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Chains of Complexes in the Crystal Structure of Bishydrazine Zinc Chloride

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The crystals of bishydrazine zinc chloride, $[Zn(N_2H_4)_2]Cl_2$, are monoclinic and always twinned. The crystal structure of this compound is characterized by chains of bridge-complexes

$$:::Zn:::(H_2N\text{–}NH_2)_2:::Zn:::(H_2N\text{–}NH_2)_2:::Zn:::$$

extending throughout the crystal, parallel to the *c* axis.

Coordination around the metal is of octahedral type. The corners of the pseudo-octahedron are occupied by four N atoms, belonging to four different hydrazine molecules, and by two Cl atoms. The distance Zn–N (2·15 Å) indicates a covalent bond; the distance Zn–Cl (2·58 Å) is nearly equal to the sum of ionic radii. The hydrazine molecule, where the distance N–N is 1·46 Å, is shown very likely to be in the 'staggered' form with symmetry C_2.

We have recently shown (Ferrari, Braibanti & Bigliardi, 1962) that compounds with the general formula $[Me(II)(N_2H_4)_2]Cl_2$, with $Me(II) = Cd, Zn, Mn$, form twins in which the twin plane is either (100) or (001) or (110).

The crystals of these compounds, which are monoclinic isostructural, are pseudo-merohedral reticular twins (Friedel, 1926). Each compound forms twins according to the various laws in different amounts. No relation can be found between the number of crystals twinned in each law and the obliquity or the twin index *S*. It has been suggested therefore that conditions at crystallization or structural changes from one compound to another may influence the formation of the twins. The importance of the conditions of crystallization is supported now by the fact that in particular cases the compound $[Zn(N_2H_4)_2]Cl_2$ can form twins according to the (100) law, which had not been observed before in other conditions of crystallization.

The present paper deals with the crystal structure of such compounds and particularly of $[Zn(N_2H_4)_2]Cl_2$.

Experimental

The crystals of $[Zn(N_2H_4)_2]Cl_2$ are colorless, monoclinic and twinned. They were prepared from a mixture of zinc chloride, ammonia and hydrazine by cooling or by evaporation; in the former case (001) twins, in the latter (100) twins, also were obtained.

The unit cell (Ferrari, Braibanti & Bigliardi, 1962) has:

$$a = 8{\cdot}99 \pm 0{\cdot}01,\ b = 7{\cdot}92 \pm 0{\cdot}01,\ c = 4{\cdot}13 \pm 0{\cdot}01\ \text{Å};\ \beta = 105^\circ\ 30'$$

and contains $Z = 2$ stoichiometric units $[Zn(N_2H_4)_2]Cl_2$. Possible space groups are $C_{2h}^3\text{–}C2/m$, $C_2^3\text{–}C2$, $C_s^3\text{–}Cm$.

The length of the *c* side of the unit cell of each compound of the series $[Me(II)(N_2H_4)_2]Cl_2$ is very near to the corresponding ones of the series of compounds $[Me(II)(N_2H_4)_2](NCS)_2$ (Ferrari, Braibanti & Lanfredi, 1961), where a pseudo-octahedral centrosymmetric complex was found. This suggests the space group $C_{2h}^3\text{–}C2/m$ as the most acceptable. The complete determination of the structure has confirmed the correctness of this choice.

Photographs for intensity measurements were taken first by rotation of a crystal around [100]. The crystal was twinned according to the (001) law. The 0*kl* spots of the two individuals are superimposed on the equatorial photograph and the twin behaves as a unique crystal. On the other hand the *hkl* spots of the two individuals are split on the upper-level photographs. In the latter photographs, absorption or interference effects of one individual on the rays diffracted by the other widely influence the intensity of the spots. Accordingly during refinement the residuals never fell particularly low. Therefore all *hkl* reflections were disregarded and a single crystal or twin with the (100) law was searched for. By evaporation some such crystals were obtained; then photographs by rotation around [001] were taken. These twins give upper-layer photographs, but not equatorial photographs, showing streaks along the rows parallel to a^* similar to those observed in other compounds by several authors (Jeffrey, 1953; Dornberger-Schiff, Liebau & Thilo, 1955; Dornberger-Schiff, 1957; Gryder, Donnay & Ondik, 1958).

Cu $K\alpha$ radiation was used throughout. Reflections for the determination of the structure were integrated and the multiple-film technique was applied. Intensities were estimated visually. Corrections for polarization and geometrical factors were graphically evaluated. Absorption correction as for cylindrical specimens was introduced according to Bond (1959) (for 0*kl* reflections: $\mu R = 2{\cdot}0$; for (*hk*0) reflections:

Table 1. *Atomic coordinates*

	Crystallog. position	Nr.	x/a	y/b	z/c	x (Å)	y (Å)	z (Å)	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Zn	(*a*)	2	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	—	—	—
Cl	(*i*)	4	0·2868	0·0000	0·0000	2·4837	0·0000	−0·6912	0·0025	—	0·0024
N	(*j*)	8	0·047	0·192	0·381	0·4070	1·5206	1·4603	0·033	0·022	0·016
H_I*	(*j*)	8	0·162	0·163	0·536	1·4029	1·2910	1·8233	—	—	—
H_{II}*	(*j*)	8	0·059	0·325	0·330	0·5109	2·5740	1·2207	—	—	—

* Values obtained from the structure of Penney & Sutherland (1934).

$\mu R = 1{\cdot}0$). Atomic scattering curves were constructed from data quoted by Sagel (1958).

Determination and refinement of the structure

A trial structure based on pseudo-octahedral complexes around the metal ion and bridges of hydrazine molecules joining the complexes in chains along the [001] direction leads to the following distribution of atoms in the asymmetric unit of the $C2/m$ space group: 2 Zn in (*a*), 4 Cl in (*i*), 8 N in (*j*).

The agreement between observed and calculated structure factors confirmed that the structure was correct.

The octahedral coordination around the metal and the chains of octahedra bridged by hydrazine molecules clearly appear in the electron-density projections $\varrho_0(X, Y)$ and $\varrho_0(Y, Z)$.

Refinement was carried on by $\varrho_0 - \varrho_c$ synthesis till the best agreement between observed and calculated structure factors was reached. Finally we obtained $R_{hk0} = 0{\cdot}094$, $R_{0kl} = 0{\cdot}057$ (observed reflections only).

Isotropic thermal parameters are different for the two projections: for $hk0$ reflections $B = 1{\cdot}5$ Å^2, for $0kl$ reflections $B = 3{\cdot}5$ Å^2. Also calculations of anisotropic thermal parameters lead to different results for the two projections. Therefore the thermal parameters could not be refined. The different conditions of crystallization and twinning might cause such discrepancies.

The positions of the H atoms were calculated by attributing to the hydrazine molecule the structure proposed by Penney & Sutherland (1934). According to their calculations the two tetrahedra:

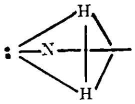


Table 2. *Main interatomic distances*

Intramolecular

$N(x, y, z)-N(\bar{x}, y, 1-z)$	$= 1{\cdot}46 \pm 0{\cdot}05$ Å	(Hydrazine)
$N(x, y, z)-Zn(0, 0, 0)$	$= 2{\cdot}15 \pm 0{\cdot}02$	Group $[Zn(N_2H_4)_{4/2}]Cl_2$
$N(x, y, z)-N(\bar{x}, y, \bar{z})$	$= 3{\cdot}03 \pm 0{\cdot}05$	
$N(x, y, z)-N(x, \bar{y}, z)$	$= 3{\cdot}04 \pm 0{\cdot}05$	
$N(x, y, z)-Cl(x, 0, z)$	$= 3{\cdot}36 \pm 0{\cdot}03$	
$N(\bar{x}, y, \bar{z})-Cl(x, 0, z)$	$= 3{\cdot}36 \pm 0{\cdot}03$	
$Zn(0, 0, 0)-Cl(x, 0, z)$	$= 2{\cdot}578 \pm 0{\cdot}003$	

Intermolecular

$N(\frac{1}{2}+x, \frac{1}{2}-y, z)-Cl(x, 0, z)$	$= 3{\cdot}45 \pm 0{\cdot}02$ Å
$N(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z})-Cl(x, 0, z)$	$= 3{\cdot}45 \pm 0{\cdot}02$
$N(\bar{x}, y, 1-z)-Cl(x, 0, z)$	$= 4{\cdot}69 \pm 0{\cdot}02$
$Cl(x, 0, z)-Cl(1-x, 0, \bar{z})$	$= 3{\cdot}833 \pm 0{\cdot}005$
$Cl(x, 0, z)-Cl(\frac{1}{2}-x, \frac{1}{2}, \bar{z})$	$= 4{\cdot}015 \pm 0{\cdot}005$

Table 3. *Observed and calculated structure factors for the (hk0) reflections*

(*hk*0)	F_o	F_c	(*hk*0)	F_o	F_c	(*hk*0)	F_o	F_c
200	38·3	43·7	130	2·2	5·4	060	70·9	67·0
400	74·7	73·9	330	53·8	50·0	260	10·0	9·9
600	19·5	19·7	530	—	−1·8	460	38·3	39·1
800	4·4	3·1	730	47·4	49·3	660	13·1	13·3
10,0,0	18·8	16·0	930	3·1	4·9	860	—	4·3
110	52·0	54·8	040	86·4	78·2	170	11·8	10·7
310	72·3	80·7	240	5·6	6·2	370	33·7	30·8
510	3·4	2·3	440	51·2	48·7	570	3·6	−1·6
710	43·8	47·2	640	18·5	17·2	770	28·0	32·1
910	10·9	−5·3	840	11·2	9·5			
11,1,0	8·9	15·5	10,4,0	15·7	20·2	080	27·7	29·8
						280	10·2	−7·9
020	73·9	67·9	150	44·0	43·4	480	24·7	23·9
220	29·1	−23·5	350	60·4	57·3	680	11·1	11·8
420	53·0	51·6	550	3·5	1·2			
620	23·3	25·0	750	33·6	33·5	190	9·4	10·8
820	14·9	18·1	950	11·7	−8·8	390	23·9	24·8
10,2,0	25·4	29·9				590	1·2	−1·8
						0,10,0	28·6	34·5
						2,10,0	2·4	4·5

Thermal parameters introduced in F_c: for Zn; $B_{11} = 2{\cdot}2$, $B_{22} = 1{\cdot}5$; for Cl: $B = 1{\cdot}3$; for N, H_I and H_{II}: $B = 1{\cdot}5$.

Table 4. *Observed and calculated structure factors for the* (0*kl*) *reflections*

(0*kl*)	F_o	F_c	(0*kl*)	F_o	F_c	(0*kl*)	F_o	F_c
020	64·4	65·3	002	68·3	70·4	004	20·0	16·0
040	68·6	68·9	022	63·2	59·2	024	28·8	27·5
060	51·6	51·4	042	43·3	45·3	044	17·8	16·8
080	17·2	15·9	062	29·1	30·4	064	9·2	9·7
0,10,0	13·3	16·0	082	17·7	17·1			
						005	15·7	15·6
001	64·3	63·7	003	52·2	51·1	025	8·6	8·8
021	111·2	111·8	023	32·4	32·0			
041	62·3	59·9	043	28·2	30·8			
061	30·9	32·8	063	21·6	22·8			
081	29·0	27·4	083	9·3	9·5			
0,10,1	5·7	8·7						

Thermal parameters introduced in F_c: for Zn: $B=3{\cdot}5$; for Cl: $B=3{\cdot}5$; for N, H_I and H_{II}: $B=2{\cdot}7$.

composing the molecule are rotated by 90 − 100°. The distance N–H is 1·04 Å, the distance N–N is 1·46 Å, the angle $H\widehat{N}H$ is 108°.

With the contributions of the hydrogen atoms the residuals became: $R_{hk0}=0{\cdot}096$ and $R_{0kl}=0{\cdot}039$.

We think that such structure for hydrazine is very probably supported by considerations given below in the discussion.

Final atomic coordinates and their standard deviations are quoted in Table 1. Standard deviations were determined by the Cruickshank (1949) method.

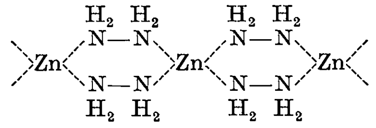
Ambiguity in the sign of the *x* co-ordinate of the N atom was resolved assuming that the distance Zn–N could not be less than 2 Å.

The main bond distances within the same chain and between two parallel chains are quoted in Table 2.

The observed and calculated structure factors are reported in Table 3 and in Table 4.

Discussion

A clinographic projection of the structure is shown in Fig. 1. The chains



extend throughout the whole crystal. The chains are similar to those found in the compound

$$[Zn(N_2H_4)_2](NCS)_2$$

(Ferrari, Braibanti & Lanfredi, 1961).

Coordination around the zinc is of octahedral type (Fig. 2). The plane passing through four N atoms — each of them belonging to a different hydrazine molecule — is normal to the line Cl–Zn–Cl. The distances between the N atoms lying on two adjacent corners of the pseudo-octahedron are N–N = 3·03 Å and N–N = 3·04 Å. The symmetry of the group $[Zn(N_2H_4)_{4/2}]Cl_2$ can be taken as D_{4h}. The bond distance between Zn and the surrounding N atoms (see Table 3) is slightly longer than that observed in the tetrahedral complex $Zn[SC(NH_2)_2.NH.NH_2]Cl_2$

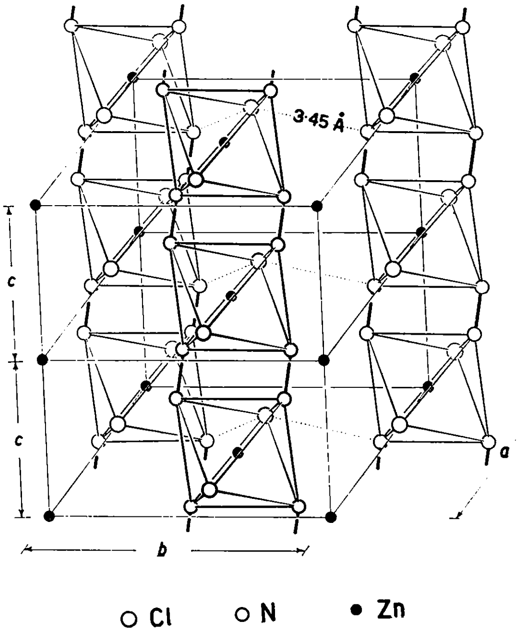


Fig. 1. Clinographic projection of the structure of $[Zn(N_2H_4)_2]Cl_2$ (two unit cells). The front chains are omitted.

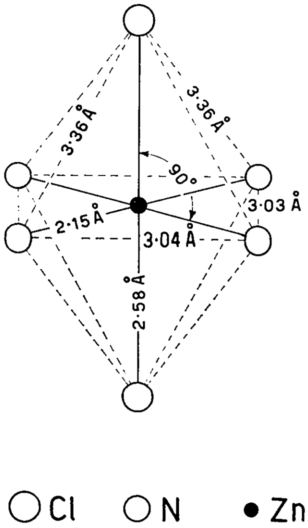


Fig. 2. Group $[Zn(N_2H_4)_{4/2}]Cl_2$.

by Cavalca, Nardelli & Branchi (1960) (Zn–Cl= 2·09 Å); it is reasonable to think of it as a weak covalent bond. The bond distance Zn–Cl is 2·58 Å which is very near to the sum of ionic radii ($r_{Zn^{++}}+r_{Cl^-}$ is 2·55 Å according to Pauling (1927) and 2·64 Å according to Goldschmidt (1926)). Such a distance is remarkably longer than that found (Zn–Cl=2·24 Å) by Cavalca, Nardelli & Branchi (1960) in the cited compound and also longer than those found by Klug & Alexander (1944) (Zn–Cl= 2·25 Å) in $(NH_4)_2ZnCl_4.NH_4Cl$ and by MacGillavry & Bijvoet (1936) (Zn–Cl=2·30 Å) in $Zn(NH_3)_2Cl_2$. In all these compounds however the coordination is tetrahedral.

Octahedral complexes are called by Pauling (1960) 'hypoligated' or 'hyperligated'. In compounds of this type implying transition elements with uncompleted *d* orbitals, magnetic properties are indicative of hypoligation or hyperligation. It is impossible to think of 'hyperligated' complexes of zinc or cadmium as their *d* orbitals are completely filled. Therefore following this theory we must consider the actual complex as 'hypoligated'.

According to the ligand field theory these are weak or external complexes. The large observed distances are in agreement with this interpretation. On the basis of the ligand field theory it is generally asserted that electronic systems d^0, d^5, d^{10} form the most stable tetrahedral complexes because of the repulsion between nitrogen atoms (Basolo & Pearson, 1958). Such repulsion would be opposed here by the rigid bond N–N of the hydrazine; the resultant complex is weak.

The structure of the hydrazine molecule is drawn in Fig. 3; hydrogen positions were calculated following Penney & Sutherland (1934). This structure can be confirmed further, at least qualitatively, if we examine

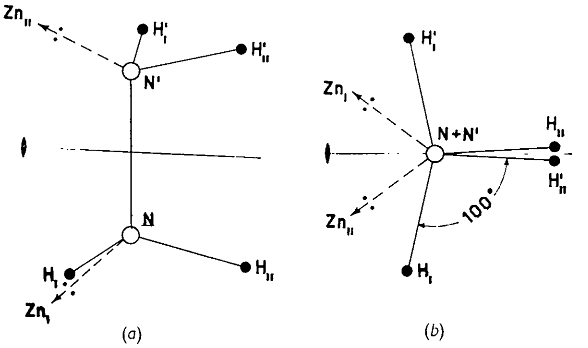


Fig. 3. The hydrazine molecule. (*a*) Clinographic projection. (*b*) Orthogonal projection on the plane normal to the line N–N. Dotted lines represent the observed bond directions Zn–N. These lines, in the projection (*b*) form a 74° angle.

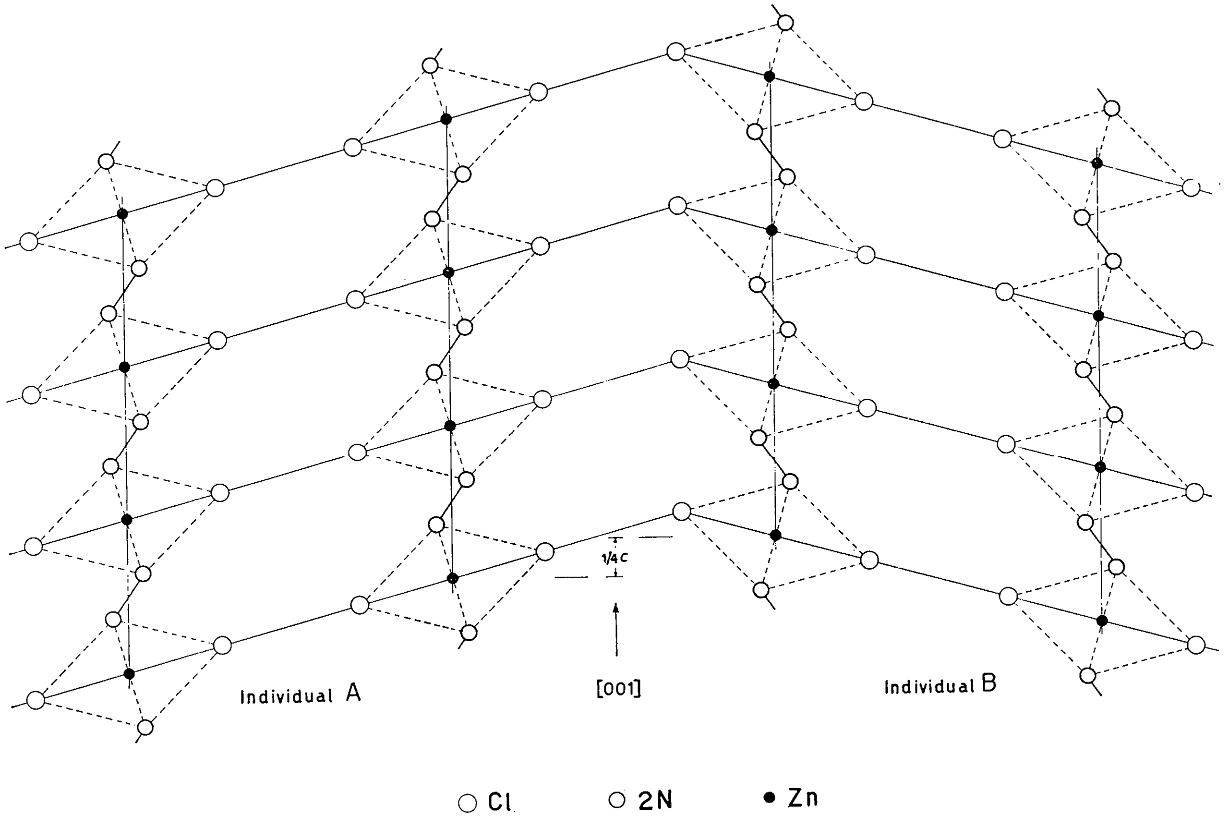


Fig. 4. Twin law (100). Structural relation between two twinned individuals in direct space. $[Zn(N_2H_4)_{4/2}]Cl_2$ groups with their centres at (*x*, 0, *z*) are represented. Twinning leaves unchanged the periodicity of the projection on the plane normal to [001].

the disposition of the Zn–N bonds in respect to the N–N direction of one hydrazine molecule. Assuming that no distortion takes place in the tetrahedral electronic structure of each N, the rotation of the two half-molecules $-NH_2$ can be calculated even from the angle between two lines joining each N to each Zn. This azimuthal angle is measured in the projection in the plane normal to N–N. The lone pair of each N atom must lie along one of these lines (see Fig. 3). The azimuthal angle is 74°. The hydrazine molecule has therefore the 'staggered' form with C_2 symmetry (Penney & Sutherland, 1934), instead of the *cis* form (Collin & Lipscomb, 1951) with C_{2v} symmetry. The distance between two N atoms in the same hydrazine molecule is 1·46 Å. It is exactly equal to that found by Collin & Lipscomb (1951) by X-rays and very near to that found by Giguére & Schomaker (1943) (N–N = 1·47 Å), by electron diffraction.

The shortest distances between parallel chains are N–Cl = 3·45 Å (see Fig. 1) and Cl–Cl = 3·83 Å (see Fig. 4).

The formation of lamellar twins — twin law (100) — can be explained by maintaining the same distances between the chains. In fact if one admits, following Buerger (1945), that one chain can join the crystal in reversed (twinned) position, the growing of the two individuals A and B and the existence of the streaks on the photographs can be understood (see Fig. 4). The individual B is shifted $\frac{1}{4}c$ in respect to the individual A; because the shift takes place after every few cells, a very long identity period is originated in the direction normal to the twin plane (100), giving origin to the streaks. The (X, Y) projection is not affected by the shift (*cf.* Fig. 4) and the whole twin behaves as a unique crystal only for the $hk0$ reflections. The structure can be considered an OD (Order–Disorder) structure (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff, 1961).

The twins of the (001) law do not present these outstanding effects, due to the increased thickness of the lamellae; but interference phenomena are probably responsible for the lack of agreement between calculated and observed hkl structure factors when $h \neq 0$.

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