


Fig. 8. A stereoscopic pair of drawings of the vicinity of the water molecules $W(4)$ and $W(9)$. The thermal ellipsoids are scaled to include 30% probability.

Na⁺ ion. *W*(1) accepts a hydrogen bond from *W*(2) and *W*(3) one from *W*(7). Both *W*(1) and *W*(3) thus belong to class 2*G* in Table 8. *W*(7) is not the acceptor of any hydrogen bond and belongs to class 1*C*. We already know that *W*(1) forms one intrinsic hydrogen bond with O(12^{vii}). The other bond is to O(4^v) in the complex layer above the actual Na layer. The hydrogen bonds donated by *W*(3) are to O(10^{viii}) and O(5^v) in the complex layer below and above respectively. *W*(7) is discussed below.

Not only all outer but also all inner (coordinated) carboxylate O atoms of the complex ions are acceptors of one hydrogen bond each, except the Ce-coordinated O(9) which only accepts a hydrogen bond from the disordered *W*(7) in position *B*, in about 27% of the cases. The outer carboxylate O(5) accepts three hydrogen bonds: from *W*(3), *W*(4), and *W*(5). O(5) is the only outer carboxylate O atom not coordinated to a Na⁺ ion. O(2) only accepts a hydrogen bond from *W*(4) in position *B*, *i.e.* in about 50% of the cases. In spite of all the hydrogen bonds accepted by the carboxylate O atoms the strongest attractive force between the complex ions should be provided by the coordination of their outer carboxylate O atoms to the Na⁺ ions. For this reason, as described in the paper dealing with the X-ray structure (Elding, 1976), the complex and Na⁺ ions should be looked upon as forming layers parallel to the *ab* plane; Na(2) connects the complexes in infinite chains in the *b* direction, while Na(1) and Na(3) connect them in zigzag-shaped chains running parallel to *a*. Between the layers of Na-bonded Ce complexes thus formed there are only van der Waals and hydrogen bonds. The hydrogen bonds are *OW*(1)–H(11)···O(4^v), those three accepted by O(5), and the bonds connecting the Na chains along [111] (Fig. 2): *OW*(2)–H(21)···*OW*(1^v), *OW*(7)–H(72)···*OW*(3^v), and *OW*(7*A*)–H(71*A*)···O(15^v). Owing to the disorder of *W*(7) the last bond is formed in only about 73% of the cases.

The disordered water molecules

The coordination around Na(2) and the hydrogen bonds in which *W*(7*A*) and *W*(7*B*) might participate are shown stereoscopically in Fig. 7. Both *OW*(7*A*) and *OW*(7*B*) have almost the same coordination distance to Na(2) (Table 6), and the angles within the coordination polyhedron of Na(2) do not deviate much for the two positions. On the other hand, both the possible hydrogen-bond distances involving *W*(7*B*), *i.e.* *OW*(7*B*)···*OW*(3^v) and *OW*(7*B*)···O(9) are very long (>3.0 Å) while at least one of the distances involving *W*(7*A*) is of normal length, *OW*(7*A*)···*OW*(3^v) 2.82 Å (Table 10). The position *B* for *W*(7) should then be energetically less favourable than position *A*, a situation reflected by the difference in occupancy: 0.73 for *W*(7*A*) and 0.27 for *W*(7*B*).

The environment of *W*(4) and *W*(9) is shown in Fig. 8. *W*(4) is distributed over two positions *A* and *B*. As

discussed in the paper describing the X-ray studies, we have chosen to regard *OW*(4*A*) as not coordinated to Na(1) since *OW*(4*B*) definitely is not coordinated (Table 6). Also *OW*(9) is not coordinated to any Na⁺ ion. It is located near the centre of symmetry (0,0, $\frac{1}{2}$) which gives one of the shortest hydrogen-bond distances in the structure, between the symmetry-related *OW*(9) and *OW*(9^{vi}), 2.73 Å. If we make the plausible assumption that a hydrogen bond always joins the two *OW*(9) of a pair, the H atom in this bond, H(91), must be statistically distributed about the centre of symmetry with an occupancy of $\frac{1}{2}$ in each position. (Symmetry alone only requires the positions to have equal occupancy.) When the structure was solved it appeared that one of the H sites near *OW*(9), *i.e.* H(92), was fully occupied. Therefore only one more site with occupancy $\frac{1}{2}$ had to be located. A half H atom was placed in position H(93) as the trough there in the difference map was about half as deep as the trough in position H(92). The distance between H(93) and H(42*A*) is only 1.13 Å meaning that both positions cannot be occupied simultaneously. Thus, when *W*(9) has its statistically distributed H atom in position H(93), *W*(4) must be in position *B* with H(93) participating in a hydrogen bond with *OW*(4*B*) as acceptor. When *W*(9) has the H atoms in H(91) and H(92), *W*(4) is in position *A* and donates a hydrogen bond to *OW*(9). The upshot of this is that the disorder of *W*(4) is a result of the disorder of *W*(9) and that the occupancy of the *A* and *B* sites of *W*(4) must be $\frac{1}{2}$ as the occupancy factors of H(91) and H(93) are assumed to be $\frac{1}{2}$. In the least-squares refinement we obtained the value 0.47 for the *A* sites (resulting in the value 0.53 for the *B* sites) in good agreement with the assumptions. As both *OW*(4*B*) and *OW*(9) accept two hydrogen bonds, *W*(4*B*) and

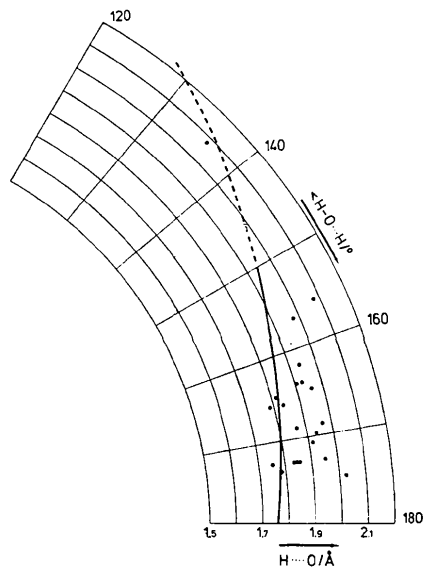


Fig. 9. The correlation between H···O(acceptor) bond length and the O–H···O angle for the hydrogen-bond geometries in TCDG. The curve is the correlation predicted by the bond-valence analysis by Brown (1976).

$W(9)$ belong to class $2E$ of Table 7. We have disregarded the $\text{Na}(1)$ contact of $\text{OW}(4A)$ and so that water molecule should be classified as belonging to type $1F$. Inclusion of $\text{Na}(1)$ changes the type to $2G$, which is the same type as $W(1)$ and $W(3)$, but definitely not the same as $W(4B)$.

The geometry of the O—H \cdots O bonds

The O \cdots O distances in the hydrogen bonds vary between 2.71 and 2.97 Å, excluding the uncertain hydrogen bonds of $W(7B)$ (Table 10). The H \cdots O (acceptor) distances are in the range 1.75–2.07 Å and the angles O—H \cdots O in the range 162–175° except in the three bonds $\text{OW}(8)\text{—H}(82)\cdots\text{OW}(4B^{xi})$ (136°), $\text{OW}(8)\text{—H}(81)\cdots\text{O}(1^{iii})$ (157°), and $\text{OW}(7A)\text{—H}(71A)\cdots\text{O}(15^a)$ (156°). From the geometrical data in the survey by Ferraris & Franchini-Angela (1972), Pedersen (1974) has shown that the equilibrium configuration for the hydrogen bond from a donor water molecule is linear and that the bending of the bond is isotropic. In a bond-valence analysis of the repulsion between the O atoms in an O—H \cdots O bond Brown (1976), on the other hand, found that weak bonds (O \cdots O greater than 2.7 Å) are generally bent and that the analysis could predict the correlation between the H \cdots O (acceptor) distance and the O—H \cdots O angle. In Fig. 9 the data in Table 10 are plotted with the predicted correlation. As the bending out of the plane of the donor water molecule is not included, Fig. 9 is a two-dimensional projection of the actual cylindrical distribution (Pedersen, 1974). Comparing Fig. 9 with Figs. 2 and 6 in the paper by Brown (1976) we conclude that all the hydrogen bonds in TCDG, including those connecting the layers of Na-bonded complex ions, are rather weak and that their geometries are mainly determined by crystal-packing considerations.

Concluding remarks

The aim of the present investigation was to gain some understanding of how the water molecules are used as a building block in TCDG and related structures. One possible description is the following: TCDG grows from concentrated water solutions containing the tris-(oxydiacetato)cerate(III) and hydrated Na^+ ions. When a complex ion is incorporated in the solid phase it must be accompanied by three Na^+ ions to compensate the negative charge. Outer carboxylate O atoms of the complex ion then replace water molecules in the inner hydrate shells of Na^+ ions, in the process also forcing other water molecules to depart for steric reasons. In this way the finite chains of six Na^+ ions surrounded by connected O polyhedra are formed (Fig. 4). Each chain has 26 O atoms of which 16 belong to water molecules [we are, at the moment, including $W(4)$ in the chain]. The Na^+ ions connect the carboxylate complexes in layers, within which all the ionic charges are compensated, so the layers in their turn

have to be connected by hydrogen and van der Waals bonds. The hydrogen bonding between the layers is accomplished by $W(1)\text{—}W(5)$ and $W(7)$ and by the carboxylate O(4), O(5), and O(15). Because of crystal-packing considerations all the hydrogen bonds in TCDG are bent and rather weak. Spaces large enough to accommodate two water molecules are formed within each layer [around $(0,0,\frac{1}{2})$ in the unit cell]. When these molecules, $W(9)$, are incorporated in TCDG, $W(4)$ is somewhat removed from $\text{Na}(1)$ to facilitate hydrogen bonds between it and $W(9)$. As $W(9)$ can only be accommodated in a disordered state, this disorder is transferred to $W(4)$ by the hydrogen bonds. $W(7)$ has been located in a somewhat larger cavity than the other water molecules. $\text{OW}(7)$ does not accept any hydrogen bond. The crystal packing in TCDG then allows $W(7)$ to occupy either site A or the energetically slightly less favourable site B .

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