

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 ^v	0.94	1.88	2.815 (3)	175
O11—H17···O8 ^v	0.94	1.95	2.870 (3)	165
N3—H23···O5 ^v	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: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *SHELXTLPC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

This work was supported by the NSFC (Nos. 29701001 and 29525101), the State Key Fundamental Research Project of MOST, the Training Project for Doctoral students of MOE, the China Postdoctoral Science Foundation and the Founder Group Corporation Foundation of Peking University.

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.

References

- Doorn, R. H. E. van, Kruidhof, H., Nijmeijer, A., Winnubst, L. & Burggraaf, A. J. (1998). *J. Mater. Chem.* **8**, 2109–2112.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Lind, M. D., Lee, B. & Hoard, J. L. (1965). *J. Am. Chem. Soc.* **87**, 1612–1613.
- Nonius (1996). *CAD-4 ARGUS Software*. Linux version. Nonius BV, Delft, The Netherlands.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pozhidaev, A. I., Polynova, T. N., Porai-Koshits, M. A. & Martynenko, L. I. (1973). *Zh. Strukt. Khim.* **14**, 947.
- Sheldrick, G. M. (1990). *SHELXTLPC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997a). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sugita, Y., Ohki, Y., Suzuki, Y. & Ouchi, A. (1987). *Bull. Chem. Soc. Jpn.* **60**, 3441–3443.
- Wiley, G. R., Lakin, M. T. & Alock, N. W. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1619–1620.
- Yan, C., Zhang, Y., Li, B., Jin, T. & Xu, G. (1996). *Polyhedron*, **15**, 2895–2899.
- Zhang, Y., Li, B., Gao, S., Jin, T. & Xu, G. (1995). *J. Rare Earths (Chin. Ed.)*, **13**, 11–14.

Acta Cryst. (1999). **C55**, 1420–1422

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

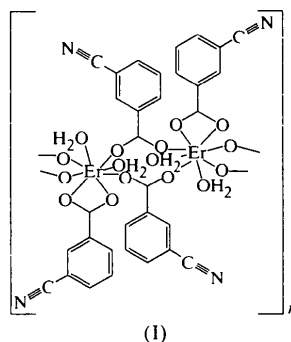
(Received 5 February 1999; accepted 4 June 1999)

Abstract

The title compound, $[\text{Er}(\text{C}_8\text{H}_4\text{NO}_2)_3(\text{H}_2\text{O})_2]_n$, 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*-cyano-benzoic acid.



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, O3ⁱ and O4, and the bottom plane defined by atoms O1ⁱⁱ, O2ⁱⁱ, O3ⁱⁱⁱ and O4ⁱⁱ 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.

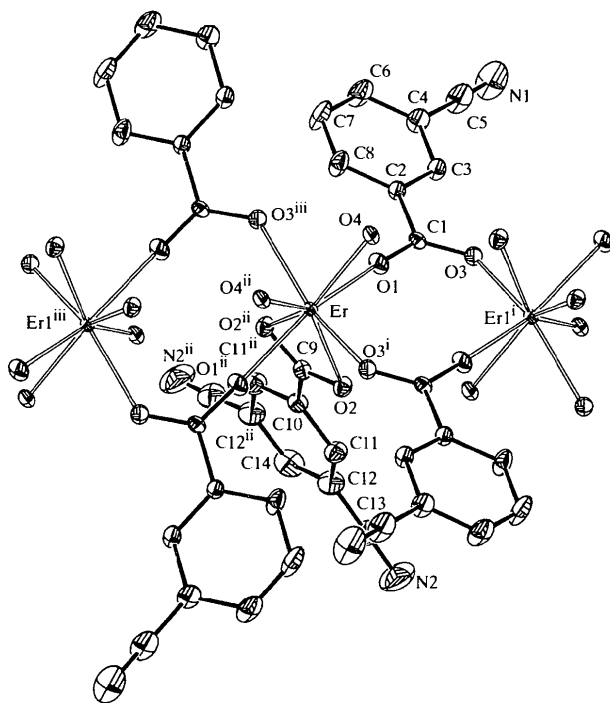


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. [Symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $1-x, y, \frac{3}{2}-z$; (iii) $1-x, 1-y, 2-z$.]

Hydrogen bonds exist *via* water molecules. The O4···O2ⁱ 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(ClO₄)₃·6H₂O (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 C₂₄H₁₆ErN₃O₈: C 44.93, H 2.50, N 6.55%; found: C 43.69, H 2.54, N 6.40%.

Crystal data

[Er(C₈H₄NO₂)₃(H₂O)₂]

M_r = 640.65

Monoclinic

*C*2/*c*

a = 22.8378(14) Å

b = 12.0426(5) Å

c = 9.5835(4) Å

β = 107.358(4)°

V = 2515.7(2) Å³

Z = 4

D_x = 1.692 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10.07–13.81°

μ = 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

θ/2θ 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 > 2σ(*I*)

R_{int} = 0.014

θ_{max} = 26.97°

h = -29 → 27

k = 0 → 15

l = 0 → 12

3 standard reflections

frequency: 60 min

intensity decay: 3.3%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*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/[σ²(*F_o*²) + (0.0204*P*)²
+ 1.3623*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.010

Δρ_{max} = 0.430 e Å⁻³

Δρ_{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)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a^i a^j$$

	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 [†]	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 - 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) 3/2 - x, 1/2 + y, 3/2 - 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: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1998). Software used to prepare material for publication: *SHELXL97*.

Financial support was from the National Natural Science Foundation of China (Nos. 29771001 and 29831010), the National Key Project for Fundamental Research and the Founder Corporation Group Foundation of Peking University.

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.

References

- Fair, C. K. (1990). *MoLEN*. Version 4.0. *An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Ma, J. F., Jin, Z. S. & Ni, J. Z. (1994). *Chin. J. Struct. Chem.* **13**, 113–116.
- Ma, J. F. & Ni, J. Z. (1996). *Prog. Chem.* **8**, 259–276.
- Nonius (1996). *CAD-4 ARGUS Software*. Linux version. Nonius BV, Delft, The Netherlands.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sakagami, N., Homma, J., Konno, T. & Okamoto, K. (1997). *Acta Cryst.* **C53**, 1378–1381.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Xing, Y., Jin, Z. S. & Ni, J. Z. (1987). *Acta Chim. Sin.* **45**, 1044–1047.
- Zsolnai, L. (1998). *XPMA and ZORTEP. Molecular Geometry and Graphics Programs*. University of Heidelberg, Germany.

Acta Cryst. (1999). **C55**, 1422–1425

Bis(4,4'-disulfanediyl)pyridinium 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

(Received 28 April 1999; accepted 14 May 1999)

Abstract

In the title compound, (C₁₀H₁₀N₂S₂)₂[Cu₂Cl₆](BF₄)₂, the [Cu₂Cl₆]²⁻ anions associate through weak Cu...Cl contacts to form polymeric [CuCl₃]_nⁿ⁻ chains. Hydrogen bonding between the chloride anions of these chains and the pyridinium protons, and between the pyridinium protons and the BF₄⁻ 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.

