Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(benzenethiolato-*S*)(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)-cadmium(II)

William F. Wacholtz[a] and Joel T. Mague[b]*

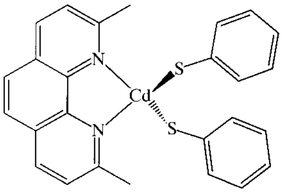
[a]Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, WI 54901, USA, and [b]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA
Correspondence e-mail: joelt@tulane.edu

Received 4 July 2001
Accepted 27 September 2001

The title compound, $[Cd(C_6H_5S)_2(C_{14}H_{12}N_2)]$, exists as monomeric molecules with offset π-stacking interactions between the phenanthroline ligands in adjacent molecules.

Comment

Highly colored and luminescent complexes can be formed when Zn^{II} or Cd^{II} is coordinated in a heteroleptic field containing *N*,*N*-heterocyclic and either one dithiolate or two monothiolate ligands. This visible transition has been described as a metal-mediated π–π* ligand-to-ligand charge-transfer (LLCT) transition (Koester, 1975; Crosby *et al.*, 1985; Truesdell & Crosby, 1985; Kutal, 1990; Burt & Crosby, 1994) and is observed for a large variety of mono- and dithiolate plus *N*,*N*-heterocyclic ligand sets (Muresan & Muresan, 1979; Fernadez & Kisch, 1984; Crosby *et al.*, 1985; Highland & Crosby, 1985; Highland *et al.*, 1986; Reddy *et al.*, 1992; Galin *et al.*, 1993; Gronlund, Burt & Wacholtz, 1995; Gronlund, Wacholtz & Mague, 1995; Halvorsen *et al.*, 1995; Zemskova *et al.*, 1998; Yam *et al.*, 1999; Wang *et al.*, 2000). A number of recent studies have indicated that unusual multinuclear Zn^{II} and Cd^{II} complexes are obtained when the mixed ligand set is a planar *N*,*N*-heterocyclic ligand in combination with a dithiolate ligand (Halvorsen *et al.*, 1995; Gronlund, Wacholtz & Mague, 1995; Wang *et al.*, 2000; Lowther *et al.*, 2001). However, when substituents are attached to the periphery of 1,10-phenanthroline ligands, only mononuclear complexes tend to be observed. In one Zn^{II} system, two different crystal forms are obtained for very subtle conformational changes in the monothiolate ligands (Jordan *et al.*, 1991). In order to investigate fully the structure–property relationships in analogous Cd^{II} complexes for comparison with these Zn^{II} systems, we have investigated the reactions of monothiolate complexes of Cd^{II} with substituted 1,10-phenanthroline ligands.



(I)

Bis(benzenethiolato)(2,9-dimethyl-1,10-phenanthroline)-cadmium(II), (I), is monomeric, in contrast to related 1,2-benzenedithiolate complexes which are dinuclear (Lowther *et al.*, 2001; Gronlund, Wacholtz & Mague, 1995). The elongated displacement ellipsoid of atom S2 is evidence of positional disorder in this atom, but attempts to model this by two or even three partially occupied sites were unsuccessful. It was evident from these attempts that no simple disorder model would be sufficient to describe alternate positions for this atom. It appears from Fig. 3 that the whole molecule is disordered over several slightly different conformations involving libration about a point near the center of the chelate ring. This is effectively an 'inversion' about this point and evidently the several conformations existing over the whole of the crystal vary considerably more in the locations of atom S2 and its attached phenyl ring than in the locations of the

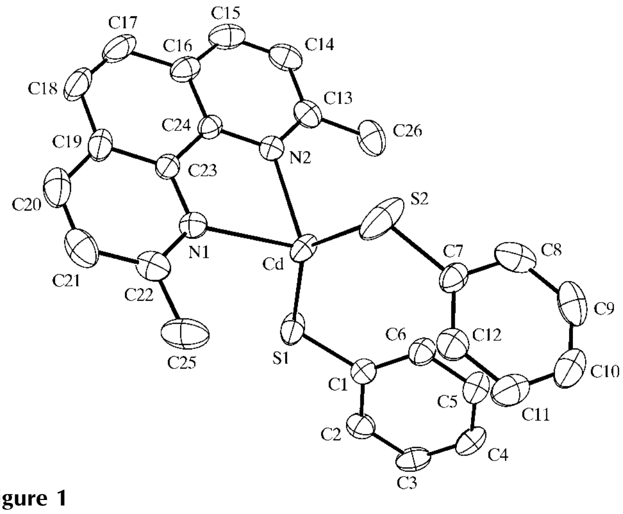


Figure 1
A perspective view of (I). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

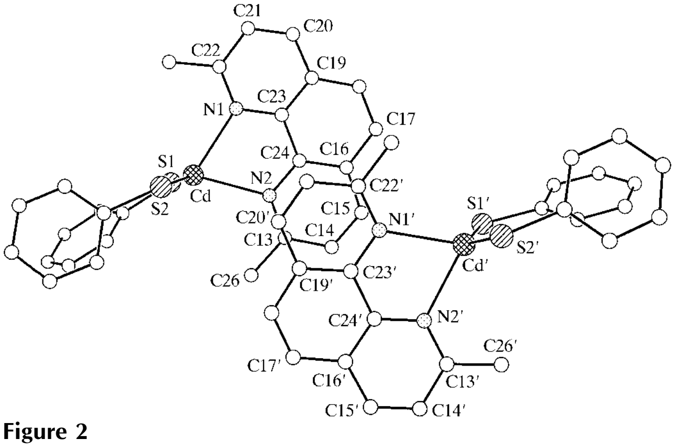


Figure 2
View of the π-stacking interaction in (I). The molecule containing primed atoms is related to the other by the operation $\frac{1}{2} - x, \frac{1}{2} + y, z$.

remaining atoms. This is likely to be the reason for the Cd—S distances (Table 1), particularly Cd—S2, appearing shorter than the usual values of around 2.50 Å. The two phenyl rings are inclined at an angle of 56.2 (1)° (Fig. 1). The phenyl ring involving C7 is nearly parallel to the mean plane of the phenanthroline ligand [dihedral angle 9.1 (2)°], while the other phenyl ring makes an angle of 64.3 (2)° with this mean plane. Fig. 2 depicts the offset π-stacking between phenanthroline ligands of neighboring molecules. The rings in question are virtually parallel, with a distance between the centers of gravity of the two rings of 3.62 (1) Å and a perpendicular distance from the center of gravity of one ring to the mean plane of the other of 3.55 (1) Å.

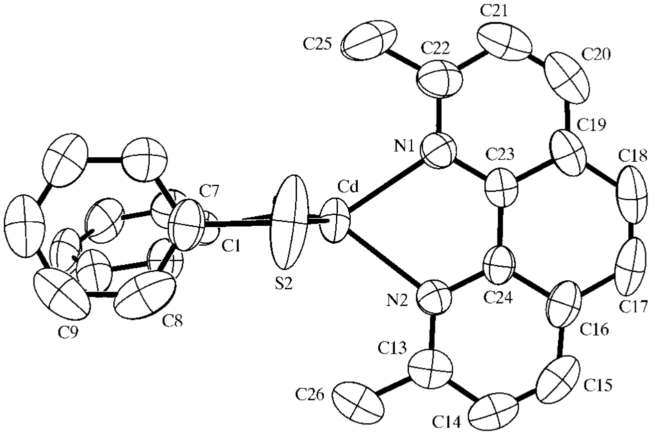


Figure 3
View of (I) perpendicular to the plane of the phenanthroline ligand, showing the apparent librational motion.

Experimental

Benzenethiol (0.21 ml, 2.1 mmol) in hot ethanol (10 ml) was added dropwise to a hot solution of cadmium acetate dihydrate (266.5 mg, 1.0 mmol) in a 1:1 (*v*/*v*) mixture (50 ml) of ethanol and dimethylformamide. The solution was brought to reflux and 2,9-dimethyl-1,10-phenanthroline monohydrate (226.3 mg, 1.0 mmol) dissolved in hot ethanol (25 ml) was added slowly with stirring. A flocculent golden yellow precipitate formed immediately and the reaction was continued for an additional 30 min. The mixture was cooled to room temperature, allowed to stand for 24 h and the solid collected by suction filtration (yield 94%). Yellow crystals were obtained by slow evaporation of a dimethylformamide solution of the complex in air. Analysis calculated for $C_{26}H_{22}CdN_2S_2$: C 57.93, H 4.12, N 5.20%; found: C 57.9, H 4.1, N 5.2%.

Crystal data

$[Cd(C_6H_5S)_2(C_{14}H_{12}N_2)]$
$M_r = 538.98$
Orthorhombic, *Pbca*
$a = 14.164$ (2) Å
$b = 12.034$ (2) Å
$c = 27.648$ (3) Å
$V = 4712.5$ (13) Å^3
$Z = 8$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.1$–15.8°
$\mu = 1.12$ mm^{-1}
$T = 293$ (2) K
Column, pale orange
0.48 × 0.28 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{min} = 0.734$, $T_{max} = 0.836$
4548 measured reflections
4548 independent reflections
2388 reflections with $I > 2\sigma(I)$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 34$
2 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.102$
$S = 1.02$
4548 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 2.7120P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—N1	2.341 (4)	Cd—S2	2.4189 (16)
Cd—N2	2.341 (3)	Cd—S1	2.4321 (14)
N1—Cd—N2	71.64 (12)	N1—Cd—S1	105.80 (9)
N1—Cd—S2	106.22 (10)	N2—Cd—S1	109.59 (9)
N2—Cd—S2	104.21 (10)	S2—Cd—S1	139.08 (5)

The H atoms were included in calculated positions (C—H = 0.93–0.96 Å) as riding, with isotropic displacement parameters 1.2 times those of the attached C atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997).

We thank the Chemistry Department of Tulane University for support of the X-ray laboratory and anonymous UW Oshkosh donors for funding to establish the Emission Spectroscopy Laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1203). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Burt, J. A. & Crosby, G. A. (1994). *Chem. Phys. Lett.* **220**, 493–496.
Crosby, G. A., Highland, R. G. & Truesdell, K. A. (1985). *Coord. Chem. Rev.* **64**, 41–52.
Enraf–Nonius (1989). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.
Fernadez, A. & Kisch, H. (1984). *Chem. Ber.* **117**, 3102–3111.
Galin, A. M., Razskakovsky, V. & Mel'nikov, M. Y. (1993). *J. Photochem. Photobiol. A*: *Chem.* **72**, 35–40.
Gronlund, P. J., Burt, J. & Wacholtz, W. F. (1995). *Inorg. Chim. Acta*, **234**, 13–18.

Gronlund, P. J., Wacholtz, W. F. & Mague, J. T. (1995). *Acta Cryst.* C**51**, 1540–1543.

Halvorsen, K., Wacholtz, W. F. & Crosby, G. A. (1995). *Inorg. Chim. Acta*, **228**, 81–88.

Harms, K. (1996). *XCAD*4. University of Marburg, Germany.

Highland, R. G., Brummer, J. G. & Crosby, G. A. (1986). *J. Phys. Chem.* **90**, 1593–1598.

Highland, R. G. & Crosby, G. A. (1985). *Chem. Phys. Lett.* **119**, 454–458.

Jordan, K. J., Wacholtz, W. F. & Crosby, G. A. (1991). *Inorg. Chem.* **30**, 4588–4593.

Koester, V. J. (1975). *Chem. Phys. Lett.* **32**, 575–580.

Kutal, C. (1990). *Coord. Chem. Rev.* **99**, 213–252.

Lowther, M. D., Wacholtz, W. F. & Mague, J. T. (2001). *J. Chem. Crystallogr.* In the press.

Muresan, N. & Muresan, V. (1979). *Rev. Roum. Chim.* **24**, 1123–1128.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reddy, H. K., Zhang, C., Schlemper, E. O. & Schrauzer, G. N. (1992). *Inorg. Chem.* **31**, 1673–1677.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Truesdell, K. A. & Crosby, G. A. (1985). *J. Am. Chem. Soc.* **107**, 1787–1788.

Wang, Q., Long, D., Hu, H., Cui, Y. & Huang, J. (2000). *J. Coord. Chem.* **49**, 201–209.

Yam, V. W., Pui, Y. & Cheung, K. (1999). *New J. Chem.* **23**, 1163–1169.

Zemskova, S. M., Prashad, G., Glinskaya, L. A., Klevtsova, R. F., Durasov, V. B., Tkachev, S. V., Gromilov, S. A. & Larionov, S. V. (1998). *Zh. Neorg. Khim.* **43**, 1644–1650.