Crystal structure of (pyridine-*N*)-bis(*N*,*N*-dibenzyldithiocarbamato)cadmium(II), $Cd(C_5H_5N)[S_2CN(C_6H_5CH_2)_2]_2$

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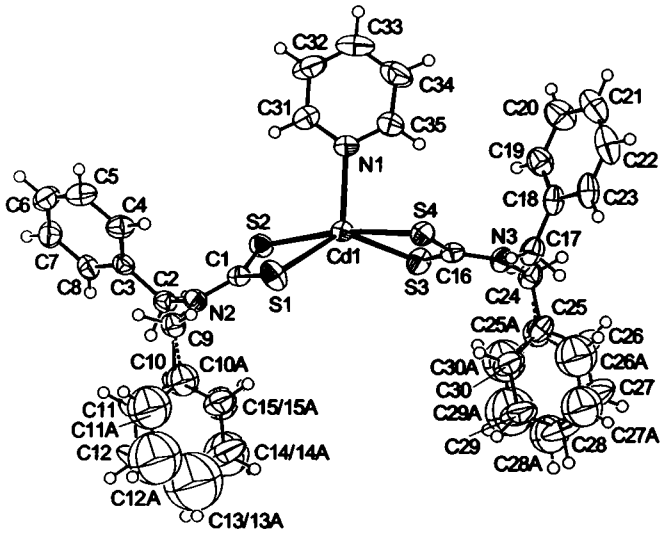

Abstract

$C_{35}H_{33}CdN_3S_4$, monoclinic, *C*12/*c*1 (no. 15), $a = 36.562(2)$ Å, $b = 9.5395(6)$ Å, $c = 19.892(1)$ Å, $\beta = 103.501(1)°$, $V = 6746.3$ Å^3, $Z = 8$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.114$, $T = 223$ K.

Source of material

Pyridine (1 mL) was added to a solution of tetrahydrofuran (THF, 40 mL) containing bis[bis(*N*,*N*-dibenzyldithiocarbamato)cadmium(II)] (1 mmol), prepared according to literature data [1]. The mixture was stirred for 1 h at room temperature and filtrated. Colorless crystal were obtained by slow evaporation of solution (m.p. 425.5-426.5 K).

Experimental details

The two phenyl rings (C10 to C15 and C25 to C30) are disordered. The rings were split into two parts. All four rings were refined as rigid hexagons. The occupancy factors varied around 60 % (part 1) and 40 % (part 2). In the final refinement they were fixed at those values and not refined. Anisotropic thermal parameters were only applied to the major parts.

Discussion

Zinc or sodium dibenzyldithiocarbamate is well known as good extractant, enrichment agent, or carrier for many metals in determination of their content by atomic absorption spectrometric or thin-film X-ray fluorescence spectrometry [2,3]. The patent on zinc dibenzyldithiocarbamate as a rubber vulcanization accelerator was applied in 1978 [4]. Then some kinds of rubber vulcanization accelerators of dibenzyldithiocarbamate complexes were reported gradually [5]. Crystal structures of some metal dibenzyldithiocarbamate have been reported [6]. Investigations of vulcanizing properties revealed that the cross-linked rubber accelerated by the Cd(II) complex has better mechanical properties than that by some other traditional accelerators (NOBS, CZ/TMTD etc.). In this study, pyridine was added to the cadmium dibenzyldithiocarbamate in order to investigate if there is some changing in the complex structure. The structure of the $\{Cd[S_2CN(CH_2Ph)_2]\}_2$ complex was reported [1]. In the dinuclear structure, two Cd(II) atoms are bridged by two of S atoms from two chelating dithiocarbamate ligands, and a four membered ring of Cd_2S_2 was formed. The Cd atoms are bonded to three S atoms from two bidentate dithiocarbamate ligands so that the square-pyramidal configuration with five-coordination was formed. The Cd atoms are located in the center of the square pyramid. The complex structure of $\{Cd[S_2CN(CH_2Ph)_2]\}_2$ was destroyed with the adding of pyridine, and the dinuclear structure became mononuclear.

In the crystal structure of $S_2CN(CH_2Ph)_2]_2$py, the cadmium(II) center is five-coordinated with pyramidal environment and bound to four sulfur atoms from two bidentate dithiocarbamate ligands and to one nitrogen atom from pyridine. The Cd—S bond lengths of *d*(Cd—S1) = 2.583 Å, *d*(Cd—S2) = 2.639 Å, *d*(Cd—S3) = 2.582 Å and *d*(Cd—S4) = 2.648 Å are longer than those in [1]. The bond angles changed too. Because of the space stoppage impact of dibenzyldithiocarbamate and the interlacing of pyridine rings, the title structure differs from that of $[Cd(C_5H_5N)_2(S_2CO\text{-}n\text{-}C_4H_9)_2]$ [7], the π-π interaction is not existing, so a supramolecular system does not form in the $\{Cd[S_2CN(CH_2Ph)_2]_2py\}$ structure. The title structure is similar to the crystal structure of $\{Zn[S_2CN(CH_2Ph)_2]_2py\}$ [8].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.38 x 0.40 x 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.24 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23368, 7742
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6965
$N(param)_{refined}$:	376
Programs:	SHELXS-97 [9], SHELXL-97 [10]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2A)	8f		0.1669	0.2490	0.2292	0.046
H(2B)	8f		0.1418	0.2816	0.1546	0.046
H(4)	8f		0.0815	0.3880	0.2430	0.058
H(5)	8f		0.0336	0.2643	0.2742	0.068
H(6)	8f		0.0330	0.0227	0.2717	0.067
H(7)	8f		0.0796	-0.0979	0.2342	0.061
H(8)	8f		0.1289	0.0241	0.2063	0.049
H(9A)	8f		0.1492	0.4151	0.3228	0.052
H(9B)	8f		0.1545	0.5732	0.3028	0.052
H(11)	8f	0.6	0.2045	0.2704	0.3635	0.075
H(12)	8f	0.6	0.2698	0.2514	0.3930	0.108
H(13)	8f	0.6	0.3067	0.4282	0.3621	0.125
H(14)	8f	0.6	0.2783	0.6240	0.3018	0.163
H(15)	8f	0.6	0.2130	0.6430	0.2723	0.105
C(10A)	8f	0.4	0.20328(7)	0.4801(4)	0.3114(2)	0.077(5)
C(11A)	8f	0.4	0.2201(1)	0.4627(6)	0.3812(1)	0.143(7)
H(11A)	8f	0.4	0.2052	0.4485	0.4131	0.172
C(12A)	8f	0.4	0.2591(1)	0.4662(6)	0.4036(2)	0.21(1)
H(12A)	8f	0.4	0.2705	0.4544	0.4508	0.254
C(13A)	8f	0.4	0.28119(7)	0.4872(7)	0.3564(3)	0.26(2)
H(13A)	8f	0.4	0.3075	0.4896	0.3715	0.315
C(14A)	8f	0.4	0.2643(1)	0.5046(7)	0.2866(3)	0.149(9)
H(14A)	8f	0.4	0.2793	0.5188	0.2546	0.179
C(15A)	8f	0.4	0.2254(1)	0.5011(6)	0.2642(2)	0.081(4)
H(15A)	8f	0.4	0.2140	0.5128	0.2170	0.097
H(17A)	8f		0.1647	1.2842	-0.0574	0.058
H(17B)	8f		0.1459	1.2487	0.0047	0.058
H(19)	8f		0.0794	1.1224	-0.1221	0.065

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(20)	8f		0.0241	1.2322	-0.1789	0.084
H(21)	8f		0.0187	1.4754	-0.1731	0.090
H(22)	8f		0.0688	1.6065	-0.1125	0.085
H(23)	8f		0.1238	1.4991	-0.0582	0.067
H(24A)	8f		0.1523	1.1174	-0.1556	0.055
H(24B)	8f		0.1550	0.9571	-0.1342	0.055
H(26)	8f	0.6	0.2062	1.1181	-0.1991	0.123
H(27)	8f	0.6	0.2715	1.1189	-0.1803	0.149
H(28)	8f	0.6	0.3085	1.0619	-0.0717	0.098
H(29)	8f	0.6	0.2802	1.0042	0.0181	0.097
H(30)	8f	0.6	0.2149	1.0035	-0.0007	0.085
C(25A)	8f	0.4	0.20671(7)	1.0380(5)	-0.1028(1)	0.058(5)
C(26A)	8f	0.4	0.2281(1)	1.1589(4)	-0.1019(3)	0.129(6)
H(26A)	8f	0.4	0.2161	1.2463	-0.1114	0.154
C(27A)	8f	0.4	0.2671(1)	1.1505(6)	-0.0869(3)	0.127(6)
H(27A)	8f	0.4	0.2815	1.2322	-0.0863	0.152
C(28A)	8f	0.4	0.28475(7)	1.0212(7)	-0.0729(2)	0.111(7)
H(28A)	8f	0.4	0.3111	1.0155	-0.0628	0.133
C(29A)	8f	0.4	0.2634(2)	0.9003(5)	-0.0738(3)	0.18(1)
H(29A)	8f	0.4	0.2754	0.8129	-0.0643	0.217
C(30A)	8f	0.4	0.2244(1)	0.9088(4)	-0.0888(3)	0.134(6)
H(30A)	8f	0.4	0.2099	0.8270	-0.0894	0.161
H(31)	8f		0.0269	0.6285	0.0645	0.069
H(32)	8f		-0.0354	0.6349	0.0064	0.084
H(33)	8f		-0.0545	0.7882	-0.0846	0.082
H(34)	8f		-0.0105	0.9396	-0.1124	0.089
H(35)	8f		0.0512	0.9265	-0.0509	0.075

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	8f		0.108599(6)	0.76264(2)	0.06373(1)	0.0331(1)	0.0440(1)	0.0431(1)	-0.00108(9)	0.00355(9)	0.00866(9)
S(1)	8f		0.13397(3)	0.71458(9)	0.19407(4)	0.0740(6)	0.0357(4)	0.0426(4)	0.0033(4)	-0.0022(4)	-0.0029(3)
S(2)	8f		0.11147(2)	0.49085(8)	0.08900(4)	0.0416(4)	0.0409(4)	0.0344(3)	-0.0021(3)	0.0008(3)	-0.0009(3)
S(3)	8f		0.14019(2)	0.81189(8)	-0.03721(4)	0.0509(4)	0.0383(4)	0.0536(4)	-0.0014(3)	0.0220(4)	-0.0033(3)
S(4)	8f		0.11857(2)	1.03522(8)	0.05034(4)	0.0425(4)	0.0416(4)	0.0409(4)	-0.0011(3)	0.0131(3)	-0.0029(3)
N(1)	8f		0.04497(7)	0.7759(3)	0.0121(1)	0.033(1)	0.049(1)	0.048(1)	-0.001(1)	0.004(1)	0.003(1)
N(2)	8f		0.14493(7)	0.4426(2)	0.2205(1)	0.038(1)	0.038(1)	0.032(1)	0.002(1)	0.0060(9)	-0.0005(9)
N(3)	8f		0.14713(7)	1.0849(3)	-0.0580(1)	0.045(1)	0.040(1)	0.038(1)	-0.008(1)	0.012(1)	-0.003(1)
C(1)	8f		0.13146(8)	0.5395(3)	0.1728(1)	0.030(1)	0.039(1)	0.035(1)	0.001(1)	0.007(1)	-0.001(1)
C(2)	8f		0.14348(8)	0.2932(3)	0.2042(2)	0.038(2)	0.037(1)	0.041(2)	0.006(1)	0.011(1)	0.003(1)
C(3)	8f		0.11066(8)	0.2188(3)	0.2227(1)	0.033(1)	0.041(1)	0.029(1)	0.003(1)	0.002(1)	0.002(1)
C(4)	8f		0.08165(9)	0.2895(4)	0.2422(2)	0.040(2)	0.047(2)	0.057(2)	0.004(1)	0.010(1)	-0.007(1)
C(5)	8f		0.0530(1)	0.2156(4)	0.2604(2)	0.038(2)	0.069(2)	0.063(2)	0.003(2)	0.013(2)	-0.010(2)
C(6)	8f		0.0524(1)	0.0721(4)	0.2585(2)	0.042(2)	0.068(2)	0.057(2)	-0.011(2)	0.012(2)	0.001(2)
C(7)	8f		0.0804(1)	0.0005(4)	0.2371(2)	0.055(2)	0.047(2)	0.052(2)	-0.004(2)	0.012(2)	0.006(1)
C(8)	8f		0.10958(9)	0.0735(3)	0.2200(1)	0.046(2)	0.043(2)	0.034(1)	0.008(1)	0.010(1)	0.006(1)
C(9)	8f		0.16084(9)	0.4761(3)	0.2941(1)	0.045(2)	0.052(2)	0.031(1)	0.001(1)	0.005(1)	0.000(1)
C(10)	8f	0.6	0.20242(7)	0.4586(4)	0.3151(2)	0.034(3)	0.067(4)	0.025(2)	-0.007(2)	-0.006(2)	0.003(2)
C(11)	8f	0.6	0.2194(1)	0.3417(4)	0.3510(2)	0.055(3)	0.045(3)	0.074(4)	0.010(3)	-0.015(3)	0.007(3)
C(12)	8f	0.6	0.2584(1)	0.3304(5)	0.3686(3)	0.072(5)	0.073(5)	0.101(6)	0.035(4)	-0.033(4)	-0.012(4)
C(13)	8f	0.6	0.28037(7)	0.4359(7)	0.3502(3)	0.027(3)	0.20(1)	0.078(5)	0.016(5)	-0.015(3)	-0.015(6)
C(14)	8f	0.6	0.2634(1)	0.5527(6)	0.3142(3)	0.048(5)	0.16(1)	0.20(1)	-0.035(6)	0.032(6)	0.02(1)
C(15)	8f	0.6	0.2244(1)	0.5640(4)	0.2966(3)	0.045(4)	0.075(5)	0.137(7)	-0.010(3)	0.009(4)	0.025(5)
C(16)	8f		0.13659(8)	0.9872(3)	-0.0187(1)	0.029(1)	0.040(1)	0.038(1)	-0.003(1)	0.005(1)	-0.002(1)
C(17)	8f		0.1437(1)	1.2347(3)	-0.0450(2)	0.058(2)	0.038(2)	0.050(2)	-0.014(1)	0.015(2)	-0.006(1)
C(18)	8f		0.1074(1)	1.2990(3)	-0.0840(2)	0.067(2)	0.037(2)	0.035(1)	-0.006(1)	0.020(1)	0.001(1)
C(19)	8f		0.0774(1)	1.2204(4)	-0.1203(2)	0.064(2)	0.043(2)	0.053(2)	0.001(2)	0.008(2)	-0.000(1)
C(20)	8f		0.0443(1)	1.2858(5)	-0.1539(2)	0.074(3)	0.066(2)	0.062(2)	0.006(2)	0.002(2)	-0.001(2)
C(21)	8f		0.0412(1)	1.4308(5)	-0.1507(2)	0.095(3)	0.071(3)	0.059(2)	0.030(3)	0.016(2)	0.017(2)
C(22)	8f		0.0710(2)	1.5085(4)	-0.1147(2)	0.119(4)	0.047(2)	0.049(2)	0.014(2)	0.024(2)	0.006(2)
C(23)	8f		0.1035(1)	1.4445(3)	-0.0823(2)	0.093(3)	0.041(2)	0.038(2)	-0.005(2)	0.026(2)	0.001(1)
C(24)	8f		0.16275(9)	1.0519(4)	-0.1180(2)	0.052(2)	0.052(2)	0.036(2)	-0.009(2)	0.014(1)	-0.002(1)
C(25)	8f	0.6	0.20422(7)	1.0607(5)	-0.1017(2)	0.046(3)	0.045(3)	0.044(3)	-0.010(2)	0.024(2)	-0.008(2)
C(26)	8f	0.6	0.2211(1)	1.0952(7)	-0.1553(2)	0.060(4)	0.19(1)	0.064(4)	-0.021(5)	0.033(4)	0.027(5)
C(27)	8f	0.6	0.2601(1)	1.0956(8)	-0.1440(2)	0.069(5)	0.22(1)	0.097(6)	-0.023(6)	0.050(5)	-0.001(7)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(28)	8*f*	0.6	0.28217(7)	1.0616(7)	–0.0793(2)	0.034(3)	0.112(6)	0.104(6)	–0.018(4)	0.028(3)	–0.031(5)
C(29)	8*f*	0.6	0.26528(8)	1.0272(6)	–0.0257(2)	0.041(3)	0.130(7)	0.068(4)	–0.020(4)	0.003(3)	–0.007(4)
C(30)	8*f*	0.6	0.22630(9)	1.0268(6)	–0.0369(1)	0.040(3)	0.122(6)	0.050(3)	–0.021(3)	0.008(2)	0.007(4)
C(31)	8*f*		0.0193(1)	0.6925(4)	0.0280(2)	0.040(2)	0.070(2)	0.062(2)	–0.008(2)	0.010(2)	0.011(2)
C(32)	8*f*		–0.0180(1)	0.6954(5)	–0.0067(2)	0.037(2)	0.095(3)	0.078(3)	–0.015(2)	0.013(2)	–0.006(2)
C(33)	8*f*		–0.0293(1)	0.7860(5)	–0.0597(2)	0.035(2)	0.092(3)	0.069(3)	0.009(2)	–0.005(2)	–0.022(2)
C(34)	8*f*		–0.0034(1)	0.8742(5)	–0.0763(2)	0.058(2)	0.085(3)	0.065(2)	0.006(2)	–0.015(2)	0.013(2)
C(35)	8*f*		0.0334(1)	0.8657(4)	–0.0392(2)	0.045(2)	0.076(3)	0.059(2)	–0.007(2)	–0.005(2)	0.019(2)

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