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The Crystal and Molecular Structure of Polymeric μ-Dichloro-imidazolocadmium (II)

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The structure of $(CdCl_2 . ImH)_\infty$ has been determined from single-crystal X-ray diffraction data collected on a four-circle diffractometer. The analysis was carried out with 655 unique reflexions and refined by full-matrix least-squares calculations to a final R of 0·024. The crystals are orthorhombic, space group $Pbn2_1$ with $a=15·305(5)$, $b=11·102(5)$, $c=3·838(5)$ Å, $Z=4$. The structure is polymeric. The Cd atoms are linked into infinite chains by double Cl bridges. Two such chains running parallel to each other are themselves linked *via* Cd–Cl bonds resulting in a cage-like structure. Each Cd is octahedrally coordinated to five Cl and one N. A trifurcated N–H···Cl interaction is postulated.

Introduction

A study of metal ion–imidazole complexes has been undertaken in view of the important role that imidazole plays in providing potential metal binding sites in proteins. Cd itself has recently gained prominence as a pollutant (Shaikh & Lucis, 1971) and is known to be present in the protein metallothionein (Kagi & Vallee, 1960). The unlikely stoichiometry of the complex which we synthesized, $CdCl_2(Im)$, made a structural determination desirable.

Experimental

The complex was prepared by mixing a saturated solution of cadmium lactate with a $1M$ solution of imidazole prepared in $5M$ hydrochloric acid. The pH of the initial lactate solution was 5·9 while that of the imidazole was 6·0. The final pH of the mixture was 5·05. The percentage composition was: found: C 14·7, H 1·7, N 11·3, Cd 44·9, Cl 26·9%; calculated for $CdCl_2.ImH$: C 14·33, H 1·60, N 11·14, Cd 44·71, Cl 28·20. The density was determined by flotation in a mixture of m-xylene and CH_2I_2. The crystals were white thin, plate-like needles. A single crystal (0·20 × 0·25 × 0·28 mm) was used. The lattice constants (Table 1) were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation.

Table 1. *Crystal data*

$C_3H_4N_2 . CdCl_2$
$M = 251·38$
Space group: $Pbn2_1$ (No. 33, C_{2v}^9)
$a = 15·305 (5)$ Å
$b = 11·102 (5)$
$c = 3·838 (5)$
$V = 652·14$ Å^3
$D_m = 2·50$ g cm^{-3}
$D_c = 2·56$ g cm^{-3} for $Z=4$
$\mu = 39·27$ cm^{-1}
$F(000) = 472$

The intensities were collected on a Philips PW1100 computer-controlled four-circle diffractometer operating in the $\omega-2\theta$ scan mode (scan width $= 1·00°$ θ, scan speed $= 0·04°$ θ s^{-1}). With graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å), 698 reflexions up to $2\theta = 50°$ were measured. With the criterion $I_{rel} > 2\sigma(I_{rel})$ for an observed reflexion, 43 reflexions were omitted as unobserved leaving 655 unique reflexions which were employed in the structural analysis. Three reference reflexions were measured after every 68 reflexions to monitor stability of operation and crystal decomposi-

tion: the variation in intensity was less than 2% of its mean value. Lorentz–polarization corrections were applied but no correction was made for absorption.

Solution and refinement of the structure

The positional parameters of the Cd atom were determined from a Patterson map while all remaining atoms were located in the subsequent electron density map. Refinement was carried out with anisotropic temperature factors for all the heavy atoms. These were of the form $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$. The unambiguous determination of N(3) of the imidazole ring was based on peak heights in an electron density map from which N(3) and C(4) had been omitted. All the H atoms were located in subsequent difference maps and refined by constraining them at 1·08 Å from their parent atoms. The isotropic temperature factors of all the H atoms were refined as one common parameter (Sheldrick, 1975). The weighting scheme was $w = 1/(\sigma^2 F + gF^2)$. The final value of $g = 0.002780$ was chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F. An isotropic extinction parameter x refined to 0·0030 (4); the correction was applied to F_c so that $F^* = F(1 - xF^2/\sin\theta)$.

After ten cycles of full-matrix least-squares refinement, $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$ converged to 0·029

with a corresponding unweighted R of 0·024.* In an attempt to establish the absolute configuration all atomic positional parameters were inverted and the refinement repeated. This yielded a virtually identical generalized R index indicating that the two enantiomorphs are indistinguishable. After the final cycle the average e.s.d. in the positional parameters and temperature factors of the non-hydrogen atoms was more than 1000 times the average parameter shift. Table 2 shows an analysis of variance computed after the final cycle. As a final check of the correctness of the structure a difference map was computed. This revealed two peaks of height 1·4 and 1·2 e Å^{-3} at distances 0·81 and 0·82 Å on either side of the Cd atom. Both peaks are thought to arise because no absorption correction had been applied. The difference map was otherwise featureless.

Scattering factors for the non-hydrogen atoms were from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The Cd was treated as Cd^0 and anomalous dispersion corrections (Mo $K\alpha$ radiation) for Cd ($\Delta f' = -0.86$; $\Delta f'' = 1.40$) and Cl ($\Delta f' = 0.10$ and $\Delta f'' = 0.20$) were applied.

Table 2. *Analysis of variance*

(a) As a function of $\sin\theta$

$\sin\theta$	0·00–0·19–0·24–0·28–0·31–0·33–0·36–0·38–0·39–0·41–0·43									
N	65	67	68	72	55	86	70	41	80	48
V	81	71	66	71	58	53	62	72	64	59

(b) As a function of $(F/F_{max})^{1/2}$

$(F/F_{max})^{1/2}$	0·00–0·17–0·22–0·25–0·29–0·34–0·39–0·42–0·49–0·59–1·0									
N	69	76	57	59	69	73	54	73	61	61
V	111	79	71	67	56	53	43	39	45	55

(c) By parity groups

	ggg	ugg	gug	uug	ggu	ugu	guu	uuu	all
N	115	82	85	93	66	78	61	72	652
V	61	56	88	61	69	65	65	58	66

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and anisotropic temperature factors* (Å$^2 \times 10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	4104 (0)	6021 (0)	0 (0)*	231 (3)	361 (3)	196 (3)	−15 (3)	−6 (4)	38 (1)
Cl(1)	4161 (1)	4276 (1)	5000 (10)	222 (6)	292 (6)	234 (7)	13 (24)	−42 (11)	12 (4)
Cl(2)	4223 (1)	7596 (1)	5000 (12)	309 (6)	311 (6)	243 (7)	−35 (12)	−72 (13)	5 (4)
N(1)	2639 (3)	5984 (3)	−79 (29)	201 (21)	396 (22)	322 (27)	−14 (33)	74 (44)	39 (13)
C(2)	2129 (4)	6877 (5)	984 (16)	349 (25)	354 (24)	281 (37)	0 (21)	31 (23)	45 (20)
N(3)	1294 (3)	6628 (4)	441 (19)	311 (22)	492 (23)	452 (34)	88 (34)	2 (30)	125 (19)
C(4)	1250 (4)	5524 (6)	−1096 (20)	314 (29)	492 (31)	425 (37)	−45 (28)	−42 (26)	−51 (25)
C(5)	2077 (4)	5127 (5)	−1341 (20)	338 (30)	385 (27)	355 (27)	−67 (26)	−70 (27)	37 (22
H(2)	2364 (4)	7701 (5)	2148 (16)						
H(3)	747 (3)	7198 (4)	1100 (19)						
H(4)	667 (4)	5061 (6)	−1947 (20)						
H(5)	2270 (4)	4262 (5)	−2371 (20)						

* Held invariant owing to space-group requirement.

The final positional and thermal parameters are given in Table 3. The isotropic temperature factor of the H atoms refined to a value of $U=0.06$ (1) Å^2.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1106 computer with the program system SHEL-X written by G. M. Sheldrick (Cambridge).

Description of the structure and discussion

The structure is shown in Fig. 1 (*PLUTO:* Motherwell, 1975). The bond lengths and angles are given in Tables 4 and 5 respectively while Table 6 lists computed least-squares planes with their equations.
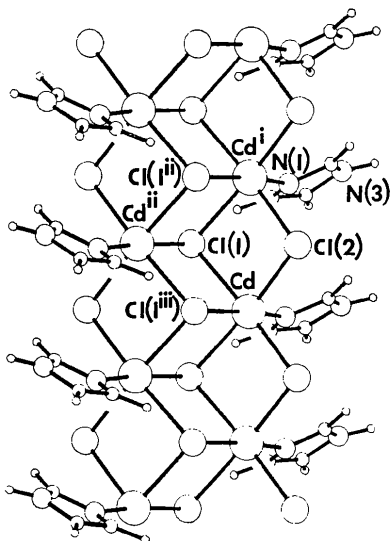

Fig. 1. The structure of (CdCl$_2$.ImH)$_\infty$.

Table 4. *Intramolecular bond lengths and their e.s.d.'s* (Å)

Cd–Cl(1)	2·729 (3)	N(1)–C(2)	1·321 (7)
Cd–Cl(2)	2·604 (4)	C(2)–N(3)	1·324 (8)
Cd–Cl(1^{iv})	2·728 (3)	N(3)–C(4)	1·367 (9)
Cd–Cl(2^{iv})	2·601 (4)	C(4)–C(5)	1·338 (9)
Cd–Cl(1^{iii})	2·676 (3)	C(5)–N(1)	1·370 (8)
Cd–N(1)	2·243 (5)		

Table 5. *Intramolecular bond angles and their e.s.d.'s* (°)

Cl(1)–Cd—Cl(2)	87·5 (1)
Cl(1)–Cd—Cl(2^{iv})	173·5 (1)
Cl(1)–Cd—Cl(1^{iii})	83·1 (1)
Cl(1)–Cd—Cl(1^{iv})	89·4 (1)
Cl(1)–Cd—N(1)	90·5 (2)
Cl(2)–Cd—N(1)	94·1 (2)
Cl(2)–Cd—Cl(2^{iv})	95·0 (1)
Cl(2)–Cd—Cl(1^{iii})	90·8 (1)
Cd—N(1)–C(2)	124·6 (4)
N(1)–C(2)–N(3)	111·4 (5)
C(2)–N(3)–C(4)	107·3 (4)
N(3)–C(4)–C(5)	107·0 (5)
C(4)–C(5)–N(1)	109·6 (5)
C(5)–N(1)–C(2)	105·2 (5)
C(5)–N(1)–Cd	130·0 (4)

The complex is polymeric. The Cd atoms are displaced one unit cell from each other in the **c** direction and are linked by double Cl bridges forming an infinite –Cd–Cl$_2$–Cd– ribbon perpendicular to the *ab* plane. This is similar to that reported for catena-μ-dichloro-bisimidazolecadmium(II) (Flook, Freeman, Huq & Rosalky, 1973). However, in the present structure, a second such ribbon, generated by the 2$_1$ axis, runs parallel to the first and is linked to the latter via Cd–Cl bonds similar to the CdCl$_2$ structure. In this way an infinite open cage-like network is generated. These

Table 6. *Least-squares planes*

The equations of the planes are expressed in orthogonalized space as $PI+QJ+RK=S$.

Plane I	through the five atoms of the imidazole ring				
Atoms defining the plane	N(1)	C(2)	N(3)	C(4)	C(5)
Distance from the plane (Å)	−0·001	−0·001	0·003	−0·004	0·003
Equation	$0.05355I+0.41497J-0.90826K=3.00174$				

Plane II	through the atoms defining face 1 of the cage			
Atoms defining the plane	Cd	Cl(1)	Cl(2)	Cd^I
Distance from the plane (Å)	−0·069	0·065	0·072	−0·069
Equation	$0.99971I-0.02389J+0.00022K=6.18830$			

Plane III	through the atoms defining face 2 of the cage			
Atoms defining the plane	Cd	Cl(1)	Cd^{II}	Cl(1^{III})
Distance from the plane	0·000	0·000	0·000	0·000
Equation	$0.08766I+0.70326J+0.70551K=5.25122$			

Plane IV	through the atoms defining face 3 of the cage			
Atoms defining the plane	Cl(1)	Cd^{II}	Cd^I	Cl(1^{II})
Distance from the plane (Å)	0·000	0·000	0·000	0·000
Equation	$0.08755I+0.70319J-0.70559K=2.54189$			

Intersection angles (°)

Planes I and II	87·6	Planes II and IV	86·0
Planes II and III	85·9	Planes III and IV	89·8

A C 32B – 17*

open cages may be regarded as incomplete 'cubes' one of which is defined in Fig. 1 by Cd, Cl(1), Cl(2), Cd^i, Cl(1^{ii}), Cd^{ii} and Cl(1^{iii}). Each Cd is thus bonded to four Cl in its own chain plus a fifth Cl in the parallel chain, the latter producing the cross-linkage. The octahedral coordination is completed by one Cd–N (imidazole) bond.

The five Cd–Cl distances (mean = 2·668 Å) are in good agreement with the 2·731 Å reported for catena-μ-dichloro-bisimidazolecadmium(II). The Cd–N (imidazole) bond length (2·243 Å) agrees favourably with that reported for the latter structure (2·248 Å) and with the mean (2·26 Å) in cis-catena-μ-sulphato-aquo-tris(imidazole)cadmium(II) (Caira, Nassimbeni & Orpen, 1975). The bond lengths in the imidazole ring lie within expected ranges although, as with dichlorobis-imidazolecadmium(II), the sharp differences between N(1)–C(2) (1·321 Å) and N(1)–C(5) (1·370 Å) indicate that the system is not completely delocalized.

The imidazole ring is planar (plane I, Table 6). This plane is approximately normal (87·6°) to the plane defined by Cd, Cl(1) and Cl(2) (plane II, Table 6). The Cd atom lies at a distance of 0·109 Å from plane I. Planes II, III and IV through the three faces of the incomplete cage are approximately perpendicular to each other intersecting at angles 85·9, 86·0 and 89·8°.

An interesting feature of the structure is the hydrogen bonding for which we adopt the criterion $d(H-B)$ $< W_H + W_B - 0·2$ Å where W_H and W_B are the van der Waals radii for H (1·2 Å) and the acceptor B (Cl: 1·8 Å) respectively (Hamilton, 1968). Thus the N(3)–H(3) group of each imidazole ring is involved in hydrogen bonding to Cl(2) in a symmetry-related ribbon with an NH···Cl distance of 2·384 (5) Å. Two weaker interactions involving the same NH group and two symmetry related Cl(1) atoms at NH···Cl distances 2·750 (6) and 3·289 (7) Å are present. These have the net effect of 'completing the cage' (Fig. 2). Table 7 lists all the relevant bond lengths and angles involved in these interactions.

Table 7. *Bond lengths* (Å) *and angles* (°) *and their e.s.d.'s involved in the hydrogen bonding and other short contacts*

Symmetry operators

(i)	x	y	$z+1$	(iv)	x	y	$z-1$
(ii)	$1-x$	$1-y$	$z+\frac{1}{2}$	(v)	$x+\frac{1}{2}$	$1\frac{1}{2}-y$	$z+\frac{1}{2}$
(iii)	$1-x$	$1-y$	$z-\frac{1}{2}$				

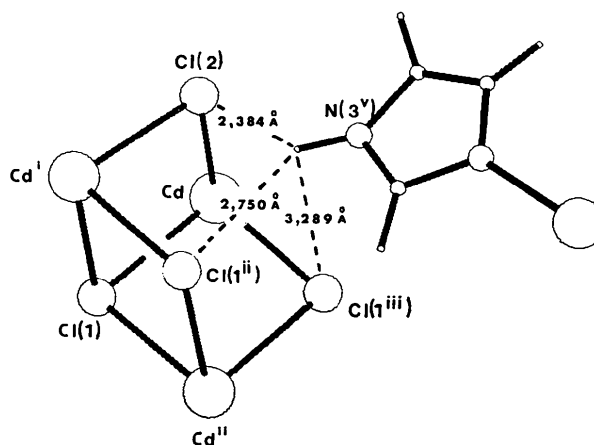| H(3^v)–Cl(2)	2·384 (5)	N(3^v)–Cl(2)	3·293 (5)
H(3^v)–Cl(1^{ii})	2·750 (6)	N(3^v)–Cl(1^{ii})	3·488 (6)
H(3^v)–Cl(1^{iii})	3·289 (7)	N(3^v)–Cl(1^{iii})	3·672 (6)
		N(3^v)–H(3^v)–Cl(2)	140·7 (5)
		N(3^v)–H(3^v)–Cl(1^{ii})	125·4 (4)
		N(3^v)–H(3^v)–Cl(1^{iii})	102·2 (5)

Fig. 2. Completion of the cage N–H···Cl hydrogen bonding.

Donohue (1968) discusses bifurcated hydrogen bonds and states that a structure in which *all* the hydrogen bonds are strained is highly unlikely, with the exception of molecules containing restraints. In the present study, although the three N–H···Cl angles deviate grossly from linearity and the corresponding H···Cl distances differ substantially, we suggest the existence of a trifurcated N–H···Cl interaction. The peculiar geometry of this interaction is dictated by the highly constrained nature of the receptor Cl atoms.

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