

The Crystal and Molecular Structure of Catena- μ -dichlorobisimidazolecadmium(II)

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(Received 4 December 1972; accepted 9 January 1973)

The structure of catena- μ -dichlorobisimidazolecadmium(II), $[\text{Cd}(\text{ImH})_2\text{Cl}_2]_\infty$, has been determined from three-dimensional X-ray counter data and refined by the full-matrix least-squares method. The final residual R is 0.039 for 2032 independent observed reflexions. The crystals are monoclinic with $a = 3.904$ (3), $b = 13.04$ (1), $c = 9.89$ (1) Å, $\beta = 93.7$ (1)°, $Z = 2$, and space group $P2_1/c$. The cadmium atoms lie in positions of $\bar{1}$ symmetry and are octahedrally coordinated. They are linked into infinite chains by double chloride bridges. Each cadmium forms, in addition to four Cd-Cl bonds [2.706 (2), 2.731 (2) Å], two Cd-N (imidazole) bonds [2.248 (3) Å] which are almost perpendicular to the plane of the Cd and Cl atoms.

Introduction

Complexes of cadmium with peptides and aminoacids are interesting as potential model compounds for Cd-protein interactions. Cadmium occurs naturally in at least one protein, metallothionein (Kagi & Vallee, 1960, 1961). It has recently been recognized increasingly as a pollutant, whose hazardous nature probably arises from its interaction with proteins in biological systems (Lucis, Shaikh & Embil, 1970; Shaikh & Lucis, 1971). A Cd(II) derivative has been used in the X-ray structure analysis of the protein concanavalin A (Weinzierl & Kalb, 1971). The possibility of solving protein structures by making isomorphous Cd derivatives and taking advantage of the anomalous dispersion of neutrons by ^{113}Cd was pointed out by Ramaseshan (1966). The complexation of Cd(II) by aminoacids and peptides in solution has been studied potentiometrically (Li, White & Doody, 1954; Li & Manning, 1955; Li & Chen, 1958; Sharma & Tandon, 1971), polarographically (Smith, Cruickshank, Donoghue & Pysz, 1962), by infrared spectroscopy (Shindo & Brown, 1965; McAuliffe, Quagliano & Vallarino, 1966; Carlson & Brown, 1966), and by n.m.r. spectroscopy (Li, Scruggs & Becker, 1962; Natusch & Porter, 1971). The imidazole groups of histidine side chains are known to be particularly important metal-binding sites in proteins.

The structures of $\text{Cd}(\text{L-His})_2 \cdot 2\text{H}_2\text{O}$, $[\text{Cd}(\text{ImH})_6](\text{NO}_3)_2$ and $[\text{Cd}(\text{ImH})_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$ which contain Cd-N(imidazole) bonds have been previously described (Candlin & Harding, 1967; Mighell & Santoro, 1971; Antti, Lundberg & Ingri, 1972). We now report the structure of $[\text{Cd}(\text{ImH})_2\text{Cl}_2]_\infty$.

Experimental

The complex crystallizes as colourless needles from an aqueous solution of cadmium(II) chloride- $2\frac{1}{2}$ -water

(0.001 mole) and imidazole (0.002 mole) in the presence of L- α -alanine (0.002 mole). The alanine was originally added to our preparations as part of an unsuccessful attempt to prepare a complex with mixed ligands. It was later observed that the imidazole complex formed much bigger and better crystals in the presence of alanine than from a pure solution.

Crystal data

$\text{C}_6\text{H}_8\text{N}_4\text{CdCl}_2$, F.W. 319.5. Monoclinic, $a = 3.904$ (3) $b = 13.04$ (1), $c = 9.89$ (1) Å, $\beta = 93.7$ (1)°, $U = 502$ (2) Å³, $D_m = 2.14$ (2) g cm⁻³ (by flotation in $\text{CHCl}_3/\text{CHBr}_3$), $D_x = 2.11$ g cm⁻³ for $Z = 2$, $F(000) = 308$, $\mu(\text{Mo } K\alpha) = 26.4$ cm⁻¹, $\lambda(\text{Mo } K\alpha_1) = 0.70926$, $\lambda(\text{Mo } K\alpha_2) = 0.71354$ Å. The space group is $P2_1/c$ (No. 14) from systematic absences ($0k0$ absent for $k = 2n + 1$, $h0l$ absent for $l = 2n + 1$). The unit-cell dimensions were fitted to the θ -values of a number of high-angle reflexions measured on an equi-inclination diffractometer.

The intensity data were recorded on a computer-controlled Supper equi-inclination diffractometer by the usual ω -scan procedure (Freeman, Guss, Nockolds, Page & Webster, 1970). The control parameters for the scan-range and scan-speed calculations as defined in the cited reference were: $\Delta\lambda = 0.007$, $\chi = 0.6^\circ$, $\varphi_m = 1.0^\circ$, $P = 0.001$, $\delta\mu = 0.05^\circ$, $\varphi_{\text{max}} = 0.25$ deg sec⁻¹, $\varphi_{\text{min}} = 0.05$ deg sec⁻¹, and $R_e = 0.02$. The intensity I of a reflexion with integrated peak count P and background counts B_1 and B_2 was given by $I = P - (B_1 + B_2)$ with variance $\sigma^2(I) = P + B_1 + B_2$. Reflexions for which $I < 3.5\sigma(I)$ were considered to be unobservably weak.

Complete sets of data to a limit of $2\theta = 85^\circ$ were recorded from two crystal specimens with dimensions $0.52 \times 0.08 \times 0.08$ mm and $0.26 \times 0.14 \times 0.12$ mm, rotated about the a and c axes, respectively. The needle axis was parallel to the a axis in both crystals. Mo $K\alpha$ radiation reflected from a graphite crystal monochromator was used. The counter was a Philips scintillation counter, PW 1964/10. Lorentz and polarization corrections were applied. For radiation reflected from a crystal monochromator, the correct form of the polariza-

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Table 1. Atomic positional parameters ($\times 10^4$) for catena- μ -dichlorobisimidazolecadmium(II), with anisotropic temperature factors ($\times 10^4$)

Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number. The form of the anisotropic temperature factors is: $\exp(-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}])$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0	0	0	329 (1)	23 (0)	57 (0)	1 (0)	-12 (0)	-1 (0)
Cl	4730 (2)	99 (0)	-1913 (1)	355 (3)	35 (0)	52 (0)	2 (1)	-17 (1)	4 (0)
N(1)	19 (6)	1718 (2)	187 (2)	372 (11)	27 (1)	53 (2)	-3 (3)	7 (4)	-3 (1)
C(1)	1535 (9)	2253 (2)	1182 (3)	666 (25)	35 (1)	70 (3)	2 (5)	-34 (7)	-11 (2)
N(2)	1009 (9)	3258 (2)	1000 (3)	821 (26)	30 (1)	91 (3)	-17 (4)	-5 (7)	-18 (2)
C(2)	-942 (11)	3381 (2)	-181 (4)	881 (32)	30 (1)	113 (4)	6 (5)	-32 (9)	8 (2)
C(3)	-1533 (9)	2430 (2)	-676 (3)	670 (24)	32 (1)	82 (3)	0 (5)	-50 (7)	4 (2)

Table 1 (cont.)

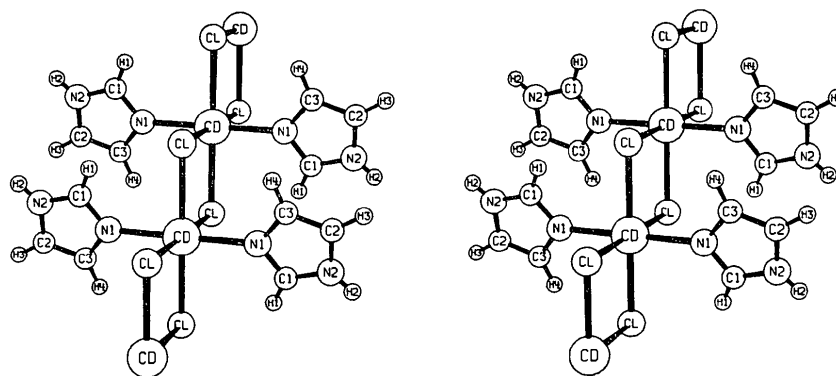
Hydrogen atom coordinates ($\times 10^3$) and isotropic temperature factors.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	283 (11)	191 (3)	192 (4)	3.5 (1.0)
H(2)	185 (12)	370 (4)	153 (5)	4.9 (1.2)
H(3)	-181 (13)	406 (3)	-49 (5)	4.5 (1.1)
H(4)	-297 (12)	219 (4)	-149 (5)	5.3 (1.2)

tion correction depends on whether the monochromator is a perfect or ideally mosaic crystal. Since the degree of perfection of the graphite monochromator was undetermined, the mean of the two possible corrections was applied to the present data. The maximum uncertainty introduced by this procedure in the case of Mo *K* radiation is about 1%. The data were also corrected for absorption using a $6 \times 6 \times 6$ grid (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965). Finally, the sets of data recorded about the two rotation axes were placed upon a common scale by the least-squares method of Rae (1965) and Rae & Blake (1966). The standard deviations of the intensities were calculated, taking into account both the random counting errors and estimated systematic errors (Freeman & Guss, 1972). The final data consisted of 3522 independent reflexions, of which 1490 were below the observable threshold of intensity.

Structure analysis and refinement

Since $Z=2$, the Cd atoms had to lie on special positions. All atoms except hydrogen were located in a single heavy-atom Fourier synthesis. Least-squares refinement with isotropic thermal parameters converged at $R=0.09$. Further refinement with anisotropic thermal parameters for the Cd and Cl atoms gave $R=0.053$. The four hydrogen atoms were located from a $(F_o - F_c)$ synthesis. They were included in the structure amplitudes as fixed contributions, with the same isotropic thermal parameters as the atoms to which they were bonded. Refinement with anisotropic thermal parameters for all the non-hydrogen atoms reduced R to 0.043. Up to this stage, the refinement had been carried out with weights $w=1$ for all reflexions. The correct weights $w=1/\sigma^2(F)$ calculated from the random and systematic errors of the observations (see above) were now introduced. This caused only an insignificant change in R , but there was an immediate drop of about 30% in the estimated standard deviations of the refined variables. Further refinement, in which five strong reflexions thought to be suffering from extinction were removed, finally reduced R to 0.039. In the last two cycles, the hydrogen atoms alone were refined isotropically but there was no further change in the residual R . A final $(F_o - F_c)$ synthesis showed no features greater than $\pm 0.4 e.\text{\AA}^{-3}$, with the exception of a negative peak of about



CD (IMH) 2CL2

CD (IMH) 2CL2

Fig. 1. Stereoscopic view of one formula unit of $[\text{Cd}(\text{ImH})_2\text{Cl}_2]_\infty$ plus nearest neighbours in chain.

$-1 \text{ e}\text{\AA}^{-3}$ on the z axis at 0.7 \AA from the Cd atom. The reason for this was not discovered.

The quantity minimized in the refinement was $\sum w(|F_o| - s|F_c|)^2$. The scattering factors used were those tabulated by Cromer & Waber (1965), and the real and imaginary parts of the anomalous dispersion corrections for cadmium and chlorine atoms were those given by Cromer (1965). The final positional and thermal parameters are listed in Table 1.*

Description and discussion of the structure

Fig. 1 is a stereoscopic drawing of the complex. The molecular structure and dimensions are shown in Fig. 2. The complex is polymeric. The Cd atoms at $(0,0,0)$ and $(0, \frac{1}{2}, \frac{1}{2})$ are linked to their neighbours in the x direction by double chloride bridges, forming infinite $-\text{Cd}-\text{Cl}_2-\text{Cd}-$ ribbons. The octahedral coordination is completed by two Cd-N(imidazole) bonds which are perpendicular (89.25°) to the plane of the Cd and Cl atoms. Similar coordination of monodentate ligands occurs in bis(biuret)cadmium(II) dichloride, $\text{Cd}(\text{Biu})_2\text{Cl}_2$ [*i.e.* catena- μ -dichlorobisbiuretcadmium(II)] (Cavalca, Nardelli & Fava, 1960), and in bis(urea)-cadmium(II) dichloride [*i.e.* catena- μ -dichlorobisurea-cadmium(II)] (Cavalca, Nardelli & Fava, 1957). The Cd-N(imidazole) bonds in the present complex are

significantly shorter [$2.248(3) \text{ \AA}$] than those in similar complexes with nitrogen and oxygen donor atoms. Cd-N(imidazole) bond lengths of $2.361(3)$ and $2.364(3) \text{ \AA}$, respectively, have been reported in $[\text{Cd}(\text{ImH})_6](\text{NO}_3)_2$ and $[\text{Cd}(\text{ImH})_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$ (Mighell & Santoro, 1971; Antti, Lundberg & Ingri, 1972). The Cd-O bond length in the cited biuret complex is $2.34(2) \text{ \AA}$. On the other hand, the increase in the bond-orders of the C-N(imidazole) bonds is accompanied by a weakening (lengthening) of the Cd-Cl bonds [$2.706(2)$ and $2.731(2) \text{ \AA}$ in $\text{Cd}(\text{ImH})_2\text{Cl}_2$; $2.55(1)$ and $2.62(1) \text{ \AA}$ in $\text{Cd}(\text{Biu})_2\text{Cl}_2$].

The Cd atom lies only 0.03 \AA from the plane of best fit of the imidazole ligand (Table 2). The dihedral angle between the imidazole plane and the plane through Cd, Cl', N(1) and N(1') is 15.4° . The bond lengths in the imidazole ring show deviations from the values which would be expected for a completely delocalized system. In particular, the difference between N(1)-C(1) and N(1)-C(3) [$1.315(4)$ and $1.375(4) \text{ \AA}$, respectively] is highly significant and shows that the canonical form in which N(1)-C(1) and C(2)-C(3) are double bonds has a large weight. The dimensions of imidazole and substituted imidazole molecules in other complexes and in crystalline imidazole itself lead to similar conclusions [*cf.* Ni(Gly) $_2$ (ImH) $_2$ (Freeman & Guss, 1972), $[\text{Cd}(\text{ImH})_6](\text{NO}_3)_2$ (Mighell & Santoro, 1971), $[\text{Cd}(\text{ImH})_6](\text{CO}_3) \cdot 5\text{H}_2\text{O}$ (Mighell & Santoro, 1971; Antti *et al.*, 1972), $\text{Ag}(\text{ImH})_2(\text{NO}_3)$ (Acland & Freeman, 1972, unpublished), $\text{Cu}(1,2\text{-dimethylimidazole})_2\text{Cl}_2$ (Huq & Skapski, 1971), imidazole (Martinez-Carrera, 1966; Bell & Freeman, 1969, unpublished)].

* The observed and calculated structure amplitudes have been deposited with the National Lending Library for Science and Technology, Boston Spa, England, as Supplementary Publication No. SUP 30054. Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Planes of best fit

Code for symmetry-related atoms		
Superscript	Atom at	
None	x ,	y , z
I	$-x$,	$-y$, $-z$
II	$-1+x$,	y , z
III	$1-x$,	$-y$, $-z$

(a) Least-squares planes

Equations of planes: $lX + mY + nZ + p = 0$, where X, Y, Z are defined by $X = ax - cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$.

Plane	Description	l	m	n	p
A	Cd, Cl, Cl', Cl'', Cl'''	0	-0.9977	-0.0681	0
B	Cd, Cl, Cl', N(1), N(1')	-0.6929	0.0577	-0.7187	0
C	Cd, Cl'', Cl''', N(1), N(1')	0.6991	0.0600	-0.7125	0
D	Imidazole	0.8635	0.0570	-0.5010	-0.0337

(b) Deviations from imidazole plane (in \AA)

The atoms marked with asterisks were *not* included in the least-squares calculation of plane D.

Atom	N(1)	C(1)	N(2)	C(2)	C(3)
Deviation	-0.002	0.002	-0.001	-0.000	0.001
Atom	Cd*	H(1)*	H(2)*	H(3)*	H(4)*
Deviation	-0.034	0.009	-0.023	-0.075	-0.052

(c) Dihedral angles between planes

Planes	$A \wedge B$	$A \wedge C$	$A \wedge D$	$B \wedge C$	$C \wedge D$
Angle	90.5°	90.6°	91.3°	88.2°	15.4°

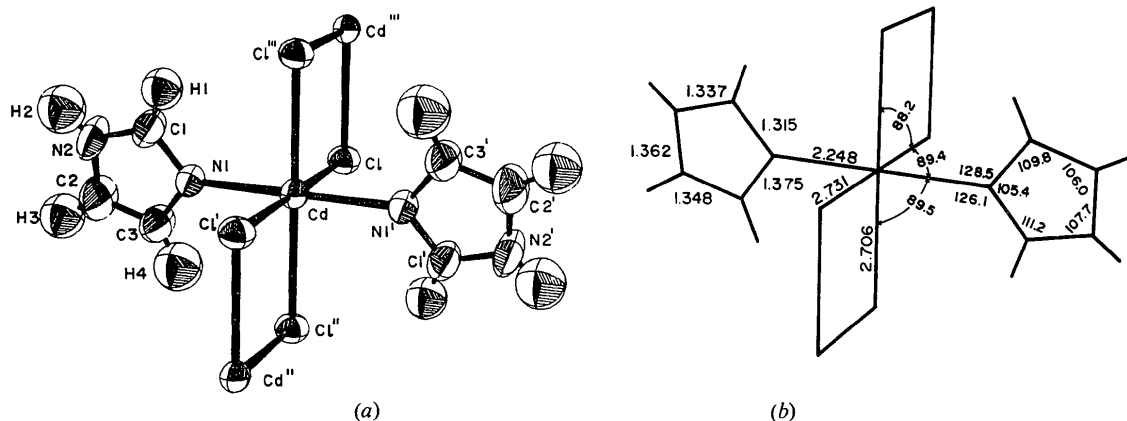


Fig. 2. (a) Thermal ellipsoids drawn at the 70% probability level, and (b) bond lengths and angles in $[\text{Cd}(\text{ImH})_2\text{Cl}_2]_\infty$. Superscripts are defined in Table 2. Average e.s.d.'s are 0.002 Å for Cd–light-atom bonds, 0.004 Å for light-atom–light-atom bonds, and 0.2° for bond-angles at the light atoms.

The lengths of the three C–H bonds (0.97, 0.99 and 1.00 Å) and the N–H bond (0.84 Å) are within the range of commonly observed values. The hydrogen atom H(2) is involved in a weak hydrogen bond from N(2) to $\text{Cl}(x-1, y, z)$. The relevant distances and angles are: $\text{N}(2)\cdots\text{Cl} = 3.25$ Å, $\text{H}(2)\cdots\text{Cl} = 2.42$ Å, $\text{N}(2)\text{--H}(2)\cdots\text{Cl} = 170^\circ$, $\text{C}(1)\text{--N}(2)\cdots\text{Cl} = 102.2^\circ$, $\text{C}(2)\text{--N}(2)\cdots\text{Cl} = 132.0^\circ$. There are no other intermolecular contacts shorter than 3.37 Å.

This work was supported by the Institute of General Medical Sciences, U.S. Public Health Service (grant GM-10867), and by the Australian Research Grants Committee (grant 65/1552).

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