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Crystal Structure of Yb_5ErCl_{13} and Yb_6Cl_{13}

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The crystal structure of Yb_5ErCl_{13}, determined by a single-crystal structural analysis, has been refined in monoclinic space groups *C*2/*c* and *I*2/*a* (No. 15). Cell data (space group *C*2/*c*) are $a = 41.44$ (2) Å, $b = 6.537$ (5) Å, $c = 7.004$ (5) Å, and $\beta = 98.48$ (10)°, with $Z = 4$. Three-dimensional intensity data were collected by a Picker automated four-circle diffractometer with Zr-filtered Mo Kα radiation in the θ–2θ scan mode. Refinement was effected by full-matrix least-squares calculation and after absorption and extinction correction yielded at convergence $R = 0.032$ and $R_w = 0.039$ for the 1012 reflections with $F^2 > 3\sigma_{F^2}$ of the 1671 observed reflections. Since the location of the Er^{3+} atoms could not be determined uniquely, the true symmetry is assumed lower than that reported. Structural and cell data for isostructural Yb_6Cl_{13} for which only twinned crystals could be isolated are also reported. These two compounds are ascribed to a series of Vernier phases of the general formula M_nX_{2n+1} and represent the $n = 6$ member.

Introduction

Rare earth halide research has produced a plethora of phases in addition to the well-characterized trihalides and dihalides. Structural details of a number of subhalides with metal valence less than 2 and intermediate halides with effective metal valence between 2 and 3 have been reported, and from these reports an organized body of structural chemistry is developing.[1-10] We undertook the research described below in an attempt to determine the structure of a partially characterized ytterbium chloride phase of the reported composition $YbCl_{2.26}$,[12] but first found the composition to be in error, and subsequently were unable to prepare suitable crystals for structural analyses. Attempts to grow crystals of structurally related phases yielded excellent single crystals of the isostructural phase Yb_5ErCl_{13}. We report herein preparatory procedures for the phases Yb_5ErCl_{13} and Yb_6Cl_{13} ($YbCl_{2.167}$) and the structural details of the former. A preliminary report of the research was presented at the 12th Rare Earth Research Conference.[13]

Table I. Comparison of Lattice Parameters of $YbCl_2$, p-$YbCl_2$, and Yb_6Cl_{13}

	$YbCl_2$[a]	p-$YbCl_2$	Yb_6Cl_{13}	axial ratio, Yb_6Cl_{13}: p-$YbCl_2$
a, Å	6.948	6.958	6.958	1:1
b, Å	6.698	6.694	40.98	6.1:1
c, Å	13.139	13.075	6.537	1:2
γ, deg	90	90	91.9	
space group	*Pbca*	*Pbca*	*I*2/*a*	

[a] See ref 19.

Experimental Section

The trichlorides of ytterbium and erbium were prepared by the method of Taylor and Carter[14] and subsequently purified by high-vacuum sublimation as described by Cox and Fong.[15] Crude $YbCl_2$, prepared by the method of DeKock and Radtke,[16] was distilled twice from an inductively heated Ta crucible onto a chilled quartz target.

Preparation of Yb_6Cl_{13}. Three procedures were used. Method A: A 100-mg sample of $YbCl_3$ was sealed in quartz under a 600-torr pressure of H_2. The sample was heated to 1000 °C, cooled slowly to 500 °C, remelted by heating to 560–570 °C, and then cooled at 10°/h to 530 °C, from which temperature it was quenched. The contents of the ampule were dropped into an Ar-filled tube, which was evacuated immediately. The material was crushed in a glovebox, and unreacted $YbCl_3$ was removed by several washings with THF that had been refluxed over sodium and distilled. The product consisted of almost colorless to dark green 0.01–0.1-mm crystals. Chlorine content was determined gravimetrically as AgCl; metal content was determined from hydroxide precipitation and subsequent calcination to the sesquioxide. Anal. Calcd for Yb_6Cl_{13}: Yb, 69.3; Cl, 30.7. Found: Yb, $69._5$; Cl, $30._5$.

Method B: A 200-mg sample of $YbCl_3$ and the amount of Zn required for reduction to $YbCl_{2.2-2.5}$ were sealed in quartz under a 1-atm pressure of Ar. Reduction was effected as in method A, with heating to a maximum temperature of 1000 °C, slow cooling at 400 °C, subsequent remelting by heating to 470 °C, and slow cooling to 430 °C. Sample workup was as described in method A. Anal. Found: Yb, $69._8$; Cl, $30._2$.

Method C: A ~100-mg sample of $YbCl_2$ and a ~60-mg sample of $YbCl_3$ were sealed in quartz under 1 atm of Ar, heated to 800 °C, agitated to achieve mixing, cooled to 500 °C, and treated subsequently as described in method A. Anal. Found: Yb, $69._5$; Cl, $30._5$.

Preparation of Yb_5ErCl_{13}. Approximately 100 mg of $YbCl_2$ and ~60 mg of $ErCl_3$ were sealed in quartz under 1 atm of Ar. The quartz ampule was heated to 750 °C, agitated to ensure mixing, cooled rapidly to 550 °C, and then cooled at a rate of 5°/h to 450 °C. Sample workup as indicated in method A above yielded clear yellow crystals. Analysis for Yb was effected by dissolving the Yb–Er oxide mixture in HCl, evaporating the excess acid and determining Yb content polarographically.[17] Other analyses were effected as described above. Anal. Calcd for Yb_5ErCl_{13}: Cl, 30.9; Ln, 69.1; Yb, 57.9. Found: Cl, 30.9 ± 0.2; Ln, 69.9 ± 1.0; Yb, 58.4 ± 2.0.

Crystallographic Data. Yb_6Cl_{13}. The crystals of Yb_6Cl_{13} evidenced sharp extinctions under polarized light and decomposed slowly in air and rapidly in H_2O to yield a yellow solution. Some 30 crystals were examined by precession and Weissenberg techniques. The photographs indicated all the crystals were identical. The majority of the reflections could be indexed in terms of a monoclinic twin with $a = 41.42$ Å, $b = 6.539$ Å, $c = 6.953$ Å, and $\beta = 98.48°$, in space group *C*2/*c* or *Cc*; a second phase, orthorhombic space group *Pbca*, $a = 6.69$ Å, $b = 13.09$ Å, and $c = 6.96$ Å, was always present.[18] The space group and lattice parameters of this latter phase indicated it to be either $YbCl_2$ or closely related thereto.[19] It is designated p-$YbCl_2$ (p =

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Table II. Experimental Data for the X-ray Diffraction Study of Yb_5ErCl_{13}

(A) Crystal Parameters at 23 °C[a]

cryst system: monoclinic
space group: $C2/c$; No. 15
$a = 41.441$ (20) Å
$b = 6.537$ (5) Å
$c = 7.004$ (5) Å
$\beta = 98.49$ (10)°
$V = 1876$ Å^3
$Z = 4$
mol wt = 1493.4
ρ(calcd) = 5.28 g cm^{-3}
$\mu = 309$ cm^{-1}

(B) Measurement of Data

diffractometer: Picker FACS-I
radiation: Mo Kα ($\bar{\lambda} = 0.71073$ Å); Zr filter
detection: scintillation, pulse height analyzed
rflctns measd: $+h, +k, \pm l$
2θ range: 4–50°
scan type: θ–2θ
scan speed: 1° (2θ)/min
scan width: 1.2° (2θ) + $\alpha_1 - \alpha_2$
bckgrd count: 10 s at each end of scan
standard rflctns: 2,0,$\bar{2}$; 12,0,0; 0,2,0 measd after each 100 rflctns; no apparent decay in intensity
rflctns collected: 1694; 1671 independent, excluding standards

[a] Unit cell parameters derived from least-squares fit to the setting angles of the unresolved Mo Kα components of 12 reflections between 45 and 50° in 2θ: $\overline{41}$,1,5; $\overline{36}$,2,6; $\overline{31}$,1,7; $\overline{19}$,3,7; $\overline{17}$,5,5; 7,3,7; 7,5,5; 11,7,2; 14,4,6; 19,1,7; 26,2,6; 43,1,1.

pseudo). Overlap between the two lattices precluded separate data collection for each phase.

In an attempt to develop the structural relationships between p-$YbCl_2$ and Yb_6Cl_{13}, the standard $C2/c$ cell was converted into an equivalent I-centered monoclinic cell. We chose the first setting of the cell and for comparative purposes called the long axis b. New axes were derived from the following transformations where the subscript i indicates the $I2/a$ cell, and the subscript c the standard $C2/c$ cell:

$$a_i = -c_c \qquad b_i = a_c + c_c \qquad c_i = -b_c$$

with a subsequent origin shift of 0, 0, $^1/_2$. The oblique angle of the transformed cell, $\gamma = 91.9°$, indicates an almost orthogonal cell closely related to that of p-$YbCl_2$ as is indicated in Table I. The data suggest that this Yb_6Cl_{13} phase can be envisioned as a stack of six half-cells of $YbCl_2$. These six subunits, each comprised of four formula units of $YbCl_2$, yield an overall composition of $Yb_{24}Cl_{48}$ in contrast with the calculated composition of $4 \times Yb_6Cl_{13} = Yb_{24}Cl_{52}$. The observation that the b axis in Yb_6Cl_{13} is slightly larger than 6 times the length of that of p-$YbCl_2$ is consistent with the need to accommodate additional chloride ions.

Our inability either to find a true single crystal or to solve the structure on the basis of the fragmentary data we could collect caused us to seek an isostructural phase.

Yb_5ErCl_{13}. The initial 23 crystals examined were twinned; the 24th was of excellent quality, and a set of diffraction data was collected on a crystal 0.12 × 0.05 × 0.07 mm. Details of the data collection are presented in Table II. Lorentz and polarization corrections were applied.[20] Trial metal atomic parameters were deduced from a model structure based on p-$YbCl_2$ (see Table I). Initial refinement was effected in space group Cc since no reasonable way to accommodate four formula units of Yb_5ErCl_{13} in a centrosymmetric space group could be found. Scattering factors for Yb^{2+}[21] were used for all three metal atoms; isotropic B parameters of 1.5 Å^2 and unit weighting yielded upon refinement[20] $R = 0.31$ for 1024 reflections with $F^2 > 3\sigma_{F^2}$, with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. Twelve Cl atoms were found from the difference Fourier synthesis; but a structural model that included them would not refine, and further calculations indicated one metal atom was misplaced. A second difference Fourier revealed the proper location of the misplaced metal atom, and subsequent refinement of metal atom positional parameters with B fixed yielded $R = 0.19$.

From a third difference synthesis, the locations of the 13 chlorine atoms were determined; refinement of the complete structure with scattering factors for Cl^- and Yb^{2+} ions[21] yielded $R = 0.064$ with isotropic temperature factors and unit weights. High correlation between the positional parameters of certain parts of atoms along with some negative or unreasonably high temperature factors indicated a high degree of centrosymmetry; subsequent refinement in centrosymmetric space group $C2/c$ with anisotropic temperature factors and individual weights equal to $1/\sigma_F{}^2$ and $\sigma_F = (F/2I)\sigma_I$ (with $I = P - C[10(B + 1)]$ and $\sigma_I{}^2 = P + C^2(B) + [D(P - B)]^2$, in which P is the integrated count, B is the measured background, C is the ratio of total peak counting time to background count time, and D is a 2% instrument drift factor) eliminated correlation and temperature factor problems and yielded $R = 0.058$.

An absorption correction was now applied to the data.[20] Because the crystal vertices were difficult to measure through the glass capillary, minor adjustments were made to the measurements with subsequent refinement with isotropic temperature parameters. The discrepancy index, R, reached a minimum of 0.049 after correction for absorption and subsequent parameter adjustment. The absorption correction factor varied from 3.220 to 5.495, with an average value of 3.655, which was used for rescaling the corrected values.

In the final cycles of refinement, the scattering factor of Yb^{2+} was used for metal position 2 as designated in Table III and the figures; a hypothetical scattering factor $[(3F_{Yb^{2+}} + F_{Er^{3+}})/4]$ was used for the remaining metal positions. A secondary extinction correction was applied by application of the equation $I_c/I_o = 1 + 2gI_c$.[22] The I_c and I_o values were derived from the respective F_c and F_o values obtained after isotropic refinement; g was derived by least-squares fit of the data. For 46 reflections with $F_o > 80$, $g = 2.284 \times 10^{-6}$; for all 1012 reflections, $g = 2.114 \times 10^{-6}$. A corrected intensity I_o(cor) computed according to $I_o(\mathrm{cor}) = I_o(1 + 2gF_c{}^2Lp)$ was applied only to the reflections with $F_o > 80$. The final refinement cycles were effected with the program CRYLSQ (1971 version) on the Karlsruhe Univac 1108.[20]

In the final cycle of refinement, the ratio of shift/esd was less than 0.08, the greatest shift being 0.02 in the anisotropic thermal parameters. The final values, $R = 0.032$ and $R_w = 0.039$, were obtained upon refinement with anisotropic temperature factors and with inclusion of a dispersion correction. Final positional and thermal parameters are tabulated in Table III.

Selected interatomic distances are presented in Table IV, and ORTEP drawings of the molecule, in space group $I2/a$, are presented in Figures 1 and 2.

In the final difference Fourier the largest peak, 1.60 e Å^{-3}, is located at $^1/_2$, 0, 0.47 in the I-centered cell, almost in the center of the Cl(1) atom cage where the structure folds. Hamilton's test, applied to determine if the anisotropic temperature factors are significant, yielded $\mathcal{R}(48,925,0.005) = 1.0414$ for the hypothesis that all atoms vibrate isotropically and $\mathcal{R}(33,925,0.005) = 1.0311$ for the hypothesis that only the chlorides vibrate isotropically.[23] Thus, the anisotropic thermal parameters are considered meaningful.

Discussion

The considerable effort expended to grow single crystals of Yb_6Cl_{13} was fruitless; only crystals that exhibited the "double phase" could be grown. When it became apparent that isostructural phases should be sought, substitution of Ca^{2+} (r = 1.20 Å, CN = 7) for Yb^{2+} (r = 1.22 Å; CN = 7) was unsuccessful and substitution of Lu^{3+} (r = 1.001 Å, CN = 6) for Yb^{3+} (r = 1.008 Å, CN = 6) produced nonisotypic crystals; substitution of Er^{3+} (r = 1.030 Å, CN = 6) yielded excellent isotypic crystals.[24]

The structure of Yb_6Cl_{13} may differ slightly from that of Yb_5ErCl_{13}. The monoclinic unit cell listed in Table I may actually represent only a basic subunit of a very long periodic

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Table III. Positional and Anisotropic Thermal Parameters (with Esd's) for Yb_5ErCl_{13},[a] in Space Group *C*2/*c*

atom	*x*	*y*	*z*	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
M(1)	0.20421 (2)	0.77451 (15)	0.62527 (12)	15.6 (5)	14.5 (5)	14.8 (5)	−0.05 (42)	2.5 (4)	1.4 (4)
Yb(2)	0.12054 (2)	0.77154 (15)	0.15104 (13)	20.1 (5)	15.4 (5)	13.8 (4)	1.4 (4)	2.4 (4)	2.7 (4)
M(3)	0.03981 (2)	0.76830 (13)	0.49039 (13)	18.3 (5)	15.2 (5)	13.2 (4)	0.2 (5)	3.9 (3)	0.4 (5)
Cl(1)	0.2428 (1)	0.9819 (9)	0.3874 (9)	26 (3)	28 (3)	31 (3)	3 (2)	14 (3)	12 (3)
Cl(2)	0.1800 (1)	0.5701 (8)	0.2844 (8)	21 (3)	28 (3)	16 (3)	2 (2)	−3 (2)	−9 (2)
Cl(3)	0.1623 (1)	0.9445 (8)	0.9016 (4)	18 (3)	25 (3)	16 (3)	−0.3 (22)	5 (2)	5 (2)
Cl(4)	0.1052 (1)	0.6038 (8)	0.4868 (8)	31 (3)	22 (3)	23 (3)	7 (2)	10 (3)	13 (2)
Cl(5)	0.0800 (1)	0.9366 (7)	0.8194 (8)	13 (2)	21 (2)	21 (2)	3 (2)	2 (2)	−5 (2)
Cl(6)	0.0341 (2)	0.6194 (9)	0.1219 (9)	63 (5)	28 (3)	22 (3)	4 (3)	1 (3)	−9 (3)
Cl(7)	0	0.9404 (10)	0.75	13 (4)	17 (4)	27 (4)		6 (3)	

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + ... + 2a^*b^*U_{12}hk + ...)]$.

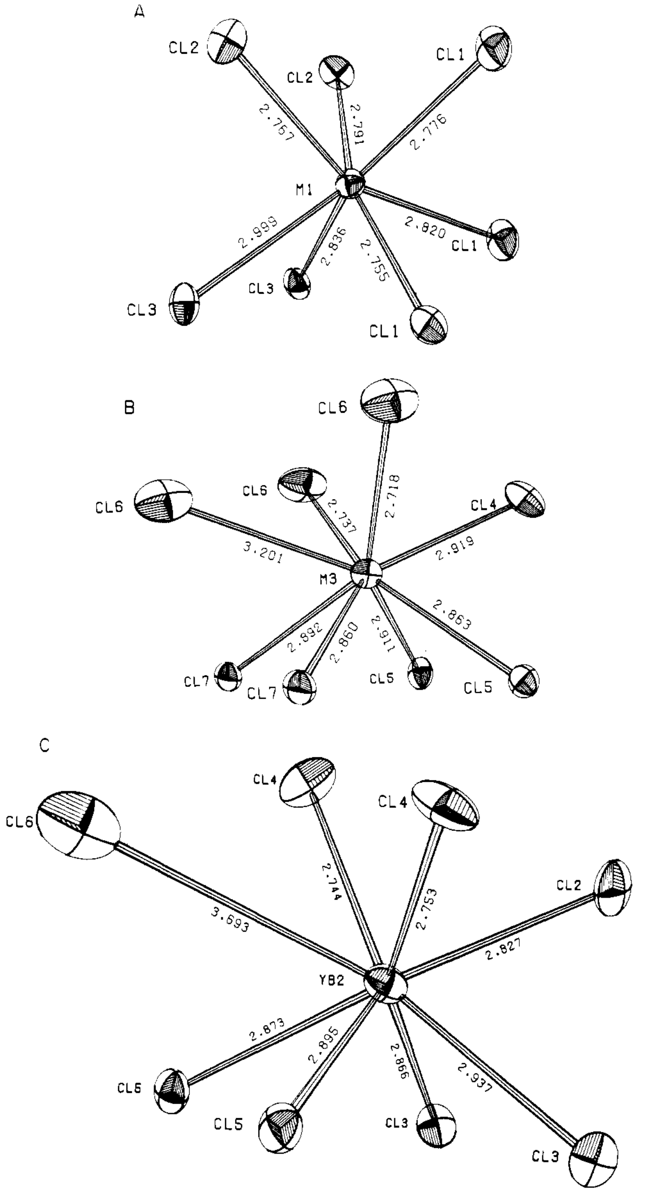

Figure 1. ORTEP drawings that illustrate the anion coordination around the three metal sites in Yb_5ErCl_{13}. The ellipsoids are presented at the 60% probability level.

superstructure with a *b* axis several times the stated value of 40.98 Å (see Table I), similar to some of the very long periodic structures found in the $YOF-YF_3$ system.[25] This suspicion is based upon the observation that sometimes a very small splitting of 0*kl* reflections occurs parallel to [001]* (*I*2/*a*).

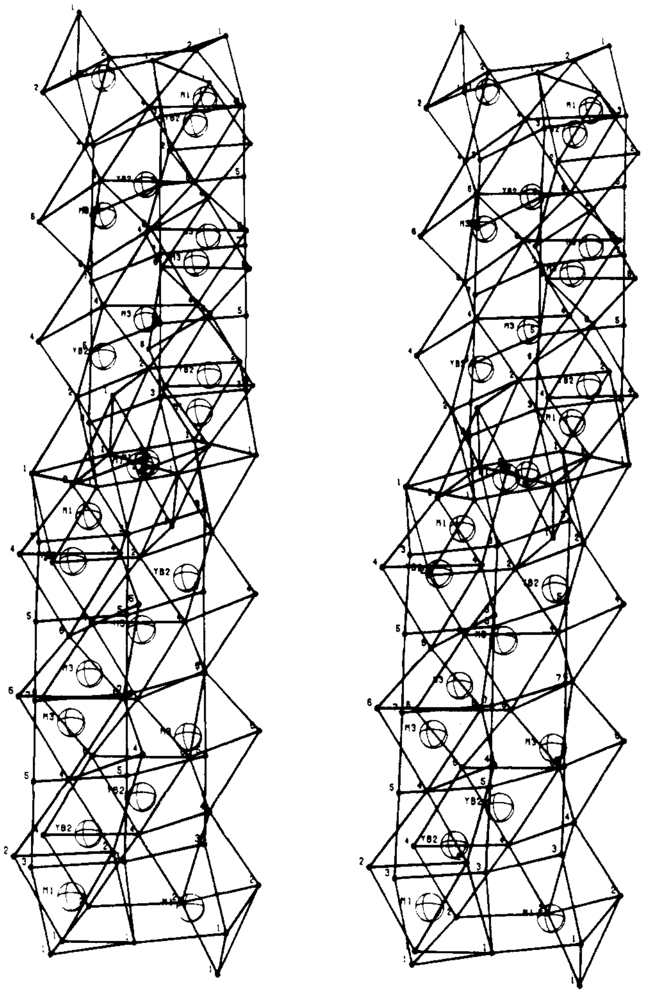

Figure 2. An ORTEP stero illustration of the unit cell of Yb_5ErCl_{13} in space group *I*2/*a* viewed down the *c* axis. The lines connect anion sites in a way that emphasizes the rectangular and the distorted hexagonal nets. Individual numbers adjacent to the apices correspond to chlorine atom numbers.

An alternate explanation for this splitting is an incomplete overlap of the two twin lattices of Yb_6Cl_{13} which should theoretically coincide exactly in the 0*kl* plane. A deviation from this coincidence might be caused either by a minute triclinic distortion of the monoclinic cell or by a small tilt between the two monoclinic lattices due to a small angle involved in the intergrowth of Yb_6Cl_{13} and p-$YbCl_2$.

The structure depicted in Figure 2 illustrates the folding of the anion nets at regular intervals to accommodate the insertion of the extra halide ions. Each anion layer consists of a series of rectangular nets (Schlaefli symbol 4^4), an interchange net, and then a series of severely distorted hexagonal nets (Schlaefli symbol 3^6). The planes of nets are stacked so

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Table IV. Selected Interatomic Distances (Å) in Yb_5ErCl_{13}

M(1)–Cl(1)	2.820 (7)
–Cl(1)	2.776 (6)
–Cl(1)	2.755 (6)
–Cl(2)	2.791 (6)
–Cl(2)	2.767 (6)
–Cl(3)	2.836 (6)
–Cl(3)	2.999 (6)
Yb(2)–Cl(2)	2.827 (6)
–Cl(3)	2.866 (6)
–Cl(3)	2.937 (6)
–Cl(4)	2.753 (6)
–Cl(4)	2.744 (6)
–Cl(5)	2.873 (6)
–Cl(5)	2.895 (6)
–Cl(6)	3.693 (8)
M(3)–Cl(4)	2.920 (6)
–Cl(5)	2.911 (6)
–Cl(5)	2.863 (6)
–Cl(6)	2.736 (6)
–Cl(6)	2.719 (6)
–Cl(6)	3.201 (6)
–Cl(7)	2.860 (4)
–Cl(7)	2.892 (5)
Cl(1)–Cl(1)	3.855 (9)
–Cl(1)	3.510 (9)
–Cl(1)	3.884 (9)
–Cl(1)	3.430 (9)
–Cl(2)	3.740 (8)
–Cl(2)	3.673 (9)
–Cl(2)	3.630 (9)
–Cl(3)	3.385 (9)
Cl(2)–Cl(2)	3.620 (8)
–Cl(3)	3.624 (8)
–Cl(3)	3.385 (8)
–Cl(3)	3.564 (8)
–Cl(4)	3.651 (8)
–Cl(4)	3.598 (9)
Cl(3)–Cl(3)	3.576 (8)
–Cl(4)	3.884 (8)
–Cl(5)	3.373 (8)
Cl(4)–Cl(4)	3.756 (8)
–Cl(5)	3.468 (8)
–Cl(5)	3.324 (7)
–Cl(5)	3.830 (7)
–Cl(6)	3.605 (10)
–Cl(6)	3.539 (10)
Cl(5)–Cl(5)	3.593 (9)
–Cl(6)	3.620 (8)
–Cl(6)	3.694 (9)
–Cl(7)	3.280 (6)
Cl(6)–Cl(6)	3.834 (9)
–Cl(6)	3.454 (10)
–Cl(6)	3.567 (12)
–Cl(7)	3.386 (9)
–Cl(7)	3.479 (8)
Cl(7)–Cl(7)	3.588 (3)

that a 3^6 section overlays a 4^4 section. Structures such as this in which stoichiometric changes can be accommodated by an alteration of anion density in the nets have been classified as Vernier structures and have been discussed in detail.[26] This structure differs from those described by Hyde et al., however, in that in this structure a folding occurs; in the true Vernier structure, folding does not occur in the unit cell as the extra atoms are in only one layer.

In the $I2/a$ presentation (Figure 2), the lower anion layer ($0 \leq y \leq {}^1/_2$) is seen to consist of a rectangular net, while the upper layer is a triangular net. The 3^6 net is considerably longer than the 4^4 counterpart (ratio = 0.91:1), and it is this greater length that probably causes net inversion at $y = {}^1/_2$. The dimensions of the 4^4 net of this structure are almost identical with those of the 4^4 net in $YbCl_2$; thus, the great difference between this compound and $YbCl_2$ lies in the 3^6 nets. This observation implies that when an M^{2+} ion in $YbCl_2$ is replaced by M^{3+}, the extra charge is compensated in the 3^6 anion net yielding the nonstoichiometric halide.

Since the unit cell of Yb_5ErCl_{13} contains only four formula units, refinement in a centrosymmetric space group with three heavy atoms in eightfold general positions leads necessarily to a structure in which one (or more) eightfold position is occupied by both Er and Yb atoms. The coordination numbers of M(1), M(2), and M(3) are 7 (6 + 1), 7, and 8 (7 + 1), respectively. The polyhedra can be described as capped octahedron, trigonal base–tetragonal base, and distorted square antiprism.[27] There is no obvious polyhedron that can be assigned by inspection as a possible Er site. A comparison of the cavity sizes (calculated by subtracting the chloride ion radius, 1.81 Å, from the average bond distances[24]) is inconclusive. But selection of M(1) and M(3) for Er sites is supported by high thermal values of the adjacent atoms Cl(1) and Cl(6). Evidence obtained from electrostatic bond strength calculations[28] indicated M(3) and possibly M(1) to be the most probable sites for Er/Yb. These calculations yielded a charge compensation of 2.19, 2.04, and 2.32 for the three sites, respectively. The largest single contribution to these values is from the very short M(3)–Cl(6) bond, whose distance is significantly shorter than the smallest distances of the two other polyhedra and shortest distance in $YbCl_2$ (2.76 Å). Carter's Voroni volume calculations of the three metal atom sites are 20.72, 21.03, and 19.29 Å^3, respectively. In comparison, the Voroni atomic volume calculated for Yb(II) in $YbCl_2$ is 21.24 Å^3 and that for the Ho(III) in $HoCl_3$, calculated on the basis of the YCl_3 structure type, is 18.03 Å^3, strongly supporting the M(3) site as the principal location of the Er atom.[29] As a consequence, the M(2) site has been designated as a Yb atom site and M(1) and M(3) are regarded as Yb/Er sites, with M(3) the principal Er site.

If the apparent statistical distribution of the Er atoms in M(1) and M(3) is incorrect, assignment to space group $C2/c$ ($I2/a$) cannot be justified since the fixing of the Er atom on any of the possible sites reduces the structure to one of lower symmetry. An alternate space group would be Cc (Ia), and M(3) would have to be regarded as the correct Er position. A model that does not require the glide plane lowers the symmetry to that of triclinic space group $P1$ ($I1$). This space group would allow single isolated Er atoms in any of the metal atom sites. Although in theory this space group accounts for all the evidence gathered against space group $I2/a$, i.e., M(1) and M(3) both evidence a higher than 2.0 calculated nuclear charge and smaller Voroni volumes than Yb(2), Cl atoms Cl(1) and Cl(6) adjacent to M(3) show high temperature factors, and Yb_6Cl_{13} shows a possible triclinic distortion, the structure does not refine well. Therefore, we conclude that the metal atoms are statistically oriented principally in position M(3).

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Supplementary Material Available: Listings of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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