

The Crystal and Molecular Structure of Di- μ -chloro-bis[thioacetamide(chloro)cadmium(II)]

BY M. M. ROLIES AND C. J. DE RANTER*

Institute of Pharmaceutical Sciences, Laboratory of Analytical Chemistry, Katholieke Universiteit te Leuven, 3000 Leuven, Belgium

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The crystal and molecular structure of di- μ -chloro-bis[thioacetamido(chloro)cadmium(II)] has been determined by three-dimensional X-ray analysis. There are four Cd(TAA)Cl₂ (TAA = thioacetamide) units in the orthorhombic unit cell: $a = 3.938$ (5), $b = 10.646$ (9), $c = 16.415$ (32) Å, space group $P2_1nb$. The structure was solved by standard heavy-atom techniques and refined by use of a block-diagonal least-squares analysis. Each Cd atom is octahedrally surrounded by one S atom from the thioacetamide ligand and five Cl atoms. The coordination polyhedra are linked by Cl bridges into double chains, running parallel to the a axis.

Introduction

In our programme of structure determination of metal-complex compounds of thioacetamide, results for bis(thioacetamide)mercury(II) chloride (Rolies & De Ranter, 1977*a*), bis(thioacetamide)zinc(II) chloride (Rolies & De Ranter, 1977*b*) and *cyclo*-tri- μ -thioacetamide-tris[chlorocopper(I)] (De Ranter & Rolies, 1977) have already been published. Nardelli & Chierici (1957) have reported the preparation of Cd(TAA)₂Cl₂ and Cd(TAA)₄Cl₂, but the structures were not solved. In the present paper the crystal structure of Cd(TAA)Cl₂ is described.

Experimental

Crystals of Cd(TAA)Cl₂ were prepared by heating a solution of cadmium chloride in HCl, and a solution of TAA in ethanol was added in proportion as the liquid was evaporated. The final CdCl₂:TAA ratio was about 2:1. On cooling to room temperature white needles separated in the course of 24 hours. The very fragile crystals (thickness 0.05 mm and length 1–2 mm) neither were well-shaped nor could be ground to a sphere. The unit-cell dimensions were initially obtained from Weissenberg and precession photographs, which showed the orthorhombic crystals to have systematic extinctions: for $h0l$, $h + l = 2n + 1$, and for $hk0$, $k = 2n + 1$, indicating space group $Pmnb$ or $P2_1nb$. The density, measured by flotation in a bromoform–benzene mixture, is 2.53 g cm⁻³ which is in good agreement with that calculated for four units of Cd(TAA)Cl₂ per unit cell.

The intensity data were collected on an automated Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation, a graphite monochromator and the θ – 2θ scan technique. Every 40 reflections a standard reflection was measured and its intensity showed no unusual fluctuations during the run. All reflections with $I < 3\sigma(I)$ were considered unobserved, so that only 442 of the 820 independent reflections were used in the analysis. Corrections for Lorentz and polarization effects were applied to the data, but no correction for absorption was made because no precise crystal size determination could be made. Crystal data: Cd(C₂H₅NS)Cl₂, $M_r = 258.4$, orthorhombic, $P2_1nb$, $a = 3.938$ (5), $b = 10.646$ (9), $c = 16.415$ (32) Å, $V = 688.2$ Å³, $D_m = 2.53$, $D_c = 2.49$ g cm⁻³, $Z = 4$, $F(000) = 488$, $\mu(\text{Cu } K\alpha) = 355.7$ cm⁻¹ (the e.s.d.'s given in parentheses are quoted in units of the last place of decimals).

Structure determination and refinement

With four molecules of Cd(TAA)Cl₂ in the unit cell, the architecture of the complex is unlikely to be symmetrical enough to allow it to lie astride the mirror planes at $x = \frac{1}{4}$ and $\frac{3}{4}$ in space group $Pmnb$, so we assumed the space group to be $P2_1nb$. The y and z coordinates of the Cd atom were obtained from a Patterson synthesis. The x coordinate was set to 0.25, considering the facts that for $x = 0.25$ the conditions of $Pmnb$ for special positions were fulfilled and that the statistics and distributions of the reflections showed high centrosymmetry. This choice was confirmed by the fact that after the structure was solved all phases were very close to 0 and 180°. The x value of the Cd atom was left constant during the whole structure determination. Using the signs of the Cd contributions to the structure factors a three-dimensional Fourier synthesis ($R =$

* To whom correspondence should be addressed.

Table 1. Atomic coordinates with e.s.d.'s for the non-hydrogen atoms

	x	y	z
Cd(01)	0.2500	0.5896 (3)	0.4050 (2)
Cl(02)	0.226 (5)	0.5946 (9)	0.5650 (6)
Cl(03)	-0.234 (6)	0.7508 (9)	0.3970 (6)
S(04)	0.202 (9)	0.502 (1)	0.2608 (8)
C(05)	0.293 (28)	0.603 (4)	0.192 (3)
C(06)	0.236 (50)	0.569 (5)	0.099 (3)
N(07)	0.477 (11)	0.710 (3)	0.206 (3)
H(08)	0.583	0.750	0.281
H(09)	0.538	0.763	0.158

0.38) revealed the positions of the Cl and S atoms. Successive electron-density maps led to the location of the other non-hydrogen atoms. Subsequently positional and isotropic thermal parameters were refined by use of a block-diagonal least-squares analysis.

A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ (Cruickshank, 1965) was used with final constants $a = 4.35$ and $b = 0.0504$. Anisotropic temperature factors were introduced and refined, the function minimized being $\sum w(|F_o| - |F_c|)^2$; R converged to 0.108. From a difference map computed at this stage only one H of the amide group, H(08), could be located; no methyl H atoms were found. The coordinates of the second amide H atom were calculated on the assumption of a trigonal planar bond configuration around N. This twofold H contribution was not included in the subsequent refinement. Final atomic parameters are given in Table 1.* All calculations were carried out on an IBM 370/158 computer with the programs of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering factors are those of Stewart, Davidson & Simpson (1965) for H, and of Cromer & Mann (1968) for the other atoms. The anomalous dispersion corrections for Cd, Cl and S were taken from *International Tables for X-ray Crystallography* (1974).

Discussion

In the following discussion, atoms belonging to different asymmetric units are labelled as shown in Table 2.

The Cd is octahedrally surrounded by one S atom from thioacetamide and five Cl atoms with bond distances and angles quoted in Tables 2 and 3. It is interesting to compare these values with those found in ammonium cadmium chloride (Rolies & De Ranter, 1978) where the environment of the Cd atom is more symmetrical. In $\text{Cd}(\text{TAA})\text{Cl}_2$ the octahedra are quite

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33684 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

significantly distorted, probably because of the thioacetamide molecule. The octahedra are linked in chains by Cl bridges as shown in Fig. 1. These chains, running parallel to the a axis, are further condensed in pairs, once again by Cl bridges.

Each Cl(03) atom lies between Cd(01) and Cd(01^{iv}) with distances of 2.57 (2) and 2.66 (2) Å which are comparable with Cd-Cl distances already found in other compounds, e.g. in bisacetamide-cadmium chloride, 2.58 and 2.66 Å (Cavalca, Nardelli & Coghi, 1957), in bisurea-cadmium chloride, 2.64 Å (Nardelli, Cavalca & Fava, 1957), in monomethylurea-cadmium chloride, 2.58 and 2.62 Å (Nardelli,

Table 2. Interatomic distances (Å)

Cd(01)—Cl(02)	2.63 (1)	C(05)—S(04)	1.61 (5)
Cd(01)—Cl(03)	2.57 (2)	C(05)—C(06)	1.58 (8)
Cd(01)—S(04)	2.55 (1)	C(05)—N(07)	1.37 (8)
Cd(01)—Cl(02 ⁱ)	2.76 (2)		
Cd(01)—Cl(02 ⁱⁱ)	2.89 (2)	N(07)—H(08)	1.37
Cd(01)—Cl(03 ⁱⁱⁱ)	2.66 (2)	N(07)—H(09)	0.99
Cl(02)—Cd(01 ⁱ)	2.89 (2)		
Cl(02)—Cd(01 ⁱⁱ)	2.76 (2)		
Cl(03)—Cd(01 ^{iv})	2.66 (2)		

Symmetry code

None	x, y, z	(iii)	$x + 1, y, z$
(i)	$x + \frac{1}{2}, 1 - y, 1 - z$	(iv)	$x - 1, y, z$
(ii)	$x - \frac{1}{2}, 1 - y, 1 - z$	(v)	$x + \frac{1}{2}, (1 - y) + \frac{1}{2}, z - \frac{1}{2}$

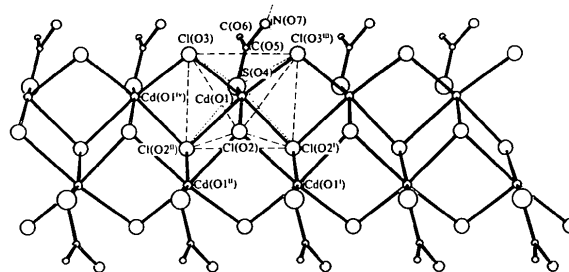


Fig. 1. Clinographic projection of a chain.

Table 3. Interatomic angles (°)

Equivalent positions of $P2_1nb$, a non-standard setting of $Pna2_1$ (C_2^2 , No. 33)

x, y, z	$\frac{1}{2} + x, \bar{y}, \bar{z}$	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	$x, \frac{1}{2} + y, \frac{1}{2} - z$
Cl(02)—Cd(01)—S(04)	158.6 (4)	Cl(02 ⁱ)—Cd(01)—Cl(03 ⁱⁱⁱ)	87.1 (5)
Cl(02)—Cd(01)—Cl(02 ⁱ)	82.0 (4)	Cl(02 ⁱⁱ)—Cd(01)—Cl(02 ⁱⁱ)	88.4 (5)
Cl(02)—Cd(01)—Cl(03)	90.6 (4)	Cl(02 ⁱⁱ)—Cd(01)—Cl(03 ⁱⁱⁱ)	172.2 (4)
Cl(02)—Cd(01)—Cl(03 ⁱⁱⁱ)	93.7 (4)		
Cl(02)—Cd(01)—Cl(02 ⁱⁱ)	79.5 (4)	Cd(01)—S(04)—C(05)	113 (2)
S(04)—Cd(01)—Cl(03)	98.2 (7)		
S(04)—Cd(01)—Cl(03 ⁱⁱⁱ)	104.3 (7)	S(04)—C(05)—C(06)	120 (5)
S(04)—Cd(01)—Cl(02 ⁱ)	87.5 (6)	S(04)—C(05)—N(07)	124 (4)
S(04)—Cd(01)—Cl(02 ⁱⁱ)	81.7 (6)	C(06)—C(05)—N(07)	115 (6)
Cl(03)—Cd(01)—Cl(03 ⁱⁱⁱ)	97.7 (5)		
Cl(03)—Cd(01)—Cl(02 ⁱⁱ)	86.1 (5)	C(05)—N(07)—H(08)	124
Cl(03)—Cd(01)—Cl(02 ⁱ)	171.4 (4)	C(05)—N(07)—H(09)	118
		H(08)—N(07)—H(09)	118

Coghi & Azzoni, 1958), in bisbiuret-cadmium chloride, 2.55 and 2.62 Å (Cavalca, Nardelli & Fava, 1960), in NH_4CdCl_3 , 2.65 Å averaged (Brasseur & Pauling, 1938; Rolies & De Ranter, 1978). On the other hand Cl(02) is bonded to three Cd atoms with distances which are significantly different. The distance between Cd(01) and Cl(02), belonging to the same asymmetric unit, is 2.63 (2) Å, but between atoms of different asymmetric units we find distances for Cd(01ⁱⁱ)-Cl(02) 2.76 (2) Å and for Cd(01ⁱ)-Cl(02) 2.89 (2) Å. This Cl atom forms the binding between adjacent chains.

Consequently the structure may be described as being built up of infinite chains of $\text{Cd}_2(\text{TAA})_2\text{Cl}_4$ units, which are linked by Cl bridges. Dimers were also found in $\text{Cd}(\text{DMTF})_2\text{Cl}_4$ (Aarts, Desseyne & Herman, 1977). From these it seems that the complex is best formulated as di- μ -chloro-bis[thioacetamide(chloro)cadmium(II)].

The thioacetamide molecule is nearly planar.* The angles within the ligand are those expected, but the distances within the thioacetamide ligand seem to be significantly different from that found in the free thioacetamide molecule (Truter, 1960). From other thioacetamide complexes, e.g. $\text{Cu}(\text{TAA})_4\text{Cl}$ (Truter & Rutherford, 1962), $\text{Ni}(\text{TAA})_4\text{Cl}_2$ (Girling, O'Connor & Amma, 1972), $\text{Hg}(\text{TAA})_2\text{Cl}_2$ (Rolies & De Ranter, 1977a), $\text{Zn}(\text{TAA})_2\text{Cl}_2$ (Rolies & De Ranter, 1977b), $\text{Cu}(\text{TAA})\text{Cl}$ (De Ranter & Rolies, 1977), it could be concluded that coordination does not significantly alter the interatomic distances of the thioacetamide molecule. More than likely the deviations found in the cadmium complex result from the poor quality of the

* The least-squares-plane equation of the TAA molecule is: $-0.8831x + 0.4623y + 0.0799z = 2.1326$; x, y and z are orthogonal coordinates.

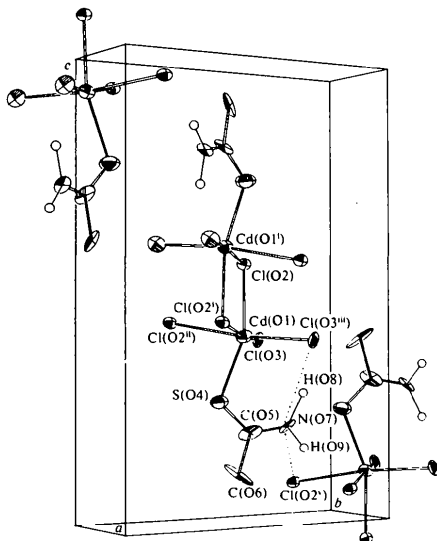


Fig. 2. ORTEP (Johnson, 1965) plot of the unit cell.

crystal and the X-ray data. Although not all the H atoms of the thioacetamide molecule could be located, those of the amide group seem to be very important ones for the stacking of the molecules. The contacts which can be considered as hydrogen bonds are: N(07)···Cl(03ⁱⁱⁱ) 3.37, N(07)···Cl(02^v) 3.25 Å, N(07)-H(08)···Cl(03ⁱⁱⁱ) 162, N(07)-H(09)···Cl(02^v) 170°. These hydrogen bonds act to strengthen the molecular packing in the dimer chains (intermolecular bridges) and the binding forces between neighbouring parallel chains (inter-chain bridges) (Fig. 2).

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