Structure of bis(dipropyldithiocarbamate) cadmium(II), [Cd₂(n-Pr₂dtc)₄] (dtc = dithiocarbamate)

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The cadmium complex of bis(dipropyldithiocarbamate), $[Cd_2(n-Pr_2dtc)_4]$ (dtc = dithiocarbamate) was crystallized from ethylether. It crystallizes in the monoclinic system, space group P_{2l}/c , with lattice parameters, a = 8.2532(1), b = 19.4519(1), c = 13.4163(2) Å, $\beta = 99.243(1)^\circ$, and Z = 4. The X-ray single-crystal structure of $[Cd_2(n-Pr_2dtc)_4]$ reveals that the complex is binuclear in the solid state and the Cd atom has a distorted square-pyramidal coordination environment and four equatorial donors are the two bidentate chelate sulfur atoms from two dtc ligands, of which the sulfur atom from the bridging dtc ligand occupies the apical position of the symmetry-related Cd atom in the dimer structure.

KEY WORDS: X-ray structure; dtc; cadmium complex.

Introduction

The development of effective antidotes for cadmium intoxication has proven to be a task of considerable difficulty. On the one hand, cadmium is much more toxic than lead, and the normal physiological processes by which it is immobilized involve its bonding to an intracellular protein in the liver and the kidney rather than the semipermanent deposition of lead in the bone;¹ on the other hand, this metal-intracellular protein complex, cadmium metallothionein (CdMT) does have a reasonably slow rate of transfer from one organ to another, which is more toxic to it than cadmium bound to high molecular weight serum protein.² Since this passage to intracellular sites occurs quite rapidly,³ these compounds are effective antagonists only while the cadmium is still in the extracellular space.⁴ In recent years it has become apparent that two types of chelating agents can effect antidotes for cadmium intoxication; uncharged vicinal dithiols⁵ and dithiocarbamates.^{6,7} Oddly enough, relatively little is known about the behavior of cadmium complexes with either of these types of chelating agents. Herewith, we report the crystal structure of bis(dipropyldithiocarbamate) cadmium.

Experimental

All chemicals were obtained from a commercial source and used without further purification. Reagent n-Pr₂dtcNa was synthesized by the reaction of n-Pr₂NH, NaOH, and CS₂ in water. To a heated aqueous solution of Na(n-Pr₂dtc) [0.01 mol] was added an EtOH solution of cadmium perchlorate $[Cd(ClO_4)_2, 0.054 \text{ mol}]$ with stirring. The white precipitate was collected by filtration, washed with water, and dried over P4O10. These were collected and submitted for elemental analysis. Anal. Calcd. For [Cd₂(n-Pr₂dtc)₄]: C, 36.16% H, 6.07%; N, 6.02%. Found: C, 36.50%; H, 6.29%; N, 6.24%. The solid of $[Cd(n-Pr_2dtc)_2]$ was dissolved in ethylether and allowed to evaporate slowly. This resulted in the formation of needle-like crystals which were then used in the crystallographic study. The IR spectra

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Color/shape	Colorless needle
CCDC deposit no.	CCDC-1003/5514
Formula	$C_{28}H_{56}Cd_2N_4S_8$
Formula weight	930.04
Crystal size (nm)	$0.62 \times 0.38 \times 0.22$
Space group	$P2_{1}/c$
Unit cell dimensions	
a, Å	8.2532(1)
b, Å	19.4519(1)
<i>c</i> , Å	13.4163(2)
α , deg	90
β , deg	99.243(1)
γ, deg	90
Vol. A ³	2125.89(4)
Ζ	2
D (calcd.), mg/m ³	1.453
Abs coeff., mm ⁻¹	1.416
F(000)	952
Radiation	Mo K_{α} ($\lambda = 0.71073$ Å)
Temp., K	293(2)
θ range, deg.	2.60-25.00
Limiting indices	$-9 \le h \le 9, 0 \le k \le 23,$
0	$0 \le l \le 15$
No. unique reflection	3731
R	0.0215
R_{ω}	0.0478
Goodness-of-fit on F^2	1.033
Largest diff. peak and hole	0.308 and $-0.410 \text{ e}\text{\AA}^{-3}$

were recorded in the 4000–400 cm⁻¹ region using KBr pellets on a Nicolet 170 SX FTIR spectrometer, which showed the characteristic bands of the complex; the band in the 1480–1510 cm⁻¹, attributed to the ν (C–N) stretching vibration,⁸ the band in the 940–990 cm⁻¹, belonging to the ν (C–SN) stretching vibration,^{8,9} which is considered indicative of dithiocarbamate acting as a bidentate ligand.¹⁰ The Raman spectra were recorded 3500–100 cm⁻¹ using RFS 100 Fourier transform Raman spectrophotometer, which showed bands in the region 450–300 cm⁻¹, due to the ν (Cd–S) stretching vibration. All bands are consistent with the expected compound.

A summary of the key crystallographic information is given in Table 1. The selected crystal of [Cd(n-Pr₂dtc)₂] was mounted on a SMART CCD diffractometer. Reflection data were measured at 20°C using graphite monochromated M_o -K_{α} ($\lambda = 0.71073$ Å) radiation with a detector distance of 4 cm and swing angle of -35° . A hemisphere of reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0,88,180°) and each exposure of 30 s covered 0.3° in ω . The collected data were reduced by using the program SAINT¹¹ and empirical absorption correction was done by using the SADABS¹² (T_{min} = 0.395 and T_{max} = 0.786) pro-



Fig. 1. Molecular structure for $[Cd_2(n-Pr_2dtc)_4]$ with the atomic numbering scheme.

gram. Reflections with $2\theta < 50^{\circ}$ were used for structure solution and refinement.

The structure was solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL¹³ software package. One of the propyl chain (C9 to C11) is found to be disordered; the occupancies of the disordered atoms were initially refined and later fixed. The populations of the major and minor components are 60 and 40%, respectively. All non-H-atoms were anisotropically refined. The hydrogen atoms were geometrically fixed and allowed to ride on the parent atoms to which they attach. The final conventional R(F) =0.215 and wR(F2) = 0.0478 for 3280 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_0^2) +$ $(0.0154P)^2 + 0.9927P$], where $P = (F_c^2)/3$. The molecular graphics were created by using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.¹⁴

Results and discussion

The X-ray structure of the cadmium complex $[Cd_2(n-Pr_2dtc)_4]$ is built up of centro-symmetric di-

Fig. 2. A view of the crystal packing down the *a* axis for $[Cd_2(n-Pr_2dtc)_4]$.

meric entities. Figure 1 shows a perspective view of the dimeric unit with the atomic numbering scheme, and Fig. 2, a perspective view of the crystal packing in the unit cell. Table 2 contains atomic positions and equivalent temperature factors for nonhydrogen atoms. Selected bond distances and angles are listed in Table 3. The coordination sphere of the cadmium ions is best described as a distorted square pyramid. The basal coordination positions are occupied by four sulfur atoms belonging to two dtc ligands. The fifth coordination is achieved by linking to a sulfur atom from a third ligand occupying the equatorial site in the coordination polyhedron of the centrosymmetrically related cadmium ion. Therefore, each bridging sulfur simultaneous occupies an equatorial coordination site on one cadmium ion and an apical site on the other Cd. The topology of the informed dimers is then viewed as edge-sharing distorted square-pyramids. As expected, the axial Cd(1) - S(4)#1 bond distance [2.6212(6) Å] is a little longer than three of the

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent IsotropicDisplacement Parameters ($A^2 \times 10^3$)

	x	у	Z	$U(eq)^a$
Cd(1)	4575(1)	5786(1)	5521(1)	47(1)
S(1)	4773(1)	6995(1)	6335(1)	53(1)
S(2)	5026(1)	5670(1)	7470(1)	50(1)
S(3)	2585(1)	5876(1)	3824(1)	74(1)
S(4)	2707(1)	4610(1)	5085(1)	45(1)
N(1)	5058(2)	6906(1)	8335(1)	48(1)
N(2)	612(3)	4802(1)	3378(2)	71(1)
C(1)	4968(3)	6557(1)	7471(2)	41(1)
C(2)	5014(4)	7662(1)	8358(2)	61(1)
C(3)	6657(4)	7996(2)	8296(2)	79(1)
C(4)	8030(5)	7781(2)	9123(3)	96(1)
C(5)	5130(4)	6549(1)	9313(2)	62(1)
C(6)	3454(5)	6411(2)	9576(2)	98(1)
C(7)	3592(8)	6042(3)	10588(3)	157(2)
C(8)	1835(3)	5071(1)	4013(2)	49(1)
$C(9A)^b$	-538(7)	5257(4)	2671(5)	69(2)
$C(10A)^{b}$	34(9)	5195(4)	1696(7)	93(2)
$C(11A)^{b}$	-1021(17)	5681(7)	907(8)	133(4)
$C(9B)^{c}$	301(9)	5095(3)	2265(6)	44(2)
$C(10B)^{c}$	-1129(10)	5607(4)	2246(6)	62(3)
$C(11B)^{c}$	-1657(20)	5908(8)	1244(10)	10(4)
C(12)	-123(3)	4124(1)	3519(2)	64(1)
C(13)	579(4)	3550(2)	2982(2)	76(1)
C(14)	-289(4)	2873(2)	3087(3)	86(1)

^{*a*} U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

^b Occupancy = 0.60.

^{*c*} Occupancy = 0.40.



Cd(1) - S(1)	2.5867(6)	Cd(1) - S(2)	2.5911(6)
Cd(1) - S(3)	2.5900(7)	Cd(1) - S(4)#1	2.6212(6)
Cd(1) - S(4)	2.7681(6)	N(1) - C(1)	1.335(3)
N(1) - C(2)	1.472(3)	N(1) - C(5)	1.476(3)
N(2) - C(8)	1.319(3)	N(2) - C(12)	1.476(3)
N(2) - C(9A)	1.516(8)	S(1) - C(1)	1.732(2)
S(2) - C(1)	1.726(2)	S(3) - C(8)	1.717(2)
S(4) - C(8)	1.749(2)	S(4) - Cd(1)#1	2.6212(6)
S(1) - Cd(1) - S(2)	70.38(2)	S(1) - Cd(1) - S(3)	107.34(2)
S(2) - Cd(1) - S(3)	149.43(3)	S(1) - Cd(1) - S(4)	146.70(2)
S(2) - Cd(1) - S(4)	97.25(2)	S(3) - Cd(1) - S(4)	67.49(2)
S(1) - Cd(1) - S(4)#1	113.49(2)	S(2) - Cd(1) - S(4)#1	107.20(2)
S(3) - Cd(1) - S(4)#1	101.57(3)	S(4) - Cd(1) - S(4)#1	99.61(2)
C(1) - N(1) - C(2)	121.9(2)	C(1) - N(1) - C(5)	121.4(2)
C(2) - N(1) - C(5)	116.7(2)	C(8) - N(2) - C(12)	124.0(2)
C(8) - N(2) - C(9A)	120.6(3)	C(12) - N(2) - C(9A)	111.9(3)
C(1) - S(1) - Cd(1)	85.13(7)	C(1) - S(2) - Cd(1)	85.10(7)
C(8) - S(3) - Cd(1)	90.10(8)	C(8) - S(4) - Cd(1)	83.77(8)
C(8) - S(4) - Cd(1)#1	98.92(8)	Cd(1) - S(4) - Cd(1)#1	80.39(2)
N(1) - C(1) - S(2)	120.8(2)	N(1) - C(1) - S(1)	119.9(2)
S(2) - C(1) - S(1)	119.3(1)	S(3) - C(8) - S(4)	118.6(1)

Table 3. Selected Bond Distances (Å) and Bond Angles (°) of $[Cd_2(n-Pr_2dtc)_4]^a$

^a Symmetry transformations used to generate equivalent atoms: #1 1-x, 1-y, 1-z.

equatorial Cd(1)-S(n) ones [n = 1,2,3,2,5867(6), 2.5900(7), and 2.5911(6) Å] and shorter than that of Cd(1)-S(4) [2.7681(6) Å]. The four basal sulfur atoms are coplanar, but the Cd atom deviates from that plane by 0.7176(2) Å showing a slight tetrahedral distortion. The bond length of Cd(1)-S(4) [2.7681(6) Å] is the longest in Cd-S equatorial bond lengths due to S(4) being a bridging atom. The bond angles S(1)-Cd(1)-S(2) and S(3)-Cd(1)-S(4) [70.38(2) and 67.49(2)°] are in agreement with the cadmium bis(dibutyldithiocarbamate)² and bis(diethyldithiocarbamate)¹⁵ complexes.

The bridging network Cd(1)-S(4)-Cd(1)#1-S(4)#1 is strictly planar owing to the inversion center, with a Cd···Cd separation of 3.4799(3) Å. The bond angles of S(4)-Cd(1)-S(4)#1 and Cd(1)-S(4)-Cd(1)#1 are 99.61(2) and 80.39(2)°, respectively. The Cd(1)-S(4)-Cd(1)#1-S(4)#1 and S(1)-S(2)-S(3)-S(4) planes are nearly perpendicular with a dihedral angle of 89.11(1)°. The carbon-sulfur bonds have an average distance of 1.73(1) Å and the ligand "bite" angle S-C-S has a mean value of 119.0(3)°. The N(1)-C(1) and N(2)-C(8) bond distances [1.335(3), 1.319(3) Å] are shorter than the other N-C bond distances which are indicative of considerable double-bond character.

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