O10—H16···O1^{ii}	0.94	1.82	2.749 (2)	166
O13—H22···O12^{iii}	0.94	1.91	2.844 (3)	173
O13—H21···O4^{iii}	0.93	2.00	2.877 (3)	156
O12—H20···O8	0.95	1.86	2.801 (3)	175
O12—H19···O11^{iv}	0.94	1.91	2.847 (3)	177
O11—H18···O13^{i}	0.94	1.88	2.815 (3)	175
O11—H17···O8^{v}	0.94	1.95	2.870 (3)	165
N3—H23···O5^{i}	0.85	2.13	2.958 (3)	165
N3—H24···O7^{v}	0.87	2.18	3.018 (2)	161
N3—H24···O10^{v}	0.87	2.37	2.924 (2)	122
N3—H26···O3^{vi}	0.87	2.24	2.990 (3)	145
N3—H25···O12^{v}	0.87	2.35	3.083 (3)	144

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, -y, -z$; (iv) $-x, -y, -z$; (v) $x, 1 + y, z$; (vi) $1 - x, 1 - y, -z$.

All H atoms were located by difference Fourier synthesis and were refined as riding atoms.

Data collection: *CAD*-4 *ARGUS Software* (Nonius, 1996). Cell refinement: *CAD*-4 *ARGUS Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1032). Services for accessing these data are described at the back of the journal.

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catena-Poly[[diaqua(3-cyanobenzoato-*O*,*O*′)-erbium]-bis-μ-(3-cyanobenzoato-*O*:*O*′)]

BAO-QING MA, SONG GAO, ZHE-MING WANG, TAO YI, CHUN-HUA YAN AND GUANG-XIAN XU

State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU, Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, People's Republic of China.
E-mail: gaosong@chemms.chem.pku.edu.cn

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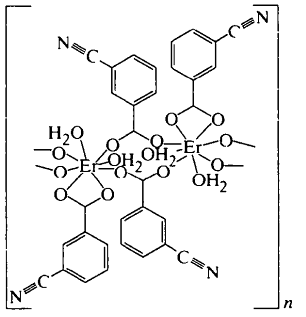
Abstract

The title compound, $[Er(C_8H_4NO_2)_3(H_2O)_2]_n$, has a one-dimensional chain structure bridged by carboxylate groups. The Er^{III} atom and one 3-cyanobenzoate ligand lie on a twofold axis and this ligand has its cyano group disordered over two sites. Each Er^{III} atom is surrounded by two O atoms from one chelating carboxylate group, four O atoms from four different bridging carboxylate groups and two water molecules, leading to a square-antiprism coordination polyhedron.

Comment

Carboxylate complexes of lanthanides play a significant role in the separation, analysis and even luminescence of rare earth elements. Structural information for these complexes will help in the estimation of the chelating ability of different carboxylic acids and may facilitate the design and/or synthesis of new extraction or luminescent systems. A number of carboxylates of lanthanides have been studied extensively and structurally characterized (Ma & Ni, 1996). In this paper, we report the structure of a novel complex, *catena*-poly[[diaqua(3-cyanobenzoato-*O*,*O*′)-erbium]-bis-μ-(3-cyanobenzoato-*O*:*O*′)], (I), which is, to our knowledge, the first lanthanide complex of *m*-cyanobenzoic acid.



(I)

In the complex, the Er atom and one 3-cyanobenzoate ligand lie on a twofold axis and this ligand has its cyano group disordered equally over two sites; each eight-coordinate Er atom is ligated by two O atoms provided by a chelating carboxylate group, four O atoms from four different bridging carboxylate groups and two water molecules, forming a distorted square-antiprism coordination environment. The dihedral angle between the top plane defined by atoms O1, O2, O3^{i} and O4, and the bottom plane defined by atoms O1^{ii}, O2^{ii}, O3^{iii} and O4^{ii} is 5.32 (7)° [symmetry codes: (i) $-x+1$, $-y+1$, $-z+2$; (ii) $-x+1$, y, $-z+\frac{3}{2}$; (iii) x, $-y+1$, $z-\frac{1}{2}$]. The Er—O bond lengths are within the ranges observed for other carboxylate–erbium complexes (Xing *et al.*, 1987), although the bond distance involving the chelating carboxylate O atom [2.439 (2) Å] is greater than that of the bridging O atoms [average 2.274 (2) Å]. This results from the fact that a four-membered chelate ring is unstable and Er—O bonding of the chelating carboxylate group is weaker than that of bridging carboxylate groups (Ma *et al.*, 1994).

Each Er atom is bridged by two carboxylate groups in a bidentate manner, which is described as a '*Z*,*E* conformation' (Sakagami *et al.*, 1997), giving rise to an infinite one-dimensional chain structure running along the *c* axis. The shortest intra- and interchain Er···Er separations are 4.8201 (6) and 12.9092 (6) Å, respectively.

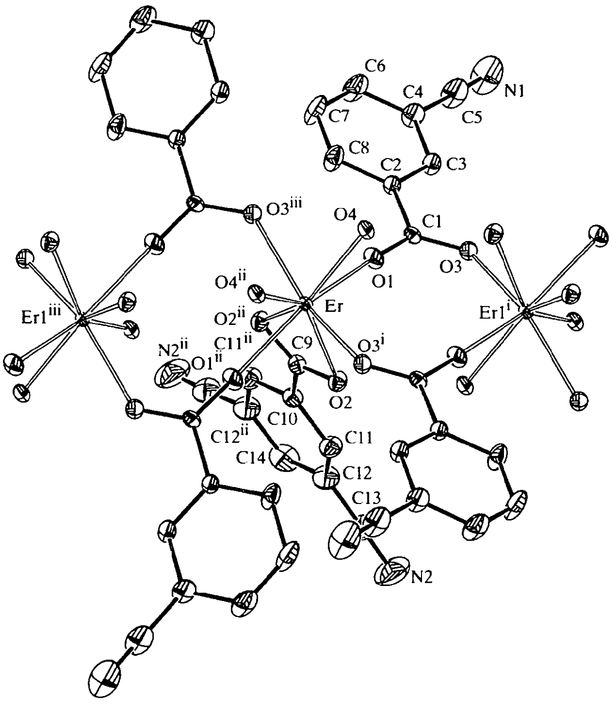


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. [Symmetry codes: (i) x, $1-y$, $z-\frac{1}{2}$; (ii) $1-x$, y, $\frac{3}{2}-z$; (iii) $1-x$, $1-y$, $2-z$.]

Hydrogen bonds exist *via* water molecules. The O4···O2^{i} and O4···N1^{iv} closest contacts are 2.782 (3) and 2.935 (4) Å, respectively [symmetry code: (iv) $-x+\frac{3}{2}$, $y+\frac{1}{2}$, $-z+\frac{5}{2}$].

The cyano group does not take part in coordination due to the relatively weak affinity of nitrogen for lanthanide ions compared with oxygen. The C13—N2 group of the chelating cyanobenzoate ligand is disordered by symmetry, so that each site is 50% occupied.

Experimental

An aqueous solution of *m*-cyanobenzoic acid (Hcba), neutralized with an equivalent molar quantity of NaOH, was added dropwise to an aqueous solution of $Er(ClO_4)_3 \cdot 6H_2O$ (molar ratio 3:2). The mixture were filtered and the filtrate allowed to stand undisturbed at room temperature. Two days later, pink needle-like single crystals were obtained. Calculated for $C_{24}H_{16}ErN_3O_8$: C 44.93, H 2.50, N 6.55%; found: C 43.69, H 2.54, N 6.40%.

Crystal data

$[Er(C_8H_4NO_2)_3(H_2O)_2]$
$M_r = 640.65$
Monoclinic
$C2/c$
$a = 22.8378\,(14)$ Å
$b = 12.0426\,(5)$ Å
$c = 9.5835\,(4)$ Å
$\beta = 107.358\,(4)°$
$V = 2515.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.692$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.07–13.81°$
$\mu = 3.387$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.30 × 0.11 × 0.11 mm
Pink

Data collection

Enraf–Nonius CAD-4 MACH3 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.638$, $T_{max} = 0.689$
2907 measured reflections
2738 independent reflections

2480 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26.97°$
$h = -29 \rightarrow 27$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 12$
3 standard reflections frequency: 60 min intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.047$
$S = 1.078$
2738 reflections
204 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 1.3623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.430$ e Å^{-3}
$\Delta\rho_{min} = -0.827$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Er	1/2	0.521683 (15)	3/4	0.01841 (6)
O1	0.56702 (9)	0.46522 (18)	0.9647 (2)	0.0359 (5)
O2	0.46523 (9)	0.34097 (17)	0.8086 (2)	0.0303 (4)
O3	0.58625 (8)	0.42206 (19)	1.1975 (2)	0.0306 (4)
O4	0.53501 (9)	0.68217 (17)	0.9027 (2)	0.0294 (4)
N1	0.83637 (17)	0.2443 (5)	1.4600 (5)	0.0979 (17)
N2†	0.3868 (4)	−0.1176 (8)	0.9039 (11)	0.092 (3)
C1	0.60188 (11)	0.4326 (2)	1.0835 (3)	0.0234 (5)
C2	0.66728 (12)	0.4057 (2)	1.0934 (3)	0.0279 (6)
C3	0.70490 (13)	0.3566 (3)	1.2181 (3)	0.0332 (7)
C4	0.76599 (14)	0.3358 (3)	1.2287 (4)	0.0459 (9)
C5	0.80512 (16)	0.2841 (4)	1.3580 (5)	0.0655 (13)
C6	0.78943 (16)	0.3633 (4)	1.1153 (5)	0.0583 (11)
C7	0.75127 (17)	0.4116 (4)	0.9902 (5)	0.0610 (13)
C8	0.69056 (15)	0.4332 (4)	0.9791 (4)	0.0460 (8)
C9	1/2	0.2893 (3)	3/4	0.0279 (8)
C10	1/2	0.1651 (4)	3/4	0.0315 (9)
C11	0.46048 (16)	0.1079 (3)	0.8081 (4)	0.0397 (7)
C12	0.4600 (2)	−0.0074 (3)	0.8063 (5)	0.0499 (9)
C13†	0.4211 (4)	−0.0680 (7)	0.8592 (9)	0.0556 (19)
C14	1/2	−0.0653 (5)	3/4	0.0563 (14)

† Site occupancy = 0.50.

Table 2. *Selected bond lengths (Å)*

Er—O1	2.2712 (19)	O3—C1	1.253 (3)
Er—O3^{i}	2.2764 (18)	N1—C5	1.131 (5)
Er—O4	2.412 (2)	N2—C13	1.164 (10)
Er—O2	2.439 (2)	C1—C2	1.503 (3)
O1—C1	1.243 (3)	C9—C10	1.496 (6)
O2—C9	1.265 (3)	C12—C13	1.359 (9)

Symmetry code: (i) $x, 1-y, z-\frac{1}{2}$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O4—H8···N1^{i}	0.918 (18)	2.09 (3)	2.935 (4)	153 (3)
O4—H7···O2^{ii}	0.901 (18)	1.92 (2)	2.782 (3)	160 (4)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{2}-z$; (ii) $1-x, 1-y, 2-z$.

All H atoms were located by difference Fourier synthesis. The water H atoms were refined with a rigid model and the other H atoms were refined isotropically.

Data collection: *CAD*-4 *ARGUS Software* (Nonius, 1996). Cell refinement: *CAD*-4 *ARGUS Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1998). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1072). Services for accessing these data are described at the back of the journal.

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Bis(4,4′-disulfanediyldipyridinium) di-μ-chloro-bis[dichlorocuprate(II)] bis(tetrafluoroborate)

Alexander J. Blake, Neil R. Champness, Paul A. Cooke and James E. B. Nicolson

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nottingham.ac.uk

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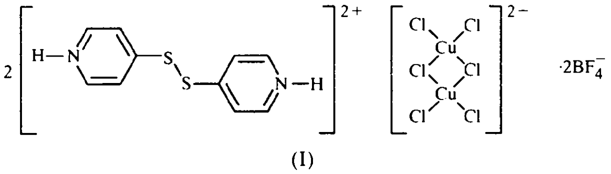
Abstract

In the title compound, $(C_{10}H_{10}N_2S_2)_2[Cu_2Cl_6](BF_4)_2$, the $[Cu_2Cl_6]^{2-}$ anions associate through weak Cu···Cl contacts to form polymeric $[CuCl_3]_n^{n-}$ chains. Hydrogen bonding between the chloride anions of these chains and the pyridinium protons, and between the pyridinium protons and the BF_4^- anions, results in the formation of weakly associated ribbons.

Comment

The title compound, (I), isolated during our studies into the formation of extended structures by copper halide complexes and bridging bipyridyl ligands, exists as an air-stable red solid.



(I)