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Structure of Rubidium Tetrachlorozincate(II), $Rb_2[ZnCl_4]$

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Abstract. $M_r = 378\cdot12$, orthorhombic, *Pnma*, $a = 9\cdot2636\ (6)$, $b = 7\cdot2859\ (11)$, $c = 12\cdot7193\ (13)$ Å, $V = 858\cdot5\ (2)$ Å^3, $Z = 4$, $D_x = 2\cdot925$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 150\cdot59$ cm^{-1}, $T = 295$ K, $R = 0\cdot037$ for 689 observed reflections. The compound is isostructural with $Cs_2[ZnBr_4]$. The $ZnCl_4^{2-}$ ion assumes a distorted tetrahedral geometry with the Zn and two Cl atoms occupying positions on the mirror plane along with the Rb^+ cations.

Introduction. Recent interest in the physical properties of tetrahalogenzincates has prompted an accurate structural determination of the title compound. The ferroelectricity of $Rb_2[ZnCl_4]$ has been studied by Sawada, Shiroishi, Yamamoto, Takashiga & Matsuo (1977) who have considered *Pmcn* to be the space group at room temperature and the unit-cell axes to be as in NH_4LiSO_4 and $RbLiSO_4$ where $b = \sqrt{3}a$. Our findings indicate agreement with the space-group assignment of *Pmcn* (conventionally *Pnma*) at room temperature and the axial lengths we have determined are commensurate with those suggested by Sawada *et al.*

Experimental. Single crystals of $Rb_2[ZnCl_4]$ grown by evaporation of an aqueous solution of $RbCl{:}ZnCl_2$, mixed stoichiometrically; absence conditions on precession photographs ($0kl$: $k + l = 2n + 1$ and $hk0$: $h = 2n + 1$) indicated *Pnma* or $Pn2_1a$, CAD-4 diffractometer, Mo $K\alpha$ radiation, ω–$(\frac{5}{3})\theta$ scans, $0 < \theta \leq 27\cdot5°$, ω speeds from 1·34 to 10·06° min^{-1}, ω-scan angle $(0\cdot65 + 0\cdot35 \tan\theta)°$ extended by 25% on each side of the peak for background measurement, horizontal aperture $= (2\cdot0 + \tan\theta)$ mm, vertical aperture 4 mm, < 1% deviation for three reference reflections monitored each hour, final cell parameters obtained by constrained least-squares fit to $\sin\theta$ for 24 planes having $12 < \theta < 20°$, data corrected for Lp and absorption (transmission factors ranged from 0·0336 to 0·1482), 1052 unique reflections measured, 689 observed with $I \geq 3\sigma(I)$ where $\sigma^2(I) = S + 2B + [0\cdot04(S-B)]^2$, S = scan count and B = time-averaged background; starting coordinates were those found for $Cs_2[ZnBr_4]$ (Morosin & Lingafelter, 1959) whose structure is of the β-K_2SO_4 type (McGinnety, 1972; Robinson, 1958); full-matrix least-squares refinement, anisotropic temperature factors, weights $w = 1/\sigma^2(F)$ [$\sigma^2(F)$ derived from the previously defined $\sigma^2(I)$], $R = 0\cdot066$ ($R_w = 0\cdot098$); subsequent refinement included anomalous scattering and anisotropic extinction corrections (Coppens & Hamilton, 1970), final $R_w = 0\cdot048$; mean and maximum parameter shifts on the last cycle 0·024 and 0·099σ, respectively; standard deviation in an observation of unit weight 1·446; including all data, $R = 0\cdot074$ and $R_w = 0\cdot048$; $F(000) = 688$; a difference Fourier map calculated after convergence showed a random distribution of density peaks and troughs with magnitudes less than 0·9 e Å^{-3}; ionic scattering factors for Rb^+, Zn^{2+} and Cl^- from Cromer & Mann (1968); anomalous-scattering factors from Cromer & Liberman (1970); program system used was *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.*

The anion assumes a tetrahedral arrangement with the Zn and two Cl atoms occupying positions on the mirror plane. The Zn—Cl distances (Table 2) range from 2·233 (4) to 2·254 (4) Å and the Cl—Zn—Cl angles lie within 106·2 (1) to 114·3 (2)°. These angular distortions from the normal tetrahedral value of 109·5° indicate, as in the isostructural compound $Cs_2[ZnBr_4]$

Table 1. *Final positional (fractional* $\times 10^4$*) and isotropic thermal parameters (*$U \times 10^3$ Å^2*) with estimated standard deviations in parentheses*

	x	y	z	U_{eq}*
Rb(1)	6318 (2)	2500	4065 (2)	66
Rb(2)	4853 (1)	2500	8194 (1)	41
Zn	2245 (2)	2500	4223 (1)	29
Cl(1)	−165 (4)	2500	4174 (3)	70
Cl(2)	3184 (4)	2500	5858 (3)	72
Cl(3)	3153 (4)	23 (4)	3414 (3)	79

* U_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix.

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* Lists of structure factors, anisotropic thermal parameters and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38196 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *with estimated standard deviations in parentheses*

Zn—Cl(1)	2·233 (4)	Zn···Rb(1)	3·779 (2)
Zn—Cl(2)	2·254 (4)	Zn···Rb(2)	3·963 (2)
Zn—Cl(3)	2·241 (3)		
Rb coordination			
Rb(1)···Cl(1)$(1+x,y,z)$	3·261 (4)	Rb(2)···Cl(2)$(\frac{1}{2}+x,\frac{1}{2}-y,\frac{3}{2}-z)$	3·312 (4)
Rb(1)···Cl(3)(x,y,z)	3·541 (3)	Rb(2)···Cl(3)$(1-x,\frac{1}{2}+y,1-z)$	3·313 (3)
Rb(1)···Cl(3)$(x,\frac{1}{2}-y,z)$	3·541 (3)	Rb(2)···Cl(3)$(1-x,-y,1-z)$	3·313 (3)
Rb(1)···Cl(2)$(1-x,\frac{1}{2}+y,1-z)$	3·673 (1)	Rb(2)···Cl(1)$(\frac{1}{2}+x,\frac{1}{2}-y,\frac{3}{2}-z)$	3·349 (4)
Rb(1)···Cl(2)$(1-x,y-\frac{1}{2},1-z)$	3·673 (1)	Rb(2)···Cl(3)$(\frac{1}{2}-x,-y,\frac{1}{2}+z)$	3·349 (4)
Rb(1)···Cl(2)(x,y,z)	3·691 (4)	Rb(2)···Cl(3)$(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z)$	3·349 (4)
Rb(1)···Cl(3)$(1-x,\frac{1}{2}+y,1-z)$	3·727 (5)	Rb(2)···Cl(2)(x,y,z)	3·350 (4)
Rb(1)···Cl(3)$(1-x,-y,1-z)$	3·727 (5)	Rb(2)···Cl(1)$(\frac{1}{2}-x,1-y,\frac{1}{2}+z)$	3·861 (1)
		Rb(2)···Cl(1)$(\frac{1}{2}-x,-y,\frac{1}{2}+z)$	3·861 (1)
Angles (°) within $ZnCl_4^{2-}$			
Cl(1)—Zn—Cl(2)	114·3 (2)	Cl(2)—Zn—Cl(3)	106·2 (1)
Cl(1)—Zn—Cl(3)	111·2 (2)	Cl(3)—Zn—Cl(3)	107·3 (2)

(Heming, Lehman, Henkel & Krebs, 1981; Morosin & Lingafelter, 1959), a displacement of the $X(2)$ halide with respect to its normal tetrahedral position; Cl(1) and Cl(3) are displaced to lesser extents. The closest approach of the Rb^+ cations (which also lie on the mirror plane) to the anion is the Rb(1)···Cl(1) distance of 3·261 (4) Å. This distance lies within the sum of the two ionic radii, 3·3 Å, and is slightly longer than the Rb···Cl distance of 3·24 Å in RbCl (Olshausen, 1925). Morosin & Lingafelter have shown that for $Cs_2[ZnBr_4]$ the Cs(2) ion is in a more confined environment than the Cs(1) ion; the smaller temperature factor for Cs(2) is consistent with this packing. A similar situation is found in the present structure in which Rb(2) (U_{eq} = 0·041 Å^2) is surrounded by seven Cl atoms at distances less than 3·35 Å, whereas Rb(1) (U_{eq} = 0·066 Å^2) has only one nearest neighbor at less than this value.

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Fluorure de Neptunium et de Sodium: $NaNp_3F_{13}$

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Abstract. $M_r = 981$, hexagonal, $P6_3/mmc$, $a = 8{\cdot}022\ (5)$, $c = 16{\cdot}513\ (9)$ Å, $V = 1062\ (2)$ Å^3, $Z = 4$, $D_m = 6{\cdot}13$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 257$ cm^{-1}, $F(000) = 1621$, $R = 0{\cdot}066$ for 599 independent reflexions. The title compound is closely related to CsU_6F_{25}, the Cs atoms being substituted by the linear groups Na—F—Na. Np ions are at the centers of trigonal tricapped prisms, the Np—F distances ranging from 2·288 (6) to 2·55 (1) Å. Na ions have a five coordination and Na—F distances vary between 2·42 (5) and 2·65 (3) Å.

Introduction. Ce travail s'insert dans le cadre d'une étude systématique des systèmes fluorures alcalins–fluorure de neptunium tétravalent. Lors de l'étude sous pression du système $NaF–NpF_4$ nous avons mis en évidence une phase dont les caractéristiques cristallographiques sont très voisines de celles du composé

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