N1—P11—Cl13	113.59 (12)	Cl15—P11—Cl14	107.09 (6)
N1—P11—Cl15	112.87 (12)	Cl18—P12—Cl16	107.34 (6)
N1—P12—Cl16	112.81 (12)	Cl18—P12—Cl17	107.13 (6)
N1—P12—Cl17	113.97 (12)	Cl20—P21—Cl19	107.64 (6)
N2—P21—Cl19	113.34 (12)	Cl20—P21—Cl21	107.06 (6)
N2—P21—Cl21	112.76 (12)	Cl22—P22—Cl23	107.57 (6)
N2—P22—Cl23	113.68 (12)	Cl22—P22—Cl24	106.80 (6)
P12—N1—P11—Cl14	−178.3 (2)	P22—N2—P21—Cl20	−176.0 (2)
P11—N1—P12—Cl18	−174.0 (2)	P21—N2—P22—Cl22	178.3 (2)

All atoms were refined with anisotropic displacement parameters without any constraints.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1304). Services for accessing these data are described at the back of the journal.

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Tricaesium Tetraiodozincate(II) Iodide, Cs_3ZnI_5

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Abstract

Cs_3ZnI_5 is isotypic with Cs_3CoI_5, $(NH_4)_3ZnCl_5$ and Cs_3HgCl_5. The structure consists of distorted $[ZnI_4]^{2-}$ tetrahedra and chains of face-sharing $[Cs_6I]^{5+}$ octahedra parallel to the x axis. The ninefold coordination around one Cs^+ ion is best described as a quadratic antiprism with one of the basal faces centred. The other Cs^+ ion is coordinated by eight I^- ions in the form of a strongly truncated 'bisdisphenoid'.

Comment

For halogenides of type A_3BX_5 (A = Cs, NH_3; B = Co, Zn, Hg; X = Cl, Br, I), two different structure types are known. Cs_3CoCl_5 (Powell & Wells, 1935; Figgis *et al.*, 1964, 1980; Williams *et al.*, 1980; Reynolds *et al.*, 1981) and Cs_3CoBr_5 (Figgis & Reynolds, 1981) crystallize with tetragonal symmetry in space group *I4/mcm*, whereas $(NH_4)_3ZnCl_5$ (Klug & Alexander, 1944; Schmitz, 1981), Cs_3HgCl_5 (Clegg *et al.*, 1976) and Cs_3CoI_5 (Städel & Seifert, 1978) have orthorhombic symmetry with space group *Pnam* (see Table 3). In both structure types, the B cation is tetrahedrally coordinated by the X^- anions; additionally, isolated X^- ions are surrounded by six A cations in the form of a slightly distorted octahedron.

A detailed comparison between $(NH_4)_3ZnCl_5$ and Ba_3SiS_5 has been given by Schmitz (1981), who pointed out the close relationship between orthorhombic A_3BX_5 compounds and Ge_3Rh_5.

During our investigations on A_2BX_4 compounds of the β-K_2SO_4 type, we obtained crystals of Cs_3ZnI_5. Their existence was first reported by Billesbach & Ullman (1992, 1993), who confirmed the orthorhombic symmetry and gave a brief description of the structure. Since no coordinates or further details were given by the authors, we decided to refine the crystal structure.

The structure of Cs_3ZnI_5 is isotypic with $(NH_4)_3$-$ZnCl_5$ (Klug & Alexander, 1944; Schmitz, 1981), Cs_3HgCl_5 (Clegg *et al.*, 1976) and Cs_3CoI_5 (Städel & Seifert, 1978). The *ab* projection of the structure of Cs_3ZnI_5 is shown in Fig. 1, with the *bc* projection shown in Fig. 2. Apart from Cs1 and I4, all ions lie on the mirror plane perpendicular to *c*.

The Zn^{2+} ions are coordinated by four I^- ions in the form of slightly distorted tetrahedra, with symmetry *m* and Zn—I distances ranging from 2.594 (1) to 2.620 (2) Å (see Table 2). The average Zn—I distance (2.602 Å) is significantly shorter than the sum of the ionic radii (2.800 Å; Shannon, 1976) indicating the covalent character of the Zn—I bonds. The average separation of the I^- ions within the tetrahedra is 4.246 Å, which corresponds well to the sum of the ionic radii (4.120 Å).

Around the isolated I3 ion, which does not form part of the tetrahedra, the Cs^{2+} ions form a slightly distorted octahedron (Fig. 2 and Table 2). Neighbouring $[Cs_6I]^{5+}$ octahedra share common faces and thus form chains of composition $[I_2Cs_6]^{4+}_{\infty}$ parallel to the x axis (Fig. 1).

The Cs1 ion is coordinated by 7+2 I^- ions in the form of a strongly distorted quadratic antiprism with one of the basal planes centred. The Cs1—I distances range from 3.798 (1) to 4.312 (2) Å; the Zn^{2+} ion is nearer to the Cs1 ion than the two most weakly

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bonded I^- ions [Cs1—Zn^{IV} 4.196 (2) Å]. The $[Cs2I_8]^{7-}$ polyhedron can be described as a strongly truncated 'bisdisphenoid', a coordination polyhedron that results from the joining of two disphenoids with a common $\bar{4}$ axis and ideal symmetry $\bar{4}2m$ (Hoard & Silverton, 1963). The symmetry of the polyhedron is reduced to m, the Cs2—I distances lie between 3.747 (2) and 3.992 (2) Å.

Resulting bond valence sums for the two A cations are 0.8 (Cs1) and 1.329 (Cs2). Comparison with other A_3BX_5 compounds shows similar bond valence sums in each case (see Table 3), even for the tetragonal Cs_3CoCl_5. The bond valence sum for the cation with higher coordination number (which is incorporated in the larger coordination polyhedron) is always smaller than the ideal value of one, while the cation with smaller coordination number (which is situated in the smaller coordination polyhedron) has bond valence sums greater then one. A similar behaviour was observed in A_2BX_4 compounds (see, for example, Fábry & Pérez-Mato, 1994) and probably plays an important role in the tendency of these compounds to undergo phase transitions. A comparison of the structures of orthorhombic A_3BX_5 and A_2BX_4 compounds is given in Friese *et al.* (1998).

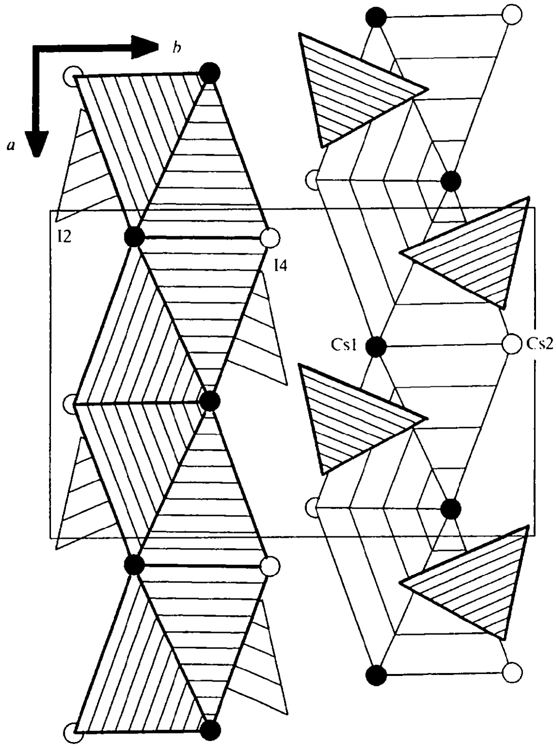

Fig. 1. An *ab* projection of the structure of Cs_3ZnI_5. $[Cs_6I]^{5+}$ octahedra and $[ZnI_4]^{2-}$ tetrahedra are drawn. Polyhedra around atoms at $z = \frac{3}{4}$ are drawn in thick lines, polyhedra around atoms at $z = \frac{1}{4}$ are drawn in thin lines.

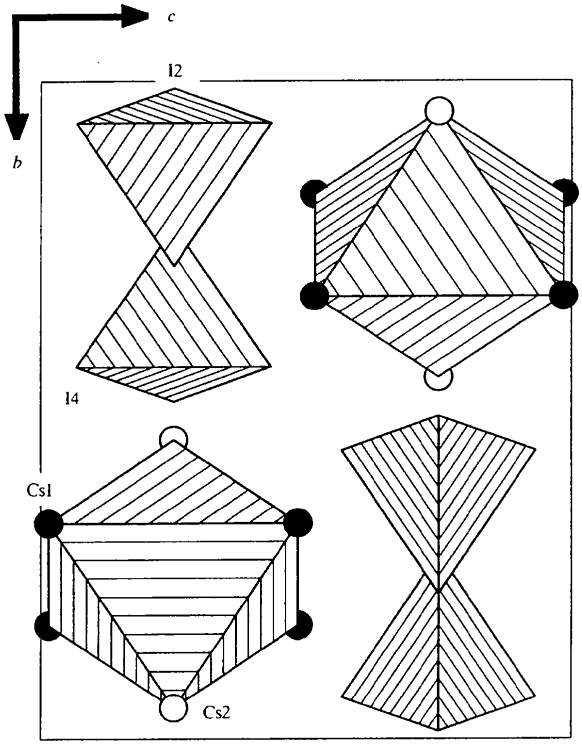

Fig. 2. A *bc* projection of the structure of Cs_3ZnI_5. $[Cs_6I]^{5+}$ octahedra and $[ZnI_4]^{2-}$ tetrahedra are shown.

Experimental

Crystals of the title compound were grown by slow evaporation (303 K, 3–4 weeks, in darkness) from an aqueous solution containing a stoichiometric molar ratio of CsI and ZnI_2. Depending on pH, the majority of the crystals were of the type Cs_3ZnI_5 (pH 2) or Cs_2ZnI_4 (pH 6). Crystals of Cs_3ZnI_5 can be easily distinguished since they show a pronounced hexagonal morphology.

Crystal data

Cs_3ZnI_5
$M_r = 1098.60$
Orthorhombic
Pnam
$a = 9.952$ (3) Å
$b = 14.687$ (2) Å
$c = 11.599$ (5) Å
$V = 1695.3$ (9) Å^3
$Z = 4$
$D_x = 4.304$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–16.6°
$\mu = 16.858$ mm^{-1}
$T = 293$ (2) K
Hexagonal prism
0.36 × 0.31 × 0.29 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Petricek & Dusek, 1996)
$T_{min} = 0.142$, $T_{max} = 0.458$
5137 measured reflections
1408 independent reflections

1274 reflections with $I > 2\sigma(I)$
$R_{int} = 0.095$
$\theta_{max} = 23.98°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -13 \rightarrow 13$
3 standard reflections every 400 reflections intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.1312$
$S = 1.127$
1408 reflections
50 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1025P)^2 + 4.8227P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.870$ e Å^{-3} (at 0.96 Å from I3)
$\Delta\rho_{\min} = -2.313$ e Å^{-3} (at 1.10 Å from I2)
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0025 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Cs1	0.41864 (8)	0.67225 (6)	0.01559 (7)	0.0488 (4)
Cs2	0.41189 (10)	0.95281 (7)	1/4	0.0376 (4)
Zn1	0.3120 (2)	0.39343 (12)	1/4	0.0323 (5)
I1	0.36317 (14)	0.21981 (8)	1/4	0.0532 (4)
I2	0.03461 (11)	0.01140 (7)	1/4	0.0409 (4)
I3	0.16945 (10)	0.73626 (8)	1/4	0.0415 (4)
I4	0.18880 (8)	0.43648 (6)	0.06062 (6)	0.0459 (4)

Table 2. *Selected geometric parameters (Å, °)*

Cs1—I3	3.7983 (14)	Cs2—I2$^{\rm vi}$	3.852 (2)
Cs1—I2$^{\rm i}$	3.9099 (15)	Cs2—I4$^{\rm vii}$	3.8811 (14)
Cs1—I3$^{\rm ii}$	3.9279 (14)	Cs2—I1$^{\rm vi}$	3.951 (2)
Cs1—I2$^{\rm iii}$	3.9999 (14)	Cs2—I3	3.992 (2)
Cs1—I1$^{\rm iv}$	4.089 (2)	Zn1—I4	2.5939 (14)
Cs1—I4$^{\rm v}$	4.1212 (13)	Zn1—I1	2.600 (2)
Cs1—I4	4.1827 (13)	Zn1—I2$^{\rm iii}$	2.620 (2)
Cs1—Zn1$^{\rm iv}$	4.196 (2)	I1—I4	4.238 (2)
Cs1—I1$^{\rm i}$	4.224 (2)	I1—I2$^{\rm iii}$	4.297 (2)
Cs1—I4$^{\rm iv}$	4.312 (2)	I4—I2$^{\rm iii}$	4.154 (2)
Cs2—I4$^{\rm v}$	3.747 (2)	I4—I4$^{\rm viii}$	4.393 (1)
Cs2—I3$^{\rm ii}$	3.779 (2)		
I4—Zn1—I4$^{\rm viii}$	115.75 (8)	Cs1—I3—Cs1$^{\rm viii}$	91.42 (4)
I4—Zn1—I1	109.37 (5)	Cs2$^{\rm ix}$—I3—Cs1$^{\rm x}$	79.65 (3)
I4—Zn1—I2$^{\rm iii}$	105.65 (5)	Cs1—I3—Cs1$^{\rm x}$	90.23 (3)
I1—Zn1—I2$^{\rm iii}$	110.95 (7)	Cs1$^{\rm viii}$—I3—Cs1$^{\rm x}$	174.32 (3)
Cs2$^{\rm ix}$—I3—Cs1	105.13 (3)	Cs2$^{\rm ix}$—I3—Cs2	174.48 (4)

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

Table 3. *Bond valence sums (according to Brese & O'Keeffe, 1991) for A_3BX_5 compounds.*

	$A1$	$A2$	B	Space group
Cs_3HgCl_5^{a}	0.802	1.235	2.446	*Pnam*
Cs_3HgBr_5^{b}	0.827	1.340	2.458	*Pnam*
Cs_3ZnI_5^{c}	0.800	1.329	2.080	*Pnam*
Cs_3CoI_5^{d}	0.846	1.293	2.165	*Pnam*
Cs_3CoCl_5^{e}	0.704	1.106	2.007	*I4/mcm*

References: (*a*) Clegg *et al.* (1976); (*b*) Pakhomov *et al.* (1978); (*c*) this work; (*d*) Stäudel & Seifert (1978); (*e*) Williams *et al.* (1980).

The computations were carried out using the program *SHELXL*93 (Sheldrick, 1993) with the coordinates of Cs_3CoI_5 (Stäudel & Seifert, 1978) as a starting model. The existence of reflections violating the glide planes and the high anisotropic displacement parameters of some of the atoms suggested a lower symmetry of the structure. Refinement was therefore also tested in $Pna2_1$, $P\bar{1}$ and $P1$. It was not possible in any of these space groups to lower the anisotropic displacement parameters. Furthermore, the resulting $R(F)$ value in $P\bar{1}$ and $P1$ for the reflections violating the glide planes was not smaller than 0.5, indicating that none of the refined models was able to reproduce satisfactorily the intensities of these 'forbidden reflections'. Space group *Pnam* was therefore assumed to be correct. Face-indexing (distances in mm) as used in the absorption correction: $\bar{6}\bar{2}\bar{1}$ 0.18, 621 0.18, $1\bar{2}\bar{2}$ 0.145, 032 0.145, $01\bar{1}$ 0.155, $0\bar{1}1$ 0.155. The largest feature of residual electron density was 0.96 Å from I3.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *JANA*96 (Petricek & Dusek, 1996). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *STRUPLO*84 (Fischer, 1984).

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