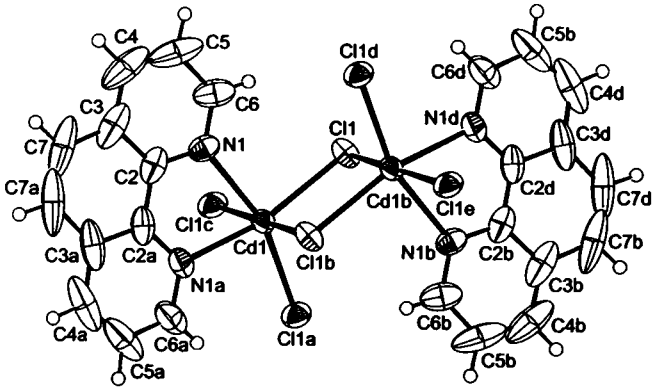
Z. Kristallogr. NCS 220 (2005) 209-210

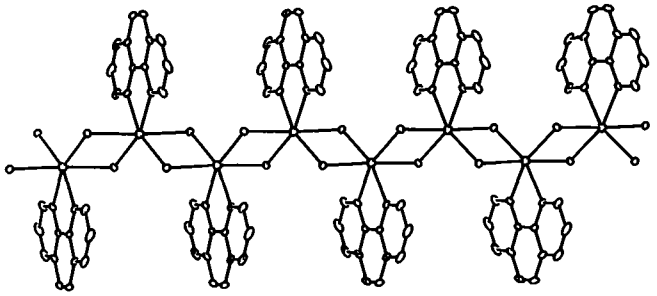
Crystal structure of bis(μ-chloro)(1,10-phenanthroline-*N*,*N*')cadmium(II), $CdCl_2(C_{12}H_8N_2)$

H.-Y. He[I], Y.-L. Zhou[I], J. Chen[I] and L.-G. Zhu*[,II]

[I] Jiaxing College, Department of Chemical Engineering, Jiaxing, 314001 P. R. China
[II] Zhejiang University, Department of Chemistry, Hangzhou, 310027 P. R. China

Received December 30, 2004, accepted and available on-line March 24, 2005; CCDC no. 1267/1491





Abstract

$C_{12}H_8CdCl_2N_2$, monoclinic, *C*12/*c*1 (no. 15),
a = 16.934(2) Å, b = 10.511(1) Å, c = 7.2284(7) Å,
β = 110.643(2)°, V = 1204.0 Å^3, Z = 4,
$R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.048, T = 293 K.

Source of material

The title compound was synthesized using three-layer solutions in a slender tube with an 0.8 cm diameter. The bottom layer solution was 5 ml *N*,*N*'-dimethylformamide (DMF) containing $CdCl_2 \cdot H_2O$ (68.6 mg, 0.37 mmol) and 2-thiopheneacetic acid (85.3 mg, 0.6 mmol), the middle layer solution was 5 ml DMF/methanol (1:1 *v*/*v*) mixed solvent system and the upper layer solution was 5 ml methanol containing 1,10-phenanthroline (60.5 mg, 0.3 mmol). After standing two weeks, colorless block crystals were obtained. They were filtered by suction and dried in air.

Experimental details

The strong anisotropies of some carbon atoms can be caused by twinning, statistical orientational disorder or temperature dependent large atomic librations.

Discussion

The system of Cd^{2+}/Cl^-/1,10-phenanthroline has been extensively studied in solid state (powder) or solution. Several species have been determined, such as $[CdCl(phen)]^+$, $[CdCl_2(phen)]$, $[CdCl(phen)_2]^+$, $[CdCl_2(phen)_2]$, and $[CdCl_3(phen)]^-$ [1-5]. The structure of a bis(1,10-phenanthroline) compound, *cis*-dichlorobis(1,10-phenanthroline)cadmium(II), was reported [6]. Here we report on the preparation and structural characterization of a mono-1,10-phenanthroline compound with one-dimensional chain, $CdCl_2(C_{12}H_8N_2)$.

The coordination environment of the cadmium atom is a distorted octahedron completed by two nitrogen donors from one 1,10-phenanthroline and four bridging chloro atoms (figure, top). Atoms Cl1(x,$-y$,$-½+z$) and Cl1($-x$,$-y$,$2-z$) are located on the axial positions of the polyhedron. The Cd1—N bond length is 2.350(2) Å and two kinds of distances of Cd1—Cl are observed. The equatorial distances are 2.5426(7) Å, but shorter than the axial bonds [2.7529(8) Å]. The bridging function of chloro atoms leads to one-dimensional chain structure (figure, bottom), in which the basic building unit is a four-membered ring, $[Cd_2(\mu_2\text{-}Cl)_2]$, and neighboring rings are nearly perpendicular each other with the dihedral angle of 76.23(2)°.

The distance of Cd···Cd separated by bridging chlorine atoms is 3.909 Å. Furthermore, there are strong π-π interactions among phen ligands from two neighboring chains and distances of π-π interactions are 3.34 Å and 3.16 Å, thus 2D stacking architecture is observed in the crystal packing. The reported species of *cis*-$[CdCl_2(phen)_2]$ [6] is a monomeric compound, in which the chlorine atoms act as terminal ligands. The average Cd—N bond length is 2.436 Å, which is longer than that in the title structure. The bond lengths of Cd—Cl are 2.505(1) Å to 2.528(1) Å, and shorter than those in the title structure. A bimetallic compound with similar stoichiometry, $NiCd(phen)_2X_4$(III) (X represents a site of mixed chloro and bromo occupancy) [7], has a very different one-dimensional structure. The two terminal phen ligands coordinate to the Ni atom, while the Cd atom adopts a tetrahedral geometry of $[CdX_4]^{2-}$. Therefore, further exploration of coordination modes in the Cd^{2+}/Cl^-/phen system, such as single-μ-chloro mode found in the structure of $[CuCl_2(2,2'\text{-bipy})]$ [8], will lead to create more diverse networks.

* Correspondence author (e-mail: chezlg@zju.edu.cn)

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.13 × 0.14 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.32 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	53°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3204, 1194
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1028
$N(param)_{refined}$:	78
Programs:	SHELXS-97 [9], SHELXL-97 [10], ORTEP-3 [11], WinGX [12]

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

Atom	Site	x	y	z	U_{iso}
H(4)	8*f*	0.1917	0.5504	1.0947	0.08
H(5)	8*f*	0.2474	0.3571	1.2192	0.08
H(6)	8*f*	0.1746	0.1750	1.0964	0.08
H(7)	8*f*	0.0630	0.6755	0.8667	0.08

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(1)	4*e*	0	0.07085(3)	¾	0.0454(2)	0.0311(2)	0.0288(2)	0	0.0032(1)	0
Cl(1)	8*f*	0.09579(5)	–0.07723(7)	1.0115(1)	0.0500(5)	0.0491(4)	0.0376(4)	0.0129(4)	0.0107(3)	0.0091(3)
N(1)	8*f*	0.0765(2)	0.2525(2)	0.9015(4)	0.044(2)	0.047(2)	0.042(1)	–0.009(1)	0.018(1)	–0.014(1)
C(2)	8*f*	0.0411(2)	0.3656(3)	0.8272(4)	0.074(2)	0.038(2)	0.054(2)	–0.010(2)	0.047(2)	–0.010(1)
C(3)	8*f*	0.0814(3)	0.4813(3)	0.9004(6)	0.122(4)	0.051(2)	0.080(3)	–0.037(2)	0.080(3)	–0.030(2)
C(4)	8*f*	0.1616(4)	0.4760(6)	1.0472(7)	0.123(5)	0.111(4)	0.095(4)	–0.080(4)	0.079(4)	–0.070(3)
C(5)	8*f*	0.1948(3)	0.3618(6)	1.1190(7)	0.063(3)	0.151(4)	0.077(3)	–0.052(3)	0.034(2)	–0.068(3)
C(6)	8*f*	0.1508(2)	0.2526(4)	1.0440(5)	0.053(2)	0.088(3)	0.054(2)	–0.012(2)	0.017(2)	–0.031(2)
C(7)	8*f*	0.0373(4)	0.5981(3)	0.8190(7)	0.235(9)	0.034(2)	0.131(6)	–0.035(3)	0.150(6)	–0.024(2)

Acknowledgment. The project was supported by the National Natural Science Foundation of China (grant no. 50073019).

References

1. Komiya, M.; Yoshida, S.; Ishiguro, S. I.: Ternary complexation of manganese(II) and cadmium(II) with 1,10-phenanthroline and halide or thiocyanato ions in *N,N'*-dimethylformamide. J. Solution Chem. **29** (2000) 165-182.
2. Yang, Z. Y.; Han, X. W.; Hu, J. H.; Ji, T.: NMR study of metallic nuclei. I. Cadmium-111, -113, tin-117, -119, and mercury-199 NMR spectra of metal complexes. Bopuxue Zazhi **2** (1985) 25-30.
4. Bujewski, A.; Grzedzicki, K.; Dobrowolski, J.: Effect of cations and conditions of synthesis on composition of halogen complexes of cadmium of the type: $[M(L\text{–}L)_3][Cd_mX_{2m+n}]$. Zesz. Nauk. Politech. Slask., Chem. **958** (1988) 355-356.
5. Demidov, V. N.; Denisov, I. A.; Belyaev, A. N.; Yakovlev, V. N.; Kukushkin, Y. N.: Thermal intramolecular rearrangement of coordinated 1,10-phenanthroline in chromium (III), cobalt(II), nickel(II), zinc(II) and cadmium(II). Koord. Khim. **17** (1991) 1717-1718.
3. Mahapatra, B. B.; Panda, D.; Pujari, S. K.; Chiranjeevi, A.: Mixed ligand anionic complexes of cadmium(II). J. Indian Chem. Soc. **59** (1982) 1022-1023.
6. Wang, H.; Xiong, R. G.; Chen, H. Y.; Huang, X. Y.; You, X. Z.: *cis*-Dichlorobis(1,10-phenanthroline)cadmium(II). Acta Crystallogr. C**52** (1996) 1658-1661.
7. Chesnut, D. J.; Haushalter, R. C.; Zubieta, J.: The hydrothermal synthesis and structural characterization of a new class of compounds: nickel organoamine-halocadmates. Inorg. Chim. Acta **292** (1999) 41-51.
8. Molina, M. H.; Platas, J. G.; Perez, C. R.; Lloret, F.; Julve, M.: Crystal structure and magnetic properties of the single-μ-chloro copper(II) chain $[Cu(bipy)Cl_2]$. Inorg. Chim. Acta **284** (1999) 258-265.
9. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
10. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
11. Farrugia, L. J.: ORTEP-3 for Windows – a version of ORTEP-III with a Graphical User Interface (GUI). J. Appl. Crystallogr. **30** (1997) 565.
12. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **32** (1999) 837-838.