

Crystal and molecular structure of tris(ethylenediamine) cadmium(II) iodide, $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{CdI}_2$

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Crystal structure / Tris(ethylenediamine)cadmium(II) iodide

Abstract. The crystal and molecular structure of the title compound is reported. Crystals are triclinic, space group $P\bar{1}$ with $Z = 4$ in a unit cell of dimensions $a = 8.835(1)$, $b = 14.294(2)$, $c = 14.570(2)$ Å, $\alpha = 107.15(1)$, $\beta = 95.50(1)$ and $\gamma = 100.97(1)^\circ$. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method to $R = 0.060$ for 3091 unique reflections. The Cd atoms of both the molecules in the same asymmetric unit have distorted octahedral configuration. Both the molecules in the same asymmetric unit have the $\lambda\lambda\lambda$ ring conformation.

Introduction

The present investigation forms a part of our research programme on the structural studies of $[\text{M}(\text{en})_3]^{2+}$ complexes. The structural details of the title compound, tris(ethylenediamine)cadmium(II) iodide, is reported here and is hereafter represented as $\text{Cd}(\text{en})_3\text{I}_2$.

Experimental

$\text{Cd}(\text{en})_3\text{I}_2$ was prepared by adding excess of ethylenediamine to an aqueous solution of CdI_2 . Colourless crystals were obtained by slow evaporation.

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The crystals acquire a white powdery surface on exposure to air. Density was measured by the method of floatation with CCl_4 and HBr_3 as lighter and denser media respectively. Unit cell parameters were obtained by least-squares refinement of the θ values of 25 high-angle reflections.

The crystal data are $M = 546.51$, triclinic, space group $P\bar{1}$, $a = 8.835(1)$, $b = 14.294(2)$, $c = 14.570(2)$ Å, $\alpha = 107.15(1)$, $\beta = 95.50(1)$, $\gamma = 100.97(1)^\circ$, $V = 1703$ Å³, $Z = 4$, $D_m = 2.174$ g cm⁻³, $D_c = 2.131$ g cm⁻³, $\text{MoK}\alpha$, $\mu = 4.564$ mm⁻¹ and $F(000) = 1024$.

A crystal of size $0.2 \times 0.375 \times 0.325$ mm was chosen for study sealed in a Lindemann tube, and three-dimensional intensity data were collected at room temperature (21 °C) on an Enraf-Nonius single crystal CAD-4 diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation. The data were collected in the $\omega/2\theta$ scan mode at a variable scan speed with a maximum of 60 s per reflection. Standard reflections (165) and (166) showed no significant change. All reflections (h : -10 to 10, k : -16 to 16, l : 0 to 16) in the range $2^\circ < 2\theta < 48^\circ$ were measured. 3091 unique reflections with $I > 3\sigma(I)$ were considered as observed. R_{int} from merging 265 equivalent reflections is 0.029. Calculation with measured density showed $Z = 4$. Since there are four molecular per unit cell, the space group was tentatively fixed as $P\bar{1}$ which proved to be correct later. Intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the heavy-atom method and refined by the method of full-matrix least-squares minimizing $\sum w(\Delta F)^2$ with SHELX-76 (Sheldrick, 1976), initially with isotropic and then anisotropic thermal parameters for the non-hydrogen atoms. Refinement of 271 positional and thermal parameters (scale factor included) converged to $R = 0.060$. Few C and N atoms [N(3), N(4), C(3), C(4) and C(11)] show higher thermal parameters (see Table 1). Since difference Fourier maps did not reveal additional peaks as evidence for these atoms occupying different sites with fractional occupancy factors during the structure analysis, large thermal factors may be due to the neglect of absorption correction to the intensity data. The final difference Fourier maps revealed the positions of only nine hydrogen atoms out of a total of fortyeight to be located. Since these H atoms did not converge to reasonable positions during refinement, they were fixed at the appeared positions and were given a temperature factor of 0.05 Å². Location of other hydrogens was not attempted. Maximum and average shift/e.s.d. are 1.05 and 0.116 respectively. Maximum height in final difference Fourier map is 1.26 eÅ⁻³ [1.07 Å away from Cd(1) atom]. A final $R_w = 0.057$ with $w = 1.00/[\sigma^2(F_o) + 0.0114|F_o|^2]$ was obtained.

The atomic scattering factors were taken from Cromer and Mann (1968) and the anomalous dispersion correction factors from Cromer and Liberman (1970).

Table 1. Final diffractational atomic coordinates ($\times 10^4$ for I and Cd atoms and $\times 10^3$ for others) and equivalent isotropic thermal parameters ($\times 10^4$ for I and Cd atoms and $\times 10^3$ for others) with estimated standard deviation in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2)*
I(1)	3084(2)	835(1)	726(1)	455(5)
I(2)	6542(2)	3334(1)	5450(1)	486(5)
I(3)	1560(2)	580(1)	6663(1)	495(6)
I(4)	8114(2)	4483(1)	1479(1)	461(6)
Cd(1)	11105(2)	2898(1)	3470(1)	359(5)
N(1)	988(2)	142(1)	221(1)	46(7)
N(2)	846(2)	304(1)	322(1)	46(7)
N(3)	1207(5)	420(2)	497(2)	122(17)
N(4)	1078(5)	213(2)	472(2)	126(14)
N(5)	1180(2)	409(2)	265(1)	57(8)
N(6)	1365(2)	275(2)	312(1)	51(7)
C(1)	832(3)	155(2)	183(2)	57(10)
C(2)	748(3)	200(2)	265(2)	54(9)
C(3)	1190(5)	394(2)	579(2)	82(14)
C(4)	1137(4)	282(2)	567(2)	86(13)
C(5)	1320(5)	390(2)	218(2)	61(10)
C(6)	1439(3)	374(2)	291(2)	71(12)
Cd(2)	7147(2)	1910(1)	8160(1)	359(5)
N(7)	913(2)	345(1)	893(1)	43(7)
N(8)	923(2)	139(1)	888(1)	42(6)
N(9)	583(2)	226(2)	950(1)	55(8)
N(10)	528(2)	280(2)	774(1)	52(7)
N(11)	782(2)	148(2)	660(1)	47(7)
N(12)	559(2)	25(1)	740(2)	57(8)
C(7)	1061(3)	315(2)	922(2)	55(10)
C(8)	1020(3)	228(2)	964(2)	51(9)
C(9)	449(3)	274(2)	928(2)	59(10)
C(10)	495(3)	339(2)	869(2)	59(10)
C(11)	668(5)	58(4)	599(2)	127(21)
C(12)	629(4)	-21(2)	653(2)	71(12)

$$* U_{\text{eq}} = 1/3 (U_{11} + U_{22} + U_{33} + U_{23} \cos \alpha + U_{13} \cos \beta + U_{12} \cos \gamma)$$

Table 2. Fractional (fixed) H-atom position (revealed by the final difference Fourier maps) coordinates ($\times 10^4$)

Atom	bonded to	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	C(7)	11077	3824	-109
H(2)	C(10)	3981	3730	8548
H(3)	N(12)	6078	-38	7842
H(4)	N(1)	9444	-1188	8353
H(5)	C(6)	4919	-3645	6394
H(6)	C(8)	9618	2393	10324
H(7)	N(8)	9562	1011	8152
H(8)	N(11)	9108	1389	6663
H(9)	N(10)	5993	3135	7233

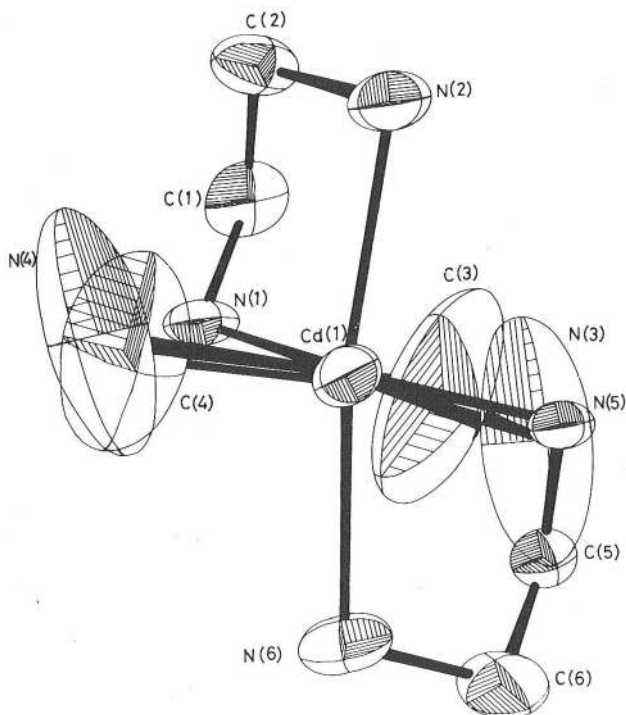


Fig. 1. Perspective view of $[\text{Cd}(\text{en})_3]^{2+}$ of molecule I

Discussion

The fractional atomic coordinates of the non-hydrogen atoms are listed in Table 1. Fractional coordinates (fixed) of the hydrogens (revealed by the final difference Fourier maps) are listed in Table 2. Tables of the relevant bond lengths, bond angles, and the anisotropic thermal parameters of the non-hydrogen atoms have been deposited¹. ORTEP plots (Johnson, 1965) of $\text{Cd}(\text{en})_3$ of molecule I and molecule II are separately shown in Figures 1 and 2 respectively.

The Cd atoms, Cd(1) and Cd(2), of molecule I and molecule II have distorted octahedral configuration. The Cd–N distances vary from 2.34(2) to 2.42(2) Å and the average value (2.38 Å) compares well with that found in $\text{Cd}(\text{en})_3\text{NO}_3)_2$ [2.41(4) Å] (Mahadevan et al.).

The bite distances of the chelate rings are 2.92(3) Å [(N(1)... N(2)), 2.85(3) Å [(N(3)... N(4)), 2.92(3) Å [(N(5)... N(6)), 2.95(3) Å

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 51 308, the names of the authors and the title of the paper

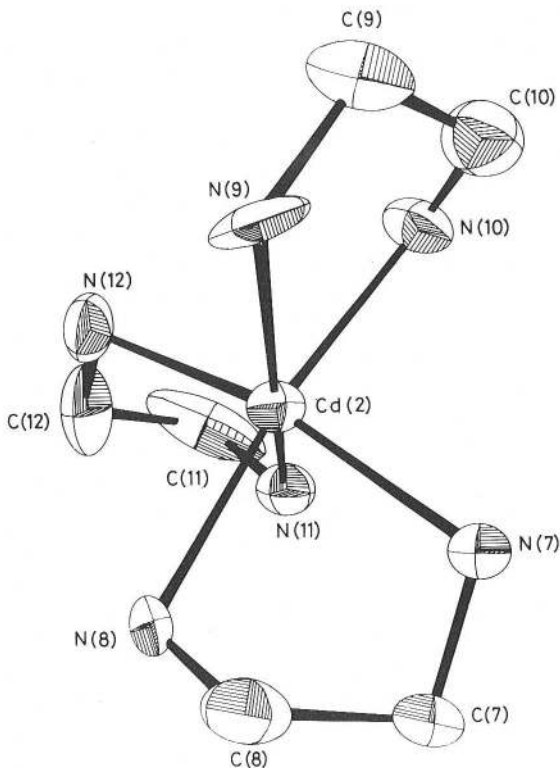


Fig. 2. Perspective view of $[\text{Cd}(\text{en})_3]^{2+}$ of molecule II

$[\text{N}(7) \dots \text{N}(8)]$, $2.91(3) \text{ \AA}$ $[\text{N}(9) \dots \text{N}(10)]$ and $2.95(3) \text{ \AA}$ $[\text{N}(11) \dots \text{N}(12)]$. The bite angles $\text{N}(1) - \text{Cd}(1) - \text{N}(2)$ $[76.5(6)^\circ]$, $\text{N}(3) - \text{Cd}(1) - \text{N}(4)$ $[73.8(8)^\circ]$, $\text{N}(5) - \text{Cd}(1) - \text{N}(6)$ $[75.7(8)^\circ]$, $\text{N}(7) - \text{Cd}(2) - \text{N}(8)$ $[75.8(8)^\circ]$, $\text{N}(9) - \text{Cd}(2) - \text{N}(10)$ $[75.6(7)^\circ]$ and $\text{N}(11) - \text{Cd}(2) - \text{N}(12)$ $[77.3(7)^\circ]$ deviate significantly from 90° .

The dihedral angles with respect to the N–C, C–C and C–N bonds of the five-membered Cd(en) rings are $46(2)$, $64(2)$, $46(2)^\circ$ [for Cd(1)–N(1)–C(1)–C(2)–N(2) ring], $46(2)$, $65(2)$, $49(2)^\circ$ [for Cd(1)–N(5)–C(5)–C(6)–N(6) ring], $41(2)$, $64(2)$, $50(2)^\circ$ [for Cd(2)–N(7)–C(7)–C(8)–N(8) ring], $36(2)$, $63(2)$, $53(2)^\circ$ [for Cd(2)–N(9)–C(9)–C(10)–N(10) ring] and $43(2)$, $62(3)$, $45(2)^\circ$ [for Cd(2)–N(11)–C(11)–C(12)–N(12) ring] which compare well with those found in similar $[\text{M}(\text{en})_3]^{2+}$ compounds. Consequently the configuration of these five five-membered Cd(en) rings can be assigned as gauche-gauche-gauche. The dihedral angles for the sixth ring $[\text{Cd}(1) - \text{N}(3) - \text{C}(3) - \text{C}(4) - \text{N}(4)]$ are $10(3)$, $13(4)$, $8(3)^\circ$ which are significantly small and quite unusual showing nearly the

cis configuration. This is also evidenced by the significantly larger Cd–N–C [116(2)° and 113(2)°] and N–C–C [117(2)° and 119(3)°] angles. The averages of these angles in all the other Cd(en) rings are 107.2(4)° (Cd–N–C) and 109.5(5)° (N–C–C).

All the N–C bond distances other than C(3)–N(3) [1.37(5) Å] and C(4)–N(4) [1.42(3) Å] vary from 1.46(4) to 1.56(4) Å which agree with N–C distances found in similar ethylenediamine complexes. Also the C–C bond distances [vary from 1.47(4) to 1.57(4) Å] agree with C–C distances found in similar ethylenediamine complexes.

Unusual cis configuration and an unusually small N–C distance [1.37(5) Å] observed in one of the Cd(en) rings [Cd(1)–N(3)–C(3)–C(4)] may be due to a total disorder of the ethylenediamine part of this ring which is clearly shown by the unusual large thermal ellipsoids (see Fig. 1).

The ring conformation for both the molecules in the same asymmetric unit is $\lambda\lambda\lambda$. Short contacts (< 3.95 Å, the van der Waals distance) between amine atoms and I[−] ions observed in the present structure are I(1) . . . N(1), I(1) . . . N(6), I(1) . . . N(8), I(1) . . . N(9), I(1) . . . N(12), I(2) . . . N(2), I(2) . . . N(3), I(2) . . . N(5), I(2) . . . N(6), I(2) . . . N(10), I(2) . . . N(11), I(3) . . . N(1), I(3) . . . N(4), I(3) . . . N(10), I(3) . . . N(11), I(3) . . . N(12), I(4) . . . N(2), I(4) . . . N(5), I(4) . . . N(7), I(4) . . . N(7) and I(4) . . . N(9) with distances 3.80(2), 3.67(2), 3.66(2), 3.79(2), 3.71(2), 3.76(2), 3.75(2), 3.81(2), 3.82(2), 3.86(2), 3.80(2), 3.78(2), 3.86(2), 3.93(2), 3.77(2), 3.78(2), 3.73(2), 3.75(2), 3.84(2), 3.69(2) and 3.67(2) Å respectively. These short contacts may be the reason for the $\lambda\lambda\lambda$ conformation in the present structure. Short contacts (less than 4 Å) between C atoms and I[−] ions are I(3) . . . C(4), I(4) . . . C(3) and I(4) . . . C(7) with distances 3.91(3), 3.95(3) and 3.82(2) Å respectively.

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