

Studies on Chelates of Hydrazinecarboxylic Acid with Bivalent Metals. The Crystal and Molecular Structure of Bis(hydrazinecarboxylato-*N'*,*O*)cadmium Monohydrate

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The crystals of bis(hydrazinecarboxylato-*N'*,*O*)cadmium monohydrate, $\text{Cd}(\text{N}'\text{H}_2\text{-NH-COO})_2 \cdot \text{H}_2\text{O}$, are orthorhombic, space group *Pbcn*. The unit cell constants are: $a = 7.402(7)$, $b = 12.360(7)$, $c = 7.828(12)$ Å, with four molecular units per cell. The structure has been determined from three-dimensional data and refined by differential syntheses. The structure is made up from distorted complexes *trans,cis,cis*-octahedral; two corners (*trans*) of the coordination polyhedron are occupied by O atoms of chelating $\text{N}'\text{H}_2\text{-NH-COO}$ groups, two corners (*cis*) by N' atoms and two corners (*cis*) by O atoms belonging to hydrazinecarboxylato groups of adjacent octahedra. The complex is of the same type as that found in the anhydrous compound $\text{Cd}(\text{N}'\text{H}_2\text{-NH-COO})_2$ but with different distortions of the five-membered chelate ring; in particular, the bonds $\text{Cd-N}'$ and N-C are rotated, around the bond N'-N , 32° from the eclipsed position in the hydrated compound but 3° in the anhydrous compound. This difference could be due either to rotational isomers of the ligand being 'frozen' in different positions in the two compounds, or to distinct stereoisomers of the ligand.

Introduction

The study of the crystal structures of bis(hydrazinecarboxylato-*N'*,*O*)cadmium monohydrate has been undertaken as part of structural and chemical researches on the chelating properties of hydrazinecarboxylic acid, $\text{N}'\text{H}_2\text{-NH-COOH}$ (Hhyc). This acid derives from hydrazine, $\text{H}_2\text{N-NH}_2$, to which a 'staggered' configuration can be assigned (Ferrari, Braibanti & Bigliardi, 1963; Ferrari, Braibanti, Bigliardi & Dallavalle, 1963; Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a,b,c*); the rotation of the two $-\text{NH}_2$ groups around the N-N axis is hindered by the lone pairs of the nitrogen atoms. If the carboxylato group is substituted for one H, several stereoisomers of the resulting acid could be formed, unless the rotation of $-\text{N}'\text{H}_2$ around N'-N becomes possible in the new molecule. The ligand hydrazinecarboxylato forms, with bivalent metals, octahedral complexes giving various sterical dispositions of the chelating molecules (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a*; Braibanti, Manotti Lanfredi & Tiripicchio, 1967; Braibanti, Bigliardi, Manotti Lanfredi & Tiripicchio, 1966; Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1968; Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967). Compounds with two hyc's and two monodentate ligands L can give rise to complexes $\text{M}^{\text{II}}\text{hyc}_2\text{L}_2$ (Fig. 1) of the following types:

complexes (A): *trans*(O), *trans*(N'), *trans*(L)

complexes (B): *trans*(O), *cis*(N'), *cis*(L),
two enantiomorphous forms

complexes (C): *cis*(O), *cis*(N'), *trans*(L)

complexes (D): *cis*(O), *trans*(N'), *cis*(L),
two enantiomorphous forms

complexes (E): *cis*(O), *cis*(N'), *cis*(L),
two enantiomorphous forms.

The complexes that have been identified in the structures of compounds of hyc so far determined are (A) and (B). The non-chelating ligands are $\text{L} = \text{H}_2\text{N-NH}_2$ in complexes (A) and $\text{L} = \text{OH}_2$ or $\text{O} = \text{hyc} <$ in complexes (B). The last notation (Braibanti, Tiripicchio, Manotti Lanfredi & Camellini, 1967) indicates a tridentate (chelating and bridging) hyc group which is bound to one metal atom through one O and chelates an adjacent metal atom through N' and the second O. Both

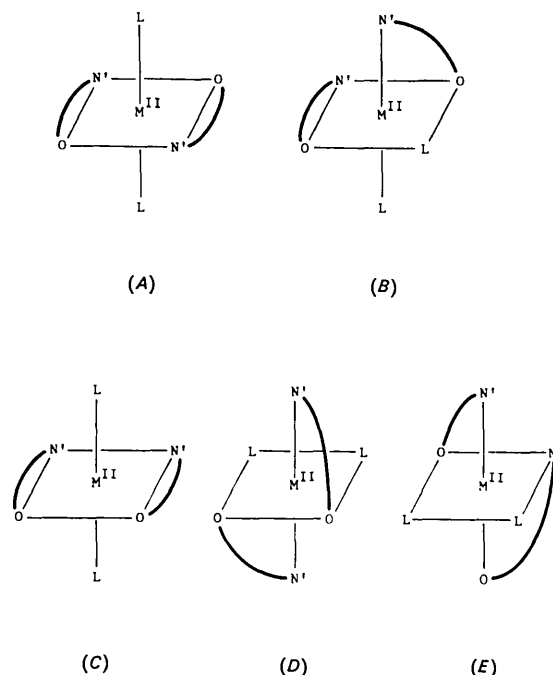


Fig. 1. Types of octahedral complexes $\text{M}^{\text{II}}\text{hyc}_2\text{L}_2$. The bold curves stand for the chelating group $\text{N}'\text{H}_2\text{-NH-COO}$ (hyc).

complexes (A) and (B) have the O atoms of the chelating group in *trans* positions, while the complexes (C), (D) and (E), which have not yet been found experimentally, have the O atoms in *cis* positions. This suggests that the oxygen atoms, having the negative charge of the anion, are bound first to the cation at opposite sides and the remaining donor atoms N' and L are then coordinated to the central metal. If this is the reaction mechanism, it should be much more difficult to obtain complexes of the last three types.

In order to clarify these chemical problems, it is of interest to search for complexes of unknown types and for differences between complexes of the known types. The crystal structure of the anhydrous compound $\text{Cd}(\text{N}'\text{H}_2\text{-NH-COO})_2$, (II), has already been determined; here, the results of the determination of the structure of the monohydrated compound (I) are presented.

Experimental

Crystals of the hydrated compound I are obtained by evaporating an aqueous solution of hydrazine hydrate and cadmium chloride, or acetate at room temperature. Under apparently the same conditions, the solid phase was sometimes formed as crystals of the anhydrous compound II, but we are not able to specify how either one of the two compounds can be obtained.

Crystal data

Compound: bis(hydrazinecarboxylato-N',O) cadmium monohydrate, $\text{Cd}(\text{N}'\text{H}_2\text{-NH-COO})_2 \cdot \text{H}_2\text{O}$, $M = 280.53$.

Crystal habit: small colourless dipyrramids.

Crystal class: orthorhombic dipyramidal.

Unit cell (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$; average of measurements from rotation and Weissenberg photographs, both around [100] and [001]):

$$a = 7.402(7), b = 12.360(7), c = 7.828(12) \text{ \AA}$$

$$V = 716.2 \text{ \AA}^3, Z = 4 \text{ stoichiometric units.}$$

$$D_m = 2.63, D_x = 2.60 \text{ g.cm}^{-3}, \mu = 257.06 \text{ cm}^{-1} \text{ (Cu } K\alpha\text{).}$$

Reflexions: $0kl$ only if $k = 2n$; $h0l$ only if $l = 2n$; hkl only if $h + k = 2n$.

Space group: $Pbcn$ [No. 60, $D_{2h}(14)$] from systematic absences.

The photographs for intensity measurements were taken by an integrating Weissenberg camera by applying the multiple film technique. The intensities of reflexions $0kl$, $1kl$, ... $5kl$ and $hk0$, hkl , ... $hk6$ were measured by a microdensitometer and the usual corrections were applied. Absorption corrections were introduced as for cylindrical specimens ($\mu\bar{R} = 4.6$ for reflexions Hkl and $\mu\bar{R} = 5.7$ for hkL reflexions). Atomic form factors were calculated by Forsyth & Wells's (1959) method with the improved constants given by Moore (1963). All the calculations were performed on the Olivetti Elea 6001/S of the Centro Calcolo Elettronico of the University of Parma.

Determination of the structure

The three-dimensional Patterson function could be interpreted on the basis of Cd-Cd vectors with Cd placed at the special position (c) of the space group $Pbcn$. Successive Fourier syntheses made it possible to identify the light atoms. The structure was refined by differential syntheses and the anisotropic thermal par-

Table 1. Fractional atomic coordinates with estimated standard deviations ($\times 10^4$)

	Position multiplicity	x	y	z
Cd	c 4	0000 (0)	2341 (1)	2500 (0)
O(1)	d 8	2559 (24)	2365 (9)	0745 (19)
C(2)	d 8	3314 (22)	1449 (9)	0476 (16)
N(3)	d 8	2931 (30)	0638 (14)	1606 (27)
N(4)	d 8	2006 (32)	0868 (9)	3145 (22)
O(5)	d 8	4326 (22)	1237 (14)	-0756 (16)
H ₂ O(6)	c 4	0000 (0)	1172 (14)	0000 (0)

Table 2. Anisotropic thermal parameters (\AA^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	3.218	0.925	1.323	0	0.382	0
O(1)	4.645	1.133	1.339	0.209	1.039	0.235
C(2)	2.779	0.858	0.645	0.072	-0.193	-0.016
N(3)	3.229	1.144	0.737	0.669	0.707	0.413
N(4)	2.923	1.791	0.201	0.033	0.152	0.118
O(5)	2.805	2.140	0.851	0.261	1.105	0.133
H ₂ O(6)	4.248	2.248	4.874	0	-0.645	0

Average and maximum shift in the last cycle

Cd $|\Delta B_{av}| = 0.031$ $|\Delta B_{max}| = 0.067$

Light atoms $|\Delta B_{av}| = 0.061$ $|\Delta B_{max}| = 0.153$

Table 3. Observed and calculated structure factors F_o followed by = is not observed.

Table with 40 columns (h, k, l, F_o, F_c) and 40 rows of numerical data representing structure factors for various metal complexes.

Table 3 (cont.)

h	k	l	10F _o	10F _c	h	k	l	10F _o	10F _c	h	k	l	10F _o	10F _c	h	k	l	10F _o	10F _c	h	k	l	10F _o	10F _c	h	k	l	10F _o	10F _c						
6	7	6	79	-61	7	0	2	92	53	7	7	3	379	-312	7	5	5	408	-341	8	3	1	45	-30	8	2	3	58	-16	8	4	5	6	74	
6	8	6	13	-197	7	1	2	79	-38	7	8	3	45	2	7	6	5	22	1	8	4	1	214	201	8	3	3	135	107	9	1	0	95	82	
7	1	0	122	-143	7	2	2	86	-59	7	9	3	306	273	7	7	5	263	254	8	5	1	69	-63	8	4	3	204	-146	9	3	0	158	-164	
7	3	0	158	-176	7	3	2	145	133	7	0	4	66	-32	7	0	6	102	62	8	6	1	201	-186	8	5	3	45	1	9	5	0	22	-67	
7	5	0	158	168	7	4	2	109	79	7	1	4	66	-8	7	1	6	99	-87	8	7	1	29	-13	8	6	3	244	210	9	1	1	260	-245	
7	7	0	237	-261	7	5	2	237	-245	7	2	4	69	-6	7	2	6	86	-48	8	8	1	198	187	8	7	3	26	-10	9	2	1	29	26	
7	9	0	320	-324	7	6	2	102	-78	7	3	4	151	-117	7	3	6	181	184	8	0	2	405	-375	8	0	4	402	352	9	3	1	257	265	
7	1	1	405	-439	7	7	2	276	253	7	4	4	69	52	7	4	6	92	64	8	1	2	58	-34	8	1	4	86	84	9	4	1	22	8	
7	2	1	69	-60	7	8	2	66	33	7	5	4	260	200	7	5	6	19	-88	8	2	2	389	353	8	2	4	353	-293	9	5	1	13	-204	
7	3	1	455	545	7	9	2	283	-252	7	6	4	55	-28	8	0	0	280	256	8	3	2	73	-50	8	3	4	42	-20	9	0	2	36	-37	
7	4	1	55	12	7	10	2	26	6	7	7	4	273	-218	8	2	0	408	-436	8	4	2	267	-232	8	4	4	313	248	9	1	2	36	5	
7	5	1	418	-493	7	1	3	498	491	7	8	4	36	-5	8	4	0	442	467	8	5	2	49	-23	8	5	4	79	-68	9	2	2	29	6	
7	6	1	82	82	7	2	3	73	-80	7	1	5	366	-314	8	6	0	280	-262	8	6	2	221	197	8	6	4	19	-252	9	3	2	63	37	
7	7	1	211	233	7	3	3	428	-392	7	2	5	39	16	8	8	0	237	225	8	7	2	73	72	8	1	5	82	59	9	4	2	19	34	
7	8	1	102	-87	7	4	3	66	15	7	3	5	514	451	8	1	1	49	8	8	8	2	19	-269	8	2	5	95	-98	9	1	3	26	253	
7	9	1	240	-235	7	5	3	523	281	7	4	5	36	4	8	2	1	49	-14	8	1	3	58	42	8	3	5	86	-63	9	2	3	22	0	
7	10	1	26	11	7	6	3	63	45																										

Table 4. Atomic peak heights (e.Å⁻³), curvatures (e.Å⁻⁵) and e.s.d.'s

		ρ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Cd	obs	151.9	1399	1832	1714	0	79	0
	calc	156.1	1421	1826	1713	0	60	0
O(1)	obs	14.4	84	172	113	-1	-21	0
	calc	14.6	85	171	117	-2	-23	-1
C(2)	obs	11.7	102	131	122	-11	-22	-22
	calc	12.1	103	134	122	-8	-21	-24
N(3)	obs	12.6	92	122	120	-4	9	14
	calc	12.8	95	124	117	-5	6	13
N(4)	obs	12.8	93	122	123	-19	0	-11
	calc	12.8	94	121	125	-19	7	-11
O(5)	obs	14.5	137	100	148	12	17	-30
	calc	15.2	141	98	152	13	12	-33
H ₂ O(6)	obs	11.1	74	111	96	0	0	0
	calc	11.6	74	113	98	0	1	0
	e.s.d.	0.7	8	8	10	5	5	5

ameters were refined by the method of Nardelli & Fava (1960) ($R_{hkl} = 13.8\%$, observed reflexions only). The final results are reported in Tables 1-4.

Discussion of the structure

The structure is represented in Fig. 2. It consists of octahedral complexes of type (B) grouped in layers

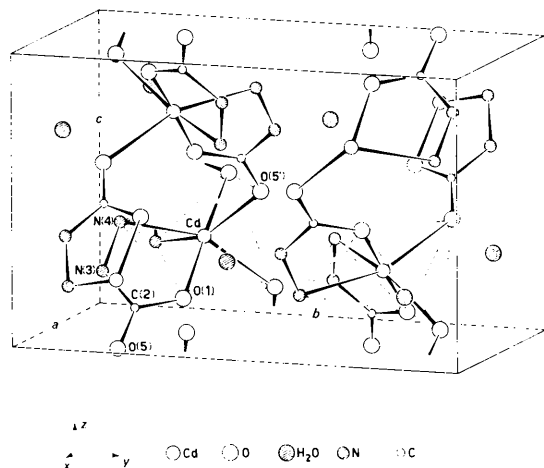


Fig. 2. Clinographic projection of the structure of bis(hydrazinecarboxylato-*N',O*)cadmium monohydrate.

parallel to (010) (Fig. 3). The complexes are held together by bridging hyc groups, each of which completes, through O(5), the coordination polyhedron of an adjacent metal atom. The layers are approximately at $y \approx \frac{1}{4}$ and $y \approx \frac{3}{4}$, each layer being composed of complexes of the same kind, enantiomorphous to those composing the following layer. The complexes in the present compound, **I**, are of the same type (B) as those found in the anhydrous cadmium compound, **II**, where, however, only one complex of the enantiomorphous pair is present in each crystal. The two complexes (Fig. 4) show some rather large differences in bond angles and distances (Table 5). One bond between cadmium and oxygen, Cd-O(1), changes from 2.34 Å in **I** to 2.24 Å in **II**; moreover in the former the two bonds are almost opposite [O(1)-Cd-O(1'') = 178.4° in **I**] while in the latter the two bonds are bent an angle 146.9°. The other metal-oxygen distances (Cd-O(5) = 2.28 Å in **I** and 2.26 Å in **II**) remain unchanged in the two compounds, as does the angle O(5')-Cd-O(5''). The metal-nitrogen bond distance does not change in the two complexes (Cd-N(4) = 2.40 Å in **I** and 2.38 Å in **II**) while the angle N(4)-Cd-N(4'') = 81.5° in **I** and 94.7° in **II** is significantly different. Also the chelate ring (Fig. 5) shows some systematic differences (Table 6).

Although the statistical significance test indicates that bond lengths N(3)-C(2) or C(2)-O(1) probably

Table 5. Comparison of distances and angles in the complexes of the monohydrate (I) and of the anhydrous (II) cadmium compound

	I	II*
Cd-O(1)	2.34 (2) Å	2.24 (2) Å
Cd-N(4)	2.40 (2)	2.38 (3)
Cd-O(5')	2.28 (2)	2.26 (2)
N(4)-Cd-O(1)	68.5 (6)°	69.2 (9)°
N(4)-Cd-O(5')	108.9 (6)	94.5 (9)
N(4)-Cd-O(5'')	147.7 (6)	163.5 (8)
N(4)-Cd-N(4''')	81.5 (6)	94.7 (8)
N(4)-Cd-O(1''')	112.7 (6)	88.2 (9)
O(1)-Cd-O(1''')	178.4 (3)	146.9 (8)
O(1)-Cd-O(5')	99.4 (5)	107.8 (7)
O(1)-Cd-O(5'')	79.5 (5)	97.5 (8)
O(5')-Cd-O(5'')	78.9 (5)	80.0 (7)

Transformations in I'
 I'' $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$
 I''' $-\frac{1}{2}+x, \frac{1}{2}-y, -z$
 I'''' $-x, y, \frac{1}{2}-z$

* Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968).

do not differ between compounds I and II, it seems to us reasonable to assume that the differences are significant, as can be assessed by the analysis of the planarity of the ring (see below): the displacements of the atoms from one another in the two compounds are consistent with a rotation of the plane containing the atoms N(3), C(2), O(1) and O(5). Then the nitrogen-carbon bond can be considered as shorter in I (N(3)-C(2) = 1.37 Å) than in II (N(3)-C(2) = 1.42 Å) whereas the carbon-oxygen bond is C(2)-O(1) = 1.28 Å in I and 1.20 Å in II. It seems that double bond character has

been transferred from carbon-nitrogen, in I, to carbon-oxygen in II; in I, the carbon-nitrogen distance is in agreement with the distances found in amines, with the nitrogen atom in hybridization state sp^3 , and in II with

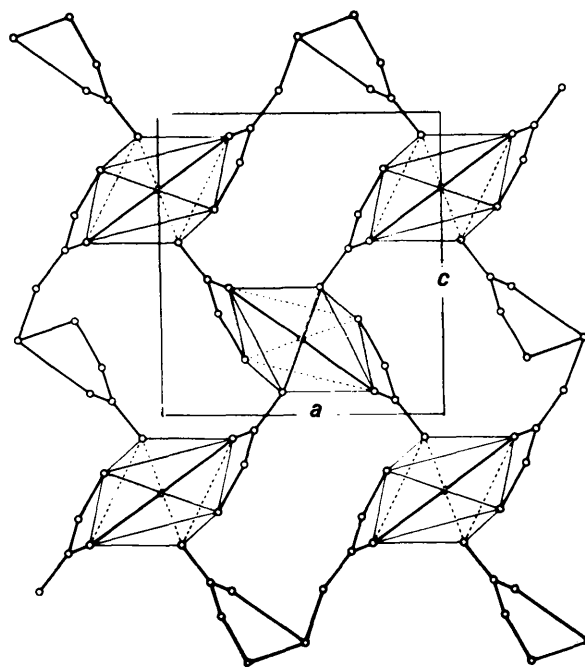


Fig. 3. One layer of octahedra CdHyc₂L₂, parallel to (010) at $y \approx \frac{1}{2}$.

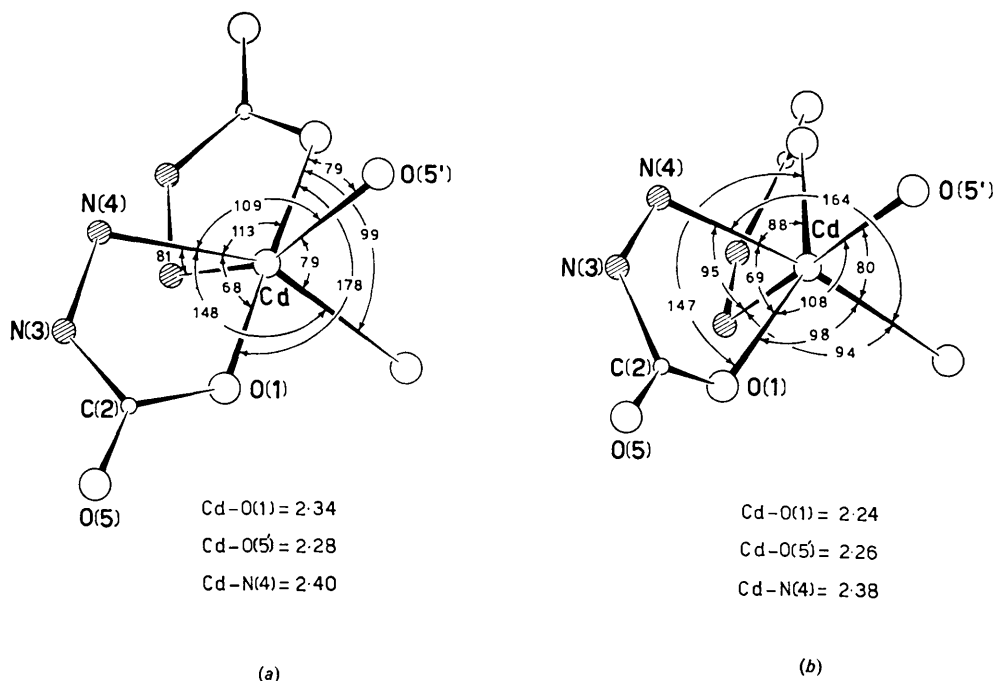
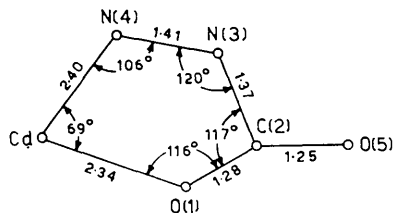


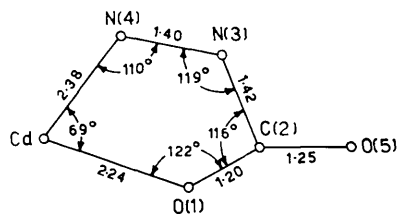
Fig. 4. The complex around Cd (Type B of Fig. 1). (a) Bis(hydrazinecarboxylato-*N'*, *O*)cadmium monohydrate, I. (b) Bis(hydrazinecarboxylato-*N'*, *O*)cadmium anhydrous, II.

distances found in amides, with the nitrogen atom in hybridization state sp^2 . The two bonds $C(2)-O(5)=1.25 \text{ \AA}$ are equal in the two compounds. Also the distances $N(3)-N(4)=1.41 \text{ \AA}$ in **I** and 1.40 \AA in **II** are equal and normal for distances in hydrazinecarboxylato group.

The shortening of the nitrogen–nitrogen bond distance in this group with respect to that obtained for hydrazine ($N-N=1.46 \text{ \AA}$) (Collin & Lipscomb, 1951) and for hydrazine complexes (Ferrari, Braibanti & Bigliardi, 1963; Ferrari, Braibanti, Bigliardi & Dalla-



(a)



(b)

Fig. 5. Chelate ring formed by hydrazinecarboxylato group: (a) bis(hydrazinecarboxylato- N' , O)cadmium monohydrate, **I**. (b) bis(hydrazinecarboxylato- N' , O)cadmium anhydrous, **II**.

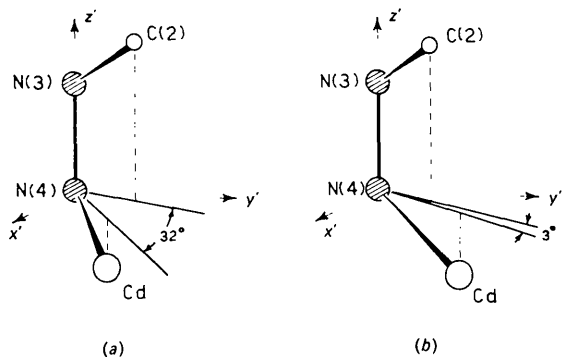


Fig. 6. Clinographic view of the rotation of the bonds $N(4)-Cd$ and $N(3)-C(2)$: (a) bis(hydrazinecarboxylato- N' , O)cadmium monohydrate, **I**. (b) bis(hydrazinecarboxylato- N' , O)cadmium anhydrous, **II**.

Table 6. Comparison of the bond distances and angles of the chelate ring in the monohydrate (**I**) and in the anhydrous (**II**) cadmium compound

	I	II*
$Cd-N(4)$	2.40 (2) Å	2.38 (3) Å
$Cd-O(1)$	2.34 (2)	2.24 (2)
$N(4)-N(3)$	1.41 (3)	1.40 (4)
$N(3)-C(2)$	1.37 (2)	1.42 (4)
$C(2)-O(1)$	1.28 (2)	1.20 (4)
$C(2)-O(5)$	1.25 (2)	1.25 (4)
$N(4)\cdots O(1)$	2.67 (2)	2.63 (4)
$O(5)-C(2)-O(1)$	125.0 (1.4)°	131.1 (3.2)°
$N(3)-C(2)-O(1)$	116.9 (1.5)	116.1 (3.2)
$O(5)-C(2)-N(3)$	118.2 (1.4)	112.8 (3.0)
$N(4)-Cd-O(1)$	68.5 (0.6)	69.2 (0.9)
$Cd-O(1)-C(2)$	116.0 (1.0)	122.3 (2.4)
$N(4)-N(3)-C(2)$	120.3 (1.5)	118.6 (3.2)
$Cd-N(4)-N(3)$	105.8 (1.1)	109.8 (2.0)

* Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968).

valle, 1963; Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a, b, c*) can be explained by assuming a 'staggered' model for the hydrazine molecule: the lone pairs of nitrogen atoms repel each other and maintain the large separation. Whenever one or both nitrogen atoms are involved in bonds 'sucking' electrons, such as in protons or conjugating groups, the repulsion between lone pairs diminishes and the bond is shortened.

Table 7. Analysis of the planarity

Equation of plane $m_1X + m_2Y + m_3Z = d$

$$\sigma_{\perp} = \{m_1^2\sigma^2(X) + m_2^2\sigma^2(Y) + m_3^2\sigma^2(Z)\}^{1/2} (\text{\AA})$$

best plane through $N(3)$, $C(2)$, $O(1)$, $O(5)$

	I	II*
m_1	+0.78966	-0.42023
m_2	+0.27583	+0.28524
m_3	+0.54803	-0.86141
d	+2.62568	-4.54887

d , distances from the plane (Å)

$N(3)$	-0.006	+0.001
$C(2)$	+0.010	-0.007
$O(1)$	-0.004	+0.001
$O(5)$	-0.003	+0.001
$\Sigma(d/\sigma_{\perp})^2$	0.61	0.05 ($\chi^2_{95\%} = 3.84$)
$N(4)$	+0.192	-0.210
Cd	-0.755	-0.717

* Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968).

The chelate ring contains the atoms $N(3)$, $C(2)$, $O(1)$ and $O(5)$, which form a conjugating group, lying in one plane (Table 7). The deviations of $N(4)$ and Cd from the plane are on opposite sides in **I** and on the same side in **II**. This means that the dihedral angle $Cd-N(4)-N(3) \wedge N(3)-N(4)-C(2)$ is $\omega = 32^\circ$ in **I** and $\omega = 3^\circ$ in **II** (Fig. 6). The lone pair of N' can be assumed to lie along the direction $Cd-N(4)$; therefore the angle ω gives the rotation of $-N'H_2$ around the bond $N'-N$.

The question now arises, can the two complexes be considered to be derived from the same acid with

-N'H₂ free to rotate around N'-N and 'frozen' at different angles? In any case it would be interesting to know if the molecule has been frozen by bonding to the metal or by packing in the crystal. No definite answer seems possible at present either on chemical or structural grounds. Alternatively the complexes can be assumed to be derived from different stereoisomers, taking into account particularly those differing both by the rotation of -N'H₂ and the hybridization state of N. The intermolecular distances and angles are quoted in Table 8. The octahedra are associated in each layer in a similar way in the two compounds, as can be shown from the intermolecular angles C(2')-O(5')-Cd = 115.6° in **I** and 117.3° in **II**, and by the distances between cadmium atoms of adjacent octahedra which are Cd...Cd = 5.40 Å in **I** and Cd...Cd = 5.31 Å in **II**. The differences in the remaining angles are a consequence of the displacement of the bridging group. The water molecule is bound through hydrogen bonds to both layers. The strongest hydrogen bonds are H₂O(6^{iv})...N(4) = 2.969 and H₂O(6) ... O(1) = 2.902 Å and those centrosymmetrically equivalent. These hydrogen bonds bind the layers to one another; further hydrogen bonds N(4)...O(1') = 3.00 Å are formed between two octahedra of the same layer.

Table 8. Intermolecular distances and angles

	I	II*
Cd...Cd'	5.401 (5) Å	5.311 (3) Å
C(2')-O(5')-Cd	115.6 (1.1)°	117.3 (1.8)
C(2')-O(5')-N(4''')	114.7 (1.0)	124.5 (1.8)
C(2')-O(5')-N(4)	79.8 (1.0)	76.7 (1.7)
C(2')-O(5')-O(1''')	111.0 (1.1)	125.7 (1.9)
C(2')-O(5')-O(1)	105.2 (1.1)	90.0 (1.8)
C(2')-O(5')-O(5'')	158.9 (1.2)	144.1 (2.0)

Hydrogen bonds in **I**

N(4)...H ₂ O(6 ^{iv})	= 2.969 Å
O(1)...H ₂ O(6 ^v)	= 2.902
N(4)...O(1')	= 3.002

Transformations in

I'	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$
I''	$-\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$-z$
I'''	$-x,$	$y,$	$\frac{1}{2}-z$
I^{iv}	$-x,$	$-y,$	$1-z$
I^v	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$

* Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli (1968).

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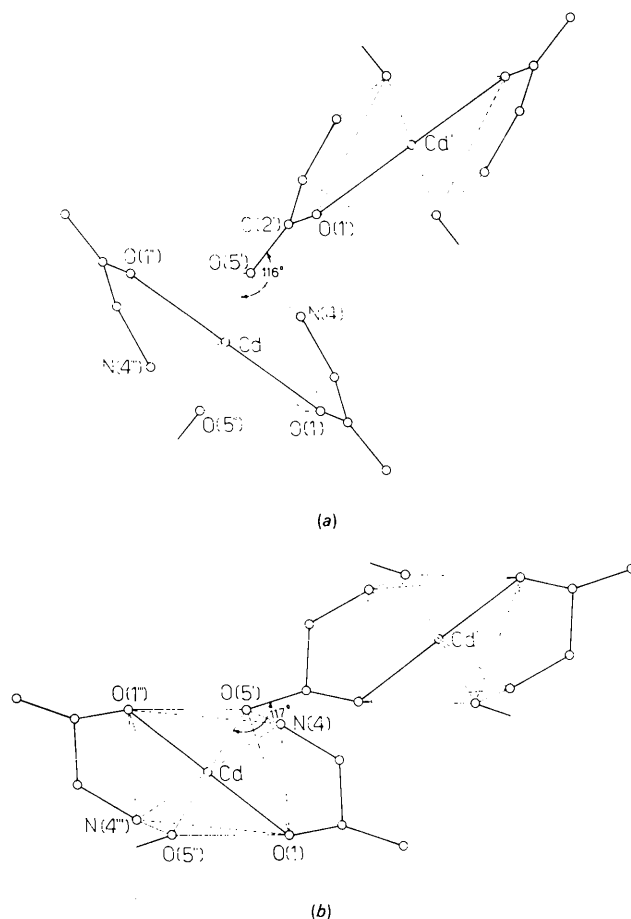


Fig. 7. Association of complexes in each layer: (a) bis(hydrazinecarboxylato-N',O)cadmium monohydrate, **I**. (b) bis(hydrazinecarboxylato-N',O)cadmium anhydrous, **II**.

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