Acta Chemica Scandinavica A 31 (1977) 21—30

Rare Earth Carboxylates. 26. The Geometry of the Mononuclear Tris(oxydiacetato)cerate(III) Complex in the Solid State

JÖRGEN ALBERTSSON and INGA ELDING

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

The crystal structure of the compound $Na_3[Ce(C_4H_4O_5)_3].2NaClO_4.6H_2O$ has been determined at 123, 163, and 295 K using X-ray intensity data collected with a four-circle single crystal diffractometer. The space group is R32 with $Z=3$. The unit cell dimensions are $a=9.805(1)$ and $c=28.545(1)$ Å at 295 K. Layers, parallel to the *ab*-plane, containing the tris(oxydiacetato)cerate(III) complexes and the perchlorate ions, interspaced with layers containing the water molecules and the sodium ions build up the structure. A slightly distorted tricapped trigonal prism of carboxylate and ether oxygen atoms surrounds the nine-coordinated cerium ion. The geometry of the complex is compared to the geometry of the tris(oxydiacetato)cerate-(III) complex in the triclinic compound $Na_3[Ce(C_4H_4O_5)_3].9H_2O$.

In a not too diluted water solution containing the trivalent cerium ion and the tridentate ligand oxydiacetate in the molar ratio 1:3, the predominant species is the tris(oxydiacetato)-cerate(III) complex.[1] Solution X-ray diffraction has shown that nine donor oxygen atoms forming a tricapped trigonal prism (TCTP) surround the lanthanoid ion.[2] The symmetry of the complex in water solution is D_3. The distortion of the coordination polyhedron from the D_{3h} symmetry of a regular TCTP depends on ligand constraints which cause the triangular faces to be slightly rotated relative to one another.[3]

The sodium salts of the tris(oxydiacetato)-cerate(III) complex can be prepared by slow evaporation of a water solution at room temperature. In the simple sodium salt, the triclinic $Na_3[Ce(C_4H_4O_5)_3].9H_2O$ (TCDG), the symmetry of the complex ion is degraded to C_1 by the packing forces.[4] The most predominant of these forces are the coordination of the outer carboxylate oxygen atoms to the sodium ions and the hydrogen bonds between the water molecules and both the outer and inner carboxylate oxygen atoms of the complex.[5] However, if sodium perchlorate is present in the mother liquor, a double salt, the trigonal $Na_3[Ce(C_4H_4O_5)_3].2NaClO_4.6H_2O$ (CDG), is formed,[3] in which the complex retains the D_3 symmetry in the solid state.

The present investigation aims at comparing the geometry of the tris(oxydiacetato)cerate-(III) complex in the triclinic and the trigonal phases. The results of both X-ray and neutron diffraction studies on the triclinic TCDG-phase have been published previously,[4,5] as well as the results of X-ray studies on the trigonal "CDG-phase" formed by the lanthanoid ions neodymium(III), gadolinium(III), and ytterbium(III).[3,6] To obtain the actual bond distances and bond angles in CDG, we have now investigated this compound with X-ray diffractometry. Due to the potential low temperature applications of CDG as a magnetic coolant and thermometer [7] the effect of cooling on the structure was also investigated by collecting data at 123 and 163 K besides room temperature, 295 K.

EXPERIMENTAL

Data collection. Crystals of CDG were prepared as described in Ref. 6. Table 1 gives information concerning the collection and reduction of the intensity data sets and the refinements based on them. The method employed in the data

Table 1. Data collection and reduction of CDG. The least-squares refinements.

	Crystal 1		Crystal 2	
Crystal size (mm³)	0.09 × 0.11 × 0.17		0.05 × 0.09 × 0.10	
Radiation	Graphite monochromated CuKα		Graphite monochromated CuKα	
ω-Interval (°) ($\omega - 2\theta$ scan)	0.80 + 0.50 tan θ		0.75 + 0.40 tan θ	
θ-Interval (°)	5 – 70		5 – 70	
Minimum number of counts in a scan	3000		3000	
Maximum recording time (min)	3		3	
μ(Cu$K\alpha$) (cm^{-1})	139.3		139.3	
Range of the transmission factor	0.28 – 0.42		0.34 – 0.58	
Temperature (K)	295	163	295	123
Number of measured reflexions	642	1162	1193	1233
Number of reflexions given zero weight [$I < 3\sigma_c(I)$]	11	29	–	–
Number of reflexions skipped due to collision	–	–	27	14
Number of independent reflexions used in the final refinements, m	598	583	594	592
Number of parameters refined, n	77	77	77	77
$R = \sum\|\|F_o\| - \|F_c\|\| / \sum\|F_o\|$	0.023	0.029	0.028	0.028
$R_w = \{\sum w(\|F_o\| - \|F_c\|)^2 / \sum w\|F_o\|^2\}^{1/2}$	0.031	0.040	0.036	0.035
$S = \{\sum w(\|F_o\| - \|F_c\|)^2 / (m-n)\}^{1/2}$	0.995	0.908	0.865	0.881
C_1 (weighting function)	0.0005	0.0009	0.0005	0.0005
C_2 ,,	0.5	2.0	0.5	0.5
$g \times 10^{-4}$ (extinction)	0.116	0.134	0.077	0.207
Mosaic spread (")	4.99×10^3	4.34×10^3	7.57×10^3	281×10^3
Domain size (cm)	0.18×10^{-4}	0.21×10^{-4}	0.12×10^{-4}	0.32×10^{-4}

collection has been described in Ref. 4 and the low temperature apparatus in Ref. 8. To certify that the derived model of CDG and its interatomic distances and angles are typical of that material duplicate measurements on two different crystals were performed. Fluctuations in the intensities in three reference reflexions were mostly within 8 % for crystal 1 and 12 % for crystal 2 and they could be described by polynomials of the second degree which were used for scaling the data sets. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization, and absorption effects. $\sigma_c(I)$ is based on counting statistics. The expression used in the polarization correction was $p = (1 + \cos^2 2\theta_M \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ with $\theta_M = 13.3°$.

Unit cell and space group. CDG, $Na_3[Ce(C_4H_4O_5)_3].2NaClO_4.6H_2O$, F.W. = 958.28, crystallizes in the trigonal system with space group **R32**. The unit cell dimensions at the different temperatures were determined with least-squares refinement of θ-values for about 40 reflexions, measured on the diffractometer with Cu$K\alpha_1$ radiation as described in Ref. 8 ($\lambda = 1.54051$ Å). The following unit cell dimensions were obtained.

	295 K	163 K	123 K
a/Å	9.8052(9)	9.7405(11)	9.7117(79)
c/Å	28.5452(14)	28.4540(17)	28.4531(118)
V/Å³	2376.7	2337.9	2324.1

The unit cell contains three formula units.[6]

Refinements. The parameters used as starting values in the least-squares refinements of CDG were those for the non-hydrogen atoms in the neodymium structure in Ref. 3. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights calculated using the equation $1/w = \sigma_c^2/4|F_o|^2 + C_1|F_o|^2 + C_2$. C_1 and C_2 are adjustable constants. An isotropic extinction correction was also included. After a few cycles of refinements R had converged to 0.056. Anomalous dispersion for Ce and Cl was included and resulted in $R = 0.093$. The other absolute configuration was then tried with the unaveraged data and one cycle of refinement gave $R = 0.027$. This absolute configuration was chosen as a model of CDG in crystal 1. CDG in crystal 2 appears to have the same absolute configuration as in crystal 1.

Only one of the hydrogen atoms of the water

Table 2. Atomic parameters with estimated standard deviations in parentheses for CDG at 295, 163 and 123 K. The H atoms were not refined.

Atom	295 K			163 K			123 K		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Ce	0	0	0	0	0	0	0	0	0
Cl	1/3	−1/3	0.0956(1)	1/3	−1/3	0.0968(1)	1/3	−1/3	0.0962(1)
Na(1)	0.0371(5)	−1/3	1/6	0.0321(5)	−1/3	1/6	0.0359(5)	−1/3	1/6
Na(2)	0	0	0.2001(1)	0	0	0.1977(1)	0	0	0.1980(1)
O(1)	−0.2615(6)	−0.2615(6)	0	−0.2604(7)	−0.2604(7)	0	−0.2638(7)	−0.2638(7)	0
O(2)	−0.0374(5)	−0.1978(5)	0.0599(1)	−0.0372(6)	−0.1991(6)	0.0595(1)	−0.0341(5)	−0.1974(5)	0.0597(1)
O(3)	−0.1709(6)	0.4153(5)	0.1008(1)	−0.1743(6)	−0.4183(6)	0.1015(2)	−0.1693(6)	−0.4153(6)	0.1021(2)
O(4)	0.1773(6)	−0.4177(14)	0.1134(2)	0.1732(7)	−0.4203(13)	0.1141(2)	0.1735(6)	−0.4195(13)	0.1135(2)
O(5)	1/3	−1/3	0.0465(3)	1/3	−1/3	0.0469(3)	1/3	−1/3	0.0470(3)
O(6)	0.1412(7)	−0.0793(7)	0.1432(1)	0.1424(7)	−0.0788(7)	0.1416(2)	0.1434(7)	−0.0776(7)	0.1425(1)
C(1)	−0.2921(8)	−0.3839(8)	0.0324(2)	−0.2955(9)	−0.3869(10)	0.0324(2)	−0.2932(10)	−0.3878(10)	0.0328(3)
C(2)	−0.1536(12)	−0.3298(5)	0.0669(1)	−0.1576(15)	−0.3322(7)	0.0671(2)	−0.1520(14)	−0.3315(7)	0.0670(2)
H(1)	−0.3852	−0.4096	0.0495	−0.3900	−0.4131	0.0491	−0.3870	−0.4148	0.0501
H(2)	−0.3061	−0.4738	0.0158	−0.3089	−0.4771	0.0156	−0.3066	−0.4784	0.0161
H(W)	0.1157	−0.1073	0.1144	0.0963	−0.1056	0.1142	0.1072	−0.1082	0.1158

molecule could be located in a difference synthesis. This atom, hydrogen bonded to O(2), and the methylene hydrogen atoms were included in the structure factor calculations with their isotropic temperature factors fixed at 5.0 Å^2. Attempts to refine these coordinates were not successful.

The parameter shifts in the last cycle of refinements were within 10 % of the estimated standard deviations, except for Ceβ_{11} in the 123 and 163 K structures (12 and 20 %, respectively), O(1)β_{23} in the 123 K structure (30 %), and O(1)β_{11} in the 295 K structure of crystal 1 (22 %). Final difference maps were featureless.

The scattering factors for Ce were taken from Cromer *et al.*[9] those for Na, Cl, O, and C from Hanson *et al.*[10] and those for H from Stewart *et al.*[11] The anomalous dispersion corrections were taken from Cromer and Liberman.[12] Tables 2 and 3 list the final positional parameters with estimated standard deviations and the thermal parameters, respectively. Lists of structure factors are available on request from the authors.

Probability plot analysis. As intensity measurements at 295 K were made with two different crystals, a probability plot of the measured structure factors was performed according to Abrahams and Keve.[13] Ordered values of $\delta m_i = (|F(1)_i| - K|F(2)_i|)/[\sigma^2 F(1)_i + K^2\sigma^2 F(2)_i]^{1/2}$ are compared with the values expected for a normal distribution with zero mean and unit variance. K is a scale factor such that $\sum(\delta m_i)^2$ is a minimum. Fig. 1a shows that the plot is linear with slope 0.48 and intercept −0.03. A half-normal probability plot of the positional and thermal coordinates (a δp-plot: $\delta p_i = ||p(1)_i| - |p(2)_i||/[\sigma^2 p(1)_i + \sigma^2 p(2)_i]^{1/2})$ is shown in Fig. 1b. This comparison results in a straight line with slope 0.97 and intercept 0.06 indicating that the systematic differences between the two determinations are very small. Together the δm- and δp-plots indicate that the systematic errors are comparable or smaller than the random errors and that the values assigned to $\sigma(F)$ are larger than the correct ones (see p. 162 in Ref. 13). δR-plots comparing model with experiment were also made for each of the two 295 K structures (Fig. 1c and d). The slopes are somewhat smaller than the S-values (Table 1): 0.93 for crystal 1 and 0.80 for crystal 2. They indicate that the $\sigma(F)$'s are overestimated by 8 and 25 %, respectively. As the slope of the δm-plot is still lower than the slopes of the δR-plots, there also appears to be an underestimation of $\Delta F_i = |F(1)_i| - K|F(2)_i|$ in the δm-plot. Parameters from crystal 1 only are given in this paper for the 295 K structure of CDG as this determination seems to be better than that of crystal 2.

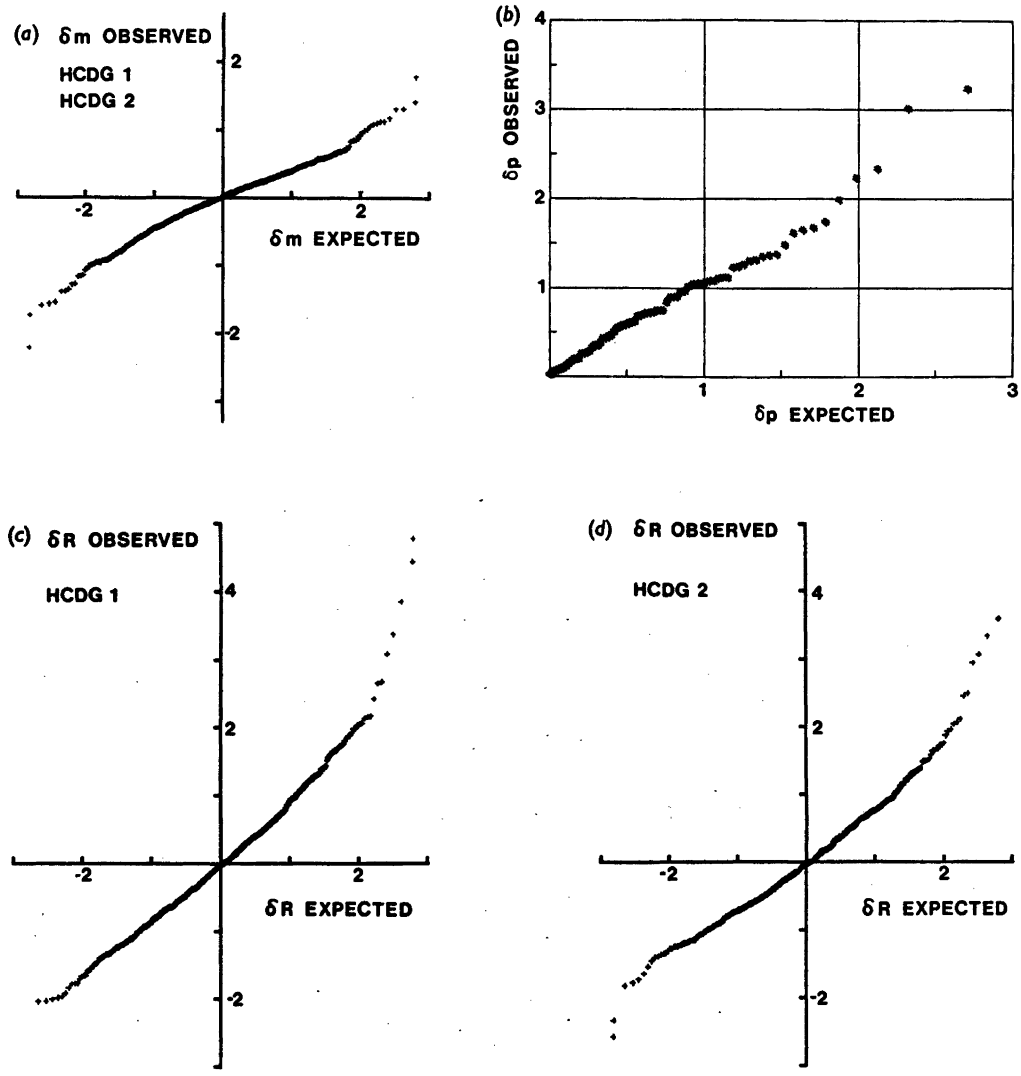

Fig. 1. Probability plot analysis of data and models of CDG at room temperature: (*a*) a δm-plot comparing the data sets for crystal 1 (HCDG1) and crystal 2 (HCDG2); (*b*) a δp-plot comparing the models derived from crystals 1 and 2; (*c*) a δR-plot comparing the model with experiment for crystal 1; (*d*) the same for crystal 2.

DISCUSSION

A description of the structure has been given in Refs. 3 and 6. The structure is composed of layers, perpendicular to **c** containing the mononuclear tris(oxydiacetato)cerate(III) complexes and the perchlorate ions alternating with layers containing the sodium ions and the water molecules. In Ref. 3 projections of the cerium layer including the perchlorate ion and the sodium layer are shown. Figs. 2–4 show stereoscopic pairs of drawings of the cerium complex, part of the sodium layer, and the vicinity of the water molecule including the perchlorate ion, respectively. Table 4 gives selected interatomic distances and angles with estimated standard deviations. The room temperature values in Table 4 are slightly at

Table 3. Thermal parameters with standard deviations ($\times 10^5$). The form of the temperature factor is exp $(-\beta_{11}h^2 - 2\beta_{12}hk \ ..)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A. 295 K						
Ce	992(10)	992(10)	43(1)	496(5)	0	0
Cl	1665(29)	1665(29)	97(2)	833(15)	0	0
Na(1)	2186(63)	1530(59)	193(6)	765(30)	28(8)	56(15)
Na(2)	1268(40)	1268(40)	100(3)	634(20)	0	0
O(1)	1265(115)	1265(115)	103(7)	459(67)	−29(19)	29(19)
O(2)	1575(62)	1424(58)	95(4)	713(52)	−19(13)	69(13)
O(3)	2059(90)	1713(63)	150(5)	928(61)	89(17)	249(16)
O(4)	1767(73)	2218(126)	229(8)	527(115)	74(19)	−92(44)
O(5)	4028(240)	4028(240)	107(9)	2014(120)	0	0
O(6)	2205(133)	2071(119)	105(4)	1075(119)	1(17)	55(16)
C(1)	1716(103)	1245(87)	131(8)	537(79)	107(24)	60(23)
C(2)	1363(128)	1264(69)	98(5)	689(94)	103(22)	58(14)
B. 163 K						
Ce	820(14)	820(14)	25(1)	410(7)	0	0
Cl	1166(32)	1166(32)	55(3)	583(16)	0	0
Na(1)	1593(64)	1240(68)	101(5)	620(34)	16(8)	32(15)
Na(2)	999(51)	999(51)	61(4)	500(26)	0	0
O(1)	969(150)	969(150)	81(8)	650(82)	19(21)	−19(21)
O(2)	1201(75)	1167(73)	60(5)	637(64)	5(16)	34(16)
O(3)	1506(97)	1300(73)	91(6)	680(69)	69(18)	142(17)
O(4)	1207(72)	1465(114)	106(6)	554(99)	30(16)	25(35)
O(5)	2138(162)	2138(162)	58(9)	1069(81)	0	0
O(6)	1464(121)	1405(112)	64(5)	632(111)	−31(18)	43(17)
C(1)	1097(107)	1090(111)	71(8)	390(89)	69(25)	18(25)
C(2)	1137(151)	973(85)	63(6)	638(117)	74(27)	47(17)
C. 123 K						
Ce	932(12)	932(12)	29(1)	466(6)	0	0
Cl	1377(33)	1377(33)	72(2)	688(16)	0	0
Na(1)	1809(65)	1421(69)	133(5)	711(35)	35(8)	70(16)
Na(2)	1116(48)	1116(48)	77(4)	558(24)	0	0
O(1)	1271(152)	1271(152)	89(8)	485(87)	−19(24)	19(24)
O(2)	1383(73)	1207(67)	71(4)	691(61)	14(14)	87(14)
O(3)	1738(95)	1566(76)	135(6)	914(69)	130(18)	221(18)
O(4)	1387(72)	1676(119)	155(6)	568(107)	58(17)	17(38)
O(5)	3028(206)	3028(206)	79(9)	1514(103)	0	0
O(6)	1935(140)	1832(126)	78(5)	975(125)	−20(18)	34(17)
C(1)	1748(136)	1337(119)	111(9)	700(106)	92(29)	39(28)
C(2)	1400(163)	1240(88)	81(6)	701(114)	92(25)	44(17)

variance with what may be expected from the values in Table 4 of Ref. 3. The probability-plot analysis indicates, however, that the present investigation of CDG must be looked upon as more accurate than the neodymium and ytterbium studies presented in Ref. 3.

The coordination polyhedron. As is the case in TCDG,[4] the cerium ion in CDG is surrounded by a distorted TCTP of carboxylate and ether oxygens (Fig. 2). To compare the distortions of the two polyhedra in CDG and TCDG, respectively, a number of quantities are collected in Table 5. The geometry of the coordination polyhedron in CDG is almost unchanged in the temperature interval 123 − 295 K. The triangular faces of the trigonal prism are only

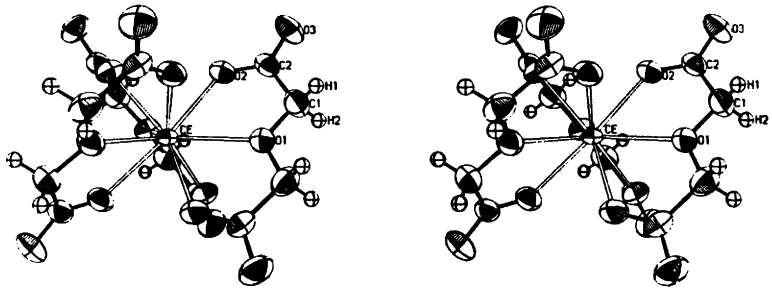

Fig. 2. The tris(oxydiacetato)cerate(III) complex. The thermal ellipsoids for the non-hydrogen atoms are scaled in Figs. 2 – 4 to include 50 % probability.

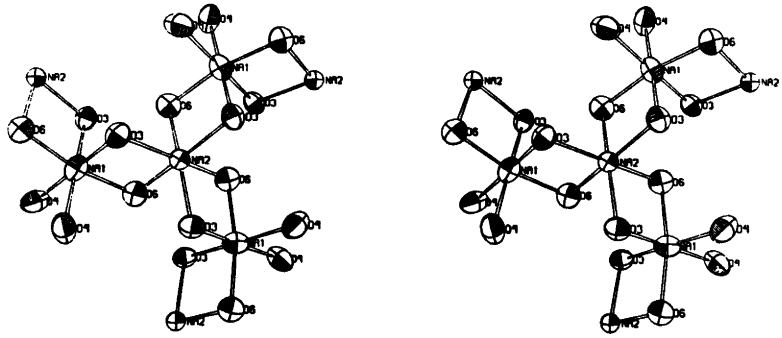

Fig. 3. The coordination around the sodium ions.

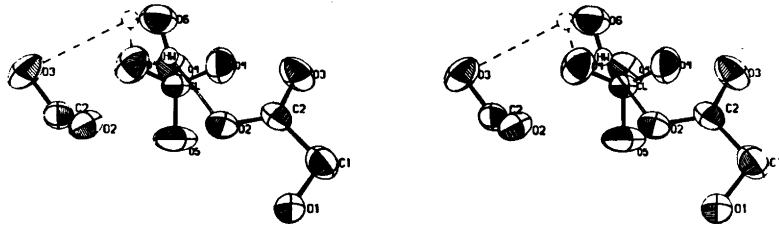

Fig. 4. The hydrogen bond O(6) – H(W)···O(2) and the perchlorate ion.

approximately equilateral in TCDG where the symmetry of the polyhedron is C_1. The edge is about 0.1 Å longer in TCDG than in CDG. The equatorial triangle has approximately the same edge length in CDG and TCDG. The height of the trigonal prism, measured as the distance between the centroids of the triangular faces in TCDG, is about 0.1 Å larger in CDG than in TCDG. In TCDG the two triangular faces of the prism are tilted 2 and 5°, respectively, to the equatorial plane and 5° to each other. The rigid oxydiacetate ligands cause the triangular faces of the prism to be rotated relative to one another. The resulting torsion angles are calculated by method 1 as given by Dymock and Palenik.[14] The average

Table 4. Selected interatomic distances (Å) and angles (°) with e.s.d.'s in CDG at 295, 163, and 123 K. The superscripts (i)–(v) indicate the following equivalent sites in the structure:

(i) $y,x,-z$ (iii) $-y,x-y-1,z$
(ii) $y-x,-x,z$ (iv) $-y,x-y,z$
(v) $1+y-x,-x,z$

	295 K	163 K	123 K
A. The cerium coordination polyhedron; distance			
Ce–O(1)	2.564(6)	2.537(7)	2.564(7)
Ce–O(2)	2.471(4)	2.461(4)	2.457(4)
O(1)–O(2)	2.602(5)	2.579(6)	2.615(6)
O(1)–O(2^{ii})	3.096(5)	3.068(6)	3.063(6)
O(2)–O(2^{ii})	3.091(7)	3.092(9)	3.075(8)
O(2^{i})–O(2^{ii})	3.476(7)	3.446(8)	3.444(7)
B. The ligand; distance			
O(1)–C(1)	1.423(7)	1.436(9)	1.435(9)
C(1)–C(2)	1.541(11)	1.532(13)	1.542(13)
C(2)–O(2)	1.241(7)	1.258(10)	1.249(9)
C(2)–O(3)	1.234(6)	1.247(8)	1.246(7)
Angle			
C(1)–O(1)–C(1^{i})	116.4(8)	113.6(8)	117.4(8)
O(1)–C(1)–C(2)	110.3(6)	108.9(6)	110.1(6)
C(1)–C(2)–O(2)	116.5(5)	116.9(6)	117.0(6)
C(1)–C(2)–O(3)	117.9(6)	118.4(8)	118.0(7)
O(2)–C(2)–O(3)	125.3(8)	124.6(9)	124.6(9)
Dihedral angle			
O(1)–C(1)–C(2)–O(2)	−4.2(0.9)	−5.8(1.1)	−4.6(1.1)
O(1)–C(1)–C(2)–O(3)	171.0(0.6)	171.3(0.8)	168.8(0.7)
C(1^{i})–O(1)–C(1)–C(2)	−176.6(0.6)	−176.3(0.7)	−176.5(0.7)
C. The sodium coordination; distance			
Na(1)–O(3)	2.589(6)	2.549(6)	2.529(6)
Na(1)–O(4)	2.455(9)	2.451(9)	2.427(9)
Na(1)–O(6)	2.270(6)	2.269(6)	2.266(6)
Na(1)–Na(2)	3.593(3)	3.526(3)	3.539(4)
Na(2)–O(3)	2.355(4)	2.334(5)	2.346(5)
Na(2)–O(6)	2.497(5)	2.476(6)	2.459(6)
D. The perchlorate ion; distance			
Cl–O(4)	1.420(5)	1.439(6)	1.433(6)
Cl–O(4)[a]	1.455(5)	1.452(6)	1.452(6)
Cl–O(5)	1.401(8)	1.420(8)	1.399(8)
Cl–O(5)[a]	1.463(10)	1.445(9)	1.441(9)
Angle			
O(4)–Cl–O(4^{iii})	107.9(2)	109.0(2)	108.8(2)
O(4)–Cl–O(5)	111.0(2)	110.0(2)	110.1(2)
E. The water molecule and possible hydrogen bonds; distance			
O(6)–H(W)	0.86	0.87	0.83
H···(W)O(2)	2.03	1.94	2.00
O(6)···O(2)	2.835(6)	2.799(6)	2.806(6)
O(6)···O(3^{iv})	3.198(8)	3.155(8)	3.142(8)
O(6)···O(4^{v})	3.290(14)	3.232(13)	3.239(13)
O(6)···O(2^{iv})	3.191(6)	3.155(7)	3.175(7)

Table 4. Continued.

Angle			
O(6)–H(W)···O(2)	154.3	169.3	164.9
O(2)···O(6)···O(3^{iv})	97.5(2)	99.1(2)	98.2(2)
O(2)···O(6)···O(4^{v})	94.5(2)	95.7(2)	94.4(2)
O(2)···O(6)···O(2^{iv})	61.4(2)	62.2(2)	61.5(2)

[a] Values corrected for thermal motion, O(4) and O(5) riding on Cl.

torsion angle in TCDG is about the same as the angle in CDG. The difference in height between the prisms is, thus, compensated by the difference in the length of the edges of the triangular faces.

The six cerium-carboxylate oxygen bond distances within the trigonal prism are 2.471 Å at room temperature. The average value in TCDG is 2.477 Å. The three equatorial cerium-ether oxygen bond distances are 2.564 Å in CDG and 2.583 Å in TCDG (average value). The equatorial bonds are significantly longer than the prismatic bonds. The symmetry requires the cerium ion to be in the equatorial plane of the CDG polyhedron. Also in the polyhedron of symmetry C_1 in TCDG, the cerium ion is located in the equatorial plane. The quotient between the equatorial and prismatic bond distances, ϱ in Table 5, has the same value in both structures. The angle θ in Table 5 is calculated as the angle between the line connecting the cerium ion and the centroid of a triangular face and the bond between cerium and a carboxylate oxygen in this triangle. The regular TCTP of symmetry D_{3h} is described by the parameters ϱ and θ.[15] The distortions of the polyhedra in TCDG and CDG from the symmetry D_{3h} are small making it possible to use ϱ and θ for an approximate description. The value of θ for a hard sphere model with $\varrho = 1.04$ is 42.6°. Kepert [15] has shown that a more stable structure is obtained for nine independent real ligand atoms by increasing the hard sphere value of θ about 3°. The values of θ for the CDG and TCDG complexes formed by three tridentate ligands are 46.3 and 48.2°, respectively, corresponding to increases from the hard sphere value of 3.7 and 5.6°.

The ligands. The oxydiacetate ion is approximately planar in CDG as can be seen from the dihedral angles (Table 4 *B*). Its conformation is, however, slightly different in CDG and TCDG at 295 K. The dihedral angles corresponding to, *e.g.*, O(1)–C(1)–C(2)–O(2) are in TCDG ligand 1: −12.5 and 10.8°, ligand 2: 2.7 and −3.2°, ligand 3: 6.0 and −14.9°. Its value is ±4.2° in CDG at 295 K. Most interatomic distances (bonded and non-bonded) less than 2.50 Å appear to be longer at 123 and 163 K than at 295 K as the geometries of the ligand at the different temperatures are uncorrected for thermal motion.

Table 5. A comparison of the coordination polyhedra in CDG and TCDG.[4] The various quantities are defined in the text.

Quantity	TCDG(295 K)		CDG		
	Range	Average	295 K	163 K	123 K
Edge of the prismatic triangles (Å)	3.10–3.22	3.20	3.09	3.09	3.08
Edge of the equatorial triangle (Å)	4.38–4.53	4.47	4.44	4.39	4.44
Height of the prism (Å)	–	3.30	3.42	3.39	3.40
Tilt angles (°)	2, 5, 5	–	–	–	–
Torsion angle (°)	19.2–21.7	20.1	20.5	20.3	18.6
ϱ	1.02–1.05	1.04	1.04	1.03	1.04
θ (°)	45.5–50.7	48.2	46.3	46.5	46.3

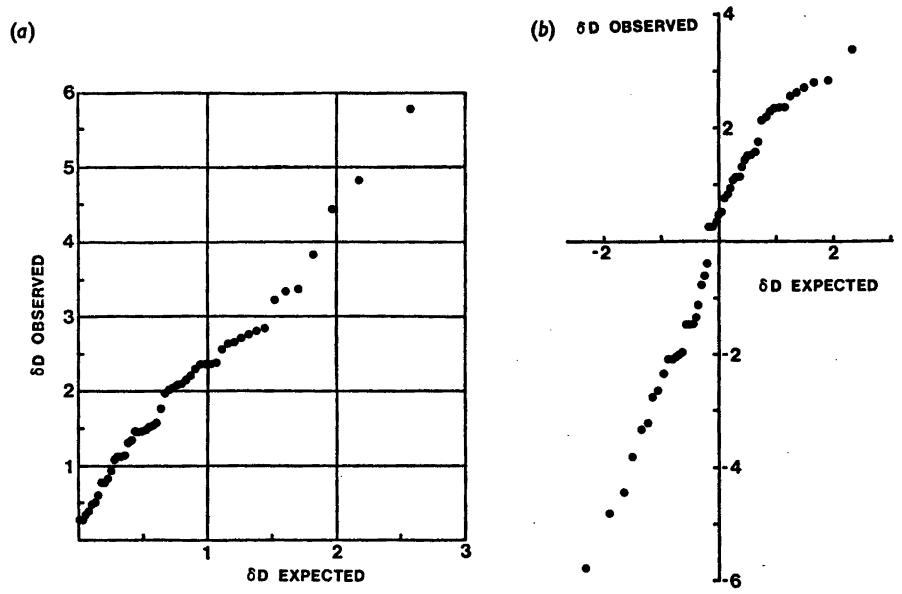

Fig. 5. A δd probability plot comparison of the bond distances and angles in the oxydiacetate ligands in CDG and TCDG at 295 K: (*a*) half-normal, (*b*) full-normal.

The oxydiacetate bond distances and bond angles within the cerium complexes in TCDG and CDG are compared at 295 K in Fig. 5. Both half-normal (*a*) and full-normal (*b*) probability plot comparisons of interatomic distances less than 2.50 Å are shown.[16,17] The non-linear plots with intercepts 0.33 and 0.10, respectively, indicate differences between the ligands in the two structures. The distance C(1)–C(2) is 1.541 Å in CDG but the corresponding average value is 1.507 Å in TCDG. The angle O(1)–C(1)–C(2) is smaller in TCDG (average value 107.9°) than in CDG (110.3°). The angle C(1)–O(1)–C(1^{i}) has also a smaller value in TCDG (average value 112.5°) than in CDG (116.4°). On the average, the geometry of the ligands of TCDG are more in agreement with the geometry of the oxydiacetate residues in the alkali hydrogen salts [18] than is the ligand in CDG.

The hydrogen bonds. The only hydrogen bond distance in the structure is between O(6) and O(2), 2.84 Å at room temperature. The water hydrogen atom found in the difference synthesis is located between these two atoms. There is a possibility for an interaction between the other water hydrogen atom and either of the oxygen atoms O(3) and O(4). The distances at 295 K are O(6)–O(3^{iv}), 3.20 Å, and O(6)–O(4^{v}), 3.29 Å. In Fig. 4 the hydrogen atom not found has been drawn dotted in a position where its distances to O(3^{iv}) and O(4^{v}) are about the same. As no peak corresponding to this hydrogen atom was found in the difference synthesis it might be disordered.

Acknowledgements. We thank Professor I. Leden and Dr. Å. Oskarsson for helpful discussions. The Swedish Natural Science Research Council gave financial support, which is gratefully acknowledged.

REFERENCES

1. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand. 17* (1963) 2101.
2. Hansson, E. *To be published.*
3. Albertsson, J. *Acta Chem. Scand. 24* (1970) 3527.
4. Elding, I. *Acta Chem. Scand. A 30* (1976) 649.
5. Albertsson, J. and Elding, I. *Acta Crystallogr. B 32* (1976) 3066.
6. Albertsson, J. *Acta Chem. Scand. 22* (1968) 1563.

7. Albertsson, J., Chen, P. Y. and Wolf, W. P. *Phys. Rev. Sect. B 11* (1975) 1943.
8. Danielsson, S., Grenthe, I. and Oskarsson, Å. *J. Appl. Crystallogr. 8* (1975) 14.
9. Cromer, D. T., Larson, A. C. and Water, J. T. *Acta Crystallogr. 17* (1964) 1044.
10. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr. 17* (1964) 1040.
11. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
12. Cromer, D. T. and Liberman, D. *J. Chem. Phys. 53* (1970) 1891.
13. Abrahams, S. C. and Keve, E. T. *Acta Crystallogr. A 27* (1971) 157.
14. Dymock, K. R. and Palenik, G. J. *Inorg. Chem. 14* (1975) 1220.
15. Kepert, D. L. *J. Chem. Soc.* (1965) 4736.
16. De Camp, W. H. *Acta Crystallogr. A 29* (1973) 148.
17. Albertsson, J. and Schultheiss, P. M. *Acta Crystallogr. A 30* (1974) 854.
18. Albertsson, J.,Herbertsson, H. and Grenthe, I. *Acta Crystallogr. B 29* (1973) 1855 and 2839.

Received June 21, 1976.