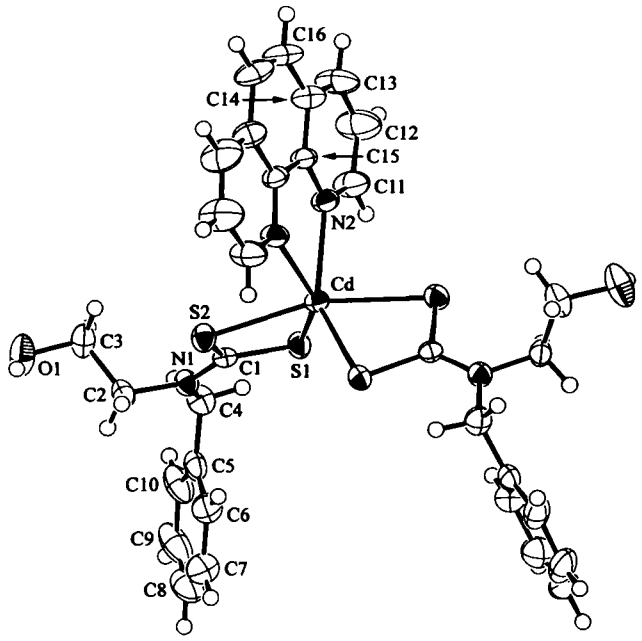
© by Oldenbourg Wissenschaftsverlag, München

Crystal structure of bis[(*N*-benzyl,*N*-hydroxyethyl)-dithiocarbamato](1,10-phenanthroline)cadmium(II), $Cd[S_2CN(C_7H_7)(C_2H_2OH)]_2(C_{12}H_8N_2)$

M. Saravanan[I], R. Ramalingam[I], B. Arulprakasam[I], G. Bocelli[II], A. Cantoni[II] and E. R. T. Tiekink*,[III]

[I] Annamalai University, Department of Chemistry, Annamalainagar 608 002, India
[II] IMEM-CNR, Parco Area delle Scineze 17/a, 43100 Parma, Italy
[III] Griffith University, School of Science, Nathan, Queensland 4111, Australia

Received July 19, 2005, accepted and available on-line August 30, 2005; CCDC no. 1267/1601



Abstract
$C_{32}H_{32}CdN_4O_2S_4$, orthorhombic, *Pbcn* (no. 60), $a = 7.2663(7)$ Å, $b = 18.606(2)$ Å, $c = 24.010(2)$ Å, $V = 3246.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.066$, $T = 223$ K.

Source of material

The title compound was prepared by reacting an ethanol solution of 1,10-phenanthroline with a hot benzene-ethanol (2:1) solution containing authenticated $Cd[S_2CN(Bz)(CH_2CH_2OH)]_2$. Crystals were obtained from the slow evaporation of a benzene-ethanol solution of the product (IR: $\nu_{C-N} = 1471$ cm^{-1}).

Experimental details

Except H1 whose position was refined, the H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation. The U_{iso}(H1) was restrained to $1.5\,U_{eq}$ of the attached O atom.

Discussion

The cadmium atom in $Cd[S_2CN(Bz)(CH_2CH_2OH)]_2$(phen) is situated on a twofold rotation axis and is coordinated by symmetrically coordinating dithiocarbamate ligands, d(Cd—S1) = 2.6529(8) Å and d(Cd—S2) = 2.6722(8) Å, and a bidentate 1,10-phenanthroline ligand, d(Cd—N2) = 2.379(2) Å. The N_2S_4 donor set defines a distorted octahedral geometry. Deviations from the ideal geometry are readily ascribed to the chelate angles with the most acute being that subtended by the dithiocarbamate, i.e. S1–Cd–S2 is 67.47(2)°. The molecular geometry reported here has several precedents in the literature, e.g. [1-5]. Molecules associate via hydrogen-bonding interactions between the hydroxyl group and the S1 atom. Thus, d(O1–H···S1^i) = 2.49 Å, d(O1···S1^i) = 3.318(3) Å, with an angle of 167° at H (symmetry operation i: $1+x,y,z$). From symmetry, these interactions occur on either side of the molecule so that a supramolecular chain, mediated by O–H···S interactions, aligned along the a-direction, is formed.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.03 × 0.14 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	9.66 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, ω/φ
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14767, 2335
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2043
$N(param)_{refined}$:	198
Programs:	DIRDIF [6], SHELXL-97 [7], ORTEP-II [8], teXsan [9]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*d*	0.778(5)	0.245(3)	0.423(1)	0.094
H(2A)	8*d*	0.5348	0.1834	0.3695	0.043
H(2B)	8*d*	0.5147	0.1412	0.4265	0.043
H(3A)	8*d*	0.4926	0.2928	0.4142	0.052
H(3B)	8*d*	0.4464	0.2535	0.4712	0.052
H(4A)	8*d*	0.0415	0.1383	0.4317	0.047
H(4B)	8*d*	0.1956	0.1591	0.4754	0.047
H(6)	8*d*	0.2925	0.0403	0.3626	0.061
H(7)	8*d*	0.3686	−0.0811	0.3732	0.079
H(8)	8*d*	0.3514	−0.1349	0.4598	0.088
H(9)	8*d*	0.2561	−0.0692	0.5352	0.090
H(10)	8*d*	0.1898	0.0516	0.5267	0.067
H(11)	8*d*	−0.3343	0.3346	0.3306	0.064
H(12)	8*d*	−0.4809	0.4386	0.3598	0.090
H(13)	8*d*	−0.3706	0.5487	0.3303	0.083
H(16)	8*d*	−0.1290	0.6195	0.2762	0.066

* Correspondence author (e-mail: etiekink@deakin.edu.au)

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	4c	0	0.27493(2)	¼	0.0336(2)	0.0225(2)	0.0341(2)	0	–0.0040(2)	0
S(1)	8d	–0.0447(1)	0.19824(4)	0.34216(3)	0.0259(4)	0.0363(4)	0.0416(5)	–0.0038(3)	–0.0035(4)	0.0046(4)
S(2)	8d	0.3156(1)	0.25439(4)	0.30487(3)	0.0308(5)	0.0391(5)	0.0367(4)	–0.0062(4)	–0.0021(4)	0.0074(4)
O(1)	8d	0.7097(3)	0.2508(2)	0.4513(1)	0.038(2)	0.104(2)	0.047(2)	–0.009(2)	–0.005(1)	–0.020(2)
N(1)	8d	0.2725(3)	0.1761(1)	0.3960(1)	0.027(1)	0.035(2)	0.034(1)	–0.001(1)	0.001(1)	0.004(1)
N(2)	8d	–0.1447(4)	0.3801(1)	0.2855(1)	0.035(2)	0.026(1)	0.044(2)	–0.002(1)	0.005(1)	–0.003(1)
C(1)	8d	0.1912(4)	0.2070(2)	0.3522(1)	0.031(2)	0.022(2)	0.033(2)	0.002(1)	–0.001(1)	–0.004(1)
C(2)	8d	0.4713(4)	0.1831(2)	0.4055(1)	0.027(2)	0.041(2)	0.040(2)	0.003(2)	–0.005(2)	0.007(2)
C(3)	8d	0.5206(4)	0.2506(2)	0.4372(1)	0.031(2)	0.063(2)	0.036(2)	–0.006(2)	–0.001(2)	–0.007(2)
C(4)	8d	0.1739(5)	0.1360(2)	0.4393(1)	0.038(2)	0.046(2)	0.034(2)	0.000(2)	0.003(2)	0.009(1)
C(5)	8d	0.2311(4)	0.0582(2)	0.4431(1)	0.024(2)	0.043(2)	0.049(2)	–0.006(2)	–0.005(2)	0.012(2)
C(6)	8d	0.2856(5)	0.0186(2)	0.3979(2)	0.050(2)	0.043(2)	0.060(2)	–0.003(2)	–0.005(2)	0.005(2)
C(7)	8d	0.3309(6)	–0.0541(2)	0.4043(2)	0.056(3)	0.048(2)	0.094(3)	–0.001(2)	–0.008(2)	–0.006(2)
C(8)	8d	0.3206(6)	–0.0861(2)	0.4556(2)	0.045(3)	0.047(3)	0.128(4)	–0.004(2)	–0.010(3)	0.034(3)
C(9)	8d	0.2657(5)	–0.0469(3)	0.5002(2)	0.036(2)	0.080(3)	0.109(4)	–0.001(2)	–0.002(3)	0.060(3)
C(10)	8d	0.2236(5)	0.0249(2)	0.4951(2)	0.036(2)	0.073(3)	0.058(2)	0.001(2)	–0.001(2)	0.032(2)
C(11)	8d	–0.2890(5)	0.3792(2)	0.3185(2)	0.052(2)	0.035(2)	0.074(3)	–0.002(2)	0.021(2)	–0.004(2)
C(12)	8d	–0.3777(6)	0.4413(2)	0.3363(2)	0.069(3)	0.053(3)	0.104(3)	0.007(2)	0.042(3)	–0.005(2)
C(13)	8d	–0.3120(6)	0.5061(2)	0.3189(2)	0.079(3)	0.043(2)	0.085(3)	0.021(2)	0.024(3)	–0.012(2)
C(14)	8d	–0.1576(5)	0.5096(2)	0.2841(1)	0.060(2)	0.030(2)	0.047(2)	0.006(2)	0.005(2)	–0.005(2)
C(15)	8d	–0.0789(5)	0.4440(2)	0.2681(1)	0.041(2)	0.022(2)	0.036(2)	0.002(1)	–0.004(1)	–0.002(1)
C(16)	8d	–0.0755(6)	0.5755(2)	0.2658(1)	0.089(3)	0.024(2)	0.052(2)	0.010(2)	0.004(2)	–0.004(2)

Acknowledgment. The Queensland Government, for the award of a Smart Returns Fellowship (ERTT), is thanked.

References

1. Guo, T.; Lai, C. S.; Tan, X. J.; Teo, C. S.; Tiekink, E. R. T.: Bis(diethyldithiocarbamato)(4,7-dimethyl-1,10-phenanthroline)cadmium(II) acetonitrile solvate. Acta Crystallogr. **E58** (2002) m439-m440.
2. Lai, C. S.; Tiekink, E. R. T.: Bis(*N,N*-diethyldithiocarbamato)(2,9-dimethyl-1,10-phenanthroline)cadmium(II). Appl. Organomet. Chem. **17** (2003) 139-140.
3. Ivanchenko, A. V.; Gromilov, S. A.; Zemskova, S. M.; Baidina, I. A.; Glinskaya, L. A.: Synthesis and crystal structure of bis(di-*n*-butyldithiocarbamato)(1,10-phenanthroline)cadmium(II). J. Struct. Chem. **39** (1998) 554-558.
4. Zemskova, S. M.; Prashad, G.; Glinskaya, L. A.; Klevtsova, R. F.; Durasov, V. B.; Tkachev, S. V.; Gromilov, S. A.; Larionov, S. V.: Volatile mixed-ligand complexes of bis(diisobutyldithiocarbamato)cadmium with 1,10-phenanthroline, 2,2'-bipyridine and 4,4'-bipyridine. Crystal and molecular structure of the complex $Cd(S_2CN(i\text{-}Bu)_2)_2(C_{12}H_8N_2)$. Zh. Neorg. Khim. **43** (1998) 1525-1531.
5. Airoldi, C.; De Oliveira, S. F.; Ruggiero, S. G.; Lechat, J. R.: Adducts of cadmium diethyldithiocarbamate with bidentate nitrogen ligands. Inorg. Chim. Acta **174** (1990) 103-108.
6. Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Smits, J. M. M.; Smykalla, C.: The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands 1992.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
8. Johnson, C. K.: ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
9. Molecular Structure Corporation: teXsan. Single Crystal Structure Analysis Software. Version 1.05. MSC, The Woodlands, Texas, USA 1997.