1979) and $TlCl_3.2$(4-pyridinecarbonitrile 1-oxide-*O*) (Gutiérrez-Puebla, Vegas & Garcia-Blanco, 1980) although other complexes are known which contain five-coordinate thallium, *e.g.* $[(p\text{-}HC_6F_4)_2TlCl(OPPh_3)]_2$ (Henrick, Matthews & McPartlin, 1980).

Bond distances and angles in $TlBr_3$.dioxane are given in Table 2. The Tl—Br distances are similar to those observed in $TlBr_3.2H_2O$ [Tl—Br=2·515 (3) Å, Glaser, 1979]. The Tl—O distance is similar to that found in the hydrate (2·59, 2·52 Å). It is greater than expected and significantly greater than in trichlorobis(4-pyridinecarbonitrile 1-oxide-*O*)thallium [2·36 (1), 2·40 (1) Å (Gutiérrez-Puebla *et al.*, 1980)] and tribromobis(triphenylphosphine oxide)thallium(III) [2·38 (2) Å (Jeffs, Small & Worrall, 1983)]. This may reflect the weak donor strength of the ligand dioxane. Distortions from trigonal bipyramidal geometry are to be expected for complexes with the axial positions occupied by low-symmetry ligands such as dioxane. These are indeed observed in the equatorial bond angles, Br(1)—Tl—Br(2), 118·4°, and Br(2)—Tl—Br(2''), 123·2°. The latter angle would be expected to be greater since torsion angles (Table 3) show that two carbon atoms C(2) are between Br(2) and Br(2'') (above and below the equatorial plane) whilst only one [C(1)] lies between Br(1), Br(2) and Br(1), Br(2''). These angular deviations are less than those observed in the analogous $AlCl_3$.2dioxane complex which contains an additional solvate dioxane molecule in the lattice. It has been proposed that interactions between dioxane solvate and bound dioxane are a contributing factor to these larger deviations (Boardman *et al.*, 1983).

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Structure of Tris(ethylenediamine)zinc(II) Chloride Dihydrate, $[Zn(C_2H_8N_2)_3]Cl_2.2H_2O$

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Abstract. $M_r = 352·61$, monoclinic, $C2/c$, $a = 8·793$ (2), $b = 13·961$ (4), $c = 12·953$ (3) Å, $\beta = 93·37$ (2)°, $V = 1587$ Å^3, $Z = 4$, $D_x = 1·474$ g cm^{-3}, $\lambda = 0·71069$ Å, $\mu = 18·05$ cm^{-1}, $F(000) = 736$, room temperature. The final R value for 1136 unique reflections is 0·074. An approximately octahedral coordination around Zn is observed. The site symmetry for Zn is 2 (C_2) and not 32 (D_3) as concluded through Raman and IR spectral studies. One of the chloride ions appears to be disordered. The site symmetry 2 of the metal atom and the centrosymmetric space group favours the presence of a racemic mixture of $\Lambda\lambda\lambda\lambda$ and $\Delta\lambda\lambda\lambda$ configurations.

Introduction. Tris(ethylenediamine) complexes are of interest because of the sixfold octahedral coordination around the metal atom. Krishnan & Plane (1966) have reported from Raman and IR spectral studies that $Zn(en_3)Cl_2.2H_2O$ has D_3 symmetry. Paramagnetic complexes doped in a diamagnetic host lattice, having D_3 symmetry, are expected to exhibit the Jahn–Teller effect in an EPR experiment. Hence, we expected this complex to form an ideal host lattice for studying the Jahn–Teller effect.

The temperature-dependent EPR spectra of Cu^{2+} in this host lattice show the presence of dynamic distortions (Shakuntala, 1980). The EPR spectra of Mn^{2+} in the same complex show several sites at room temperature whereas the Cu^{2+} spectra show only one site. The

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results on Cu^{2+} cannot be unambiguously understood in terms of the Jahn–Teller effect alone. In order to resolve the above difficulties, we have determined the structure of the compound by X-ray diffraction. Also a detailed crystal structure would be needed to understand the relations between the principal axes of the different sites and to some extent the relative magnitude of the EPR parameters.

Experimental. $Zn(en)_3Cl_2.2H_2O$ prepared by adding excess ethylenediamine to an aqueous solution of $ZnCl_2$. Colourless crystals obtained by slow evaporation.

Unit-cell parameters from least-squares refinement of θ values of 25 high-angle reflections. Crystal $0{\cdot}15 \times 0{\cdot}175 \times 0{\cdot}3$ mm, three-dimensional intensity data, $\theta_{\max} = 26°$ ($-10 \le h \le 10$, $0 \le k \le 16$, $0 \le l \le 15$), Enraf–Nonius single-crystal CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan mode, maximum counting time for each reflection 60 s, 1136 unique reflections with $I > 3\sigma(I)$, no correction for absorption. During refinement of the atomic parameters in space group *Cc*, strong correlations among the parameters were observed and hence the centrosymmetric *C*2/*c* was chosen; no extra systematic absences observed. Zn atoms assigned special positions $0,y,\frac{1}{4}$; $0,\bar{y},\frac{3}{4}$; $\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$; $\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$ with point symmetry 2. *y* coordinate for Zn atom obtained from three-dimensional Patterson map, all non-hydrogen atoms from successive difference Fourier maps. One of the Cl atoms occupies the special position. Difference Fourier maps did not reveal any other special position for the second Cl atom, but two peaks persistently appeared near a special position, the distance between the peaks being 1·12 Å. This indicated disorder of the Cl atom and hence both positions were included with occupancy factors of $\frac{1}{2}$ in subsequent refinements. Refined occupancy factors indicated equal occupancy of the two sites. The distance between the two positions after refinement is 1·04 (2) Å. Final difference Fourier maps revealed 11 of the 14 H atoms. Their positions were refined once. Final maximum $\Delta\rho$ excursion 3·2 e Å^{-3}, 0·73 Å from the O atom of the water molecule. Structure refined by full-matrix least squares minimizing $\sum w(\Delta F)^2$ [*SHELX*76 (Sheldrick, 1976)], initially with isotropic and then anisotropic thermal parameters for the non-hydrogen atoms. Refinement showed a higher temperature factor for the disordered Cl atom [$U = 0{\cdot}090\,(3)$ Å^2] than for the other Cl atom [$U = 0{\cdot}041\,(1)$ Å^2]. Atomic scattering factors for zinc (Zn^{2+}) from Cromer (1965) and for other non-hydrogen atoms from Cromer & Mann (1968), anomalous-dispersion-correction factors from Cromer & Liberman (1970); H-atom scattering factors from Stewart, Davidson & Simpson (1965). Final $R = 0{\cdot}074$, $R_w = 0{\cdot}080$, $w = 0{\cdot}0156/[\sigma^2(F_o) + 0{\cdot}5656|F_o|^2]$, $(\Delta/\sigma)_{\max} = 1{\cdot}68$.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^4$ *for* Zn, $\times 10^3$ *for others*) *with estimated standard deviations in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i U_{ii}.$$

	x	*y*	*z*	$U_{\rm eq}$ (Å^2)
Zn	0	2283 (1)	2500	311 (6)
N(1)	1416 (10)	3485 (6)	3112 (7)	40 (3)
N(2)	1418 (10)	2160 (7)	1137 (7)	44 (3)
N(3)	−1355 (11)	1216 (6)	1585 (7)	40 (3)
C(1)	891 (13)	4348 (8)	2539 (13)	60 (4)
C(2)	889 (16)	1316 (10)	518 (10)	58 (4)
C(3)	−867 (16)	1258 (9)	527 (9)	52 (4)
Cl(1)	0	−964 (2)	2500	46 (1)
Cl(2)	50 (12)	3152 (6)	7100 (7)	70 (2)
O	−9 (4)	3851 (3)	5588 (3)	27 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°) *within* $[Zn(en)_3]^{2+}$

A prime denotes the point-symmetry equivalent position $\bar{x}, y, \frac{1}{2} - z$.

Zn—N(1)	2·209 (9)	Zn—N(2)	2·23 (1)
Zn—N(3)	2·209 (9)	N(1)—C(1)	1·47 (2)
N(2)—C(2)	1·48 (2)	N(3)—C(3)	1·46 (2)
C(1)—C(1′)	1·57 (2)	C(2)—C(3)	1·55 (2)
N(1)···N(1′)	2·87 (1)	N(2)···N(3)	2·86 (1)
N(1)···N(2)	3·16 (1)	N(1)···N(3′)	3·19 (1)
N(3)···N(3′)	3·26 (1)		
N(1)—Zn—N(1′)	81·1 (4)	N(2)—Zn—N(3)	80·3 (4)
N(1)—Zn—N(2)	90·8 (3)	N(1)—Zn—N(3)	168·5 (4)
N(1)—Zn—N(2′)	96·0 (4)	N(1)—Zn—N(3′)	92·6 (3)
N(2)—Zn—N(3′)	93·6 (3)	N(2)—Zn—N(2′)	171·2 (4)
N(3)—Zn—N(3′)	95·2 (5)	Zn—N(1)—C(1)	106·6 (7)
Zn—N(2)—C(2)	108·5 (7)	Zn—N(3)—C(3)	107·3 (7)

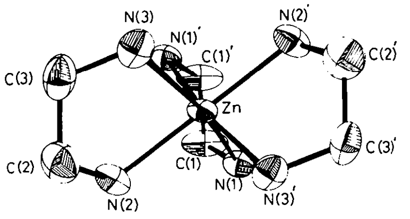

Fig. 1. Perspective view of $[Zn(en)_3]^{2+}$.

Discussion. The fractional atomic coordinates with equivalent isotropic thermal parameters are listed in Table 1.* Table 2 contains the interatomic distances and angles within $[Zn(en)_3]^{2+}$. Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of the cation, with the numbering scheme.

The Zn atom has an approximately octahedral configuration with all the four equatorial Zn—N distances equal to 2·209 (9) Å and the two axial distances equal to 2·227 (10) Å. The bite angles of the

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* Lists of structure factors, H-atom coordinates, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38781 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chelate rings N(1)—Zn—N(1′) [81·1 (4)°] and N(2)—Zn—N(3) [80·3 (4)°] deviate significantly from 90°. This deviation compares well with those found in $[Ni(en)_3]^{2+}$ [82 (1)°] (Swink & Atoji, 1960), $[Cu(en)_3]^{2+}$ [80·9 (1)°] (Cullen & Lingafelter, 1970), $[Cr(en)_3]^{3+}$ [82·5 (1)°] (Whuler, Brouty, Spinat & Herpin, 1975), $[Rh(en)_3]^{3+}$ [83·6 (2)°] (Whuler, Brouty, Spinat & Herpin, 1976) and $[Ru(en)_3]^{2+}$ [81·6 (3)°] (Smolenaers, Beattie & Hutchinson, 1981). The C—N and C—C distances in the en group are not significantly different from single-bond distances. The N—N separations in the chelate rings, the so-called bite distances, are 2·87 (1) and 2·86 (1) Å in two different chelate rings of the same cation.

The shortest distance between the chloride ions is 3·098 (9) Å. The minimum distances between the chloride ions and the metal atom are Cl(1)···Zn = 4·534 (3) Å and Cl(2)···Zn = 4·40 (1) Å. The closest approach of the metal atom and O atom of the water molecule is 4·560 (4) Å.

The dihedral angles with respect to the N—C, C—C and C—N bonds of the five-membered Zn(en) rings are 44 (1), 61 (1) and 44 (1), and 38 (1), 56 (1) and 44 (1)° for two different rings of the same cation. The third ring is the symmetry equivalent of the second. Consequently, the configuration of the five-membered Zn(en) rings can be assigned as *gauche-gauche-gauche*. The dihedral angles of 61 (1) and 56 (1)° between the planes determined by the C—C and C—N bonds compare well with that found in $[Cu(en)_3]SO_4$, 57·5° (Cullen & Lingafelter, 1970).

The intermolecular hydrogen bonds between N atoms and chloride ions are Cl(1)···N(1), Cl(2)···N(2), Cl(1)···N(3) and Cl(2)···N(3) with distances 3·383 (9), 3·39 (1), 3·45 (1) and 3·39 (1) Å respectively. These can be considered as hydrogen-bonding distances, even though longer than the average bond of 3·10 (8) Å listed in *International Tables for X-ray Crystallography* (1968). The average hydrogen-bond distance between the O atom of the water molecule and the disordered chloride ion is 2·67 (1) Å which is very strong when compared to the normal hydrogen bond between chlorine and oxygen [2·95 (2) Å] (*International Tables for X-ray Crystallography*, 1968).

Because of the *gauche* conformations, for $M(en)_3$ complexes there are in general eight possible isomers for both the absolute configurations Λ and Δ. These are designated as $\Lambda\delta\delta\delta$, $\Lambda\delta\delta\lambda$, $\Lambda\delta\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\delta\delta\delta$, $\Delta\delta\delta\lambda$, $\Delta\delta\lambda\lambda$ and $\Delta\lambda\lambda\lambda$. Because of the twofold site symmetry of the Zn atom in $Zn(en)_3Cl_2.2H_2O$, the bond C(1)—C(1′) is always oblique to the C_3 axis of the octahedron. The other two C—C bonds are also oblique. Consequently, $\Lambda\lambda\lambda\lambda$ and $\Delta\lambda\lambda\lambda$ are the only possible isomers in this case. Since the space group is centrosymmetric, a racemic mixture of both is present, as in the case of $[Cr(en)_3]^{3+}$ (Raymond & Ibers, 1968).

Krishnan & Plane (1966) concluded, for the present structure, through Raman and IR spectral studies, that it has the site symmetry D_3 (32). But the present structure determination using full three-dimensional X-ray diffraction data shows that the site symmetry is C_2 (2) which is contrary to the above conclusion. Consequently it can be concluded that the present complex $Zn(en)_3Cl_2.2H_2O$ is not an ideal host lattice for the study of the Jahn–Teller effect.

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