Fig. 1. The crystal structure of mercury(I) orthoarsenate projected along the *b* axis.

The dimensions within the AsO_4 tetrahedron are similar to those found in other arsenates (Poulsen & Calvo, 1967; Ferraris & Chiari, 1970; Khan, Straumanis & James, 1970; Linnros, 1970). One As–O distance is longer (1·78 Å) than the other three (average value 1·68 Å) and this oxygen [O(4)] is the one bonded to three different Hg–Hg pairs. The tetrahedral angles show smaller differences and range between 106 and 113° (mean value 109·5°).

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The Crystal and Molecular Structure of Di-(2-pyridyl)amine

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The crystal and molecular structure of the low-melting polymorph of di-(2-pyridyl)amine has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic, space group *Pccn*, with $a = 18·42 \pm 0·005$, $b = 12·29 \pm 0·005$, $c = 7·69 \pm 0·007$ Å, and $Z = 8$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to a final discrepancy index $R = 3·8\%$ for 565 observed reflections. Hydrogen bonds between molecules lead to the formation of dimeric units possessing twofold crystallographic symmetry and lying approximately parallel to the *ab* plane.

Introduction

The structural study of di-(2-pyridyl)amine was undertaken to obtain accurate structural parameters for this moiety since it has been widely used as a ligand in transition metal complexes. The crystal structures of three copper(II) complexes with this ligand (Johnson & Jacobson, 1971, 1973a,b) have been determined in this laboratory and McWhinnie (1970) has recently reviewed the ligand behavior of this compound.

The preparation of di-(2-pyridyl)amine was first reported by Wibaut & Dingemanse (1923). Two crystalline modifications of the compound are known, one melting at 84° and a second that melts at 94°C. The structure of the low-melting polymorph was determined in this study.

Experimental

Crystal data

Di-(2-pyridyl)amine, $C_{10}H_9N_3$, $M = 171$. Orthorhombic, *Pccn*, $a = 18·416 \pm 0·005$, $b = 12·294 \pm 0·005$,

$c = 7.691 \pm 0.007$ Å, $V = 1741.3$ Å^3, $\varrho_c = 1.31$ g cm^{-3}, $Z = 8$, $F(000) = 720$, Mo $K\alpha (\lambda = 0.7107$ Å), $\mu = 1.03$ cm^{-1}, m.p. 84°.

Recrystallization of reagent grade di-(2-pyridyl)-amine from carbon tetrachloride yielded large colorless crystals of rectangular needlelike habit and well formed faces. Precession and Weissenberg photographs exhibited mm Laue symmetry with the following systematic extinctions: $h0l$ when $l = 2n + 1$, $0kl$ when $l = 2n + 1$, and $hk0$ when $h + k = 2n + 1$. These absences uniquely determine the space group as $Pccn$. The unit-cell parameters and their standard deviations were determined by a least-squares fit to 12 independent reflection angles (Williams, 1964) whose centers were determined by left-right, top-bottom beam splitting on a previously aligned four-circle diffractometer.

For data collection a crystal of dimensions $0.10 \times 0.25 \times 0.50$ mm along the a, b, c crystal axes respectively and housed in a thin-walled Lindemann glass capillary was mounted so that the c axis was along the spindle axis of the goniometer. Data were collected at room temperature (24°) with an automated four-circle diffractometer designed and built in the Ames Laboratory (for further details, see Schroeder & Jacobson, 1973). A variable-step symmetric-scan technique was employed, with scans ranging from $1.12°$ in 2θ at low 2θ values to $1.72°$ at large 2θ angles. Stationary-crystal, stationary-counter background counts of one-half the time required to scan the peak were taken at the beginning and end of each scan. Before the scan was made each peak was maximized in ω. Also if the reflection did not exceed the background by seven counts or more, which corresponds to approximately three standard deviations in the background for larger values of 2θ, no further measurements were made on the reflection.

As a general check on electronic and crystal stability, the intensities of three standards were remeasured every 25 reflections. These standards showed no decrease over the entire period of data collection. A total of 1771 reflections were recorded in the hkl and $\bar{h}kl$ octants.

The intensity data were corrected for Lorentz polarization effects. Because of the small linear ab-sorption coefficient, no absorption correction was made. The minimum and maximum transmission factors were 0.95 and 0.99 respectively. The individual values of F_o^2 from the equivalent octants were averaged to yield 809 unique F_o^2 values. The standard deviation in each intensity was estimated from the average total count and background values by

$$[\sigma(I)]^2 = [C_t + C_b + (0.05\ C_t)^2 + (0.05\ C_b)^2] .$$

Of the 809 unique reflections, 567 had $F_o^2 \geq 3.0\sigma(I)$. The estimated standard deviation in each structure factor was calculated by the method of finite differences (Lawton & Jacobson, 1968). The reciprocals of the squares of the structure factor variances were used as weights in the least-squares refinement.

Solution and refinement

The program $MULTAN$ (Main, Woolfson & Germain, 1971) was employed to obtain phases for all reflections with E's greater than 1.0 and the E map (Hubbard, Quicksall & Jacobson, 1971) that resulted unambiguously showed the positions of all 13 heavy atoms in the structure. The ring nitrogen positions were readily determined by their low temperature factors and by their shorter bond distances on refinement. With all atoms isotropic, R was 11.00%, and the weighted R index, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$, was 12.90% for the 567 observed reflections. The scattering factors used for carbon and nitrogen were those of Hansen, Herman, Lea & Skillman (1964). Three additional cycles of anisotropic refinement of all heavy atoms reduced the discrepancy index to 9.8% and R_w to 11.3%. A subsequent difference map clearly indicated all nine hydrogen atom positions.

At this stage two reflections, 202 and 220, appeared to be severely affected by extinction and were removed from the refinement. Hydrogen positions were included using the contracted hydrogen atom scattering factor of Stewart, Davidson & Simpson (1965). A final discrepancy index of 3.8% was obtained, with $R_w = 4.3\%$ for the 565 observed reflections. At this point two

Table 1. *Final heavy atomic coordinates and thermal parameters for di-(2-pyridyl)amine*

Standard deviations of the coordinates are for the least significant figure. The β_{ij} and their standard deviations are $\times 10^4$. The β_{ij} are defined by:

$$T = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})] .$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.4805 (2)	0.8697 (4)	0.2168 (5)	31 (2)	85 (4)	259 (10)	11 (2)	−7 (3)	1 (5)
C(2)	0.4524 (2)	0.7692 (4)	0.1838 (5)	30 (2)	94 (4)	240 (9)	−3 (2)	−12 (3)	−24 (5)
C(3)	0.4955 (2)	0.6806 (4)	0.2183 (5)	43 (2)	73 (4)	253 (10)	−5 (2)	−8 (3)	−25 (5)
C(4)	0.5635 (2)	0.6964 (3)	0.2846 (5)	34 (2)	61 (3)	249 (9)	3 (2)	−15 (3)	−20 (5)
C(5)	0.5876 (2)	0.8018 (3)	0.3162 (4)	22 (1)	69 (3)	173 (8)	6 (2)	2 (2)	−8 (4)
C(6)	0.6912 (2)	0.9073 (3)	0.4451 (4)	26 (1)	55 (3)	172 (7)	0 (2)	0 (3)	5 (4)
C(7)	0.6558 (2)	1.0030 (3)	0.4934 (5)	31 (2)	69 (3)	218 (9)	11 (2)	−6 (3)	−14 (4)
C(8)	0.6964 (2)	1.0868 (3)	0.5580 (5)	39 (2)	66 (3)	241 (9)	10 (2)	−6 (3)	−15 (5)
C(9)	0.7704 (2)	1.0761 (3)	0.5742 (5)	42 (2)	66 (4)	224 (9)	−5 (2)	−4 (3)	−8 (5)
C(10)	0.8007 (2)	0.9783 (3)	0.5273 (5)	28 (2)	82 (4)	231 (9)	−2 (2)	−8 (3)	2 (5)
N(1)	0.5469 (2)	0.8888 (2)	0.2825 (4)	25 (1)	75 (3)	249 (7)	5 (1)	−10 (2)	−4 (3)
N(2)	0.6564 (2)	0.8157 (3)	0.3834 (4)	26 (1)	54 (3)	257 (8)	7 (2)	−6 (2)	−4 (4)
N(3)	0.7630 (2)	0.8946 (2)	0.4624 (4)	26 (1)	59 (2)	226 (7)	1 (1)	−4 (2)	1 (3)

final cycles of least-squares calculations (Busing, Martin & Levy, 1962) were run with all 807 uniquely measured reflections yielding $R = 6 \cdot 2\%$ and $R_w = 5 \cdot 3\%$. No appreciable shifts in atom positions occurred.

In Table 1 are listed the final positional and thermal parameters of the heavy atoms together with their standard deviations. The refined positional and isotropic thermal parameters and their standard deviations for the hydrogen atoms are given in Table 2. Standard deviations given were obtained from the inverse matrix of the final least-squares refinement cycle. A list of all 807 unique recorded and calculated structure factors ($\times 10$) is found in Table 3. The bond lengths and bond angles with standard deviations are given in Tables 4 and 5 and in Fig. 1 (Johnson, 1965). Significant nonbonded distances are listed in Table 6 with least squares plane information provided in Table 7.

Table 2. Refined hydrogen atom parameters

The number of the hydrogen atom is that of the carbon to which it is attached.

	x	y	z	$B(\text{Å}^2)$
H(1)	0·454 (2)	0·935 (3)	0·190 (4)	4·5 (9)
H(2)	0·403 (3)	0·763 (3)	0·131 (4)	5·1 (9)
H(3)	0·479 (2)	0·611 (3)	0·190 (5)	6·4 (10)
H(4)	0·594 (2)	0·635 (3)	0·307 (4)	4·0 (8)
H(5)*	0·681 (2)	0·756 (3)	0·396 (4)	4·1 (9)
H(7)	0·605 (2)	1·008 (2)	0·481 (4)	4·0 (8)
H(8)	0·668 (2)	1·156 (3)	0·589 (5)	6·5 (10)
H(9)	0·800 (2)	1·135 (3)	0·622 (5)	6·3 (10)
H(10)	0·850 (2)	0·967 (3)	0·541 (4)	3·7 (8)

* H(5) is the amine hydrogen attached to N(2).

Table 3. Observed and calculated structure factors ($\times 10$) for di-(2-pyridyl)amine

Table 4. Interatomic distances and angles in di-(2pyridyl)amine

Distances (Å)

C(1)–C(2)	1·362 (5)	C(9)—C(10)	1·374 (5)
C(2)–C(3)	1·374 (5)	C(1)—N(1)	1·345 (4)
C(3)–C(4)	1·367 (5)	C(5)—N(1)	1·332 (4)
C(4)–C(5)	1·391 (4)	C(5)—N(2)	1·379 (4)
C(6)–C(7)	1·395 (5)	C(6)—N(2)	1·380 (4)
C(7)–C(8)	1·367 (5)	C(6)—N(3)	1·338 (4)
C(8)–C(9)	1·375 (5)	C(10)–N(3)	1·337 (4)

Angles (°), e.s.d. = 0·4°

N(1)–C(1)–C(2)	125·1	N(3)—C(10)–C(9)	124·0
C(1)–C(2)–C(3)	117·6	C(10)–C(9)—C(8)	117·6
C(2)–C(3)–C(4)	119·2	C(9)—C(8)—C(7)	120·3
C(3)–C(4)–C(5)	119·4	C(8)—C(7)—C(6)	118·4
C(4)–C(5)–N(1)	122·3	C(7)—C(6)—N(3)	122·3
C(5)–N(1)–C(1)	116·4	C(6)—N(3)—C(10)	117·5
N(1)–C(5)–N(2)	119·4	N(3)—C(6)—N(2)	113·5
N(2)–C(5)–C(4)	118·3	N(2)—C(6)—C(7)	124·2
C(5)–N(2)–C(6)	131·1		

Table 5. Interatomic distances and angles involving hydrogen atoms

Distances (Å), e.s.d. = 0·03 Å

C(1)–H(1)	0·96	C(10)–H(10)	0·92
C(2)–H(2)	0·99	C(9)—H(9)	0·98
C(3)–H(3)	0·94	C(8)—H(8)	1·03
C(4)–H(4)	0·95	C(7)—H(7)	0·94
N(2)–H(5)	0·87	H(5)···N(3′)*	2·18

Angles (°), e.s.d. = 2·0°

H(1)–C(1)–N(1)	113	H(10)–C(10)–N(3)	116
H(1)–C(1)–C(2)	122	H(10)–C(10)–C(9)	120
H(2)–C(2)–C(1)	120	H(9)—C(9)—C(8)	121
H(2)–C(2)–C(3)	123	H(9)—C(9)—C(10)	121
H(3)–C(3)–C(2)	119	H(8)—C(8)—C(7)	116
H(3)–C(3)–C(4)	121	H(8)—C(8)—C(9)	124
H(4)–C(4)–C(5)	121	H(7)—C(7)—C(6)	120
H(4)–C(4)–C(3)	119	H(7)—C(7)—C(8)	122
H(5)–N(2)–C(5)	114	H(5)—N(2)—C(6)	114

* Hydrogen bond. N(3′) is related to N(3) by the symmetry operation $\frac{3}{2}-x,\frac{3}{2}-y,z$.

Table 6. Nonbonded interatomic distances (Å) for di-(2-pyridyl)amine

N(1)····H(7)	2·38	C(10)···C(7ᵛⁱ)	3·69
H(1)····H(7ⁱⁱ)	2·84	C(9)····C(6ᵛⁱ)	3·60
H(2)····H(8ⁱⁱⁱ)	2·52	N(3)····C(6ᵛⁱ)	3·81
H(3)····H(7ⁱⁱⁱ)	2·39	N(2)····C(4ᵛ)	3·53
H(9)····H(8ⁱᵛ)	2·64	N(1)····H(10ᵛⁱⁱ)	2·83
C(3)····C(5ᵛ)	3·53	N(2)····C(10ᵛⁱⁱ)	3·48
C(3)····N(1ᵛ)	3·59		
C(4)····N(2ᵛ)	3·53		
C(10)···C(6ᵛⁱ)	3·33		

* Roman numerals denote the following symmetry transformations:i $\frac{3}{2}-x,\frac{3}{2}-y,z$; ii $1-x,2-y,1-z$; iii $-\frac{1}{2}+x, 1-y,\frac{1}{2}-z$; iv $\frac{3}{2}-x,\frac{3}{2}-y,z$; v $x,\frac{3}{2}-y,\frac{1}{2}+z$; vi $\frac{3}{2}-x,y,\frac{1}{2}+z$; vii $\frac{3}{2}-x,y,\frac{1}{2}+z$.

Table 7. Least-squares planes for di-(2-pyridyl)amine

The planes $lX+mY+nZ+k=0$ are referred to coordinates (Å) oriented along the orthogonal a,b,c crystal axes.

	l	m	n	k
Plane 1	−0·373	−0·041	0·927	2·19
Plane 2	−0·129	−0·354	0·926	2·42

Deviations from plane (Å)

Plane 1		Plane 2	
C(1)	−0·003	C(6)	−0·008
C(2)	0·005	C(7)	0·005
C(3)	0·000	C(8)	0·004
C(4)	−0·003	C(9)	−0·011
C(5)	0·004	C(10)	0·008
N(1)	−0·001	N(3)	0·000
H(1)	−0·05	H(7)	0·014
H(2)	−0·03	H(8)	−0·013
H(3)	−0·05	H(9)	0·007
H(4)	−0·02	H(10)	0·034

Description of the structure and discussion

The low-melting polymorph of di-(2-pyridyl)amine contains pairs of molecules hydrogen bonded to one another, the dimeric unit possessing twofold crystallographic symmetry. Within the molecule the carbon–carbon bonds adjacent to the bridgehead nitrogen are found to be significantly different in length [1·395 (5) Å] compared with the remaining carbon–carbon distances [1·369 (5) Å]. The latter are somewhat shorter than the pyridine C–C distances previously reported (Kennard, 1962). The carbon–nitrogen distances in the pyridine rings average 1·338 (4) Å with no significant deviations and are virtually identical with the 1·340 Å C–N distance reported for pyridine. The two bridging C–N bond distances are identical at 1·380 Å. The bond angles within the pyridine rings vary between 117·6° [C(1)–C(2)–C(3), C(8)–C(9)–C(10)] and 125·1° [N(1)–C(1)–C(2)]. The bond angles about chemically equivalent atoms in the two pyridine rings are equal within the standard deviations. Bond angles involving the bridging nitrogen are reasonable in the light of repulsive and attractive forces present. The C(6)–N(2)–C(5) angle of 131·1° reflects the nonbonded repulsions between H(7) and N(1) at 2·38 Å. The hydrogen bonding between the moieties probably accounts for the 113·5° angle found for the N(3)–C(6)–N(2). It should be noted that the geometry about the amine nitrogen is planar within experimental error, the sum of the three angles about it being 359·1°.

The carbon–hydrogen bond distances range from 0·92 Å [C(10)–H(10)] to 1·03 Å [C(8)–H(8)], the average being 0·96 Å. The N–H distance is 0·87 Å with H–N–C bond angles of 114° (Table 5).

The rings in the molecule are approximately parallel to the ab plane. As expected, the largest component of anisotropic thermal motion of the heavier atoms is in a direction perpendicular to this plane, with approximately equal r.m.s. deviations in this direction for all the heavy atoms. The hydrogen isotropic thermal parameters range from 3·7 Å² [H(10)] to 6·5 Å² [H(8)].

The pyridine ring containing N(1) is strictly planar with a maximum deviation of 0·005 Å from the mean plane, while in the second ring C(9) is displaced by 0·011 Å from the mean plane, a deviation of borderline significance.

Steric hindrance within the ligand is relieved by a twist of the two rings giving rise to a 23° dihedral angle between them (Fig. 2.)

The hydrogen bond joining the two molecules is nearly linear with a N(3')···H(5)–N(2) angle of 172°. The distance between the hydrogen and receptor atom is 2·18 Å while the N(3')···N(2) distance is 3·02 Å. In spite of the short distance between N(1) and H(7), 2·38 Å, it is unlikely that there is an appreciable linkage between these atoms due to the unfavourable N(1)–H(7)–C(7) angle of 117°.
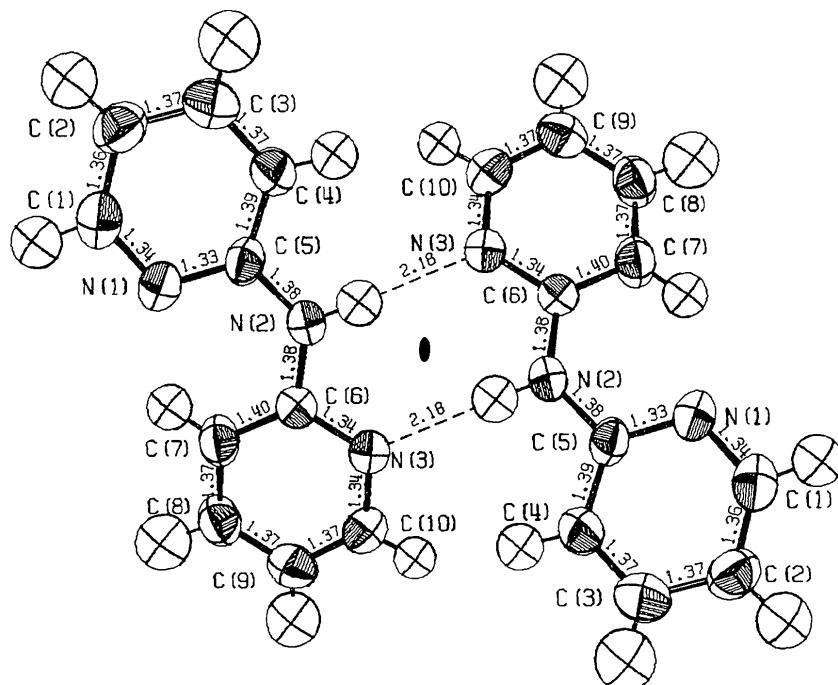
Fig. 1. A dimeric unit of di-(2-pyridyl)amine displaying the twofold symmetry.
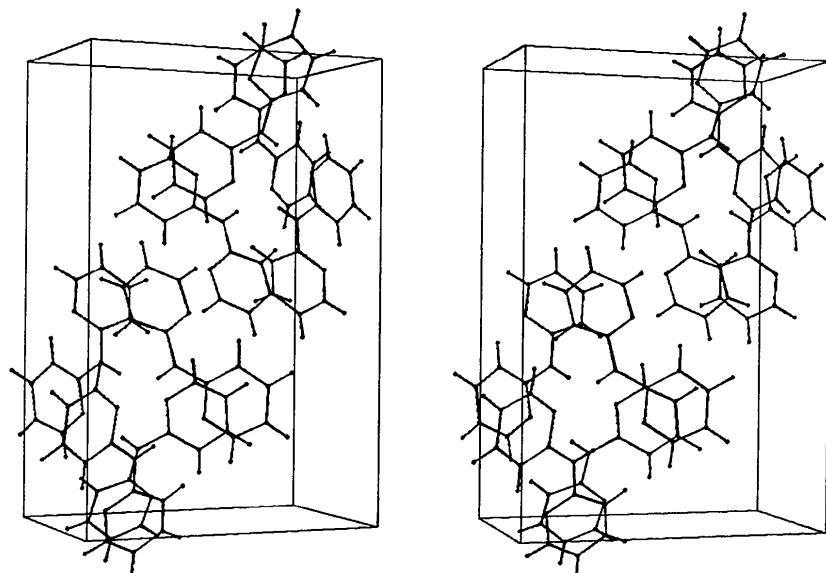
Fig. 2. A stereographic view of the unit cell of di-(2-pyridyl)amine. The origin is in the lower left corner with x up, y across, and z into the page.

The crystallographic twofold axes at $x=\frac{1}{4}$, $y=\frac{1}{4}$, and $x=\frac{3}{4}$, $y=\frac{3}{4}$ are those running through the center of the dimeric units and these units are layered approximately perpendicularly to the z direction (Fig. 2). The distance between these layers is nearly 3·7 Å, a value typical of layered aromatic structures. Distances between dimeric units in the same layer approximate those values expected for van der Waals contacts, the shortest being 2·39 between H(3) and H(7). All short intermolecular contacts are listed in Table 6.

It is interesting to speculate on the structural changes that may occur in the transformation of the low-melting form to the high-melting form of di-(2-pyridyl)amine. If the ring containing N(1) is rotated about the N(2)–C(5) bond to attempt to bring N(1) and H(10) into proximity, the distance between H(4) and H(7) would be reduced to approximately 1·6 Å, making this an unacceptable configuration. This steric interaction could be relieved by a change from the planar geometry about the amine nitrogen to one approximating a tetrahedron (including the lone pair of electrons). If this change does account for the increased stability then it is likely due to more favourable packing of dimers than the actual strengthening of the dimeric unit, since in the melting process one would expect the van der Waals forces to be overcome before the dimer is destroyed.

With the structural data presently available for transition metal complexes with di-(2-pyridyl)amine, it is not possible to make a meaningful comparison between the coordinated and free ligand. It is hoped that future structure determinations (X-ray and/or neutron) of metal complexes with this ligand will provide structural parameters of sufficient accuracy to allow meaningful comparisons to be made.

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Feeble Occurrence of Polytypism Based on the 2*H* Basic Phase in Cadmium Iodide Crystals

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In cadmium iodide, the most stable phase is the 4*H* structure. The next stable phase is the two-layered hexagonal structure known as the 2*H* polytype. Most of the polytypes of cadmium iodide are generally found to result from the 4*H* basic structure; but there seem to be only a few polytypes which are based on the 2*H* basic structure. The rare occurrence of polytypic structures based on the 2*H* basic phase seems somewhat strange and, until now, there seems to have been no explanation of this strange behaviour of CdI₂ polytypes. The purpose of this communication is, therefore, to explain this salient feature of cadmium iodide polytypes.

Recently Prasad & Srivastava (1972) have shown that the polytypes of cadmium iodide based on the 4*H* basic structure are formed through a layer-transposition mechanism involving only I/I glide and that the Cd/I glide produces structures which are energetically unfavourable. If the same idea is applied to the crea-