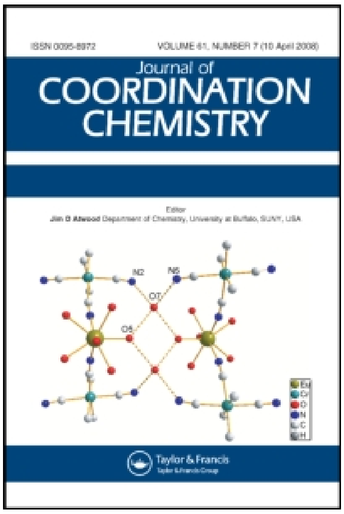


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF [$Cd_2(OS_2CSC_6H_2Bu^{<i>t</i>}_3$-2,4,6$)_4(C_2H_5OH)_2$] · C_2H_5OH. A PRODUCT OF INSERTION OF CARBON DISULFIDE INTO Cd-S BONDS

Xianglin Jin[a]; Kaluo Tang[a]; Tianbing Xia[a]; Youqi Tang[a]
[a] Institute of Physical Chemistry, Peking University, Beijing, P.R. China

To cite this Article Jin, Xianglin , Tang, Kaluo , Xia, Tianbing and Tang, Youqi(1995) 'SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF [$Cd_2(OS_2CSC_6H_2Bu^{<i>t</i>}_3$-2,4,6$)_4(C_2H_5OH)_2$] · C_2H_5OH. A PRODUCT OF INSERTION OF CARBON DISULFIDE INTO Cd-S BONDS', Journal of Coordination Chemistry, 34: 2, 187 — 194

To link to this Article: DOI: 10.1080/00958979508055398

URL: http://dx.doi.org/10.1080/00958979508055398

J. Coord. Chem., 1995, Vol 34, pp. 187–194
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[Cd_2(OS_2CSC_6H_2Bu^t{}_3\text{-}2,4,6)_4(C_2H_5OH)_2]\cdot C_2H_5OH$. A PRODUCT OF INSERTION OF CARBON DISULFIDE INTO Cd-S BONDS

XIANGLIN JIN, KALUO TANG,* TIANBING XIA and YOUQI TANG

Institute of Physical Chemistry, Peking University, Beijing 100871, P.R. China

(Received April 16, 1994; in final form September 7, 1994)

The title compound, $C_{82}H_{134}Cd_2O_7S_{12}$, formed by reaction of the corresponding cadmium thiolate with CS_2 and recrystallization from acetone/ethanol in air. Crystals belong to the triclinic space group $P\bar{1}$, with $Z = 2$, cell dimensions $a = 14.647(13)$, $b = 19.140(20)$, $c = 20.967(10)$Å, $\alpha = 64.79(6)$, $\beta = 79.56(5)$, $\gamma = 71.48(7)°$, $V = 5034$Å^3. The structure was solved by direct methods and was refined to an R of 0.098 for 3754 observed reflections. All the Cd-S bonds were inserted by CS_2, then the ligands were oxidized to form unusual $ArSCS_2O^-$ groups. Cadmium atoms have distorted octahedral geometry. The distance between the two Cd atoms is 3.753Å.

KEYWORDS: cadmium, CS_2, trithiocarbonate, synthesis, X-ray structure

INTRODUCTION

In recent years, we have investigated the insertion of carbon disulfide into M-S (M = Cu, Ag) bonds extensively. This reaction is a promising approach to new sulfur-containing metal clusters. Some insertion products of copper and silver complexes have been synthesized by this method and structurally determined by us.[1-6] From previous work, we have found that with the use of more bulky thiolate ligands, the insertion can proceed more readily, and the aggregation of copper and silver alkyl (or aryl) trithiocarbonate complexes decreases with higher proportions of CS_2 insertion.

In the case of zinc and cadmium, this kind of reaction is rarely reported. The only crystal structure presented in literature is of a mononuclear cadmium complex with a bidentate donor ligand reported by Tuck *et al.*[7] Now we present a dinuclear cadmium complex which undergoes insertion with CS_2. This is the first structure with respect to our systematic research on insertion of CS_2 into Cd-S and Zn-S bonds and follows previous work in this laboratory on thiolate derivatives of Cd and Zn.[8-11]

---

* Author for correspondence.

EXPERIMENTAL

Preparation

Reactions were performed on a standard Schlenk Line and solvents were dried and distilled before used. Cadmium salts were used as supplied. A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.302 g, 0.98 mmol) in ethanol (5 cm^3) was added dropwise into a solution of 2,4,6-tri-*tert*-butylthiophenol (TBT)[12] (0.502 g, 1.81 mmol) and Et_3 N (0.3 cm^3, 4.4 mmol) in ethanol (20 cm^3) at room temperature within 10 minutes. The mixture was stirred for 10 hours and remained clear. Many colourless rod-like crystals formed after cooling the mixture in a refrigerator (0.310 g efflorescent crystals collected, yield 51%). The crystals decompose above 150°C. Anal. for $C_{36}H_{58}CdS_2$: C,64.79; H, 8.76; Cd, 16.84; S, 9.61%. Found: C, 64.31; H, 8.55; Cd, 16.29; S, 9.80%.

The abovementioned colourless crystals (0.05 g) were dissolved in CS_2 (20 cm^3). The solution quickly turned yellow and was stirred for 10 hours. The yellow powder obtained by removing the solvent is soluble in THF, DMF, diethyl ether, benzene, toluene, pyridine, $CHCl_3$, CCl_4, cyclohexane, acetone, pentane, slightly soluble in CH_2Cl_2 (turns white), and insoluble in acetonitrile, methanol and ethanol. Recrystallization from acetone/ethanol by evaporation yielded the final product as yellow flakes. Crystals are air-stable, effloresce at 110°C and melt at 130°C, then colourless microcrystals form above 150°C. The infrared spectrum of the yellow crystals was obtained on a Perkin Elmer 983G spectrophotometer. IR (KBr pellet, cm^{-1}): 3390(w), 2961(vs), 2867(s), 2679(m), 2492(w), 1719(w), 1688(w), 1654(w), 1586(m), 1543(w), 1476(w), 1385(vs), 1360(vs), 1240(m), 1214(m), 1034(s), 876(s), 834(w), 755(m), 652(w), 541(w), 454(w), 391(w), 234(w). Anal. for $C_{82}H_{134}Cd_2O_7S_{12}$: C, 53.48; H, 7.34; Cd, 12.21; S, 20.89%. Found: C, 52.89; H, 7.06; Cd, 11.88; S, 21.38%.

Crystallography

Diffraction data were collected from a crystal with approximate dimensions 0.3 × 0.3 × 0.1 mm on a Siemens R3 diffractometer with MoK_α radiation (λ = 0.71073Å) in the range $3.0 \leq 2\theta \leq 40.0°$ using the θ-2θ scan mode at room temperatures. Crystal data: molecular formula $C_{82}H_{134}Cd_2O_7S_{12}$, M = 1841.4, space group $P\bar{1}$, a = 14.647(13), b = 19.140(20), c = 20.967(10))Å, α = 64.79(6), β = 79.56(5), γ = 71.48(7)°, V = 5034(7)$Å^3$, Z = 2, Dc = 1.215 g cm^{-3}, $F(000)$ = 1940, μ = 0.702 mm^{-1}. The SHELXTL PLUS program package was used to solve and refine the structure. The coordinates of Cd atoms were found by direct methods. Remaining non-hydrogen atoms were located from successive difference Fourier maps. The structure was refined by full-matrix block least-squares methods. Hydrogen atoms were located by theoretical calculations. With anisotropic thermal parameters for Cd, S, O atoms and isotropic thermal parameters for C atoms, refinement yielded the final discrepancy R = 0.098 for 9473 independent reflections, of which 3754 are observed $(F > 4.0\sigma(F)]$. Atomic coordinates for non-hydrogen atoms are listed in Table 1, and selected bondlengths and angles are given in Tables 2 and 3, respectively.

Table 1 Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x/a	y/b	z/c	U(eq)
Cd(1)	5751(2)	-1113(1)	-1717(1)	57(1)
Cd(2)	3985(2)	848(1)	-2672(1)	67(1)
S(11)	7466(6)	-995(5)	-1665(5)	73(5)
S(12)	6382(6)	650(5)	-2592(5)	64(5)
S(13)	8489(5)	170(5)	-2588(4)	56(4)
O(1)	5528(14)	272(13)	-2221(9)	69(12)
C(1)	7382(19)	-46(16)	-2278(14)	45(8)
C(11)	8086(20)	1205(17)	-3254(15)	49(8)
C(12)	7928(22)	1271(19)	-3962(16)	65(10)
C(13)	7459(21)	2020(18)	-4383(17)	64(9)
C(14)	7172(21)	2648(18)	-4197(16)	58(9)
C(15)	7441(21)	2595(18)	-3567(15)	59(9)
C(16)	7902(19)	1800(16)	-3069(14)	40(8)
C(121)	8296(26)	557(21)	-4215(19)	82(11)
C(122)	8238(33)	883(27)	-5008(22)	159(20)
C(123)	9316(26)	175(22)	-4154(20)	113(14)
C(124)	7795(26)	-92(21)	-3889(19)	105(13)
C(141)	6570(28)	3484(23)	-4722(20)	93(12)
C(142)	5703(38)	3873(33)	-4321(29)	236(30)
C(143)	7149(33)	4043(27)	-4996(24)	165(20)
C(144)	6073(38)	3454(32)	-5229(27)	211(27)
C(161)	8222(23)	1801(19)	-2399(17)	70(10)
C(162)	7676(24)	1355(20)	-1728(17)	91(12)
C(163)	9288(21)	1447(18)	-2345(16)	71(10)
C(164)	8076(26)	2622(20)	-2412(19)	102(13)
S(21)	5876(7)	-2577(5)	-1476(5)	84(6)
S(22)	6569(7)	-1837(5)	-2976(5)	75(5)
S(23)	7188(7)	-3603(5)	-2136(5)	82(5)
O(2)	5934(16)	-1094(12)	-2873(9)	77(13)
C(2)	6526(20)	-2658(17)	-2209(15)	56(8)
C(21)	7878(21)	-3428(17)	-2998(15)	53(9)
C(22)	8740(21)	-3296(16)	-3056(15)	50(8)
C(23)	9112(23)	-3006(17)	-3741(16)	67(10)
C(24)	8685(23)	-2947(18)	-4317(16)	64(9)
C(25)	7864(20)	-3213(16)	-4201(15)	54(8)
C(26)	7468(23)	-3503(18)	-3508(17)	65(10)
C(221)	9335(24)	-3374(20)	-2482(18)	72(10)
C(222)	8967(25)	-2727(20)	-2229(18)	99(12)
C(223)	9456(30)	-4187(24)	-1876(21)	137(17)
C(224)	10386(28)	-3416(25)	-2726(22)	141(17)
C(241)	9154(28)	-2658(29)	-5069(17)	150(19)
C(242)	8539(32)	-2478(29)	-5654(23)	178(22)
C(243)	10241(29)	-2875(39)	-5164(36)	331(46)
C(244)	9076(44)	-1772(32)	-5272(36)	371(50)
C(261)	6621(29)	-3872(24)	-3421(22)	106(13)
C(262)	5613(28)	-3311(24)	-3286(21)	132(16)
C(263)	6513(32)	-3970(26)	-4096(22)	150(18)
C(264)	6791(28)	-4698(22)	-2821(19)	118(14)
S(31)	2297(7)	714(6)	-2705(6)	109(6)
S(32)	3355(6)	-911(5)	-1734(5)	62(5)
S(33)	1402(6)	-596(5)	-2143(4)	70(5)
O(3)	4109(13)	-478(12)	-1867(10)	66(11)
C(3)	2367(24)	-259(20)	-2182(17)	73(10)
C(31)	1735(22)	-1641(18)	-1501(16)	60(9)
C(32)	1546(19)	-1811(16)	-790(15)	50(8)
C(33)	1977(19)	-2572(16)	-327(15)	47(8)
C(34)	2582(20)	-3142(17)	-559(15)	52(8)

Table 1 *Continued*

	x/a	y/b	z/c	U(eq)
C(35)	2703(21)	-2982(18)	-1286(15)	58(9)
C(36)	2316(23)	-2195(20)	-1759(17)	70(10)
C(321)	838(21)	-1231(17)	-494(16)	68(10)
C(322)	1198(22)	-542(18)	-563(16)	76(11)
C(323)	-146(23)	-917(20)	-803(18)	91(12)
C(324)	604(26)	-1648(21)	317(17)	99(13)
C(341)	3130(27)	-3976(24)	-38(20)	97(13)
C(342)	3390(44)	-4599(35)	-268(32)	274(37)
C(343)	3842(35)	-3917(34)	368(27)	227(29)
C(344)	2421(41)	-4331(38)	538(28)	308(42)
C(361)	2393(27)	-2107(22)	-2525(20)	90(12)
C(362)	1485(26)	-1748(22)	-2902(20)	116(14)
C(363)	2790(30)	-2884(24)	-2628(22)	142(17)
C(364)	3077(27)	-1617(23)	-3004(20)	117(15)
S(41)	3909(8)	2328(5)	-3549(5)	89(6)
S(42)	3311(9)	2150(6)	-2024(5)	122(7)
S(43)	2927(7)	3711(5)	-3224(4)	74(5)
O(4)	3902(28)	1289(15)	-1786(14)	307(49)
C(4)	3425(19)	2681(16)	-2924(14)	43(8)
C(41)	2405(22)	3856(17)	-2430(16)	58(9)
C(42)	2969(24)	3934(19)	-1986(18)	71(10)
C(43)	2551(22)	3864(17)	-1316(16)	66(10)
C(44)	1708(19)	3721(16)	-1098(13)	48(8)
C(45)	1132(19)	3684(15)	-1511(14)	46(8)
C(46)	1445(22)	3810(19)	-2226(17)	72(10)
C(421)	3938(25)	4149(21)	-2265(18)	77(11)
C(422)	4765(29)	3506(24)	-2338(22)	140(17)
C(423)	4237(32)	4421(27)	-1772(23)	158(19)
C(424)	3740(31)	4942(24)	-2926(21)	144(18)
C(441)	1380(22)	3543(19)	-328(14)	74(10)
C(442)	1330(38)	4233(26)	-137(27)	212(27)
C(443)	347(25)	3541(32)	-97(27)	217(28)
C(444)	2106(35)	2954(30)	215(26)	267(34)
C(461)	690(22)	3820(20)	-2661(17)	73(10)
C(462)	-290(27)	3856(24)	-2321(21)	122(15)
C(463)	959(26)	3046(21)	-2812(19)	105(14)
C(464)	620(28)	4515(22)	-3333(19)	123(15)
O(5)	5264(20)	-1302(15)	-524(10)	108(16)
C(5)	5026(47)	-1966(38)	54(35)	235(32)
C(6)	4276(50)	-1976(47)	356(39)	379(62)
O(6)	4810(17)	342(13)	-3555(12)	97(14)
C(7)	4324(51)	543(43)	-4232(34)	248(34)
C(8)	4668(57)	980(45)	-4589(40)	408(70)
O(7)	4097(54)	151(44)	9552(39)	342(34)
C(9)	3638(73)	464(71)	9864(61)	573(136)
C(10)	2804(44)	622(39)	9810(34)	272(37)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

The synthesis of neutral cadmium thiolate $[Cd(SC_6H_2Bu^t_3\text{-}2,4,6)_2]_n$ was achieved using cadmium nitrate and the corresponding thiolate in the ratio 1:2 (approximately) and in the presence of Et_3N. This cadmium thiolate reacts with CS_2 readily, although in the case of the unsubstituted thiophenolate as the ligand, the cadmium

Table 2 Selected Bond lengths (Å).

Cd(1)-S(11)	2.618(11)	Cd(1)-O(1)	2.332(22)
Cd(1)-S(21)	2.577(11)	Cd(1)-O(2)	2.376(22)
Cd(1)-O(3)	2.335 (17)	Cd(1)-O(5)	2.375 (21)
Cd(2)-O(1)	2.349 (20)	Cd(2)-S(31)	2.583 (12)
Cd(2)-O(3)	2.343 (18)	Cd(2)-S(41)	2.618 (9)
Cd(2)-O(4)	2.317 (35)	Cd(2)-O(6)	2.409 (27)
S(11)-C(1)	1.700 (25)	S(12)-O(1)	1.560 (24)
S(12)-C(1)	1.647 (25)	S(13)-C(1)	1.742 (30)
S(13)-C(11)	1.850 (24)	S(21)-C(2)	1.694 (31)
S(22)-O(2)	1.511 (23)	S(22)-C(2)	1.712 (25)
S(23)-C(2)	1.715 (30)	S(23)-C(21)	1.853 (30)
S(31)-C(3)	1.690 (33)	S(32)-O(3)	1.501 (25)
S(32)-C(3)	1.696 (31)	S(33)-C(3)	1.706 (42)
S(33)-C(31)	1.838 (27)	S(41)-C(4)	1.670 (33)
S(42)-O(4)	1.503 (26)	S(42)-C(4)	1.726 (26)
S(43)-C(4)	1.734 (27)	S(43)-C(41)	1.798 (35)

Table 3 Selected Bond angles (°).

S(11)-Cd(1)-O(1)	77.8(6)	S(11)-Cd(1)-S(21)	108.9(3)
O(1)-Cd(1)-S(21)	165.1(6)	S(11)-Cd(1)-O(2)	98.0(6)
O(1)-Cd(1)-O(2)	88.6(7)	S(21)-Cd(1)-O(2)	77.5(6)
S(11)-Cd(1)-O(3)	147.8(6)	O(1)-Cd(1)-O(3)	71.1(7)
S(21)-Cd(1)-O(3)	103.3(6)	O(2)-Cd(1)-O(3)	89.8(8)
S(11)-Cd(1)-O(5)	95.5(8)	O(1)-Cd(1)-O(5)	100.0(8)
S(21)-Cd(1)-O(5)	92.6(8)	O(2)-Cd(1)-O(5)	165.3(10)
O(3)-Cd(1)-O(5)	81.9(8)	O(1)-Cd(2)-S(31)	149.3(6)
O(1)-Cd(2)-O(3)	70.7(7)	S(31)-Cd(2)-O(3)	78.6(5)
O(1)-Cd(2)-S(41)	107.1(6)	S(31)-Cd(2)-S(41)	103.6(3)
O(3)-Cd(2)-S(41)	177.7(6)	O(1)-Cd(2)-O(4)	75.0(11)
S(31)-Cd(2)-O(4)	107.1(11)	O(3)-Cd(2)-O(4)	92.8(8)
S(41)-Cd(2)-O(4)	85.9(6)	O(1)-Cd(2)-O(6)	81.3(8)
S(31)-Cd(2)-O(6)	98.3(8)	O(3)-Cd(2)-O(6)	88.6(7)
S(41)-Cd(2)-O(6)	91.7(5)	O(4)-Cd(2)-O(6)	154.3(12)
Cd(1)-S(11)-C(1)	100.0(11)	O(1)-S(12)-C(1)	107.0(12)
C(1)-S(13)-C(11)	100.3(12)	Cd(1)-O(1)-Cd(2)	106.6(10)
Cd(1)-O(1)-S(12)	121.6(10)	Cd(2)-O(1)-S(12)	121.8(9)
S(11)-C(1)-S(12)	126.5(18)	S(11)-C(1)-S(13)	114.1(14)
S(12)-C(1)-S(13)	119.4(15)	Cd(1)-S(21)-C(2)	100.7(11)
O(2)-S(22)-C(2)	108.9(13)	C(2)-S(23)-C(21)	103.5(13)
Cd(1)-O(2)-S(22)	117.5(9)	S(21)-C(2)-S(22)	122.1(18)
S(21)-C(2)-S(23)	116.7(14)	S(22)-C(2)-S(23)	121.2(18)
Cd(2)-S(31)-C(3)	103.8(13)	O(3)-S(32)-C(3)	109.2(15)
C(3)-S(33)-C(31)	103.5(15)	Cd(1)-O(3)-Cd(2)	106.7(8)
Cd(1)-O(3)-S(32)	124.1(11)	Cd(2)-O(3)-S(32)	124.5(10)
S(31)-C(3)-S(32)	123.5(25)	S(31)-C(3)-S(33)	117.0(18)
S(32)-C(3)-S(33)	119.4(19)	Cd(2)-S(41)-C(4)	92.4(9)
O(4)-S(42)-C(4)	113.2(16)	C(4)-S(43)-C(41)	103.1(13)
Cd(2)-O(4)-S(42)	108.6(17)	S(41)-C(4)-S(42)	128.4(17)
S(41)-C(4)-S(43)	115.6(14)	S(42)-C(4)-S(43)	116.0(18)
Cd(1)-O(5)-C(5)	131.0(40)	O(5)-C(5)-C(6)	126.5(56)
Cd(2)-O(6)-C(7)	121.9(27)	O(6)-C(7)-C(8)	98.4(84)

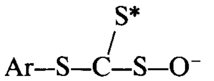
thiolate is insoluble in normal organic solvents and difficult to react with CS_2.[7] This phenomenon indicates the influence of substitution of aromatic ring on the reactivity of thiolate compounds. The crude product of insertion of CS_2 was recrystallized from acetone-ethanol in air, leading to the title compound.

$$Cd(NO_3)_2 \cdot 4H_2O + 2[HSC_6H_2Bu^t_3\text{-}2,4,6] + 2Et_3N \rightarrow [Cd(SC_6H_2Bu^t_3\text{-}2,4,6)_2]_n$$

$$[Cd(SC_6H_2Bu^t_3\text{-}2,4,6)_2]_n + CS_2 \rightarrow \xrightarrow[\text{recrystallization (in air)}]{\text{acetone/ethanol}} \text{title compound}$$

Crystal structure determination indicates that the title compound is a neutral dinuclear cadmium complex, with four oxidized trithiocarbonate and two ethnaol ligands. The core and the whole structures of the molecule are shown in Figures 1 and 2, respectively.

The unusual ligand groups, formed by insertion of CS_2 into all Cd-S bonds and an unexpected oxidization, are shown below.



$$Ar{-}S{-}\overset{S^*}{C}{-}S{-}O^-$$

In the ligands, the oxygen and one of the sulfur atoms (S^*) act as coordinating atoms. The O atoms are probably derived from air during recrystallization. Sulfur-containing compounds are easily oxidized and the oxidization products vary, depending on conditions of oxidation. The above oxidation state usually exists as an unstable intermediate which can be further oxidized.[13] Each set of Cd, C, O and two S atoms forms a stable five-membered ring, which contributes to the stability of the whole molecule. The two cadmium atoms are hexacoordinated, forming distorted octahedra.

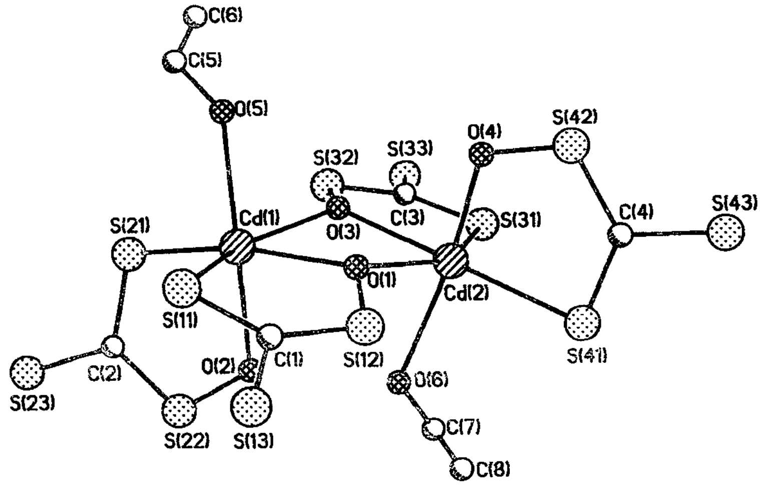


Figure 1 The core of $[Cd_2(OS_2CSC_6H_2Bu^t_3\text{-}2,4,6)_4(C_2H_5OH)_2] \cdot C_2H_5OH$.

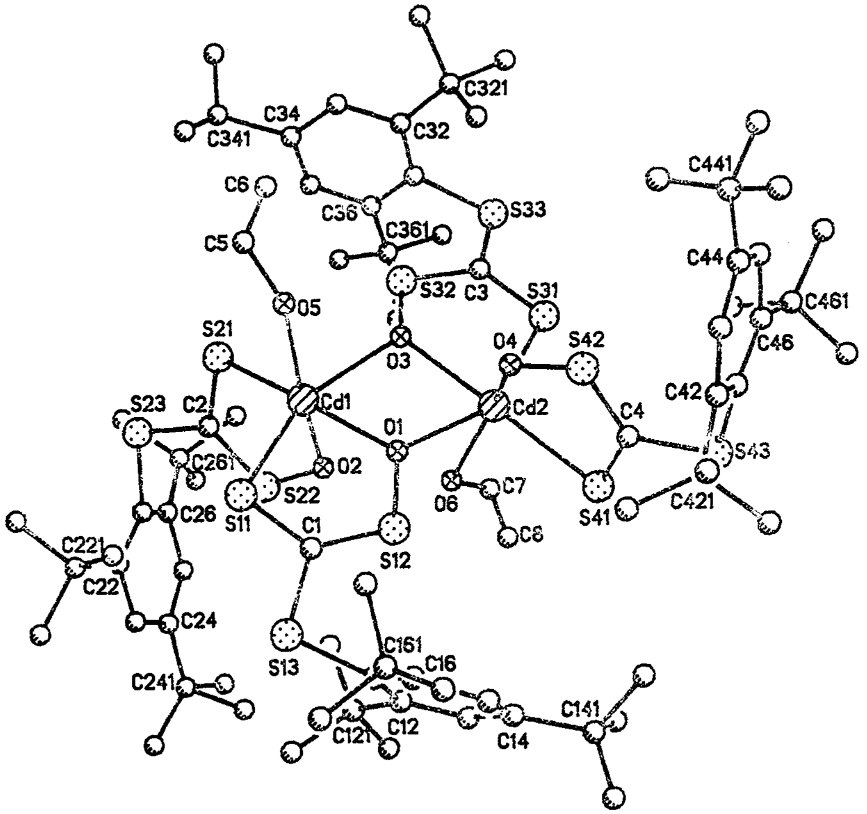


Figure 2 The molecular structure of [$Cd_2(OS_2CSC_6H_2Bu^t{}_3$ -2,4,6$)_4(C_2H_5OH)_2$].

Each Cd atom is coordinated by two sulfur atoms and four oxygen atoms. The two S atoms come from two oxidized trithiocarbonate ligands; the four O atoms include one from the ethanol ligand ($O_{t'}$) and three from oxidized trithiocarbonate ligands among them, two are bridging O atoms (O_b) and the other is a terminal O atom (O_t). The two Cd atoms are approximately symmetrically bridged by two O_b atoms and lie 3.753Å away from each other, indicating that there is no direct interaction. The mean distance between Cd and O_b is 2.340Å (2.332-2.349Å). The Cd_2O_2 four-membered ring forms a butterfly conformation, the dihedral angle of the two CdO_2 planes being 20.2°.

Although the ligands are *trans* ,the circumstances of the two Cd atoms are not exactly the same. The five atoms Cd_2, O_1, O_3, S_{31} and S_{41} are coplanar (mean deviation 0.005Å), while the five atoms, Cd_1, O_1, O_3, S_{11}, S_{21}, are not. There are four Cd-S-C-S-O five-membered rings, but only the ring formed by Cd_2, S_{31}, C_3, S_{32} and O_3 is approximately coplanar (mean deviation 0.036Å); the conformations adopted by the remaining three are "envelope" in shape with the Cd atoms about 1Å out of the CS_2O four-membered planes.

As observed previously for insertion of CS_2 into Cu-S or Ag-S bonds,[1-6] the four CS_3 groups formed by insertion of CS_2 into Cd-S bonds in the title complex are coplanar, and the C-S bondlengths are around 1.7Å (1.647–1.742Å). The presence of peaks at 1034 and 876 cm^{-1} and weak absorptions at 1543 ands 454 cm^{-1} in the infrared spectrum are characteristic of the CS_3 group, and are assigned to $\nu(C=S)$ and $\nu(C\text{-}S)$, respectively.

There are two coordinating ethanol molecules, each of which bonds to one Cd atom, so that the title compounds is a mixed-ligand complex. Ethanol molecules enter the cluster during the recrystallization. Because the whole molecule is neutral, the coordinating ethanol molecules are neutral. An additional ethanol molecule is present in the unsymmetric unit as solvent of crystallization. Infrared absorptions (weak band) at 3390 cm^{-1} are attributed to hydroxyl groups.

Supplementary Material

Lists of anisotropic and isotropic thermal parameters, bondlengths and angles, and tables of observed and calculated structure factors are available from the authors upon request.

Acknowledgments

We wish to express our gratitude for financial support of this work by China's National Natural Science Foundation.

References

1. K. Tang, Q. Xing, J. Yang, Q. Yang and Y. Tang, *Acta Chim. Sinica,* **48**, 242 (1990).
2. K. Tang, J. Yang, Q. Yang and Y. Tang, *J. Chem. Soc., Dalton Trans.,* 2297 (1989).
3. K. Tang, D. Wu, X. Jin and Y. Tang, *Acta Chim. Sinica,* **51**, 52 (1993).
4. K. Tang, D. Wu, X. Jin and Y. Tang, *Heteroatom Chemistry,* **3**, 655 (1992).
5. K. Tang, D. Wu, X. Jin and Y. Tang, *J. Struct. Chem.,* **11**, 314 (1992).
6. K. Tang, D. Wu, X. Jin and Y. Tang, *Acta Scien. Natur., Univ. Peking,* **28**, 446 (1992).
7. S. J. Black, F. W. B. Einstein, P.C. Hayes, R. Kaman, and D.G. Tuck, *Inorg. Chem.,* **25**, 4181 (1986).
8. K. Tang, A. Li, X. Jin, Y. Tang, *J. Chem. Soc. Chem. Commun.,* 1590 (1991).
9. K. Tang, X. Jin, A. Li, S. Li, Z. Li and Y. Tang, *J. Coord. Chem.,* **31**, 305 (1994).
10. K. Tang, A. Li, X. Jin and Y. Tang, *Chemical Journal of Chinese Universities,* **13**, 441 (1992).
11. K. Tang, A. Li, X. Jin and Y. Tang, *Chemical Journal of Chinese Universities,* **14**, 310 (1993).
12. D. E. Pearson and M. G. Frazer, *Synthesis,* 621 (1976).
13. D. N. Jones, "Comprehensive Organic Chemistry", (Pergamon Press, Oxford, 1979), Vol. 3, p. 438.