

- Perrin, A., Leduc, L. & Sergent, M. (1991). *Eur. J. Solid State Inorg. Chem.* **28**, 919–931.
- Perrin, A. & Sergent, M. (1988). *New J. Chem.* **12**, 337–355.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Speziali, N. L., Berger, H., Leicht, G., Sanjinés, R., Chapuis, G. & Lévy, F. (1988). *Mater. Res. Bull.* **23**, 1597–1604.
- Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). *The XRAY72 System*. Version of June 1972. Technical Report TR-192. Computer Science Center, University of Maryland, College Park, Maryland, USA.

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Ba₂ErCl₇

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Abstract

Dibarium erbium heptachloride has a network structure composed of ErCl₇ and BaCl₉ polyhedra. Since the array of the Ba and Er atoms is isostructural with the alloy Co₂Si, the structure can be considered as a stuffed Co₂Si-type structure. The mean bond distances are 2.704 Å for ErCl₇, 3.221 Å for Ba1Cl₉, and 3.212 Å for Ba2Cl₉. Some of the Cl atoms form tunnels running parallel to the *c* axis.

Comment

An efficient infrared-to-green up-conversion luminescence has been reported for ErCl₃–BaCl₂ compounds by Wang & Ohwaki (1993). In the systems RECl₃–BaCl₂ (*RE* = La, Sm, Gd and Yb), the presence of a 1:2 compound such as REBa₂Cl₇ is reported by Blachnik, Alberts & Enninga (1985). No detailed crystallographic information on the Ba–Er–Cl system has been reported so far. The present study has thus been undertaken in the course of a survey to find potent materials showing superior up-conversion properties.

The structure of Ba₂ErCl₇ is shown in Figs. 1 and 2. The Er and Ba atoms are coordinated by seven and nine Cl atoms, respectively. The ErCl₇ polyhedron is

surrounded by the Ba1Cl₉ and Ba2Cl₉ polyhedra to form a network. The mean Er–Cl distance in the ErCl₇ polyhedra is 2.704 Å, which is about 3.3% longer than reported for the ErCl₆ octahedra in Na₃ErCl₆ (2.616 Å;

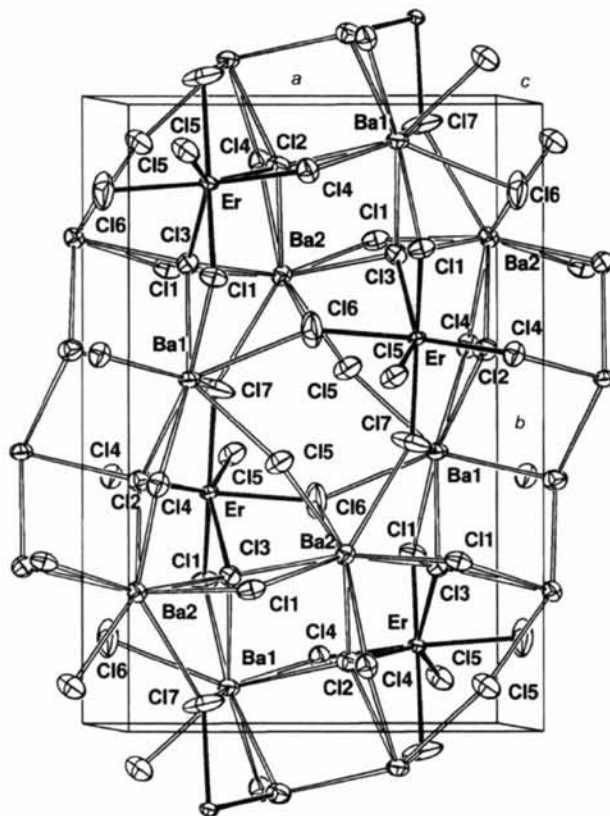


Fig. 1. The crystal structure of Ba₂ErCl₇ viewed approximately along the *c* axis. Displacement ellipsoids are shown at the 90% probability level.

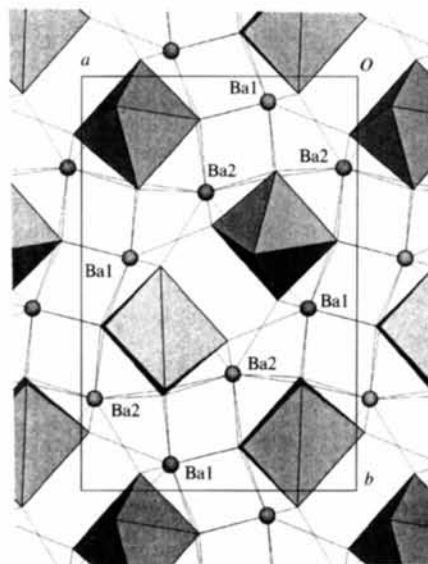


Fig. 2. The ErCl₇ polyhedra in Ba₂ErCl₇ viewed along the *c* axis.

Meyer, Ax, Schleid & Irmeler, 1987). The Cl5, Cl6 and Cl7 atoms form tunnels parallel to the *c* axis, as shown at the centre and at the origin in Fig. 1. The diameter of the tunnel is approximately 3.5 Å. Since the tunnel size is small, the Cl atoms by the tunnel wall are expected to have less charge than the fully ionized Cl⁻ anion in order to reduce their electrostatic repulsion. The presence of a tunnel composed of such Cl atoms may accelerate the reaction of the crystal with water, which can easily diffuse through the tunnel. This may be the reason why the crystal degrades rapidly in moist air.

The array of the Er and Ba cations is isostructural with Co₂Si (Geller & Wolontis, 1955), with Er atoms surrounded by six Ba atoms forming a trigonal prism, like Si in Co₂Si. In this respect, the structure of Ba₂ErCl₇ can be considered to be a stuffed Co₂Si-type structure.

Experimental

Er₂O₃ (purity 99.9%) and BaCl₂ (99.995%) were mixed in a 1:2 molar ratio of Er:Ba with carbon powder. The mixture was chlorinated at 1173 K under a Cl₂ atmosphere and sealed into a silica glass tube. Single crystals of 2.5–4.5 mm diameter and 50–200 mm length were obtained by the zone-melting technique.

Crystal data

Ba ₂ ErCl ₇	Mo <i>K</i> α radiation
<i>M_r</i> = 690.09	λ = 0.7107 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2 ₁ / <i>a</i>	θ = 23.31–25.02°
<i>a</i> = 10.500 (5) Å	μ = 16.16 mm ⁻¹
<i>b</i> = 15.507 (4) Å	<i>T</i> = 300 K
<i>c</i> = 6.804 (4) Å	Irregular
β = 90.48 (5)°	0.41 × 0.41 × 0.41 mm
<i>V</i> = 1107.8 (9) Å ³	Pink
<i>Z</i> = 4	
<i>D_x</i> = 4.138 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Rigaku AFC-5R diffractometer	2760 reflections with <i>F</i> > 3σ(<i>F</i>)
θ/2θ scans	<i>R</i> _{int} = 0.09
Absorption correction: refined from Δ <i>F</i> (Walker & Stuart, 1983)	θ _{max} = 35°
<i>T</i> _{min} = 0.020, <i>T</i> _{max} = 0.049	<i>h</i> = -14 → 14
12 921 measured reflections	<i>k</i> = -21 → 21
3193 independent reflections	<i>l</i> = -9 → 9
	4 standard reflections every 150 reflections
	intensity decay: none

Refinement

Refinement on <i>F</i>	(Δ/σ) _{max} = 0.001
<i>R</i> = 0.032	Δρ _{max} = 1.67 e Å ⁻³
<i>wR</i> = 0.029	Δρ _{min} = -2.75 e Å ⁻³
<i>S</i> = 1.527	Extinction correction: none
2760 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
91 parameters	
Weighting scheme based on measured s.u.'s	

Table 1. Selected bond lengths (Å)

Er ^I —Cl1 ^{II}	2.6953 (16)	Ba1—Cl2 ^{III}	3.2247 (18)
Er ^I —Cl2 ^{III}	2.7777 (16)	Ba1—Cl4 ^{IV}	3.2191 (17)
Er ^I —Cl3 ^{III}	2.7532 (16)	Ba1—Cl6 ^V	3.330 (2)
Er ^I —Cl4 ^{IV}	2.6986 (16)	Ba2 ^{IX} —Cl1 ^{II}	3.3081 (18)
Er ^I —Cl5 ^{IV}	2.7000 (19)	Ba2 ^{IX} —Cl5 ^{IX}	3.0755 (17)
Er ^I —Cl6 ^V	2.651 (2)	Ba2 ^{IX} —Cl3 ^{VIII}	3.1573 (17)
Er ^I —Cl7 ^{VI}	2.651 (2)	Ba2 ^{IX} —Cl6 ^V	3.295 (3)
Ba1—Cl1 ^{II}	3.1604 (17)	Ba2 ^{IX} —Cl7 ^{IX}	3.277 (2)
Ba1—Cl3 ^{III}	3.2105 (17)	Ba2 ^{IX} —Cl2 ^{VIII}	3.2197 (17)
Ba1—Cl4 ^{IV}	3.3152 (17)	Ba2 ^{IX} —Cl3 ^X	3.1509 (17)
Ba1—Cl5 ^{IV}	3.0743 (17)	Ba2 ^{IX} —Cl1 ^I	3.1605 (18)
Ba1—Cl2 ^{III}	3.2236 (16)	Ba2 ^{IX} —Cl4 ^{VIII}	3.2676 (17)
Ba1—Cl7 ^{VI}	3.233 (2)		

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

The maximum in the final difference map was at *x* = 0.731, *y* = 0.149, *z* = 0.879 and the minimum at the Er position.

Cell refinement: *Xtal3.4 LATCON* (Hall, King & Stewart, 1995). Data reduction: *Xtal3.4 ADDREF SORTRF*. Program(s) used to solve structure: *Xtal3.4 GENTAN*. Program(s) used to refine structure: *Xtal3.4 CRYLSQ*. Molecular graphics: *Xtal3.4 BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1137). Services for accessing these data are described at the back of the journal.

References

- Blachnik, R., Alberts, G. & Enninga, E. (1985). *Z. Anorg. Allg. Chem.* **522**, 207–216.
- Geller, S. & Wolontis, V. M. (1955). *Acta Cryst.* **8**, 83–87.
- Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). *Xtal3.4 Users Manual*. University of Western Australia, Australia.
- Meyer, G., Ax, P., Schleid, T. & Irmeler, M. (1987). *Z. Anorg. Allg. Chem.* **554**, 25–33.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Wang, Y. & Ohwaki, J. (1993). *J. Appl. Phys.* **74**, 1272–1278.