Octakis(ε-caprolactam-κO)erbium(III) hexaisothiocyanatochromate(III)

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The title compound, $[Er(C_6H_{11}NO)_8][Cr(NCS)_6]$, is a new structure type for $[Ln(\varepsilon\text{-caprolactam})_8][Cr(NCS)_6]$, where Ln is a lanthanide. There are two independent cations and two independent anions in the asymmetric unit. The Er atom is in a distorted square-antiprismatic environment of eight O atoms of the organic ligands; Er—O bond distances are in the range 2.29–2.44 Å. The coordination environment of the Cr atom is a slightly distorted octahedron; Cr—N bond distances vary from 1.99 to 2.01 Å. The mutual packing of the cations and the anions follows a distorted NaCl motif. One cation has the Er atom on a twofold axis and one of the anions has the Cr atom on a twofold axis.

Comment

Mixed-ligand bimetallic complexes are expected to be prospective compounds for the design of both polyfunctional materials and their molecular and ionic precursors. The work presented here is part of a systematic study of coordination compounds of metals with organic ligands and the large inert hexaisothiocyanatochromate(III) anion (Cherkasova, 1994; Cherkasova et al., 2006). This anion is useful if one needs to precipitate compounds from a mixture of labile complexes in organic aqueous solutions. According to Golub et al. (1981), the bidentate nature of NCS^- may lead to various structures of isothiocyanates, both molecular and polymeric. To the best of our knowledge, no traditional $[Cr(NCS)_6]^{3-}$ salts have been structurally characterized. Surprisingly, according to a search of the Cambridge Structural Database (CSD, Version 1.9, update of January 2007; Allen, 2002), only 11 structural characterizations have been reported for the $[Cr(NCS)_6]^{3-}$ anion. These are mostly with various organic cations and there is one bimetal complex, $[Ho(C_5H_4NCOOH)_3(H_2O)_2][Cr(NCS)_6] \cdot 2H_2O$ (Kay et al., 1972). In most of these structures, the anion serves as a counter-anion and is not discussed by the authors. Recently, Thetiota et al. (2003) and Mas-Torrent et al.

(2003) used $[Cr(NCS)_6]^{3-}$ as a paramagnetic anion to participate in magnetic exchange interactions with tetrathiafulvalene derivatives. All of these structures contain isolated $[Cr(NCS)_6]^{3-}$ anions, except $[M(en)_3]_n[\{M(en)_2Cr(NCS)_6\}_{2n}]$ (M is Ni or Zn and en is ethylenediamine), which is a one-dimensional polymeric structure involving μ-N:S thiocyanate groups (Wrzeszcz et al., 2002).

Metal complexes with ε-caprolactam (L) are still poorly studied. The reason is probably due to the conformational flexibility of the seven-membered caprolactam ring and, therefore, its pronounced tendency to be disordered in the crystalline state. Thus, the CSD contains data on fewer than 30 crystal structures containing ε-caprolactam, and only ten of these are Ln^{III} complexes (Cherkasova et al., 2006, and references therein). Only two complexes have the coordination environment of Ln^{III} fully occupied by the caprolactam molecules, namely $[PrL_8](CF_3SO_3)_3$ (Alvarez et al., 1998) and the recently reported complex for the cerium group lanthanide, $[NdL_8][Cr(NCS)_6]$, (II) (Cherkasova et al., 2006). We report here a new structural type for $[LnL_8][Cr(NCS)_6]$ compounds, found for the title complex, $[ErL_8][Cr(NCS)_6]$, (I).
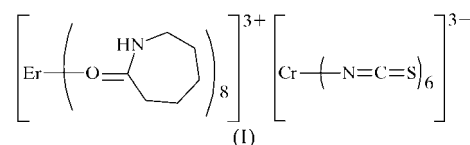
The X-ray structural analysis of compound (I) reveals that it is ionic and consists of two independent and isolated $[ErL_8]^{3+}$ cations (Fig. 1) and two independent $[Cr(NCS)_6]^{3-}$ anions (Fig. 2). One cation–anion pair lies on a twofold axis (Wyckoff position 4e) of the space group C2/c, while the other pair is in a general position. The molecular structure of the anions is typical, with the environment of the Cr atoms being a slightly distorted octahedron (Cherkasova, 1994; Cherkasova et al., 2006; Thetiota et al., 2003; Mas-Torrent et al., 2003). The coordination polyhedron of Er^{3+} for both independent cations is a square antiprism formed by eight O atoms of the caprolactam ligands (Table 1).

In the crystal structure, the anions and cations alternate to avoid undesired contacts between equally singly charged ions. The crystal packing of the complex cations and anions resembles the mutual cation–anionic packing in the crystal structure of NaCl (Fig. 3a), but in (I) the packing motif is distorted compared with the highly symmetrical face-centred cubic packing of NaCl.

In addition to Coloumbic interactions, the cations form intramolecular N—H···O=C (Fig. 1) and intermolecular N—H···S hydrogen bonds with the anions (Fig. 2). Almost all of the caprolactam ligands are involved in intramolecular hydrogen bonding, with N···O distances in the range 2.788 (5)–2.904 (5) Å (Table 2). All of the caprolactam ligands that do not participate in the intramolecular hydrogen bonds, together with some of those that do, are involved in intermolecular N—H···S hydrogen bonding with the NCS groups of the complex anions; the N···S distances are in the range

3.309 (4)–3.563 (4) Å. The intermolecular N—H···S contacts join all the complex anions and cations to form a three-dimensional network.

A comparison of the molecular structure of the cation for all three structural investigations of $[LnL_8]^{3+}$ cations, where Ln = Pr (Alvarez *et al.*, 1998), Nd [for (II)] or Er [for (I)], demonstrates the expected shortening of the Ln—O distances, from Pr—O (2.41–2.50 Å) and Nd—O (2.37–2.54 Å) to Er—O (2.29–2.44 Å).

The fact that the nearest analogues, (I) and (II), are both ionic is in accordance with Pearson's concept of hard and soft acids and bases (Pearson, 1963). They crystallize in different structure types, triclinic and monoclinic, respectively, but despite the different symmetry, the crystal packing in both compounds resembles that of NaCl (Figs. 3*b* and 3*c*). Moreover, their cell dimensions are mathematically related to each other. The triclinic unit cell of (II) can be transformed into a pseudo-monoclinic cell, with $a' = 36.877$, $b' = 23.395$, $c' = 24.557$ Å, $\alpha' = 91.58$, $\beta' = 108.71$, $\gamma' = 89.21°$ and $V' = 20059$ Å^3 (transformation matrix $(221/\bar{1}10/\bar{1}\bar{1}1)$, which resemble the cell parameters for (I). Conversely, in (II) the cell parameters a and b are rather close to one another [14.2438 (6) and 14.5641 (6) Å, respectively], as are α and β [92.518 (1) and 91.013 (1)°, respectively], which shows a tendency for the cell to be pseudo-monoclinic. It was very difficult to find a single crystal of compound (II), probably due to systematic pseudo-merohedral twinning: poor crystals were readily indexed in a 'monoclinic C' cell with high σ values and unacceptable results for the orientation matrix refinement. The rather close rela-
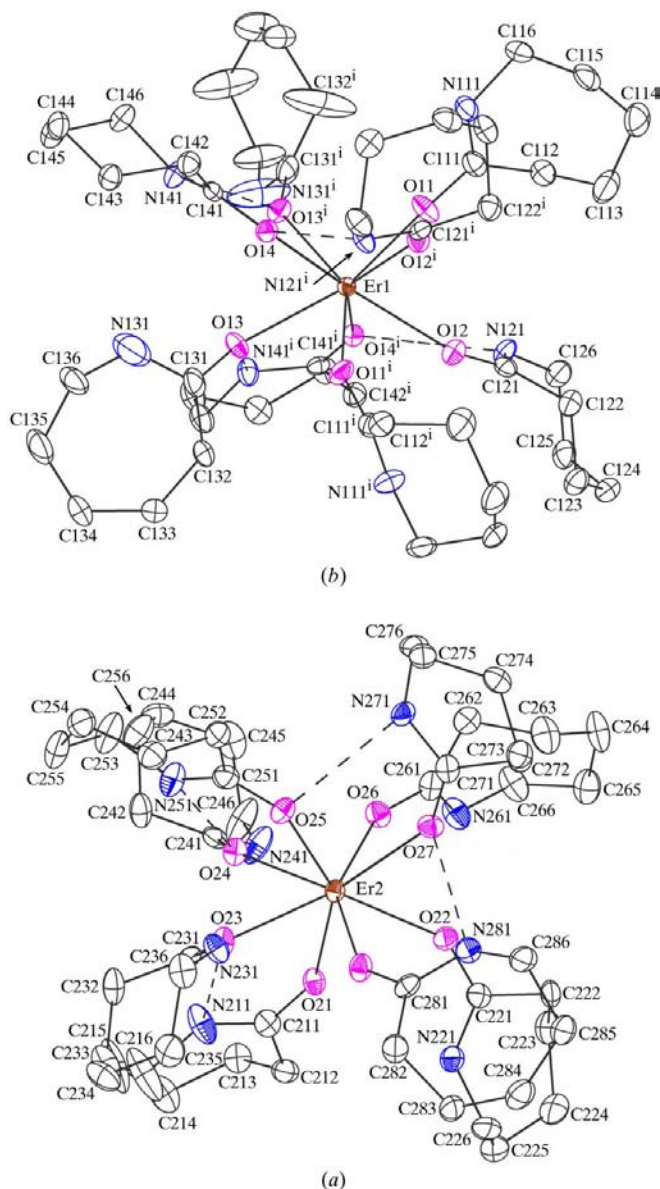

Figure 1
A view of the structure of the two crystallographically independent $[ErL_8]^{3+}$ cations in compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms of the caprolactam ligands have been omitted for clarity. Dashed lines show intramolecular N—H···O hydrogen bonds. [Symmetry code: (i) $2 - x, y, \frac{3}{2} - z$.]
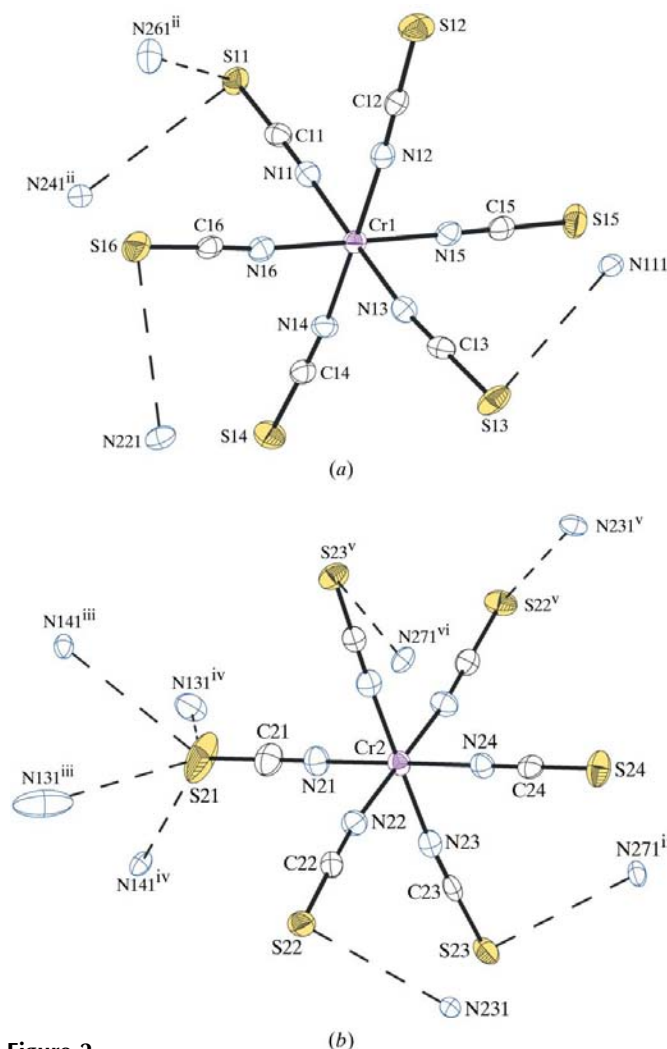

Figure 2
A view of the structure of the two crystallographically independent $[Cr(NCS)_6]^{3-}$ anions in compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intermolecular N—H···S hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii) $x, -y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{3}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$; (v) $1 - x, y, \frac{1}{2} - z$; (vi) $1 - x, -y, 1 - z$.]

tionship between the unit-cell parameters for (I) and (II) explains the quite similar theoretical powder diffraction patterns and, even more importantly, the similarity of their crystal packing, which in both cases resembles that found for the NaCl-related motif. It is worth mentioning that the NaCl motif is found to be the most frequent, as well as that of NiAs, amongst ionic and covalent compounds of different nature and composition (Ilyushin *et al.*, 2004; Blatov & Zakutkin, 2002).

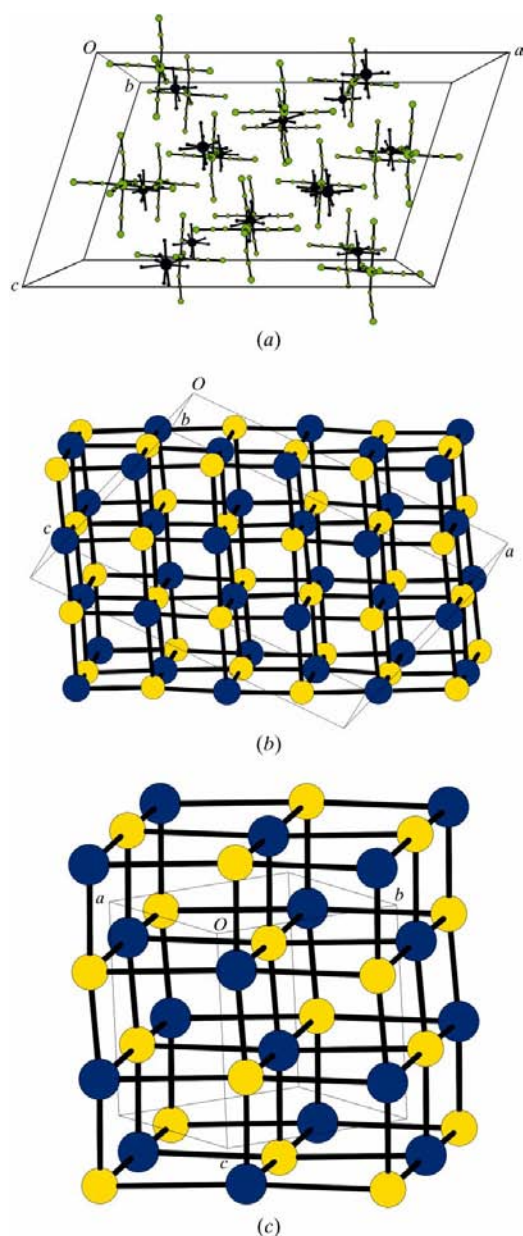There is no evident reason why compound (I) should crystallize in a different structural type from (II), as they have the same coordination numbers and only minor changes in the Ln—O bond distances due to the size of the Ln cation. The latter, however, might cause some conformational difficulties with the caprolactam ligands. This could influence the outer shape of the complex cation and, therefore, the mutual packing of the complex cations and anions, and ultimately drive the structure type to change.

Experimental

Compound (I) was prepared employing the same technique as for (II) (Cherkasova *et al.*, 2006), using a moderately concentrated aqueous solution of $ErCl_3 \cdot 6H_2O$, $K_3[Cr(CNS)_6]$ and ε-caprolactam (L). The results of the chemical analysis are in good accordance with the formula $C_{54}H_{88}CrErN_{14}O_8S_6$. Further analytical details are given in the archived CIF. A crystal suitable for X-ray analysis was grown by slow evaporation of a solution in water at room temperature, after many attempts at crystallization (each crystallization attempt took *ca* one month). Nevertheless, the quality of the crystals was very poor.

Crystal data

$[Er(C_6H_{11}NO)_8][Cr(NCS)_6]$	$V = 20002.9 (16)$ Å^3
$M_r = 1473.00$	$Z = 12$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 39.627 (2)$ Å	$\mu = 1.66$ mm^{-1}
$b = 22.3406 (11)$ Å	$T = 90.0 (2)$ K
$c = 23.7155 (10)$ Å	$0.12 \times 0.10 \times 0.10$ mm
$\beta = 107.687 (2)°$	

Data collection

Bruker X8 APEX CCD area-detector diffractometer	83013 measured reflections
	22829 independent reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)	14450 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.065$
$T_{min} = 0.736$, $T_{max} = 0.851$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	1139 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 2.56$ e Å^{-3}
22829 reflections	$\Delta\rho_{min} = -1.76$ e Å^{-3}

The H atoms were included in calculated positions and treated as riding atoms, with N—H = 0.88 Å and C—H = 0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(N,C)$. Caprolactam rings possess strong conformational flexibility, and hence the anisotropic displacement parameters of certain C and N atoms reflect this feature, resulting in some short C—C bonds, high U_{eq} values, elongated ellipsoids, Hirshfeld test alerts, *etc*. The terminal thiocyanate anions possess high thermal motion and one of the thiocyanate groups was constrained by a special position on a twofold axis.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *TOPOS* (Version 4.0 Professional; Blatov, 2006); software used to prepare material for publication: *SHELXTL*.

Figure 3
A comparison of the crystal packing in compounds (I) and (II). (*a*) The crystal packing in compound (II), with the N and C atoms of the caprolactam rings omitted for clarity. (*b*) A schematic view of the NaCl packing motif in (II). (*c*) A schematic view of the NaCl packing motif in (I). Dark and light balls denote the centres of the cations and anions, respectively, and thin lines show cell edges.

Table 1
Selected geometric parameters (Å, °).

Er1—O11	2.292 (3)	Er2—O27	2.441 (3)
Er1—O13	2.347 (3)	Cr1—N15	1.993 (4)
Er1—O12	2.359 (3)	Cr1—N13	1.993 (4)
Er1—O14	2.382 (3)	Cr1—N11	1.996 (4)
Er2—O26	2.290 (3)	Cr1—N16	2.003 (4)
Er2—O28	2.292 (3)	Cr1—N12	2.008 (4)
Er2—O21	2.305 (3)	Cr1—N14	2.011 (4)
Er2—O25	2.307 (3)	Cr2—N21	1.999 (6)
Er2—O22	2.330 (3)	Cr2—N23	2.000 (5)
Er2—O24	2.401 (3)	Cr2—N22	2.003 (4)
Er2—O23	2.439 (3)	Cr2—N24	2.007 (6)
O11^i—Er1—O11	140.65 (16)	O26—Er2—O28	147.06 (11)
O11^i—Er1—O13^i	144.84 (11)	O26—Er2—O21	93.38 (11)
O11—Er1—O13^i	73.47 (11)	O28—Er2—O21	94.22 (11)
O11^i—Er1—O13	73.47 (11)	O26—Er2—O25	100.67 (11)
O11—Er1—O13	144.84 (11)	O28—Er2—O25	91.02 (11)
O13^i—Er1—O13	75.31 (15)	O21—Er2—O25	145.18 (11)
O11^i—Er1—O12	72.35 (11)	O26—Er2—O22	75.14 (11)
O11—Er1—O12	76.54 (12)	O28—Er2—O22	76.68 (11)
O13^i—Er1—O12	139.30 (10)	O21—Er2—O22	72.66 (11)
O13—Er1—O12	120.16 (11)	O25—Er2—O22	141.73 (11)
O11^i—Er1—O12^i	76.54 (11)	O26—Er2—O24	72.60 (11)
O11—Er1—O12^i	72.35 (11)	O28—Er2—O24	140.20 (11)
O13^i—Er1—O12^i	120.16 (11)	O21—Er2—O24	74.35 (11)
O13—Er1—O12^i	139.30 (10)	O25—Er2—O24	79.71 (11)
O12^i—Er1—O12^i	74.48 (15)	O22—Er2—O24	131.67 (11)
O11^i—Er1—O14	79.76 (11)	O26—Er2—O23	141.28 (10)
O11—Er1—O14	113.25 (11)	O28—Er2—O23	71.64 (11)
O13^i—Er1—O14	76.44 (10)	O21—Er2—O23	77.63 (11)
O13—Er1—O14	74.00 (10)	O25—Er2—O23	71.46 (11)
O12—Er1—O14	141.87 (10)	O22—Er2—O23	134.26 (11)
O12^i—Er1—O14	74.12 (10)	O24—Er2—O23	68.70 (10)
O11^i—Er1—O14^i	113.25 (11)	O26—Er2—O27	76.01 (11)
O11—Er1—O14^i	79.76 (11)	O28—Er2—O27	78.58 (11)
O13^i—Er1—O14^i	74.00 (10)	O21—Er2—O27	142.59 (10)
O13—Er1—O14^i	76.44 (10)	O25—Er2—O27	72.14 (11)
O12—Er1—O14^i	74.12 (10)	O22—Er2—O27	69.96 (11)
O12^i—Er1—O14^i	141.87 (10)	O24—Er2—O27	132.54 (10)
O14—Er1—O14^i	142.41 (14)	O23—Er2—O27	131.82 (11)

Symmetry code: (i) $-x + 2, y, -z + \frac{3}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3006). Services for accessing these data are described at the back of the journal.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N111—H11$K\cdots$S13	0.88	2.60	3.429 (4)	157
N141—H14$K\cdots$S21^{ii}	0.88	2.88	3.563 (4)	135
N131—H13$K\cdots$S21^{ii}	0.88	2.93	3.499 (7)	124
N231—H23$K\cdots$S22	0.88	2.72	3.445 (4)	141
N221—H22$K\cdots$S16	0.88	2.82	3.545 (4)	141
N241—H24$K\cdots$S11^{iii}	0.88	2.89	3.563 (4)	135
N261—H26$K\cdots$S11^{iii}	0.88	2.46	3.309 (4)	161
N271—H27$K\cdots$S23^{iii}	0.88	2.71	3.429 (4)	139
N121—H12$K\cdots$O14^i	0.88	2.19	2.864 (5)	133
N141—H14$K\cdots$O13^i	0.88	2.14	2.793 (5)	131
N211—H21$K\cdots$O23	0.88	2.03	2.801 (6)	145
N251—H25$K\cdots$O24	0.88	2.02	2.788 (5)	145
N271—H27$K\cdots$O25	0.88	2.29	2.904 (5)	127
N281—H28$K\cdots$O27	0.88	2.11	2.845 (5)	140

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

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