Table 3. *Observed and predicted bond lengths* (Å) *in* $P_2As_2S_3$

Averaged As—S, P—S, As—As and P—P distances for α- and β-As_4S_3 and P_4S_3 in Table 2 and relative compositions for the sites *A*(1,2,3) from Table 1 are used.

Bond	Predicted bond length (e.s.d.'s *ca* 0·01 Å)	Observed
A(1)—S(1) *A*(1)—S(2)	0·19 (2·225) + 0·81 (2·086) = 2·112	2·120
A(2)—S(2)	0·57 (2·217) + 0·43 (2·095) = 2·165	2·193
A(3)—S(1)	0·65 (2·209) + 0·35 (2·092) = 2·168	2·194
A(2)—*A*(3)	0·61 (As—As) + 0·39 (P—P) 0·61 (2·452) + 0·39 (2·235) = 2·367 [0·61 (2·498) + 0·39 (2·25) = 2·401]*	2·390
A(3)—*A*(3′)	0·65 (As—As) + 0·35 (P—P) 0·65 (2·465) + 0·35 (2·236) = 2·385 [0·65 (2·498) + 0·35 (2·25) = 2·411]*	2·426

* Using As—As and P—P distances in As_7^{3-} and P_7^{3-}.

(As_{apex}—S_{bridge}) and 2·173 (3) Å (As_{base}—S_{bridge}) (Christian *et al.*, 1981). No similar trends in the average bond angles in $P_2As_2S_3$ are observed and it is notable that bond angles in the apex of $P_2As_2S_3$ are slightly larger [99·7 (1)°] than those in either P_4S_3 or As_4S_3, while the angles in the base are generally smaller than expected. The crystal packing is the same as that of β-dimorphite.

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Electron-Density Distribution in Crystals of Ammonium Tetrachlorozincate(II) Chloride at 120 K

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Abstract. $[NH_4]_3[ZnCl_4]Cl$, $M_r = 296{\cdot}76$, orthorhombic, *Pnma*, $a = 8{\cdot}6597\ (9)$, $b = 9{\cdot}8307\ (6)$, $c = 12{\cdot}4588\ (7)$ Å, $V = 1060{\cdot}6\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}86$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70930$ Å, $\mu = 3{\cdot}59$ mm^{-1}, $F(000) = 592$, $T = 120\ (1)$ K, $R = 0{\cdot}042$ for 2456 observed unique reflections up to $\sin\theta/\lambda = 0{\cdot}91$ Å^{-1}. The Zn^{2+} ion is surrounded tetrahedrally by Cl^- ions with mean Zn—Cl bond distance 2·2613 (7) Å. The charge distribution around the Zn^{2+} ion is slightly aspherical. In the deformation density there is a trough of −0·42 (7) e Å^{-3} on the Zn—Cl bond axis at 0·4 Å from the Zn nucleus and a peak of 0·29 (10) e Å^{-3} on the bisector of the Cl—Zn—Cl angle and at 0·7 Å from the Zn atom. This asphericity suggests that the 3*d* shell of the Zn^{2+} ion is not closed and the electronic configuration can be expressed as $(3d\colon e^4t_2^{6-x})(4s)^x$, $0 < x < 2$.

Introduction. Simple crystal field theory tells us that the charge distribution around the Zn^{2+} ion will be spherical because of fully occupied 3*d* orbitals. Recently Sakabe, Sasaki & Sakabe (1984) detected a charge asphericity around the Zn atom in 2Zn insulin. To reveal the origin of the asphericity, several examinations should be performed for small molecules with high symmetry. The title complex was selected first, because the tetrahedral environment is suitable to distinguish the aspherical charge distribution of the non-bonding *d*

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electrons from the effect of the anharmonic thermal vibrations of the metal atom. If the population of the non-bonding *e* orbitals is greater than that of t_2, a positive peak appears on the bisector of the Cl—Zn—Cl bond angle in the deformation density as observed in the $[CoO_4]^{6-}$ tetrahedron (Toriumi, Ozima, Akaogi & Saito, 1978). If the anharmonic vibration of the Zn atom is dominant, a positive peak appears on the extension of the Cl—Zn bond axis as observed in the $[MgO_4]^{6-}$ tetrahedron at 1933 K (Yamanaka, Takéuchi & Tokonami, 1984).

Experimental. Crystals nearly equi-dimensional in all directions grown from a mixture of $ZnCl_2$ and NH_4Cl aqueous solutions ($NH_4^+/Zn^{2+} = 3$). A spherical crystal of diameter 0·30 (2) mm ground by Bond's (1951) method. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation and blowing cold N_2 gas. No phase transition. Cell parameters refined by least squares of 18 2θ values ($60 < 2\theta < 70°$). 7735 reflections measured by θ–2θ scan with speed 6° min^{-1} in θ ($2\theta \leq 40°$, h $-8\rightarrow 8$, k $0\rightarrow 9$, l $-12\rightarrow 12$; $40 < 2\theta \leq 80°$, h $0\rightarrow 15$, k $0\rightarrow 17$, l $-22\rightarrow 22$), 5272 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 2456 unique reflections ($R_{\rm int} = 0{\cdot}023$). In ψ scan, $|F_o|_{\rm max}/|F_o|_{\rm min} = 1{\cdot}04$ for 111. Mean ratio of five standard reflections, $0{\cdot}984 < \sum(|F_o|/|F_o|_{\rm initial})/5 < 1{\cdot}006$. Absorption correction ($\mu r = 0{\cdot}538$, $0{\cdot}457 < A < 0{\cdot}475$). Atomic parameters refined with full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0{\cdot}015|F_o|)^2$. Atomic coordinates reported by Klug & Alexander (1944) utilized as initial parameters except Cl(*B*), which was moved to a symmetry-related position ($\frac{1}{2} + x$, y, $\frac{1}{2} - z$). Anisotropic thermal parameters for non-H atoms ($R = 0{\cdot}048$). All the H atoms found from difference synthesis with height 0·8 to 1·2 e Å^{-3} and refined with isotropic thermal parameters ($R = 0{\cdot}045$). Isotropic secondary-extinction correction parameter, $g = 1{\cdot}27\,(17) \times 10^{-4}$ (Zachariasen, 1967). Smallest extinction factor (F_o^2/F_c^2) = 0·84 for 040. Final $R = 0{\cdot}042$, $wR = 0{\cdot}033$, $S = 1{\cdot}12$.* Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). $\Delta/\sigma < 0{\cdot}05$. Reflection/parameter = 33·6.

Discussion. Final atomic coordinates and interatomic distances and angles are presented in Tables 1 and 2. The tetrahedral Zn complex is drawn in Fig. 1. The Zn, Cl(*A*) and Cl(*B*) atoms lie on a mirror plane and Cl($D^{\rm i}$)

Table 1. *Positional parameters* (×10^5; *for* H ×10^3) *and equivalent isotropic temperature factors* (*Hamilton,* 1959)

	x	*y*	*z*	$B/B_{\rm eq}$(Å^2×10)
Zn	31512 (3)	25000	10621 (2)	8 (1)
Cl(*A*)	37253 (8)	25000	28285 (5)	17 (1)
Cl(*B*)	54055 (7)	25000	1125 (5)	12 (1)
Cl(*C*)	16680 (7)	25000	−23646 (5)	11 (1)
Cl(*D*)	19089 (5)	5611 (4)	6328 (4)	13 (1)
N(1)	41966 (28)	25000	−45437 (19)	11 (1)
N(2)	41122 (20)	1742 (17)	−17563 (14)	13 (1)
H(N11)	489 (5)	250	−401 (3)	33 (9)
H(N12)	334 (6)	250	−423 (4)	57 (13)
H(N13)	431 (3)	177 (3)	−492 (2)	45 (7)
H(N21)	485 (4)	65 (3)	−164 (2)	40 (7)
H(N22)	398 (4)	−31 (4)	−106 (3)	58 (9)
H(N23)	331 (3)	79 (3)	−188 (2)	44 (8)
H(N24)	420 (4)	−34 (3)	−232 (3)	47 (8)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Zn—Cl(*A*)	2·2562 (7)	Zn—Cl(*D*)	2·2531 (7)
Zn—Cl(*B*)	2·2827 (7)		
Cl(*A*)—Zn—Cl(*B*)	108·49 (2)	Cl(*B*)—Zn—Cl(*D*)	106·58 (2)
Cl(*A*)—Zn—Cl(*D*)	109·68 (2)	Cl(*D*)—Zn—Cl($D^{\rm i}$)	115·55 (2)
Cl(*C*)···N($1^{\rm ii}$)	3·199 (2)	Cl(*C*)···H(N23)	2·28 (3)
Cl(*C*)···H($N11^{\rm ii}$)	2·30 (4)	Cl(*B*)···N($2^{\rm iii}$)	3·359 (2)
Cl(*C*)···N(2)	3·207 (2)	Cl(*B*)···H($N22^{\rm iii}$)	2·51 (4)

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

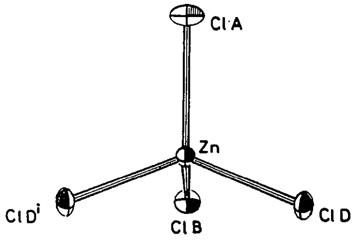

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the complex ion with thermal ellipsoids scaled at the 50% probability level.

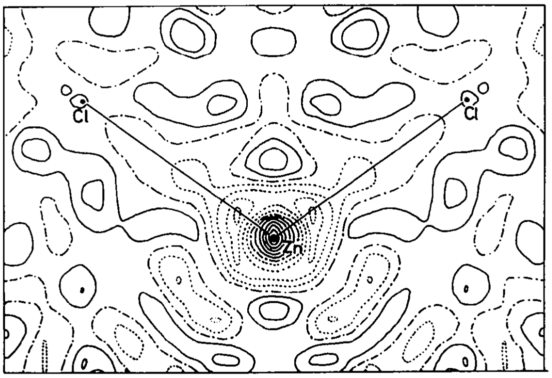

Fig. 2. Mean deformation density on the $ZnCl_2$ plane. Contour intervals at 0·1 e Å^{-3}. Negative contours are broken, zero contours chain-dotted.

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* Lists of structure factors, anisotropic thermal parameters and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43366 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is a mirror image of the Cl(*D*) atom. Root-mean-square displacement of the Zn atom is almost isotropic, 0·102 ±0·003 Å. The Zn—Cl(*B*) bond length is longer by 0·028 (1) Å than the other Zn—Cl distances. It may be due to the weak hydrogen bond of $\mathrm{Cl}(B)\cdots\mathrm{H}(\mathrm{N22}^{\mathrm{iii}})$—$\mathrm{N}(2^{\mathrm{iii}})$ (symmetry code is given in Table 2). An averaged deformation density of the $ZnCl_2$ plane assuming T_d symmetry is presented in Fig. 2. The charge distribution around the Zn atom is not perfectly isotropic. On the Zn—Cl bond axis a negative trough of −0·42 (7) e $Å^{-3}$ is observed at 0·4 Å from the Zn nucleus. A postive peak of 0·29 (10) $Å^{-3}$ lies on the bisector of the Cl—Zn—Cl angle and 0·7 Å from the Zn atom. The asphericity around the Zn atom agrees qualitatively with that observed around the Co atom in $CoAl_2O_4$ (Toriumi, Ozima, Akaogi & Saito, 1978). It suggests that the electron configuration of the Zn^{2+} ion is $(3d\text{-}e)^4(3d\text{-}t_2)^{6-x}(4s)^x$ with $0 < x < 2$. However, there is some noise in the deformation density. Investigations including theoretical calculations should be continued to exclude the possibility of anharmonic thermal vibration conclusively.

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Structures of Cadmium Nitrite Dihydrate and Cadmium Dipotassium Tetranitrite

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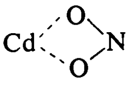
Abstract. $Cd(NO_2)_2.2H_2O$ (I), $M_r = 240·4$, orthorhombic, *Pbcn*, $a = 7·4446$ (4), $b = 7·8889$ (5), $c = 9·5992$ (7) Å, $V = 563·8$ (1) $Å^3$, $Z = 4$, $D_m(C_2H_2Br_4/CCl_4) = 2·71$ (2), $D_x = 2·83$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0·70930$ Å, $\mu = 3·83$ mm^{-1}, $F(000) = 452·2$, $T = 299$ (1) K, final $R = 0·042$ for 716 observed unique reflections. $Cd(NO_2)_2.2KNO_2$ (II), $M_r = 374·7$, orthorhombic, *Pnma*, $a = 12·1935$ (5), $b = 11·7154$ (8), $c = 6·5520$ (4) Å, $V = 936·0$ (1) $Å^3$, $Z = 4$, $D_m = 2·64$ (2), $D_x = 2·66$ Mg m^{-3}, Mo $K\alpha_1$, $\mu = 3·25$ mm^{-1}, $F(000) = 710·3$, $T = 296$ (1) K, final $R = 0·024$ for 1844 reflections. In (I) the Cd atom lies on a twofold axis and is octacoordinated by two nitrite N atoms, four nitrite O atoms and two water O atoms. The Cd atom in (II) lies on a mirror plane and is surrounded by eight O atoms of four NO_2^- ions. Each nitrite ion in both (I) and (II) forms a nearly coplanar  unit with Cd···O distances 2·357 (3) to 2·581 (4) Å.

Introduction. Coloration of nitrite ion is caused by certain post-transition-metal cations (McGlynn, Azumi & Kumar, 1981). The arrangement of post-transition-metal cations around NO_2^- has been studied in crystals of $K_3[Hg(NO_2)_4]NO_3$ (Power, King & Moore, 1976), $K_2Pb(NO_2)_3(NO_3).H_2O$ (Nardelli & Pelizzi, 1980), $AgNO_2$ (Ohba & Saito, 1981), $TlBa_2(NO_2)_5$ (Gasparri, Nardelli & Fermi, 1984), $Pb(NO_2)_2.H_2O$ (Ohba, Nosé & Saito, 1985), and $Hg_2(NO_2)_2$ and $Ag_2Li(NO_2)_3$ (Ohba, Matsumoto, Ishihara & Saito, 1986). Structures of the title Cd^{II} salts have been determined to study further the relation between the color and the structure.

Experimental. (I): Colorless tabular (010) crystals grown from filtrate of a mixture of $CdCl_2$ and $AgNO_2$ aqueous solutions, hygroscopic. A rectangular crystal of 0·12 × 0·32 × 0·55 mm sealed in a glass capillary. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Laue group *mmm*, systematic absences *hk*0 with *h*+*k* odd, *h*0*l* with *l* odd and 0*kl* with *k* odd; cell parameters refined by least

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