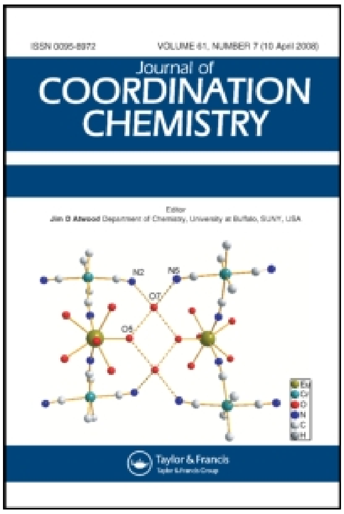

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURES OF DICHLOROTETRAKIS-(PHENYLTHIOUREA) CADMIUM(II) AND *CATENA*-BIS(THIOCYANATE) BIS(PHENYLTHIOUREA)CADMIUM(II)

Guang Yang[a]; Gao-Feng Liu[a]; Shao-Liang Zheng[a]; Xiao-Ming Chen[a]
[a] School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, P.R. China

To cite this Article Yang, Guang , Liu, Gao-Feng , Zheng, Shao-Liang and Chen, Xiao-Ming(2001) 'SYNTHESIS AND STRUCTURES OF DICHLOROTETRAKIS-(PHENYLTHIOUREA) CADMIUM(II) AND *CATENA*-BIS(THIOCYANATE) BIS(PHENYLTHIOUREA)CADMIUM(II)', Journal of Coordination Chemistry, 53: 3, 269 — 279

To link to this Article: DOI: 10.1080/00958970108022910

URL: http://dx.doi.org/10.1080/00958970108022910

J. Coord. Chem., 2001, Vol. 53, pp. 269–279
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STRUCTURES OF DICHLOROTETRAKIS-(PHENYLTHIOUREA) CADMIUM(II) AND *CATENA*-BIS(THIOCYANATE) BIS(PHENYLTHIOUREA)CADMIUM(II)

GUANG YANG, GAO-FENG LIU, SHAO-LIANG ZHENG
and XIAO-MING CHEN*

*School of Chemistry and Chemical Engineering, Zhongshan University,
Guangzhou, 510275, P.R. China*

(Received 7 June 2000; In final form 20 September 2000)

Two new cadmium(II) complexes with phenylthiourea (PTU), namely Cd(PTU)$_4$Cl$_2$ (**1**) and [Cd$_2$(NCS)$_2$(μ_2-SCN)$_2$(PTU)$_2$(μ_2-PTU)$_2$]$_n$ (**2**), have been prepared and characterized structurally by X-ray diffraction. Complex **1** crystallizes in the monoclinic space group $C2/c$, with $a = 27.057(13)$, $b = 8.108(3)$, $c = 16.751(8)$ Å, $\beta = 114.46°$, $V = 3345(3)$ Å^3, $Z = 4$. Complex **2** crystallizes in the triclinic space group $P-1$, with $a = 9.336(3)$, $b = 14.686(5)$, $c = 16.911(5)$ Å, $\alpha = 71.36(2)$, $\beta = 84.31(2)$, $\gamma = 72.470(10)°$, $V = 2095.0(12)$ Å^3, $Z = 4$. The structural analysis shows that each metal atom in both the mononuclear complex **1** and polynuclear complex **2** is octahedrally coordinated by four sulfur atoms and two chloro ligands or two nitrogen atoms from the thiocyanate groups, respectively. The PTU ligand can serve as either a monodentate ligand or a μ_2-bridging ligand upon coordination to a metal atom.

Keywords: Cadmium(II) complexes; Phenylthiourea; Crystal structure

INTRODUCTION

A number of cadmium(II) complexes with S-containing ligands are of considerable interest in material science. For instance, CdS nanowires could be prepared by thermolysis of cadmium bis(diethyldithiocarbamate); some cadmium(II) complexes with thiourea or its derivatives demonstrate strong

---

*Corresponding author. Fax: 86 20 84112245, e-mail: cescxm@zsu.edu.cn second harmonic generation efficiency [1 – 3]. In contrast with thiourea, little is known about the coordination chemistry of phenylthiourea (PTU). As far as we know, only one metal complex with PTU, namely Zn(acac)$_2$ (PTU) (acac = acetylacetate), has been structurally characterized [4]. In this paper, we report the synthesis and crystal structures of two novel cadmium(II) complexes of PTU, namely, Cd(PTU)$_4$Cl$_2$ (**1**) and [Cd$_2$(NCS)$_2$ (μ_2-SCN)$_2$(PTU)$_2$(μ_2-PTU)$_2$]$_n$ (**2**).

EXPERIMENTAL

Physical Measurement

The C, H, N microanalyses were performed with a Elementar Vario EL elemental analyzer. IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Nicolet Impact 420 FT-IR spectrometer.

Preparation

Phenylthiourea was prepared by the reaction of aniline with NH$_4$SCN in aqueous HCl solution [5]. Other reagents were used as received.

Cd(PTU)$_4$Cl$_2$ (1)

PTU (2 mmol, 0.304 g) was dissolved in 30 mL of warm water and the pH value was adjusted to ca. 4 by dilute HCl solution. An aqueous solution of CdCl$_2$·2.5H$_2$O (1 mmol, 0.226 g) was added to the above solution and white precipitate formed immediately. The mixture was heated to near boiling with stirring until all of the solids were dissolved. The resulting solution was slowly cooled to room temperature to give pale yellow crystals in 70% yield. Anal. Calcd. for C$_{28}$H$_{32}$CdCl$_2$N$_8$S$_4$(%): C, 42.48; H, 4.05; N, 14.16. Found: C, 42.59; H, 3.98; N, 14.01. IR (KBr disc): ν_{NH}, 3416(m), 3395(m), 3296(s), 3177(s) cm^{-1}; δ_{NH_2}, 1616(vs) cm^{-1}; ν_{ArH}, 3029(w), 3001(w) cm^{-1}.

[Cd$_2$(NCS)$_2$(μ_2-SCN)$_2$(PTU)$_2$(μ_2-PTU)$_2$]$_n$ (2)

PTU (2 mmol, 0.304 g), KSCN (2 mmol, 0.194 g) and Cd(NO$_3$)$_2$·4H$_2$O (1 mmol, 0.308 g) were dissolved in ethanol with stirring. The resulting mixture was allowed to evaporate to give well-shaped colorless crystals within two weeks in 70% yield. Anal. Calcd. for $C_{32}H_{32}Cd_2N_{12}S_8$ (%): C, 36.06; H, 3.03; N, 15.77; S, 24.06. Found: C, 35.69; H, 3.26; N, 15.71; S, 24.19. IR (KBr disc): ν_{NH}, 3421(m), 3376(m), 3259(s), 3194(s) cm^{-1}; δ_{NH_2}, 1623(vs) cm^{-1}; ν_{ArH}, 3036(w), 3015(w) cm^{-1}; $\nu_{C\equiv N}$(bridging), 2117(s), 2078(vs) cm^{-1}; ν_{CS}(bridging), 851(vw), 700(s) cm^{-1}; $\nu_{C\equiv N}$(*N*-bonded), 2034(vs) cm^{-1}; ν_{CS}(*N*-bonded), 752(s) cm^{-1}; δ_{NCS}(*N*-bonded), 499(m) cm^{-1}.

X-ray Crystallography

The X-ray intensity data were collected at 293 K on a Siemens R3m diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation with the ω-scan mode. Empirical absorption corrections were applied. The structures were solved with the Patterson methods of SHELXS-97 and refined with full-matrix least-squares technique using SHELXL-97 [6, 7]. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms of the organic ligands were generated geometrically. Other important crystallographic data were summarized in Table I. The non-hydrogen atomic coordinates and selected bond lengths and bond angles for these two complexes are presented in Tables II and III, respectively. Drawings were produced with SHELXTL [8].

TABLE I Crystal data and structure refinement parameters for 1 and 2

	1	2
Formula	$C_{28}H_{32}CdCl_2N_8S_4$	$C_{16}H_4CdN_6S_4$
Formula weight	792.16	532.99
Crystal system	Monoclinic	Triclinic
Space group	*C2/c*	*P*−1
a, Å	27.057(13)	9.336(3)
b, Å	8.108(3)	14.686(5)
c, Å	16.751(8)	16.911(5)
α,°	90	71.36(2)
β,°	114.46	84.31(2)
γ,°	90	72.470(10)
V, Å^3	3345(3)	2095.0(12)
Z	4	4
D_{calc}, g cm^{-3}	1.573	1.690
μ (Mo-Kα), cm^{-1}	10.96	14.55
F(000)	1608	1064
Reflections collected	3987	8717
Independent reflections	3857 [$R_{int} = 0.0425$]	8183 [$R_{int} = 0.0448$]
No. of parameters refined	196	488
Goodness-of-fit	1.019	0.984
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$; $wR_2 = 0.0846$	$R_1 = 0.0510$; $wR_2 = 0.0946$
R indices (all data)	$R_1 = 0.0535$; $wR_2 = 0.0929$	$R_1 = 0.0962$; $wR_2 = 0.1090$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.548, −0.517	0.736, −0.460

TABLE II Atomic coordinates and isotropic thermal factors ($\text{Å}^2 \times 10^3$) for **1** and **2**

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^{a}$
Cd(PTU)$_4$Cl$_2$ (1)				
Cd(1)	0	0	0	33(1)
Cl(1)	-992(1)	-852(1)	-17(1)	36(1)
S(1)	407(1)	-2639(1)	949(1)	38(1)
N(1)	934(1)	-3053(3)	-56(2)	40(1)
N(2)	778(1)	-5362(3)	579(2)	49(1)
C(11)	1136(1)	-3842(4)	-617(2)	40(1)
C(12)	809(2)	-4898(5)	-1259(3)	60(1)
C(13)	999(3)	-5544(6)	-1832(3)	83(2)
C(14)	1502(3)	-5123(6)	-1781(4)	91(2)
C(15)	1820(2)	-4087(7)	-1144(4)	85(2)
C(16)	1643(2)	-3442(5)	-548(3)	60(1)
C(17)	728(1)	-3772(4)	454(2)	33(1)
S(2)	-246(1)	-1729(1)	-1515(1)	33(1)
N(3)	-1232(1)	-456(3)	-2114(2)	35(1)
N(4)	-772(1)	-190(3)	-3000(2)	45(1)
C(21)	-1710(1)	456(4)	-2605(2)	35(1)
C(22)	-1975(1)	387(5)	-3506(2)	50(1)
C(23)	-2448(2)	1270(6)	-3927(3)	63(1)
C(24)	-2662(2)	2190(6)	-3460(3)	69(1)
C(25)	-2398(2)	2218(5)	-2570(3)	63(1)
C(26)	-1923(1)	1378(5)	-2132(2)	47(1)
C(27)	-795(1)	-718(4)	-2271(2)	32(1)
[Cd$_2$(NCS)$_2$(μ_2-SCN)$_2$(PTU)$_2$(μ_2-PTU)$_2$]$_n$ (2)				
Cd(1)	-2661(1)	-712(1)	-239(1)	37(1)
Cd(2)	2446(1)	-772(1)	-4995(1)	37(1)
S(1)	-4179(2)	-3696(1)	1510(1)	59(1)
S(2)	2320(2)	-1247(1)	1037(1)	41(1)
S(3)	-5589(2)	283(1)	-1047(1)	33(1)
S(4)	-1612(2)	-933(1)	-1655(1)	47(1)
S(5)	264(2)	-3627(1)	-3728(1)	60(1)
S(6)	4678(2)	-1634(1)	-3801(1)	43(1)
S(7)	4266(2)	-1062(1)	-6227(1)	39(1)
S(8)	227(2)	-259(1)	-3935(1)	33(1)
N(1)	-3195(7)	-2211(4)	321(3)	50(2)
N(2)	-469(6)	-1102(4)	454(3)	52(2)
N(3)	-5349(6)	-685(4)	-2144(3)	45(1)
N(4)	-6641(6)	-1247(4)	-944(3)	40(1)
N(5)	-1464(6)	-2055(4)	-2603(3)	54(2)
N(6)	-1957(7)	-2771(4)	-1230(3)	53(2)
N(7)	1661(6)	-2182(4)	-4629(3)	49(1)
N(8)	6902(6)	-747(4)	-4674(3)	42(1)
N(9)	4806(6)	-2218(4)	-7191(3)	43(1)
N(10)	3937(6)	-2902(4)	-5886(3)	46(1)
N(11)	-815(5)	994(3)	-3062(3)	40(1)
N(12)	1394(5)	1121(3)	-3755(3)	37(1)
C(1)	-3598(7)	-2833(4)	815(4)	38(2)
C(2)	666(8)	-1145(4)	688(3)	37(2)
C(3)	-5891(6)	-631(4)	-1405(3)	31(1)
C(4)	-6904(7)	-2060(4)	-1153(3)	36(1)
C(5)	-7505(7)	-1901(5)	-1921(4)	39(1)
C(6)	-7688(8)	-2706(5)	-2120(4)	54(2)
C(7)	-7314(9)	-3638(6)	-1560(5)	67(2)

TABLE II (Continued)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
C(8)	−6798(9)	−3787(6)	−770(5)	73(2)
C(9)	−6575(8)	−3005(5)	−564(4)	59(2)
C(10)	−1683(7)	−2001(5)	−1833(4)	40(2)
C(11)	−1910(7)	−3718(5)	−1321(4)	43(2)
C(12)	−3085(9)	−3835(6)	−1660(5)	65(2)
C(13)	−3030(10)	−4767(6)	−1726(5)	75(2)
C(14)	−1799(10)	−5556(6)	−1468(5)	73(2)
C(15)	−622(10)	−5445(6)	−1141(6)	83(3)
C(16)	−665(9)	−4520(6)	−1074(5)	72(2)
C(17)	1063(7)	−2785(4)	−4249(3)	35(1)
C(18)	5975(7)	−1106(4)	−4315(3)	31(1)
C(19)	4327(6)	−2137(4)	−6449(3)	34(1)
C(20)	3870(7)	−3814(4)	−6008(3)	38(1)
C(21)	2513(7)	−4013(5)	−5919(4)	52(2)
C(22)	2465(9)	−4916(5)	−5993(5)	63(2)
C(23)	3726(9)	−5592(5)	−6152(4)	60(2)
C(24)	5081(8)	−5391(5)	−6238(4)	58(2)
C(25)	5176(7)	−4494(5)	−6157(4)	48(2)
C(26)	278(6)	701(4)	−3559(3)	31(1)
C(27)	1468(6)	1934(4)	−3490(4)	35(1)
C(28)	1442(6)	1855(4)	−2655(3)	36(1)
C(29)	1403(7)	2681(5)	−2413(4)	43(2)
C(30)	1424(7)	3565(5)	−2999(4)	46(2)
C(31)	1519(7)	3644(5)	−3847(4)	47(2)
C(32)	1535(6)	2826(5)	−4092(4)	40(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

Structure of $Cd(PTU)_4Cl_2$ (1)

The structure of complex 1 with the atom numbering scheme is depicted in Figure 1. The Cd(II) atom, being located at an inversion center, is coordinated by four PTU ligands and two Cl^- anions in a *trans*-octahedral arrangement (Cd—S = 2.621(1), 2.729(1) Å; Cd—Cl = 2.759(1) Å). The bond lengths of Cd—S and Cd—Cl are longer than those in tetrahedral $Cd(TU)_2Cl_2$ (Cd—S = 2.45 Å; Cd—Cl = 2.50, 2.51 Å), respectively [9]. Each PTU acts as monodentate S-donor ligand in this neutral mononuclear complex. The C(17) and C(27) atoms of the PTU ligands are sp^2 hybridized, which can be demonstrated by the bond geometry (ca. 120° for S—C—N and N—C—N) and the coplanarity of S(1), C(17), N(1), N(2) (or S(2), C(27), N(3), N(4)) atoms. The dihedral angles between the plane defined by the thiourea group and the plane of the phenyl ring within each PTU ligand are different for the four PTU ligands, for instance, 62° for the plane (S(1),

TABLE III Selected bond distances(Å) and bond angles(°) for **1** and **2**

Cd(PTU)$_4$Cl$_2$(**1**)			
Cd(1)—S(1)	2.6213(11)	Cd(1)—S(2)	2.7294(13)
Cd(1)—Cl(1)	2.7589(14)		
S(1a)—Cd(1)—S(2)	88.61(4)	S(1)—Cd(1)—S(2)	91.39(4)
S(1)—Cd(1)—Cl(1a)	92.04(3)	C(27)—S(2)—Cd(1)	104.21(10)
S(1)—Cd(1)—Cl(1)	87.96(3)	S(2)—Cd(1)—Cl(1)	90.00(2)
C(17)—S(1)—Cd(1)	108.44(11)		
[Cd$_2$(NCS)$_2$(μ_2-SCN)$_2$(PTU)$_2$(μ_2-PTU)$_2$]$_n$(**2**)			
Cd(1)—N(2)	2.286(5)	Cd(1)—N(1)	2.286(5)
Cd(1)—S(4)	2.5772(17)	Cd(1)—S(3a)	2.7096(16)
Cd(1)—S(2b)	2.8605(19)	Cd(1)—S(3)	2.9214(18)
Cd(2)—N(7)	2.283(5)	Cd(2)—N(8c)	2.369(5)
Cd(2)—S(7)	2.6145(17)	Cd(2)—S(8)	2.6950(16)
Cd(2)—S(6)	2.7633(19)	Cd(2)—S(8d)	2.9435(18)
N(2)—Cd(1)—N(1)	98.7(2)	S(7)—Cd(2)—S(6)	94.49(6)
N(2)—Cd(1)—S(4)	100.15(14)	S(8)—Cd(2)—S(6)	95.15(5)
N(1)—Cd(1)—s(4)	98.23(13)	N(7)—Cd(2)—S(8d)	87.69(15)
N(2)—Cd(1)—S(3a)	93.69(14)	N(8c)—Cd(2)—S(8d)	90.50(13)
N(1)—Cd(1)—S(3a)	81.90(13)	S(7)—Cd(2)—S(8d)	94.25(5)
S(4)—Cd(1)—S(3a)	165.95(5)	S(8)—Cd(2)—S(8d)	76.04(5)
N(2)—Cd(1)—S(2b)	87.99(14)	S(6)—Cd(2)—S(8d)	171.07(5)
N(1)—Cd(1)—S(2b)	173.34(15)	C(2)—S(2)—Cd(1b)	102.3(2)
S(4)—Cd(1)—S(2b)	80.95(5)	C(3)—S(3)—Cd(1a)	116.6(2)
S(3a)—Cd(1)—S(2b)	97.28(5)	C(3)—S(3)—Cd(1)	102.8(2)
N(2)—Cd(1)—S(3)	165.17(14)	Cd(1a)—S(3)—Cd(1)	101.29(5)
N(1)—Cd(1)—S(3)	92.91(15)	C(10)—S(4)—Cd(1)	115.9(2)
S(4)—Cd(1)—S(3)	87.27(6)	C(18)—S(6)—Cd(2)	99.1(2)
S(3a)—Cd(1)—S(3)	78.71(5)	C(19)—S(7)—Cd(2)	113.1(2)
S(2b)—Cd(1)—S(3)	80.47(5)	C(26)—S(8)—Cd(2)	116.3(2)
N(7)—Cd(2)—N(8c)	175.8(2)	C(26)—S(8)—Cd(2d)	99.5(2)
N(7)—Cd(2)—S(7)	100.32(13)	Cd(2)—S(8)—Cd(2d)	103.96(5)
N(8c)—Cd(2)—S(7)	83.65(13)	C(1)—N(1)—Cd(1)	157.4(5)
N(7)—Cd(2)—S(8)	81.60(13)	C(2)—N(2)—Cd(1)	167.4(5)
N(8c)—Cd(2)—S(8)	94.23(13)	S(7)—Cd(2)—S(8)	170.07(5)
N(7)—Cd(2)—S(6)	92.55(15)	C(17)—N(7)—Cd(2)	159.4(4)
N(8c)—Cd(2)—S(6)	88.65(13)	C(18)—N(8)—Cd(2c)	139.7(4)

Symmetry codes:
1 (a) $-x,\ -y,\ -z$.
2 (a) $-x-1,\ -y,\ -z$ (b) $-x,\ -y,\ -z$ (c) $-x+1,\ -y,\ -z-1$ (d) $-x,\ -y,\ -z-1$.

C(17), N(1), N(2)) and 37.3° for the plane (S(2), C(27), N(3), N(4)). Thus the phenyl ring can rotate in some extent in a PTU complex. In complex 1, there are two intramolecular hydrogen bonds (Cl(1)···N(1a) or Cl(1a)···N(1) = 3.170(3) Å; Cl(1)···N(3) or Cl(1a)···N(3a) = 3.312(3) Å) involving two chloro ligands and the NH groups of PTU to generate additional six-membered rings. Similar hydrogen bonds are also observed for Cd(TU)$_2$Cl$_2$ [9].

As shown in Figure 2, each PTU ligand forms two intermolecular hydrogen bonds with the Cl atoms and S atoms of the adjacent molecules

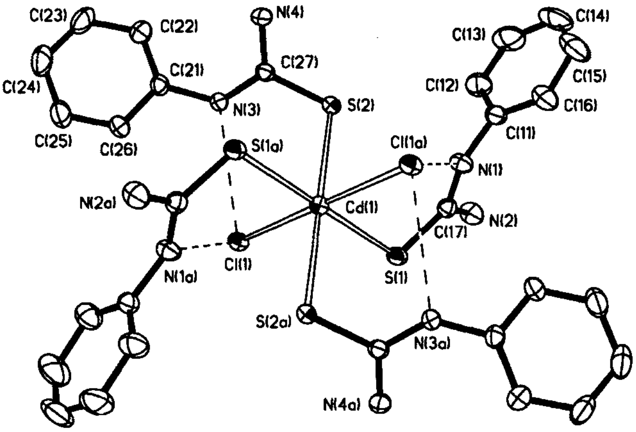

FIGURE 1 ORTEP drawing of Cd(PTU)$_4$Cl$_2$, showing the intramolecular hydrogen bonds.

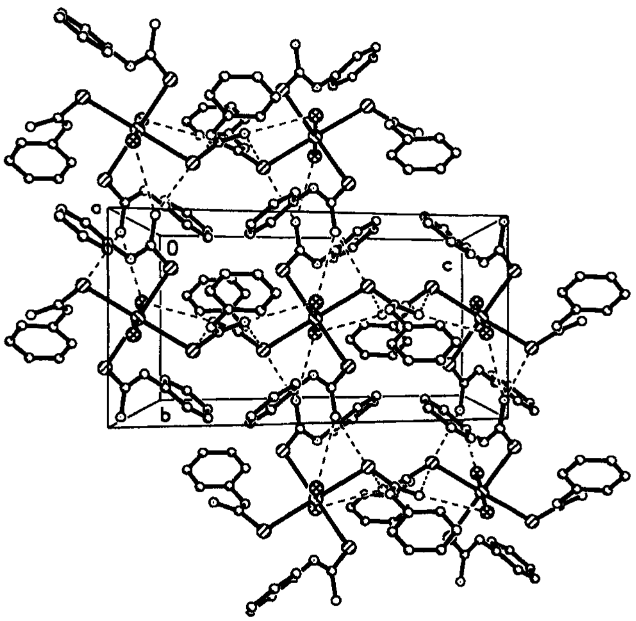

FIGURE 2 Packing diagram viewed down the *a*-axis showing the intermolecular hydrogen bonds in 1.

using NH$_2$ groups as donors. The distances of N(2)···S(2b), N(2)···Cl(2b), N(4)···S(2c) and N(4)···S(2d) are 3.457(3), 3.331(3), 3.414, 3.289(3), respectively (symmetry codes: *b*: $-x, -y-1, -z$; *c*: $-x, y, -z-1/2$; *d*: $x, -y, z-1/2$).

Structure of $[Cd_2(NCS)_2(\mu_2\text{-}SCN)_2(PTU)_2(\mu_2\text{-}PTU)_2]_n$ (2)

This complex exhibits chain-like structures in which each pair of Cd(II) atoms is bridged alternatively by either two μ_2–SCN^- or two μ_2–PTU ligands. Each Cd(II) atom is coordinated by three PTU and three SCN^- ligands in a distorted N_2S_4 octahedral geometry with the bond lengths of Cd—S and Cd—N being in the ranges of 2.577(2) – 2.944(2) Å and 2.283(5) – 2.369(5) Å, respectively. Interestingly, two kinds of chains, crystallographically independent, are distinguishable for the configurations of the Cd(II) coordination octahedra. As shown in Figure 3, the Cd(1) atom in chain A is ligated by two SCN^- nitrogen atoms in the *cis*-configuration, while the Cd(2) atom in chain B is ligated by two SCN^- nitrogen atoms in the *trans*-configuration. Therefore, chains A and B can be regarded as a pair of geometric isomers. Among the four independent SCN^- groups, two act in a μ_2-S,N mode to ligate two adjacent Cd(II) atoms related by an inversion center, yielding a ring in a chair configuration, while the other two act in a monodentate mode, using their nitrogen ends to ligate Cd(II) atoms. Such

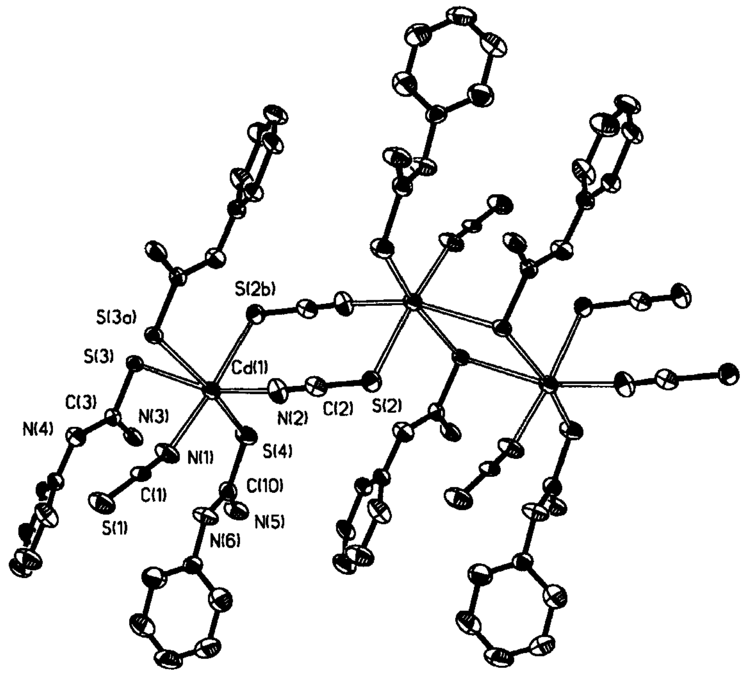

FIGURE 3 Drawings of the infinite chain in 2. (a) Chain A with *cis*-configuration; (b) Chain B with *trans*-configuration.

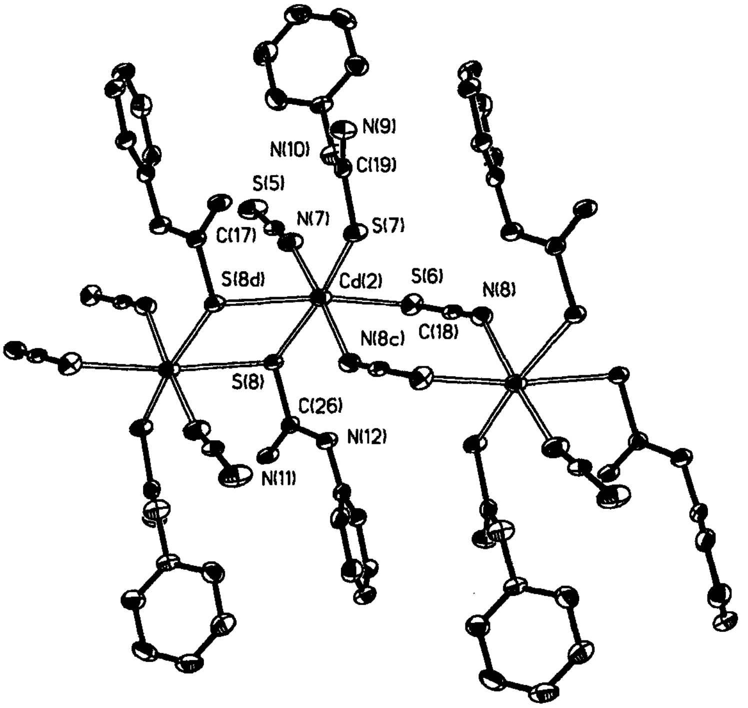

FIGURE 3 (Continued).

an arrangement consisting of two Cd(II) atoms and two bridging NCS^- ligands has been documented [10–12]. Similarly, two μ_2-PTU ligands bridge, by the μ_2-S end, a pair of Cd(II) atoms to form a Cd_2S_2 four-membered ring with the separation between the Cd(II) atoms being 4.443(1) Å, whereas the other two PTU ligands function in a monodentate mode to ligate Cd(II) atoms. Thus, the crystal structures demonstrate that the PTU ligand can serve as either a monodentate ligand or μ_2-bridging ligand upon coordination to metal ions, which is similar to the coordination behavior of its prototype thiourea [13–17].

In the crystal, there are extensive hydrogen bonds involving the N–H of the PTU (as donor) and the S atoms (from PTU or NCS^-) or N atoms (from NCS^-) as acceptors. The N···N distances of the hydrogen bonds are in the range of 3.014(8)–3.076(8) Å, while those of N···S are in the range of 3.292(6)–3.589(6) Å. Some of these hydrogen bonds contribute to further stabilization of the chains, and the others to formation of layers in which the two kinds of chains are packed in an ···ABABAB··· fashion (See Fig. 4). The layers are packed together through the offset $\pi-\pi$ stacking between the

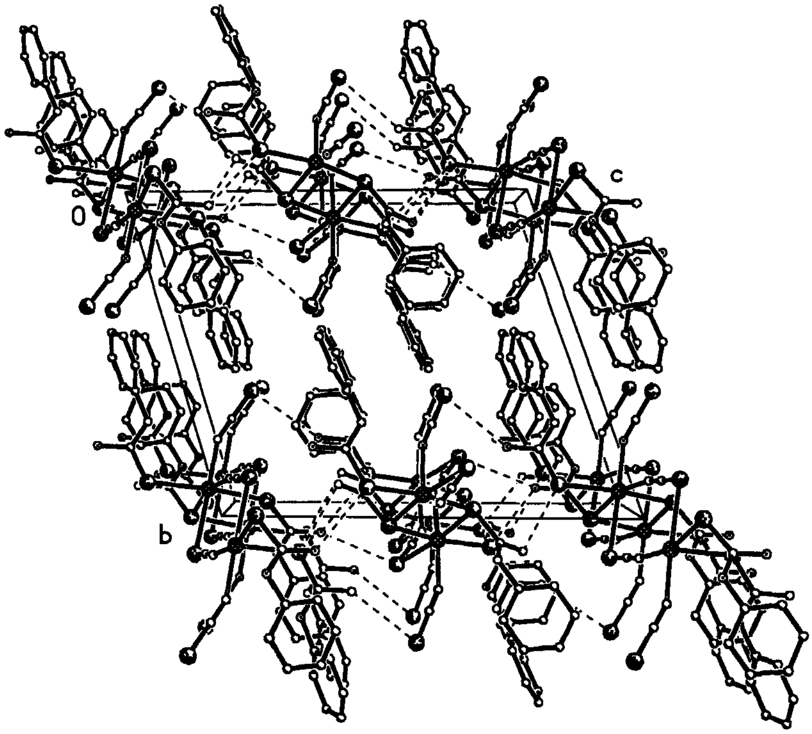

FIGURE 4 Packing diagram indicating the interchain hydrogen bonds in 2.

adjacent phenyl rings of PTU ligands with the face-to-face distances being ca. 3.64 Å.

Supplementary Data

Tables of X-ray crystallographic data in CIF format for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 145412 and CCDC 145413. Copies of the available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.acuk).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (29625102, 29971033) and the Higher Education Bureau of

Guangdong Province. We are indebted to the Chemistry Department of the Chinese University of Hong Kong for donation of the diffractometer.

References

[1] P. Yan, Y. Xie, Y. Qian and X. Liu, *Chem. Commun.* p. 1293 (1999).
[2] G. Xing, M. Jiang, Z. Shao and D. Xu, *Chin. J. Lasers* **14**(5), 302 (1987).
[3] Y. P. Tian, C. Y. Duan, C. Y. Zhao, X. Z. You, T. C. W. Mak and Z. Z. Zhang, *Inorg. Chem.* **36**, 1247 (1997).
[4] J. Qin, D. Liu, C. Dai, C. Chen, B. Wu, C. Yang and C. Zhan, *Coord. Chem. Rev.* **188**, 23 (1999).
[5] B. Liu, H. Q. Gao and X. J. Zhou, *Huaxue Tongbao* (5), p. 42 (1994).
[6] G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, Göttingen University, Germany (1997).
[7] G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, Göttingen University, Germany (1997).
[8] G. M. Sheldrick, SHELXTL, Version V, Siemens Industrial Automation Inc., Madison, Wisconsin, U.S.A. (1997).
[9] M. Nardelli, L. Cavalca and A. Braibanti, *Gazz. Chim. Ital.* **87**, 137 (1957).
[10] H.-J. Chen, G. Yang and X.-M. Chen, *Acta Crystallogr., Sect. C* **55**, 2012 (1999).
[11] G. G. Ram, P. H. William, J. O. Marc and L. B. Andre, *Inorg. Chem.* **20**, 3924 (1981).
[12] M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.* **60**, 4172 (1987).
[13] L. Cavalca, P. Domiano, G. F. Gasparri and P. Boldrini, *Acta Crystallogr.* **22**, 878 (1967).
[14] S. Natarajan, *Acta Crystallogr.* **23**, 1096 (1967).
[15] E. Corao and S. Baggio, *Inorg. Chim. Acta* **3** 617 (1969).
[16] L. Cavalca, A. C. Villa, A. Mangia and C. Palmieri, *Inorg. Chim. Acta* **4**, 463 (1970).
[17] R. Petrova, O. Angelova and J. Macicek, *Acta Crystallogr., Sect. C* **52**, 1935 (1996).