

## Structural Studies on the Rare Earth Carboxylates. 25. The Crystal Structure of Trisodium Tris(oxydiacetato)- cerate(III) Nonahydrate

INGA ELDING

Physical Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The crystal structure of the triclinic compound  $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 9\text{H}_2\text{O}$  has been determined using X-ray intensity data collected with a four-circle single crystal diffractometer. The space group is  $P1$  with  $Z=2$  and unit cell dimensions  $a=10.3597(7)$ ,  $b=11.6189(12)$ ,  $c=12.7957(9)$  Å,  $\alpha=113.001(4)$ ,  $\beta=90.227(4)$ , and  $\gamma=92.065(7)^\circ$ . The oxydiacetate ions act as tridentate ligands making the cerium ion nine-coordinated. The coordination polyhedron is a distorted tricapped trigonal prism. The structure is composed of layers of these negatively charged mononuclear tris(oxydiacetato)cerate(III) complexes alternating with layers containing the sodium ions and the water molecules. The sodium ions are surrounded by octahedra and trigonal bipyramids of oxygen atoms belonging to the carboxylate groups and the water molecules. These polyhedra form six-membered chains by sharing corners, edges and faces. The chains are held together by hydrogen bonds and the two layers are connected by carboxylate oxygens and by hydrogen bonds.

The trivalent cerium ion has a single  $4f$  electron and ground state  $^2F_{5/2}$ , which splits in a crystal field. At liquid helium temperatures only the lowest doublet is expected to be populated, which makes it possible to use a fictitious spin  $S'=1/2$  to describe the magnetic properties of the ion. A cerium(III) compound with large  $\text{Ce}^{3+}-\text{Ce}^{3+}$  separations will thus have very simple magnetic properties and can be used as a magnetic coolant and thermometer in the mK region. The most widely applied material of this type is CMN:  $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ , but at temperatures below 10 mK the effects of magnetic ordering are complicating its use.

In a search for new materials which might supplement CMN in the ultra-low temperature technique, it was noticed that the solid mononuclear tris(oxydiacetato) and tris(dipicolinato) lanthanoidate complexes all have very long distances (8–10 Å) between the central ions.<sup>1–6</sup> The magnetic properties of some of these compounds have been investigated by Wolf and coworkers<sup>7–9</sup> and by Webb and Wheatley.<sup>10</sup> In one attempt to grow large single crystals of the trigonal oxydiacetate compound  $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$  (CDG), single crystals of a new triclinic phase of trisodium tris(oxydiacetato)cerate(III) nonahydrate (TCDG) were obtained. Like the other compounds TCDG has a smaller value of the magnetic heat capacity than CMN.<sup>9</sup> Besides the potential low temperature application of TCDG another reason to determine its structure is the comparatively large water content. As large single crystals are prepared, neutron diffraction can be employed to unravel the hydrogen bond system. In this paper the X-ray investigation of TCDG is reported. The study using neutron diffraction data will be reported separately. To compare the complex in this structure with that in the trigonal CDG the latter compound has been investigated with X-ray diffractometry. This comparison will be the subject of a third communication.

### EXPERIMENTAL

*Preparation and analysis.* A water solution of CDG ( $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ ), prepared as described in Ref. 1, was concentrated

at 50 °C and then slowly evaporated in a desiccator over concentrated sulfuric acid at room temperature. A few large crystals of stout prismatic habit were obtained. They were colourless. An analysis for Ce, Cl, C, H, and H<sub>2</sub>O gave: 17.6 % Ce, 18.8 % C, 4.3 % H, 22.8 % H<sub>2</sub>O and no Cl. Calc. for Na<sub>3</sub>[Ce(C<sub>4</sub>H<sub>4</sub>O<sub>5</sub>)<sub>3</sub>].9H<sub>2</sub>O: 18.3 % Ce, 18.8 % C, 3.9 % H, and 21.1 % H<sub>2</sub>O. The cerium analysis was carried out using EDTA-titration.

*Single crystal work.* Weissenberg photographs showed the compound to be triclinic. A crystal of the approximate dimensions 0.15 × 0.20 × 0.25 mm<sup>3</sup> was cut from a larger one. The intensities were recorded at 295 K with a four-circle diffractometer (CAD-4) using graphite monochromated CuK $\alpha$ -radiation. The  $\omega$ - $2\theta$  scan technique was used with  $\Delta\omega = 0.80 + 0.50 \tan\theta$ . A fast prescan was used to determine the scan speed at which a predetermined minimum number of counts (1000) was received by the detector. However, the recording time for a reflexion was limited to 90 s. The scan interval,  $\Delta\omega$ , was extended 25 % at both ends for the background measurements. Three reference reflexions were measured after every 50th reflexion to check the stability of the crystal and the electronics. The fluctuation in their intensities was 10 % and could be described by a polynomial of the second degree. This function was used for scaling of the data set. The intensities of 3106 reflexions within the interval  $5^\circ < \theta < 50^\circ$  were measured. Of these 308 had negligible intensities (less than 100 in the prescan) and were given zero weight in the subsequent refinements.

The values of  $I$  and  $\sigma_c(I)$ , where  $\sigma_c(I)$  is based on counting statistics, were corrected for Lorentz, polarization and absorption effects. In the polarization correction the expression used was  $p = (\cos^2 2\theta_M + \cos^2 2\theta) / (1 + \cos^2 2\theta_M)$  with  $\theta_M = 13.3^\circ$ . The transmission coefficient, evaluated by numerical integration, varied in the interval 0.161–0.414.

## UNIT CELL AND SPACE GROUP

TCDG, Na<sub>3</sub>[Ce(C<sub>4</sub>H<sub>4</sub>O<sub>5</sub>)<sub>3</sub>].9H<sub>2</sub>O, F.W. = 767.6, crystallizes in the triclinic system (space group  $P1$  or  $P\bar{1}$ ).

The unit cell dimensions were determined with least-squares refinement of  $\theta$ -values for 60 reflexions, measured on the diffractometer as described in Ref. 11. The density,  $D_m$ , was determined from the loss of weight in benzene. The following crystal data were obtained:

$$\begin{array}{ll} a = 10.3597(7) \text{ \AA} & \alpha = 113.001(4)^\circ \\ b = 11.6189(12) \text{ \AA} & \beta = 90.227(4)^\circ \\ c = 12.7957(9) \text{ \AA} & \gamma = 92.065(7)^\circ \\ V = 1416.6 \text{ \AA}^3 & Z = 2 \end{array}$$

$$\begin{array}{ll} D_m = 1.78 \text{ g cm}^{-3} & \mu(\text{CuK}\alpha) = 132.6 \text{ cm}^{-1} \\ D_x = 1.80 \text{ g cm}^{-3} & \end{array}$$

## STRUCTURE SOLUTION AND REFINEMENT

The structure was assumed to belong to the centrosymmetric space group  $P\bar{1}$ . A Patterson synthesis gave the coordinates of the cerium ion. The other non-hydrogen atoms were found in a difference synthesis, and all the coordinates together with a scale factor were refined in least-squares programs, first using a block-diagonal approximation and for the last cycles a full-matrix least-squares refinement. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with weights  $w$  calculated using the equation  $1/w = (C_1\sigma_c)^2 / (4F_o^2) + (C_2F_o)^2$ , where  $C_1$  and  $C_2$  are adjustable constants. The refinement was performed with individual isotropic temperature factors ( $B$ ) for all atoms except cerium, which was given anisotropic temperature coefficients. The convergence was followed by the conventional  $R$ -factor ( $R = \sum[|F_o| - |F_c|] / \sum|F_o|$ ) and the weighted  $R$ -factor ( $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ).

In the first series of refinements one of the water oxygens, OW(4), received a value of  $B$  as high as 12. When this oxygen atom was removed, a difference map showed two nearly equal peaks 1.3 Å apart. Half an oxygen atom was placed at each position, resulting in lower  $B$ -values and a drop in the  $R$ -values. The occupancy factor was also refined assuming a total of one water oxygen in positions A and B and resulted in a factor of 0.49 for position A and 0.51 for position B.

For  $C_1 = 4.0$  and  $C_2 = 0.05$ , which gave the best constancy of  $\langle w(|F_o| - |F_c|)^2 \rangle$  in different  $|F_o|$ -intervals,  $R$  was 0.050 and  $R_w$  0.072. 170 parameters were refined. The shifts in the parameters were mostly within 10 % of the e.s.d.'s and never more than 15 %. A final difference map showed a peak of 1.7 e/Å<sup>3</sup> near the position of OW(7). Also this water oxygen might thus be distributed over two positions, as is also indicated by its rather high  $B$ -value. However, no attempt was made to investigate this point further using the X-ray data.

The scattering factors for Ce were obtained from Cromer *et al.*<sup>12</sup> and those for Na, O, and C from Hanson *et al.*<sup>13</sup> Correction for anomalous

Table 1. Atomic parameters with e.s.d.'s in parentheses. *B* denotes the isotropic temperature factor.

Atom	$x/a (\times 10^4)$	$y/b (\times 10^4)$	$z/c (\times 10^4)$	<i>B</i> (Å <sup>2</sup> )
Ce	2407.7(5)	2382.9(5)	2451.7(4)	<sup>a</sup>
Na(1)	-1258(4)	6057(4)	2144(4)	3.3(1)
Na(2)	2632(4)	6947(4)	1848(3)	2.6(1)
Na(3)	4006(4)	8594(4)	4336(3)	2.7(1)
O(1)	4171(6)	2012(6)	3568(5)	2.3(1)
O(2)	6185(6)	1611(7)	3882(6)	2.9(1)
O(3)	4577(5)	1667(6)	1455(5)	1.5(1)
O(4)	2565(6)	1960(6)	383(5)	2.1(1)
O(5)	3660(7)	1682(7)	-1187(6)	3.0(1)
O(6)	1218(6)	2361(7)	4119(5)	2.5(1)
O(7)	556(7)	3164(8)	5920(7)	3.9(2)
O(8)	2514(6)	4359(6)	4289(5)	2.2(1)
O(9)	3621(6)	4261(7)	2470(6)	2.9(1)
O(10)	4152(7)	6300(7)	3131(6)	2.9(1)
O(11)	2281(6)	69(6)	1827(6)	2.4(1)
O(12)	1310(6)	-1835(7)	1140(6)	2.9(1)
O(13)	235(5)	1175(6)	1630(5)	1.7(1)
O(14)	544(6)	3576(7)	2308(6)	2.4(1)
O(15)	-1511(7)	3846(7)	1953(6)	3.2(1)
OW(1)	-958(7)	6709(7)	603(6)	3.3(1)
OW(2)	934(6)	5451(7)	1545(6)	2.8(1)
OW(3)	-3587(9)	6175(10)	1914(9)	6.1(2)
OW(4A) <sup>b</sup>	-1971(14)	8422(15)	3022(13)	3.3(4)
OW(4B)	-2307(13)	9549(15)	3127(12)	3.4(4)
OW(5)	4112(6)	8735(7)	2490(6)	2.4(1)
OW(6)	1750(7)	8082(7)	3742(6)	3.0(1)
OW(7)	3147(11)	6046(12)	-80(10)	8.1(3)
OW(8)	6279(7)	9144(7)	4848(6)	2.9(1)
OW(9)	205(7)	10079(7)	3972(6)	3.0(1)
C(1)	5315(9)	1775(9)	3265(8)	1.5(2)
C(2)	5713(10)	1705(10)	2118(9)	2.5(2)
C(3)	4861(10)	1745(10)	393(8)	2.5(2)
C(4)	3617(10)	1795(10)	-169(9)	1.9(2)
C(5)	1185(10)	3235(10)	5091(9)	2.2(2)
C(6)	1934(12)	4455(12)	5319(11)	3.9(2)
C(7)	3091(11)	5547(12)	4365(10)	3.7(2)
C(8)	3658(9)	5336(9)	3236(8)	1.6(2)
C(9)	1311(9)	-667(9)	1449(8)	1.3(2)
C(10)	10(9)	-133(10)	1351(9)	2.3(2)
C(11)	-946(9)	1821(10)	1751(9)	2.5(2)
C(12)	-606(10)	3188(10)	2007(9)	2.1(2)

<sup>a</sup> The anisotropic thermal parameters for cerium, calculated from the expression  $\exp[-(h^2\beta_{11} + 2hk\beta_{12} + \dots)]$ , are  $\beta_{11} = 0.00299(8)$ ,  $\beta_{22} = 0.00266(8)$ ,  $\beta_{33} = 0.00211(6)$ ,  $\beta_{12} = 0.00015(5)$ ,  $\beta_{13} = 0.00010(4)$  and  $\beta_{23} = 0.00134(5)$ . <sup>b</sup> The occupancy factor for OW(4A) was refined to 0.49(2) resulting in the value 0.51(2) for OW(4B).

dispersion was made on the scattering factors for Ce and Na. The data for this correction were obtained from Cromer and Liberman.<sup>14</sup>

An isotropic extinction correction (Zachariasen<sup>15</sup>) was applied,  $|F_{o,corr}| = |F_o| (1 + g|F_c|^2 \bar{T} - 2.75 \times 10^{-3})^{1/4}$ , where  $g$  is the extinction parameter and  $\bar{T} = -\ln A/\mu$ .  $A$  is the transmission factor. The refined value of  $g$  was  $2.27 \times 10^4$ .

The extinction coefficient on  $F_o$  varied in the interval 1.00–1.39, the largest corrections being applied to the reflexions  $11\bar{4}$  (1.39),  $2\bar{2}\bar{2}$  (1.35) and 130 (1.33).

The final positional and thermal parameters with estimated standard deviations are given in Table 1. Selected interatomic distances and angles are given in Tables 2 and 3. A list of

Table 2. The cerium coordination and the oxydiacetate ligands. Selected interatomic distances (Å) and angles (°) with estimated standard deviations.

Distance		Distance	
Ce—O(1)	2.466(6)	Ce—O(14)	2.464(7)
Ce—O(4)	2.503(6)	Ce—O(3)	2.588(6)
Ce—O(6)	2.476(6)	Ce—O(8)	2.564(6)
Ce—O(9)	2.470(7)	Ce—O(13)	2.597(6)
Ce—O(11)	2.485(7)		
Distance		Angle	
Ligand 1			
O(3)—C(2)	1.437(12)	C(2)—O(3)—C(3)	113.2(7)
O(3)—C(3)	1.428(12)	O(1)—C(1)—O(2)	124.0(9)
O(1)—O(2)	2.223(9)	O(1)—C(1)—C(2)	119.5(8)
O(4)—O(5)	2.229(9)	O(2)—C(1)—C(2)	116.6(8)
C(1)—O(1)	1.255(11)	O(4)—C(4)—O(5)	122.8(9)
C(1)—O(2)	1.263(12)	O(4)—C(4)—C(3)	120.2(9)
C(4)—O(4)	1.280(12)	O(5)—C(4)—C(3)	117.0(9)
C(4)—O(5)	1.259(12)	O(3)—C(2)—C(1)	109.1(8)
C(1)—C(2)	1.498(14)	O(3)—C(2)—C(4)	108.0(8)
C(3)—C(4)	1.488(14)		
Ligand 2			
O(8)—C(6)	1.416(14)	C(6)—O(8)—C(7)	112.0(8)
O(8)—C(7)	1.451(14)	O(6)—C(5)—O(7)	124.2(10)
O(6)—O(7)	2.243(10)	O(6)—C(5)—C(6)	119.4(9)
O(9)—O(10)	2.229(10)	O(7)—C(5)—C(6)	116.4(10)
C(5)—O(6)	1.263(13)	O(9)—C(8)—O(10)	124.5(9)
C(5)—O(7)	1.275(13)	O(9)—C(8)—C(7)	119.8(9)
C(8)—O(9)	1.250(12)	O(10)—C(8)—C(7)	115.7(9)
C(8)—O(10)	1.269(12)	O(8)—C(6)—C(5)	107.5(9)
C(5)—C(6)	1.514(17)	O(8)—C(6)—C(8)	107.2(9)
C(7)—C(8)	1.495(15)		
Ligand 3			
O(13)—C(10)	1.429(12)	C(10)—O(13)—C(11)	112.2(7)
O(13)—C(11)	1.435(12)	O(11)—C(9)—O(12)	125.3(9)
O(11)—O(12)	2.234(10)	O(11)—C(9)—C(10)	119.1(9)
O(14)—O(15)	2.234(10)	O(12)—C(9)—C(10)	115.6(8)
C(9)—O(11)	1.259(11)	O(14)—C(12)—O(15)	125.6(10)
C(9)—O(12)	1.256(12)	O(14)—C(12)—C(11)	117.6(9)
C(12)—O(14)	1.262(12)	O(15)—C(12)—C(11)	116.7(9)
C(12)—O(15)	1.249(13)	O(13)—C(10)—C(9)	107.2(8)
C(9)—C(10)	1.528(13)	O(13)—C(10)—C(12)	108.2(8)
C(11)—C(12)	1.519(15)		

structure factors is available, on request, from the author. As the refinement in space group  $P\bar{1}$  was satisfactory, no attempt was made to try the non-centrosymmetric  $P1$ .

## DISCUSSION

As shown in Figs. 1 and 2 the structure can be described as composed of layers of the negatively charged mononuclear tris(oxydi-

acetato)cerate(III) complexes alternating with layers containing the sodium ions and the water molecules. The layers are parallel to the plane (01 $\bar{1}$ ). The cerium ion is nine-coordinated. The sodium ions are surrounded by distorted octahedra or trigonal bipyramids of oxygen atoms belonging to the carboxylate groups and the water molecules, forming finite chains with six sodium ions in each. The sodium chains are held together by hydrogen bonds. The

Table 3. The sodium coordination. Selected interatomic distances (Å) with estimated standard deviations. (i)  $-x, 1-y, 1-z$ ; (ii)  $x, 1+y, z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $1-x, 2-y, 1-z$ .

Distance		Distance	
Na(1)–O(7 <sup>i</sup> )	2.382(9)	Na(3)–O(2 <sup>iii</sup> )	2.391(8)
Na(1)–O(15)	2.488(9)	Na(3)–O(10)	2.515(8)
Na(1)–OW(1)	2.390(9)	Na(3)–OW(5)	2.434(8)
Na(1)–OW(2)	2.439(8)	Na(3)–OW(6)	2.435(8)
Na(1)–OW(3)	2.445(11)	Na(3)–OW(8)	2.436(8)
Na(1)–OW(4A)	2.664(17)	Na(3)–OW(8 <sup>iv</sup> )	2.449(8)
Na(1)–OW(4B)	3.946(17)		
Na(2)–O(10)	2.602(8)	Na(1)–Na(2)	4.179(6)
Na(2)–O(12 <sup>ii</sup> )	2.415(8)	Na(2)–Na(3)	3.292(5)
Na(2)–OW(2)	2.348(8)	Na(3)–Na(3 <sup>iv</sup> )	3.599(8)
Na(2)–OW(5)	2.402(8)		
Na(2)–OW(6)	2.461(8)		
Na(2)–OW(7)	2.345(13)		

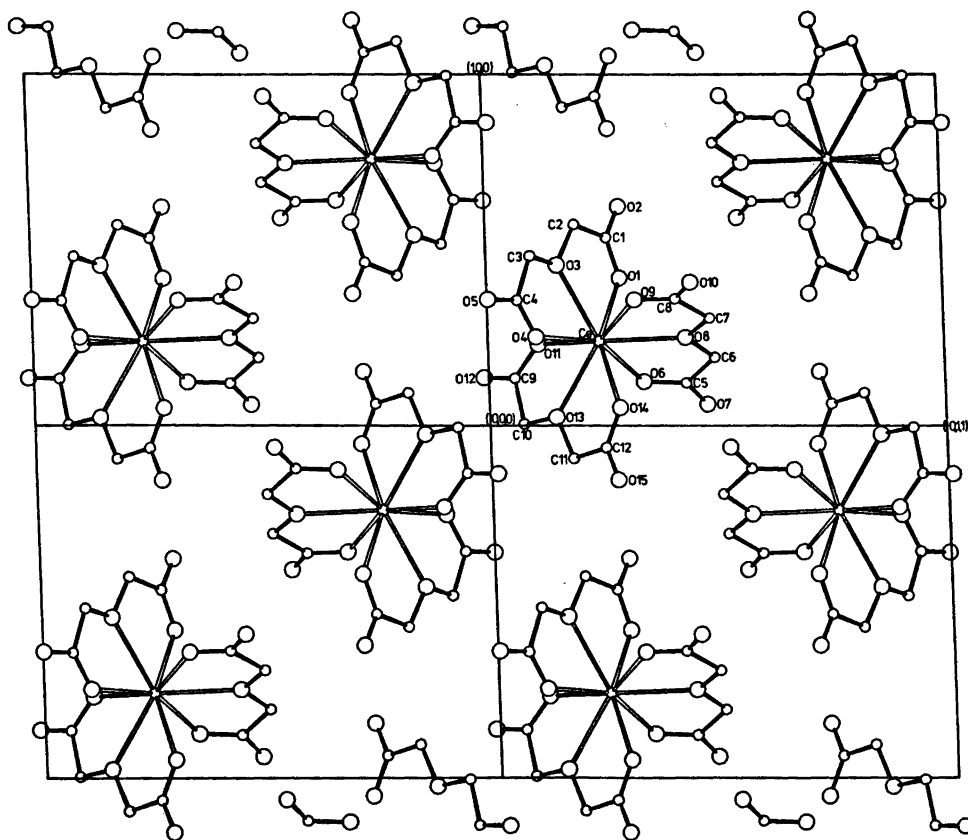
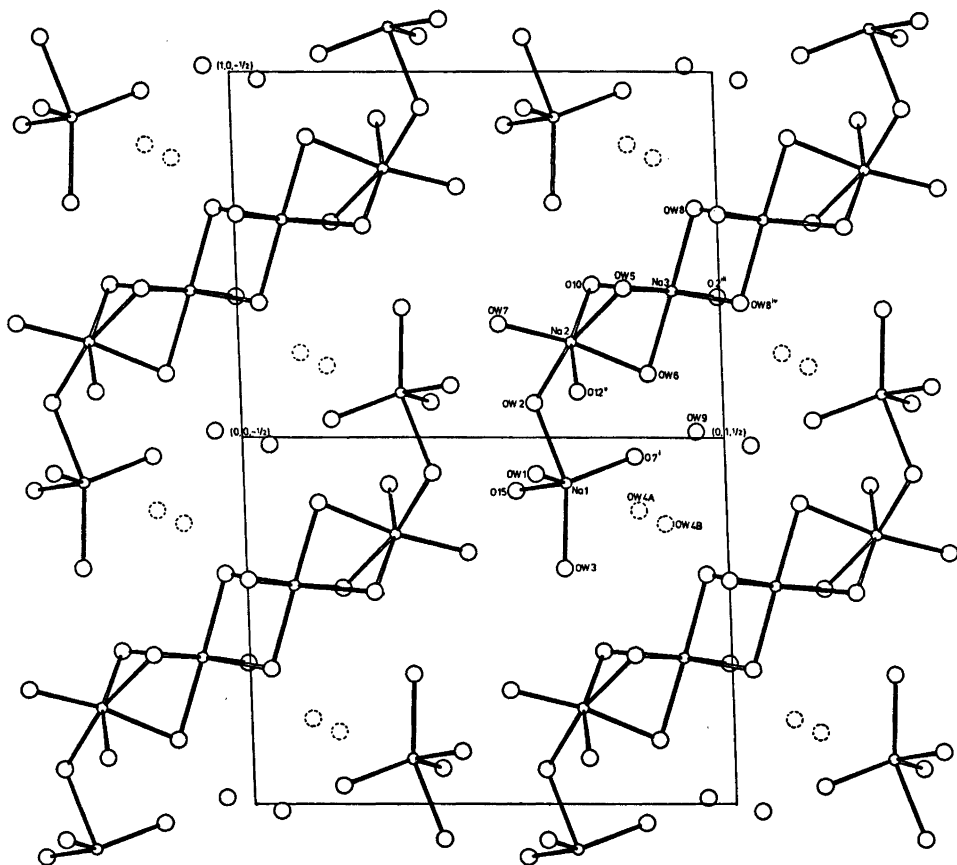
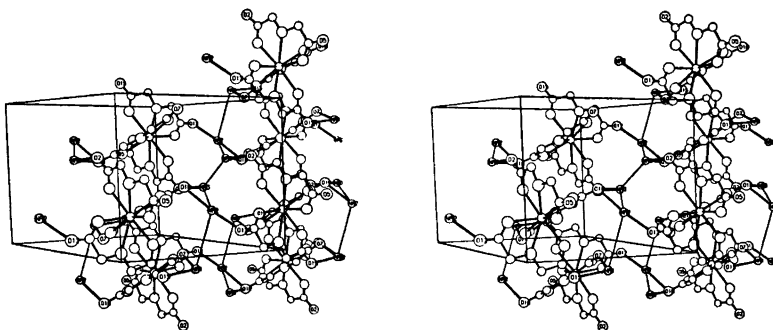


Fig. 1. The layer containing the tris(oxydiacetato)cerate(III) complexes projected on the plane (011).



*Fig. 2.* The layer containing the sodium chains and the water molecules projected on the plane (011).



*Fig. 3.* A stereoscopic pair of drawings showing the connection of the tris(oxydiacetato)cerate(III) complexes by the sodium ions. The sodium chain is shown, but the water oxygens are excluded. The unit cell edges are **b** to the right, **a** upwards and **c** to the left into the figure.



ordination polyhedron of CDG will be given in a following paper.

The shortest distance between two cerium ions is 8.10 Å. Three more cerium ions are at distances of 8.61–8.71 Å and two at 10.36 Å. All these nearest neighbours are in the same cerium layer. Six cerium ions from other layers are at distances of 11.16–11.62 Å. The separations of the cerium ions are thus not as large as in CDG, where the shortest distance Ce–Ce is 9.81 Å.

The atoms in each ligand are nearly coplanar. The deviations of the atoms from the least-squares planes through the ligand molecules are less than about 0.1 Å. The distances and angles within the ligand molecules are in good agreement with those found in the acid salts of alkali metal ions.<sup>18,19</sup>

Six sodium ions, Na(1)–Na(2)–Na(3)–Na(3<sup>iv</sup>)–Na(2<sup>iv</sup>)–Na(1<sup>iv</sup>), form a chain across a center of symmetry, the surrounding polyhedra of oxygen atoms sharing corners, edges and faces (Fig. 5). Na(1) and Na(2) share one oxygen atom [OW(2)], Na(2) and Na(3) three [O(10), OW(5) and OW(6)], and Na(3) and Na(3<sup>iv</sup>) two [OW(8) and OW(8<sup>iv</sup>)]. The sodium-oxygen distances to the six nearest oxygen atoms around each sodium ion range between 2.35 and 2.52 Å (Table 3), except the distance Na(2)–O(10) (2.60 Å) and Na(1)–OW(4A) (2.66 Å). OW(4B) is not coordinated to a sodium ion. The coordination to each sodium ion can be described by distorted octahedra. However, as the occupancy factor of the statistically distributed oxygen atom OW(4) is about the same in both positions in spite of the different distances to Na(1), the interaction between OW(4A) and Na(1) must be very small. This fact and the large deviation of the angle O(7)–Na(1)–OW(1) from the octahedral value (135° compared to 180°) indicate that the coordination polyhedron around Na(1) might be better described by a distorted trigonal bipyramid than by a distorted octahedron. The oxygen-oxygen distances along the edges of the polyhedra are in the interval 3.00–4.41 Å.

*Acknowledgements.* My thanks are due to Dr. Jörgen Albertsson for the supply of a sample of TCDG crystals, and for helpful advice and discussions. I also wish to thank Professor Ido Leden for his kind interest in

this work. The Swedish Natural Science Research Council gave financial support, which is gratefully acknowledged.

#### REFERENCES

1. Albertsson, J. *Acta Chem. Scand.* 22 (1968) 1563.
2. Albertsson, J. *Acta Chem. Scand.* 24 (1970) 3527.
3. Albertsson, J. *Acta Chem. Scand.* 24 (1970) 1213.
4. Albertsson, J. *Acta Chem. Scand.* 26 (1972) 985.
5. Albertsson, J. *Acta Chem. Scand.* 26 (1972) 1005.
6. Albertsson, J. *Acta Chem. Scand.* 26 (1972) 1023.
7. Doran, J. C., Erich, U. and Wolf, W. P. *Phys. Rev. Lett.* 28 (1972) 103.
8. Wu, C. Y., Alben, R. and Wolf, W. P. *Solid State Commun.* 11 (1972) 1599.
9. Albertsson, J., Chen, P. Y. and Wolf, W. P. *Phys. Rev. B* 11 (1975) 1943.
10. Webb, R. A. and Wheatley, J. C. *Phys. Rev. Lett.* 29 (1972) 1150.
11. Danielsson, S., Grenthe, I. and Oskarsson, Å. *J. Appl. Crystallogr.* 9 (1976) 14.
12. Cromer, D. T., Larson, A. C. and Water, J. T. *Acta Crystallogr.* 17 (1964) 1044.
13. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
14. Cromer, D. T. and Liberman, D. *J. Chem. Phys.* 53 (1970) 1891.
15. Zachariasen, W. H. *Acta Crystallogr.* 23 (1967) 558.
16. Helmholtz, L. *J. Am. Chem. Soc.* 61 (1939) 1544.
17. Sikka, S. K. *Acta Crystallogr. A* 25 (1969) 621.
18. Albertsson, J., Grenthe, I. and Herberthson, H. *Acta Crystallogr. B* 29 (1973) 1855.
19. Albertsson, J., Grenthe, I. and Herberthson, H. *Acta Crystallogr. B* 29 (1973) 2839.

Received March 12, 1976.