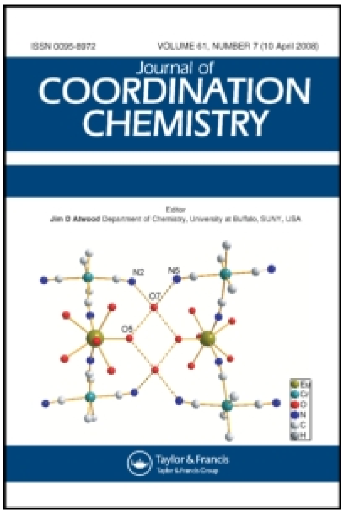

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X-ray Structure Analysis of the Isomorphous Complexes Triaquatris(2-Furancarboxylato)-Yttrium(III) and Erbium(III)

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X-RAY STRUCTURE ANALYSIS OF THE ISOMORPHOUS COMPLEXES TRIAQUATRIS(2-FURANCARBOXYLATO)-YTTRIUM(III) AND ERBIUM(III).

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The crystal structures of isomorphous triaquatris(2-furancarboxylato)yttrium(III) and erbium(III) have been determined from three-dimensional X-ray intensity data. Both complexes crystallize in the monoclinic space group *C*2/*c* with unit cell dimensions $a = 22.132(9)$, $b = 15.984(7)$, $c = 10.182(5)$ Å, $\beta = 99.99(5)^\circ$ for yttrium and $a = 22.115(9)$, $b = 15.961(8)$, $c = 10.145(6)$ Å, $\beta = 100.04(6)^\circ$ for the erbium compound. The structures have been solved by direct methods and refined to a final *R* values of 0.0525 and 0.0365 for the yttrium and erbium complexes, respectively. Two of three 2-furancarboxylate anions are bidentate and bridged ligands; the third one is monodentate and disordered between two positions. Also, one of the three water molecules present in the structure is disordered. Eight oxygen atoms are involved in the coordination of Y(Er); the coordination sphere includes three water molecules and five carboxylate oxygen atoms. The geometry around the metal ion indicates that the polyhedron is a slightly distorted dodecahedron with symmetry close to $\bar{4}2m$. The M–O distances range from 2.261(5) to 2.526(5) Å.

Keywords: Furancarboxylic acid, yttrium, lanthanides, erbium, complex, X-ray structure

INTRODUCTION

Triaquatris(2-furancarboxylato)yttrium(III) and lanthanide(III) were prepared by a double decomposition reaction by adding equivalent amounts of an ammonium 2-furancarboxylate (pyromucate) solution to a solution of yttrium(III) or a lanthanide(III) nitrate, respectively.[1,2] Henceforth, the 2-furancarboxylate anion will be abbreviated as 2-fCOO. The complexes were recrystallized from aqueous solutions and when heated in air, lost waters of crystallization in one step. The anhydrous complexes decomposed to M_2O_3 with the intermediate formation of oxysalts.[2] The powder diffraction patterns indicated that the complexes were crystalline, their structures having large unit cells and low symmetry. A preliminary study of single crystals permitted the determination of the lattice parameters[3] and showed that the yttrium and erbium complexes were isomorphous as well as isomorphous with the corresponding Nd(III)–Yb(III) complexes. They crystallize in the monoclinic system in the space group *C*2/*c*. IR spectra indicated that the carboxylate groups in these complexes occur both as bidentate and bridging ligands, and that the water molecules are coordinated.[1]

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In a previous paper[4] the crystal and molecular structure of diaquatris(2-fCOO)-praseodymium(III) was described. Its structure is isomorphous with those of the La(III) and Ce(III) complexes with 2-fCOOH. As a continuation of our work on the determination of crystal structures of rare earth complexes with organic ligands, we report now the complete crystal structures of triaquatris(2-fCOO)yttrium(III) and erbium(III), and the metal ion coordination geometry observed in those complexes.

EXPERIMENTAL

The colourless crystals of triaquatris(2-fCOO)yttrium(III) [$Y(2fCOO)_3(H_2O)_3$] and erbium(III) [$Er(2fCOO)_3(H_2O)_3$] were obtained by recrystallization from an aqueous solution. Crystal data for the analyzed complexes and conditions of diffraction data collection are presented in Table I. Intensities of reflections were measured on a Nicolet R3m diffractometer at room temperature.

TABLE I

Crystal data, experimental details and results of the refinement of the $M(2\text{-fCOO})_3 \cdot 3H_2O$ complexes.

	M = Y	M = Er
Formula	$C_{15}H_{15}O_{12}Y$	$C_{15}H_{15}O_{12}Er$
Formula weight	476.18	554.54
Space group	*C2/c*	*C2/c*
a (Å)	22.132(9)	22.115(9)
b (Å)	15.984(7)	15.961(8)
c (Å)	10.182(5)	10.145(6)
β (°)	99.99(5)	100.04(6)
Volume (Å^3)	3547.4(9)	3526.3(9)
Z,*F*(000)	8, 1920	8, 2152
Density (calcd, obsd) g cm^{-3}	1.78, 1.78	2.09, 2.06
(flotation in bromobenzene + bromoethylene)		
Crystal size (mm)	0.2 × 0.2 × 0.5	0.47 × 0.17 × 0.25
Radiation	Mo Kα (graphite monochromator)	$\lambda = 0.71069$ Å
μ (cm^{-1})	34.5	49.9
Range of 2θ (°)	1.5–47.0	1.5–47.0
Scan mode	θ–2θ	θ–2θ
Scan speed (° min^{-1})	2.1–29.3	2.1–29.3
Scan range (°)	±1.05	±1.05
Orientation matrix: 25 reflections		
2θ range	6.0–27.0	6.5–25.0
Number of collected data	2920	2752
Number of unique data	2807	2637
Number of observed ($F_o/\sigma \geq 2$)	2340	2326
Range of *hkl*	0–24, 0–18, ±11	0–24, 0–17, ±11
Number of parameters	289	289
H-atoms	all from D-map	13 from D-map, 2 missing
Shift/esd in last cycle (max)	0.008	0.022
Weighting scheme	0.0385, $w = 1/\sigma^2$	0.0362, $w = 1/\sigma^2$
GOF	2.75	3.41
$\Delta\delta$ (eÅ^{-3}): min, max	−0.80, .82	−1.64, 2.14

Efforts to solve the erbium complex structure both by Patterson synthesis and lirect methods were unsuccessful. However, application of direct methods (the ;OLV procedure[5]) to the yttrium complex data gave the position of the cation. The)osition of the heavy atom at $x \approx 1/4$, $y \approx 3/4$, $z \approx 3/4$ (close to the 2_1 axis), which is lot a special position in the space group $C2/c$, caused difficulties in the location of igand atoms in the erbium complex.

Subsequent Fourier syntheses, with the Y atom included, and least-squares efinement showed the atomic positions of the ligands; two anions and two water nolecules are ordered, while one anion and one water molecule are disordered)etween two positions, each with the site occupancy factor 0.5. A difference Fourier ynthesis which followed the refinement of non-hydrogen atom parameters revealed ıll the H-atoms of the yttrium complex, including those of the disordered part of the tructure. Fixed coordinates and isotropic thermal factors ($U_{iso} = 0.05$ Å^2 for all ıtoms) for the H-atoms were included in the structure factor calculations.

Positional parameters of the non-hydrogen atoms found for the yttrium complex vere used as a starting model in the refinement of the erbium complex structure. \fter the refinement of the structure with anisotropic thermal parameters, a differ-:nce map showed positions of 13 H-atoms. The H-atom parameters were not refined)ut included in the calculation of structure factors. The SHELXTL 86[5] and SHELX '6[6] systems of crystallographic computer programs were used for the calculations.

To avoid this disordered structure, the non-centrosymmetric space group *Cc* might)e also considered. This possibility can be discarded because the E-statistics calcu-ated for all unique reflections indicated a centrosymmetric structure and the efinement in the space group $C2/c$ converged without problems. These are sufficient ndications for the centrosymmetric space group $C2/c$, according to suggestions)resented by Marsh.[7,8]

TABLE II

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å^2 $\times 10^3$) for the complexes.

	x/a	*y/b*	*z/c*	*U**
complex				
'	2437(1)	7555(1)	7513(1)	22(1)
:(1A)	835(2)	7548(4)	9878(4)	22(2)
:(2A)	610(3)	7559(5)	11024(5)	44(2)
:(3A)	−34(3)	7672(5)	10670(6)	53(3)
:(4A)	−159(3)	7717(4)	9316(6)	41(2)
)(1A)	364(2)	7647(3)	8801(3)	34(1)
:(5A)	1454(2)	7445(4)	9600(5)	24(2)
)(2A)	1539(1)	7496(3)	8414(3)	29(1)
)(3A)	1868(2)	7306(2)	10580(4)	33(1)
:(1B)	1347(2)	9153(3)	4149(5)	22(2)
:(2B)	1195(3)	9486(4)	2893(5)	32(2)
:(3B)	823(3)	10198(4)	3027(6)	39(2)
:(4B)	767(3)	10238(4)	4331(7)	46(3)
)(1B)	1087(2)	9611(3)	5033(4)	38(2)
:(5B)	1735(2)	8436(3)	4655(5)	23(2)
)(2B)	1821(2)	8303(3)	5862(4)	39(2)
)(3B)	1940(2)	8006(2)	3809(4)	37(2)
:(1C)$^{\neq}$	3807(5)	9731(7)	6679(11)	27(4)
:(1C')$^{\neq}$	3719(6)	9668(8)	4730(14)	40(5)
:(2C')$^{\neq}$	3823(6)	10449(8)	5259(14)	45(5)

TABLE II (continued)

	x/a	*y/b*	*z/c*	*U**
Y complex				
C(23C)	4164(4)	10465(5)	6479(7)	88(4)
C(3C)[‡]	4500(6)	10445(9)	5717(14)	50(6)
C(4C)[‡]	4524(7)	9628(10)	5387(14)	53(6)
C(4C′)[‡]	4447(6)	9608(9)	6600(13)	56(6)
O(1C)	4098(2)	9158(3)	5770(5)	53(2)
C(5C)[‡]	3300(5)	9416(7)	7279(10)	28(4)
C(5C′)[‡]	3288(5)	9318(7)	3738(11)	32(4)
O(2CW)	3119(2)	8610(3)	6948(4)	48(2)
O(3C)	3011(2)	10034(3)	7928(4)	51(2)
Ow(1)	2621(2)	6234(2)	8618(4)	37(2)
Ow(2)	2220(2)	8920(2)	8584(4)	31(1)
Ow(3C)	1820(2)	6527(3)	6165(4)	50(2)
Er complex				
Er	2437(1)	7556(1)	7515(1)	21(1)
C(1A)	836(3)	7545(5)	9871(7)	24(2)
C(2A)	611(4)	7548(7)	11025(8)	45(3)
C(3A)	−31(4)	7667(7)	10659(10)	54(4)
C(4A)	−160(4)	7725(6)	9323(10)	42(3)
O(1A)	368(2)	7648(4)	8818(5)	32(2)
C(5A)	1460(3)	7442(4)	9600(7)	22(2)
O(2A)	1543(2)	7494(3)	8407(5)	28(2)
O(3A)	1871(2)	7299(3)	10576(5)	32(2)
C(1B)	1344(3)	9155(4)	4127(7)	21(2)
C(2B)	1199(4)	9490(5)	2906(8)	33(3)
C(3B)	827(4)	10197(5)	3026(9)	38(3)
C(4B)	763(4)	10236(6)	4296(10)	41(3)
O(1B)	1085(3)	9614(4)	5028(6)	38(2)
C(5B)	1734(3)	8438(4)	4650(7)	21(2)
O(2B)	1826(3)	8306(3)	5877(5)	39(2)
O(3B)	1932(3)	8001(3)	3799(6)	38(2)
C(1C)[‡]	3802(7)	9744(10)	6660(16)	27(5)
C(1C′)[‡]	3736(7)	9653(10)	4827(17)	30(6)
C(2C′)[‡]	3829(9)	10459(11)	5311(20)	47(7)
C(23C)	4151(7)	10472(7)	6488(12)	82(6)
C(3C)[‡]	4490(9)	10459(12)	5766(23)	45(8)
C(4C)[‡]	4503(8)	9629(14)	5394(20)	50(8)
C(4C′)[‡]	4453(8)	9612(15)	6582(20)	54(8)
O(1C)	4102(3)	9157(4)	5774(7)	53(3)
C(5C)[‡]	3297(7)	9410(10)	7256(16)	29(6)
C(5C′)[‡]	3290(7)	9302(9)	3751(15)	24(5)
O(2CW)	3124(3)	8612(4)	6946(7)	47(2)
O(3C)	3010(3)	10043(4)	7909(7)	51(3)
Ow(1)	2625(3)	6235(3)	8616(6)	38(2)
Ow(2)	2211(3)	8921(3)	8594(6)	32(2)
Ow(3C)	1818(3)	6524(4)	6167(7)	48(2)

[‡] Site occupancy factor 0.5. * Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE III
H-Atom coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) for the complexes.

	x/a	*y/b*	*z/c*	*U*
Y complex				
H(2A)	881	7458	11991	50
H(3A)	−396	7653	11041	50
H(4A)	−572	7724	8594	50
H(2B)	1327	9226	2076	50
H(3B)	619	10635	2393	50
H(4B)	508	10744	4691	50
H(23C)	4164	10827	7227	50
H(3C)[a]	4808	11000	5583	50
H(4C)[a]	4704	9265	4703	50
H(2C′)[a]	3530	10810	5052	50
H(4C′)[a]	4702	9228	7276	50
H(1W1)	2380	5758	8295	50
H(2W1)	2584	6194	9561	50
H(1W2)	1793	9040	8323	50
H(2W2)	2443	9376	8333	50
H(1CW)[a]	3501	8183	6426	50
H(2CW)[a]	3265	8754	6474	50
H(3CW)[a]	1726	6597	5020	50
H(4CW)[a]	1889	5947	6464	50
Er complex				
H(2A)	858	7554	12031	60
H(3A)	−280	7791	11282	60
H(4A)	−561	7808	8621	60
H(2B)	1370	9243	2247	60
H(3B)	568	10597	2308	60
H(4B)	602	10768	4732	60
H(23C)	4248	11000	7165	60
H(4C)[a]	4882	9387	5007	60
H(4C′)[a]	4900	9262	7049	60
H(1W1)	2563	6242	9447	60
H(2W1)	2280	5918	7981	60
H(1W2)	1867	9225	8044	60
H(2W2)	2424	9217	8112	60
H(1CW)[a]	3602	8456	7155	60
H(2CW)[a]	2844	8982	7118	60
H(4CW)[a]	1686	6488	4996	60

[a] S.o.f. = 0.5

The results of the final least-squares refinement of the yttrium and erbium complexes are given in Table I. The final atomic parameters are listed in Tables II and III. The numbering system used for the 2-fCOO anion is shown in Figure 1. Lists of observed and calculated structure factors and anisotropic thermal parameters of the non-hydrogen atoms can be obtained from the Editor on request.

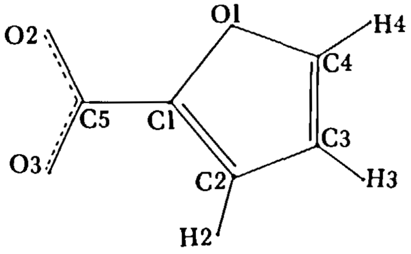

FIGURE 1 The numbering scheme for atoms in the 2-fCOO anion.

DISCUSSION

In the isomorphous structures M(2-fCOO)$_3$(H$_2$O)$_3$, M = Y or Er, the asymmetric unit contains one cation, three anions (two ordered and one disordered), and three water molecules (two ordered and one disordered). The carboxyl groups of the two ordered anions A and B bridge two metal atoms related by a centre of symmetry to form chains parallel to 001 (see Figures 2 and 3). The two ordered water molecules are also coordinated to the metal ion. The coordination sphere is completed by the disordered water molecule and one carboxyl oxygen atom from the disordered anion C. When O(2Cw) is coordinated, Ow(3c) is the water molecule, and when O(2Cw) is a water molecule, then Ow(3C) is a carboxyl oxygen atom. The result is an overall site-occupancy factor of 1 for each of the two oxygens and a final coordination number of 8 for the metal ion. None of the three 2-fCOO anions is chelating in contrast with the Pr(2-fCOO)$_3$(H$_2$O)$_2$ complex where two of the anions were chelated to the Pr ion.[4]

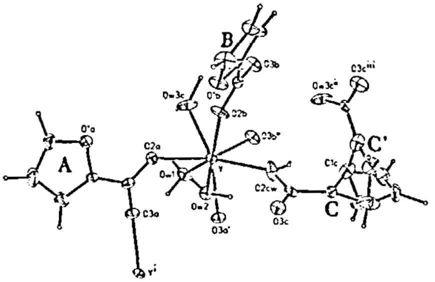

FIGURE 2 The Y(2-fCOO)$_3$(H$_2$O)$_3$ complex (for symmetry codes see Table IV).

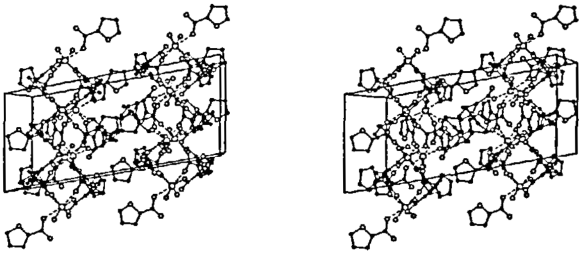

FIGURE 3 Stereoscopic view of the crystal structure along the *b* axis.

TABLE IV
Bond lengths (Å) in the complexes

	Y complex	Er complex
M-O(2A)	2.331(3)	2.315(5)
M-O(2B)	2.305(4)	2.288(5)
M-O(2CW)	2.400(4)	2.406(6)
M-Ow(1)	2.394(4)	2.388(5)
M-Ow(2)	2.523(4)	2.526(5)
M-Ow(3C)	2.407(4)	2.410(6)
M-O(3A)(i)	2.269(3)	2.261(5)
M-O(3B)(ii)	2.273(4)	2.272(6)
C(1A)-C(2A)	1.345(8)	1.350(12)
C(1A)-O(1A)	1.384(5)	1.362(8)
C(1A)-C(5A)	1.457(7)	1.462(10)
C(2A)-C(3A)	1.421(8)	1.416(12)
C(3A)-C(4A)	1.360(9)	1.338(13)
C(4A)-O(1A)	1.355(7)	1.360(10)
C(5A)-O(2A)	1.256(6)	1.258(9)
C(5A)-O(3A)	1.251(6)	1.242(8)
C(1B)-C(2B)	1.372(7)	1.336(11)
C(1B)-O(1B)	1.362(7)	1.372(10)
C(1B)-C(5B)	1.471(7)	1.476(10)
C(2B)-C(3B)	1.424(9)	1.414(12)
C(3B)-C(4B)	1.356(9)	1.323(14)
C(4B)-O(1B)	1.357(7)	1.364(11)
C(5B)-O(2B)	1.230(6)	1.244(9)
C(5B)-O(3B)	1.246(7)	1.247(10)
C(1C)-C(23C)	1.450(14)	1.423(21)
C(1C)-O(1C)	1.523(13)	1.528(18)
C(1C)-C(5C)	1.456(17)	1.460(24)
C(1C′)-C(2C′)	1.363(18)	1.379(24)
C(1C′)-O(1C)	1.477(13)	1.390(17)
C(1C′)-C(5C′)	1.382(16)	1.449(21)
C(2C′)-C(23C)	1.338(15)	1.279(22)
C(23C)-C(3C)	1.164(18)	1.136(29)
C(23C)-C(4C′)	1.503(17)	1.523(26)
C(3C)-C(4C)	1.352(21)	1.379(30)
C(4C)-O(1C)	1.316(16)	1.275(22)
C(4C′)-O(1C)	1.265(14)	1.257(21)
C(5C)-O(2CW)	1.373(11)	1.351(17)
C(5C)-O(3C)	1.403(12)	1.419(18)
C(5C′)-O(3C)(iii)	1.397(12)	1.421(15)
C(5C′)-Ow(3C)(ii)	1.379(13)	1.346(16)

(i) $1/2 - x$, $3/2 - y$, $2 - z$; (ii) $1/2 - x$, $3/2 - y$, $1 - z$; (iii) x, $2 - y$, $1/2 + z$.

Bond lengths and angles (Tables IV and V) in the two ordered anions A and B are normal. The geometry in the disordered anion C is poorly defined. The furan rings are planar within experimental error. The dihedral angle between the planes of the two disordered rings C and C′ is 87.8°. The carboxylate groups are rotated about the C(1)-C(5) bond by about 4° in A and B and about 15° in C and C′.

TABLE V
Bond angles (°) in the complexes

	Y complex	Er complex
O(2A)-M-O(2B)	82.6(1)	82.5(2)
O(2A)-M-O(2CW)	137.6(1)	137.9(2)
O(2A)-M-Ow(1)	82.3(1)	82.5(2)
O(2A)-M-Ow(2)	68.0(1)	67.7(2)
O(2A)-M-Ow(3C)	76.1(1)	75.7(2)
O(2A)-M-O(3A)(i)	99.5(1)	99.6(2)
O(2A)-M-O(3B)(ii)	149.7(1)	150.2(2)
O(3A)(i)-M-O(3B)(ii)	98.9(1)	98.6(2)
O(2B)-M-O(2CW)	77.2(1)	77.1(2)
O(2B)-M-Ow(1)	146.2(1)	146.5(2)
O(2B)-M-Ow(2)	74.6(1)	74.2(2)
O(2B)-M-Ow(3C)	74.6(1)	75.0(2)
O(2B)-M-O(3A)(i)	143.1(1)	142.6(2)
O(2B)-M-O(3B)(ii)	96.6(1)	97.1(2)
O(2CW)-M-Ow(1)	132.0(1)	131.7(2)
O(2CW)-M-Ow(2)	70.8(1)	71.4(2)
O(2CW)-M-Ow(3C)	131.4(2)	131.5(2)
O(2CW)-M-O(3A)(i)	77.0(1)	76.9(2)
O(2CW)-M-O(3B)(ii)	70.3(1)	69.9(2)
Ow(1)-M-Ow(2)	126.1(1)	126.1(2)
Ow(1)-M-Ow(3C)	72.5(1)	72.3(2)
Ow(1)-M-O(3A)(i)	69.5(1)	69.7(2)
Ow(1)-M-O(3B)(ii)	81.9(1)	81.6(2)
Ow(2)-M-Ow(3C)	134.9(1)	134.4(2)
Ow(2)-M-O(3A)(i)	72.4(1)	72.4(2)
Ow(2)-M-O(3B)(ii)	141.1(1)	141.3(2)
Ow(3C)-M-O(3A)(i)	141.9(1)	142.0(2)
Ow(3C)-M-O(3B)(ii)	74.6(1)	75.2(2)
C(2A)-C(1A)-O(1A)	110.2(4)	109.5(6)
C(2A)-C(1A)-C(5A)	132.2(4)	131.8(6)
O(1A)-C(1A)-C(5A)	117.6(4)	118.6(6)
C(1A)-C(2A)-C(3A)	106.7(5)	106.2(7)
C(2A)-C(3A)-C(4A)	106.3(6)	107.5(8)
C(3A)-C(4A)-O(1A)	110.6(5)	109.3(7)
C(1A)-O(1A)-C(4A)	106.2(4)	107.5(6)
C(1A)-C(5A)-O(2A)	118.8(4)	118.3(6)
C(1A)-C(5A)-O(3A)	116.6(5)	116.9(6)
O(2A)-C(5A)-O(3A)	124.6(5)	124.7(6)
C(2B)-C(1B)-O(1B)	110.1(5)	110.1(7)
C(2B)-C(1B)-C(5B)	131.4(5)	132.4(7)
O(1B)-C(1B)-C(5B)	118.4(5)	117.4(6)
C(1B)-C(2B)-C(3B)	105.8(5)	106.8(8)
C(2B)-C(3B)-C(4B)	106.5(5)	106.5(8)
C(3B)-C(4B)-O(1B)	110.6(6)	111.2(8)

TABLE V (continued)

	Y complex	Er complex
C(1B)-O(1B)-C(4B)	106.9(4)	105.4(6)
C(1B)-C(5B)-O(2B)	117.6(5)	118.3(7)
C(1B)-C(5B)-O(3B)	116.6(5)	116.0(7)
O(2B)-C(5B)-O(3B)	125.7(5)	125.7(7)
C(23C)-C(1C)-O(1C)	95.9(8)	97.4(12)
C(23C)-C(1C)-C(5C)	144.9(10)	145.1(12)
O(1C)-C(1C)-C(5C)	119.0(9)	117.4(12)
C(1C)-C(23C)-C(3C)	119.9(10)	119.9(15)
C(23C)-C(3C)-C(4C)	104.5(13)	104.0(8)
C(3C)-C(4C)-O(1C)	114.6(13)	115.9(18)
C(1C)-O(1C)-C(4C)	103.8(8)	102.2(12)
C(1C)-C(5C)-O(2CW)	115.8(9)	117.0(14)
C(1C)-C(5C)-O(3C)	113.6(9)	111.7(12)
O(2CW)-C(5C)-O(3C)	129.6(9)	130.4(13)
C(2C′)-C(1C′)-O(1C)	100.8(10)	104.6(13)
C(2C′)-C(1C′)-C(5C′)	135.0(12)	131.9(15)
O(1C)-C(1C′)-C(5C′)	122.3(10)	122.6(13)
C(1C′)-C(2C′)-C(23C)	114.4(11)	111.9(15)
C(2C′)-C(23C)-C(4C′)	102.6(9)	102.1(13)
O(1C)-C(4C′)-C(23C)	105.4(9)	105.4(13)
C(1C′)-O(1C)-C(4C′)	111.8(9)	109.9(13)
C(1C′)-C(5C′)-Ow(3)(ii)	116.8(9)	115.9(12)
C(1C′)-C(5C′)-O(3C)(iii)	108.0(10)	109.7(12)
Ow(3)(ii)-C(5C′)-O(3C)(iii)	134.8(8)	133.9(11)

(i) $1/2 - x$, $3/2 - y$, $2 - z$; (ii) $1/2 - x$, $3/2 - y$, $1 - z$; (iii) x, $2 - y$, $1/2 + z$.

The M–O distances and bond angles involving the yttrium and erbium ions are listed in Tables IV and V. The M–O bonds found in both complexes are equal within the limits of error and are in good agreement with previously reported values for other eight-coordinate Y(III) and Er(III) complexes with carboxylic acids: *e.g.*, 2.307–2.411 Å in yttrium and 2.293–2.389 Å in erbium formate dihydrate,[9] 2.19–2.43 Å in diaquaerbium(III) isonicotinate,[10] 2.27–2.57 Å in bis(μ-2-p-hydroxybenzoato)triaquatetrakis(*p*-hydroxybenzoato)diyttrium(III) monohydrate,[11] 2.318–2.502 Å in sodium aquatetraformatoyttrium(III) monohydrate,[12] and 2.240–2.396 Å in (hydroxyethyltriacetato)ethylenediamineerbium(III) pentahydrate.[13]

The most frequently observed polyhedra in the eight-coordinate structures are the dodecahedron (symmetry $\bar{4}2m$) and the square antiprism (symmetry $\bar{8}2m$). The analysis of the Y(III) and Er(III) coordination geometry (Figure 4) showed that the polyhedron is the distorted dodecahedron. Using the dodecahedron description given by Drew,[14] the water oxygen atoms [Ow(1), Ow(3C), and Ow(2)] and the disordered oxygen atom occupy the A sites, while the carboxylate oxygen atoms [O(2A), O(3A)(i), O(2B) and O(3B)(ii)] are in sites type B.

There are several parameters which can be used to describe an ideal dodecahedron. The angles between the metal–ligand bonds and the $\bar{4}$ axis are $\theta_A = 36.9°$ and $\theta_B = 69.5°$. The angles between faces related by the 2-fold axis are $\delta = 29.5°$. The angles describing the deviations from the ideal mirror symmetry φ are 0°. The angles between the mirror planes are $\gamma = 90°$. The mean values found in the Y(Er) complexes are: $\theta_A = 36.1(35.9)$; $\theta_B = 73.1(73.2)$; $\delta = 27.9(27.6)$; $\varphi = 4.5(4.4)$ and $\gamma = 88.1°(87.7°)$. Therefore, deviations from an ideal dodecahedron are small for both complexes. The fact that there are no shared corners or edges but chains of discrete polyhedra may account for the small deviations from ideal geometry.

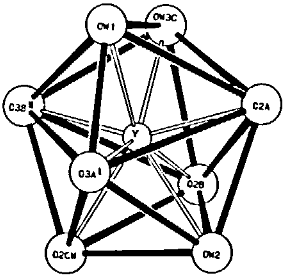

FIGURE 4 The YO_8 coordination polyhedron.

TABLE VI
Geometry of hydrogen bonds and other O...O contacts in the complexes.

D-H...A	D-A (Å)	D-H (Å)	H...A (Å)	<D-H...A (°)
Y complex				
Ow(1)-H(2w1)...Ow(2)(i)	2.82	0.98	1.87	162
Ow(1)-H(1w1)...O(3C)(iv)	2.71	0.95	1.81	157
Ow(1)-H(1w1)...Ow(3C)	2.84	0.95	2.61	94
Ow(2)-H(2w2)...O(3C)	2.66	0.94	1.74	165
O(2CW)-H(1CW)...O(1C)	2.79	1.27	2.22	103
O(2CW)-H(2CW)...O(1C)	2.79	0.67	2.19	152
O(2CW)-H(1CW)...O(3B)(ii)	2.69	1.27	2.13	102
O(2CW)... O(3C)	2.51	—	—	—
Ow(3C)-H(3CW)...O(2CW)(ii)	3.20	1.15	2.12	155
Ow(3C)-H(4CW)...O(3C)(iv)	2.56	0.98	1.59	175
Ow(3C)-H(3CW)...O(1C)(ii)	2.80	1.15	2.22	108
Er complex				
Ow(1)-H(1w1)...Ow(2)(i)	2.80	0.88	1.98	155
Ow(1)-H(2w1)...O(3C)(iv)	2.69	1.04	1.72	152
Ow(1)-H(2w1)...Ow(3C)	2.83	1.04	2.17	120
Ow(2)-H(2w2)...O(3C)	2.69	0.87	1.88	152
O(2CW)-H(1CW)...O(1C)	2.78	1.07	2.23	110
O(2CW)... O(3B)(ii)	2.68	—	—	—
O(2CW)-H(2CW)...O(3C)	2.51	0.89	1.88	93
Ow(3C)-H(4CW)... O(2CW)(ii)	3.19	1.17	2.09	155
Ow(3C)... O(3C)(iv)	2.55	—	—	—
Ow(3C)-H(4CW)... O(1C)(ii)	2.79	1.17	2.06	117

(i) $1/2 - x, 3/2 - y, 2 - z$; (ii) $1/2 - x, 3/2 - y, 1 - z$; (iv) $1/2 - x, -1/2 + y, 3/2 - z$.

Small shifts in the H-atom positions in the Y complex relative to the Er complex result in slightly different hydrogen bonding in the two structures. Despite these differences, the OH...O hydrogen bonds involving ordered water molecules as donors are strong while those involving the disordered molecules are weak (see Table VI). Hydrogen bonds are formed between ligands coordinated to the metal ion and, in addition, link ligands in polymeric chains. Adjacent chains are hydrogen bonded to give layers parallel to the (011) planes. The contacts between the hydrophobic parts of the layers correspond to normal van der Waals interactions. The nearest intermolecular contacts (C...C and C...O >3.4 Å) between the atoms of the C(C′) anion together with the weak hydrogen bonds may account for the disorder in this anion.

CONCLUSIONS

Yttrium(III) and lanthanide(III) complexes with 2-furancarboxylic acid form two series of isomorphous structures.[3,4] The lanthanum, cerium and praseodymium ions form diaquatris(2-furancarboxylato) compounds with a metal coordination number of nine. Neodymium to ytterbium and yttrium are all eight-coordinate in their triaquatris(2-furancarboxylato) complexes. Changes of this type are common for lanthanide salts and can be correlated with ionic radii. In lanthanide 2-furancarboxylates structures, cations having a crystal radius for coordination number 8[15] greater than 1.25 Å (*i.e.*, La, Ce, Pr) adopt a higher coordination number and an ordered structure by changing coordination modes.

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