

# The preparation of zinc(II) and cadmium(II) complexes of the pentadentate $N_3S_2$ ligand formed from 2,6-diacetylpyridine and *S*-benzylthiocarbamate ( $H_2SNNNS$ ) and the X-ray crystal structure of the novel dimeric $[Zn_2(SNNNS)_2]$ complex

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## Abstract

The pentadentate chelating agent, 2,6-diacetylpyridinebis(*S*-benzylthiocarbamate) ( $H_2SNNNS$ ) reacts with zinc(II) and cadmium(II) ions forming stable complexes of empirical formula,  $[M(SNNNS)]$  ( $M = Zn^{2+}$ ,  $Cd^{2+}$ ;  $SNNNS^2 =$  doubly deprotonated anionic form of the Schiff base). These complexes have been characterized by a variety of physico-chemical techniques. IR and  $^1H$  NMR spectral evidence indicate that the Schiff base coordinates to the zinc(II) and cadmium(II) ions via the pyridine nitrogen atoms, the azomethine nitrogen atoms and the mercaptide sulfur atoms. The crystal and molecular structure of the zinc(II) complex has been determined by X-ray diffraction. The complex is a dimer in which the pyridine nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom from one ligand coordinate to one of the zinc(II) ions whereas the azomethine and thiolate sulfur atoms from another ligand complete pentacoordination around the zinc(II) ion, the ligands being coordinated in their deprotonated forms. The coordination geometry about each zinc(II) can be considered as intermediate between a square-pyramid and trigonal-bipyramid. The cadmium(II) complex is also assigned with a dimeric structure.

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## 1. Introduction

Metal complexes of thiosemicarbazones [1–15] and Schiff bases derived from *S*-alkyl/aryl esters of dithiocarbamic acid [16–23] have been studied quite extensively in view of their interesting physico-chemical properties [11–15] and potentially useful biological activities [2,4–7,16–20]. However, the majority of studies on such ligands involved metal complexes of tridentate and quadridentate chelating agents; pentadentate ligands and their metal complexes did not receive much attention. We have previously reported some metal complexes of the pentadentate  $N_3S_2$  ligand (Fig. 1(a);

$R = SCH_3$ ) formed from 2,6-diacetylpyridine and *S*-methylthiocarbamate [16]. The ligand and some of its metal complexes have been shown to exhibit marked activity against a range of pathogenic fungi. However, because of the very poor solubility of its metal complexes in most polar and non-polar organic solvents, attempts to grow crystals suitable for X-ray diffraction study have so far been unsuccessful. In a recent study, we found that substitution of the methyl groups on the sulfur atoms by benzyl groups in the above ligand readily afforded the pentadentate ligand (Fig. 1(a);  $R = SCH_2Ph$ ) which was not only found to exhibit marked antileukemic activity but it also readily reacted with a nickel(II) salts yielding a novel pyridine–nitrogen-bridged dinuclear nickel(II) complex whose structure has been confirmed by X-ray diffraction [17]. As part of our on-going study of metal complexes of

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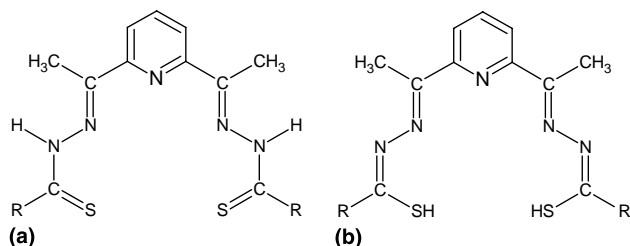


Fig. 1. The thione (a) and the thiol (b) forms of  $H_2SNNNS$  ( $R = SCH_2Ph$ ).

dithiocarbazates, we report here the synthesis and spectroscopic characterization of zinc(II) and cadmium(II) complexes of the 2,6-diacetylpyridine Schiff base of *S*-benzylthiocarbamate and the X-ray crystal structure of the  $[Zn(SNNNS)]_2$  complex.

## 2. Experimental

### 2.1. Physical measurements

The  $^1H$  NMR spectra were recorded in DMSO- $d_6$  on a Bruker Advance 300 DPX FT-NMR spectrometer using  $Si(CH_3)_4$  as an internal standard. All other physical measurements and analytical procedures were similar to those reported previously [17].

### 2.2. Preparation of the ligand

This compound was prepared following the literature procedure [17]. m.p. 203–204 °C; lit. 202–204 °C [17];  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  12.70 (s, 2H, NH), 4.48 (s, 4H,  $CH_2$ ), 2.50 (s, 6H,  $CH_3$ ), 8.05 (d, 2H, py-H), 7.90 (t, 1H, py-H), 7.20–7.45 (m, 5H, Ph-H).

### 2.3. Preparation of the complexes

#### 2.3.1. Preparation of $[Zn_2(SNNNS)_2]$

A solution of zinc(II) acetate dihydrate (0.209 g, 0.95 mmol) dissolved in abs. ethanol (50 ml) was mixed with a boiling solution of the ligand (0.50 g, 0.96 mmol) in a 9:1 mixture (250 ml) of dichloromethane and abs. ethanol and the mixture heated on a water bath for 20 min. The solution was then left to stand overnight whereupon the yellow compound that had formed was filtered off, washed with abs. ethanol followed by cold dichloromethane and dried in a desiccator over anhydrous silica gel. Yield: 0.34 g, 60%.  $^1H$  NMR (DMSO- $d_6$ ): 2.50 (s, 12H,  $CH_3$ ), 4.45 (d, 4H,  $CH_2$ ), 4.25 (d, 4H,  $CH_2$ ), 8.28 (t, 2H, py-H), 8.07 (d, 4H, py-H), 7.20–7.35 (m, 10H, Ph-H); UV(DMF) [ $\lambda_{max}/nm$   $\epsilon/M^{-1}cm^{-1}$ ]: 400 sh, 358 sh, 319 (31,622). *Anal.* Calc. for  $C_{50}H_{50}N_{10}S_8Zn_2$ : C, 51.1; H, 3.9; N, 11.5. Found: C, 51.3; H, 3.7; N, 11.9%.

#### 2.3.2. Preparation of $[Cd(SNNNS)]$

A solution of cadmium(II) nitrate tetrahydrate (0.29 g, 0.94 mmol) in abs. ethanol (20 ml) was mixed with a hot solution of the ligand (0.50 g, 0.96 mmol) in a 9:1 mixture (300 ml) of dichloromethane and abs. ethanol. The mixture when heated on a water bath for 20 min produced a yellow solution which on cooling deposited a microcrystalline powder. The crude product was recrystallized from a DMF-diethyl ether mixture. Yield: 0.42 g, 72%.  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  4.40 (s, 8H,  $CH_2$ ), 2.50 (s, 12H,  $CH_3$ ), 8.20 (t, 2H, py-H), 8.07 (d, 4H, py-H), 7.20–7.35 (m, 10H, Ph-H). UV(DMF) [ $\lambda_{max}/nm$  ( $\epsilon/M^{-1}cm^{-1}$ )]: ca. 400 sh, ca. 385 sh, 324 (25 119). *Anal.* Calc. for  $C_{50}H_{50}N_{10}S_8Cd_2$ : C, 47.4; H, 3.6; N, 11.0%. Found: C, 47.1; H, 3.9; N, 11.5%.

### 2.4. Crystallographic measurement

A bright yellow crystal of the  $Zn_2(SNNNS)_2$  complex was mounted on a glass fibre with Supa Glue. Cell constants were determined by a least squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD4 four-circle diffractometer using graphite monochromated MoK radiation (0.71073) and operating in the  $\omega$ - $2\theta$  mode within the range  $2 < 2\theta < 50^\circ$ . Data reduction and empirical absorption corrections ( $\Psi$ -scans) were performed with the WINGX [24] suite programmes. The structure was solved by direct method with SHELXS86 [25] and refined by full-matrix least-squares analysis with SHELXL97 [26]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were included at estimated positions. Drawings of molecules were produced with the programme ORTEP [27]. Crystal data and structure determination are given in Table 1.

## 3. Results and discussion

The 2,6-diacetylpyridine Schiff base of *S*-benzylthiocarbamate (Fig. 1(a);  $R = SCH_2Ph$ ) has a thioamide,  $-NH-C(=S)$  functional group and therefore, like all other Schiff bases derived from *S*-alkyl- and *S*-aryl esters of dithiocarbamic acid, it could, in principle, exhibit thione–thiol tautomerism.

It was previously shown that, in the solid state the Schiff base remains in the thioketo tautomeric form but, in solution and in the presence of nickel(II) ion, it quickly converted to the thiol form with the concomitant formation of a novel dimeric nickel(II) complex containing the deprotonated thiolate form of the ligand [17]. The reaction of  $H_2SNNNS$  with zinc(II) and cadmium(II) salts also yields complexes of empirical formula,  $[M(SNNNS)]$  ( $M = Zn^{2+}, Cd^{2+}$ ) containing the deprotonated form of the ligand as evidenced by the IR spectroscopic and X-ray results (see later). The related

Table 1  
Summary of crystal data, data collection and structure refinement parameters for  $[\text{Zn}_2(\text{SNNNS})_2]$

Chemical formula	$\text{C}_{50}\text{H}_{46}\text{N}_{10}\text{S}_8\text{Zn}_2$
Formula weight	1174.19
Crystal class	monoclinic
Space group	$C2/c$
Unit cell parameters	
$a$ (Å)	18.414(8)
$b$ (Å)	18.2020(10)
$c$ (Å)	18.100(10)
$\gamma$ (°)	119.80(3)
Volume (Å <sup>3</sup> )	5264(4)
$Z$	4
Mo $K\alpha$ (Å)	0.71073
$T$ (K)	296(2)
$\rho_{\text{calc}}$ (Mg <sup>-3</sup> )	1.481
$\mu$ (mm <sup>-1</sup> )	1.275
Sample dimension (mm)	0.60 × 0.50 × 0.40
$\theta$ range for data collection (°)	1.70–24.97
$F(000)$	2416
Total number of reflections	4791
Independent reflections	4638 [ $R_{\text{int}} = 0.0212$ ]
Absorption correction	$\Psi$ -scan
Maximum and minimum transmission	0.6296 and 0.5151
Data/restraints/parameters	4638/0/317
Goodness of fit on $F^2$	1.033
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0259$ , $wR_2 = 0.0679$
$R$ indices (all data)	$R_1 = 0.0372$ , $wR_2 = 0.0371$
Extinction coefficient	0.00167(9)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.257 and -0.23

2,6-diacetylpyridine-bis(thiosemicarbazone) (Fig. 1(a);  $\text{R} = \text{NH}_2$ ;  $\text{H}_2\text{daptsc}$ ) ligand has been shown to react with metal salts forming complexes containing both protonated and deprotonated forms [28–30] of the ligand. Its reaction with zinc(II) salts has been shown to be very interesting in that, depending on the nature of the zinc(II) salts, reaction conditions and solvents used for preparation of the complexes, three different types of zinc(II) complexes were obtained. Thus, in the presence of nitric acid, zinc(II) nitrate reacted with the ligand producing a seven-coordinate zinc(II) complex,  $[\text{Zn}(\text{H}_2\text{daptsc})(\text{H}_2\text{O})_2](\text{NO}_3)_2$  whereas with zinc(II) chloride in methanol, a dimeric complex,  $[\text{Zn}_2(\text{daptsc})_2] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$  containing the completely deprotonated form of the ligand resulted. The latter complex

contains both six- and four-coordinate zinc(II) ions in the same dimer[30]. When the reaction of zinc(II) chloride and the ligand was carried out in DMF, a third dimeric complex,  $[\text{Zn}_2(\text{daptsc})_2] \cdot \text{MeOH} \cdot 2\text{DMF}$  which is an isomer of  $[\text{Zn}_2(\text{daptsc})_2]$ , containing the deprotonated forms of the ligand was obtained. However, the present Schiff base, irrespective of nature of the zinc(II) salt used, yields complexes containing only the deprotonated mercaptide form of the ligand. The tendency of  $\text{H}_2\text{SNNNS}$  to deprotonate, even in the presence of mineral acids, may be attributed to the stabilization gained by delocalization of electrons in the C–N–N–C system. The above examples clearly demonstrate that, although Schiff bases derived from *S*-alkyl/aryl esters of dithiocarbazic acid are structurally analogous to thiosemicarbazones, they do not react with metal ions in similar ways.

The IR spectra of the complexes when compared with that of the free ligand show that the  $\nu\text{NH}$  band of the free ligand disappears in the spectra of the complexes supporting deprotonation of the ligand upon complex formation. The  $^1\text{H}$  NMR spectra of the zinc(II) and cadmium(II) complexes also do not contain the NH proton signal of the free ligand lending further support to the infrared evidence that the ligand coordinates to the zinc(II) and cadmium(II) ions in its deprotonated thiolate form. The IR spectra of the complexes exhibit the azomethine CN band ca.  $1600\text{ cm}^{-1}$  similar to that of the free ligand. In the past, evidence of coordination of thiosemicarbazones and dithiocarbazate ligands to metal ions via the azomethine nitrogen atom was based on the shifting of the azomethine C=N band of the free ligand from higher to lower wave numbers [31]. However, shifting of the  $\nu(\text{C}=\text{N})$  band to both higher [32,33] and lower [34] wave numbers has been reported. Since the azomethine C=N band is expected to couple with other bands, its shifting will also be dependent on how much it is in combination with other bands. In the IR spectra of the present zinc(II) and Cd(II) complexes the C=N band of the ligand is very little affected but the  $\nu(\text{N}-\text{N})$  band of the free ligand at  $1102\text{ cm}^{-1}$  is shifted to higher wavenumbers (Table 2) supporting coordination of the ligand via the azomethine nitrogen atom [35]. The splitting of the  $\nu_{\text{a}}$  CSS band of the free ligand at  $993$

Table 2  
Selected IR abnds ( $\text{cm}^{-1}$ ) for  $\text{H}_2\text{SNNNS}$  and its zinc(II) and cadmium(II) complexes

Compound <sup>a</sup>	IR bands			
	$\nu\text{NH}$	$\nu\text{CN}$	$\nu\text{NN}$	$\nu_{\text{a}}\text{CSS}$
$\text{H}_2\text{SNNNS}$	3170 m,br	1600 m	1102 m	993 w
$[\text{Zn}_2(\text{SNNNS})_2]$		1597 s	1131 m 1030 s	1005 sh
$[\text{Cd}(\text{SNNNS})]$		1600 m	1134 s 1006 sh	1028 s

<sup>a</sup>  $\text{H}_2\text{SNNNS} = 2,6$ -diacetylpyridinebis(*S*-benzylidithiocarbazate).

$\text{cm}^{-1}$  in the spectra of the complexes is strong evidence that the ligand coordinates to the zinc(II) and cadmium(II) ions through one of the sulfur donors of the CSS group [36].

### 3.1. The X-ray crystal and molecular structure of $[\text{Zn}_2(\text{SNNNS})_2]$

The structure of the complex along with the atom numbering scheme adopted, is shown in Fig. 2. The inter-atomic distances and angles between bonds are given in Table 3. The structure shows that the zinc(II) complex is not a monomer but a dimer in which each of the two zinc(II) ions adopts a five-coordinate geometry with a  $\text{N}_3\text{S}_2$  donor environment. The thiolate sulfur, the azomethine nitrogen and the pyridine nitrogen atoms of one ligand coordinate to a zinc(II) ion and a thiolate sulfur and an azomethine nitrogen atom of the second ligand complete the coordination sphere around the same zinc(II) ion. Both ligands in the dimer are coordinated in their deprotonated thiolate forms. While coordinating in the deprotonated iminothiolate form, the negative charge generated upon loss of the proton from the thiol sulfur atom, is delocalized in the C–N–N–C system as is shown by the intermediate C(1)–N(1) {1.299(3) Å}, C(9)–N(5) {1.300(3) Å}, N(1)–N(2) {1.388(2) Å}, N(4)–N(5) {1.394(2) Å}, C(8)–N(4) {1.293(3) Å} and C(2)–N(2) {1.293(3) Å} bond distances. Similar observations have also been made in complexes of other dithiocarbazate ligands systems [16–21]. It should be noted that  $\text{H}_2\text{SNNNS}$  was also previously found to react with nickel(II) ions producing a dimeric nickel(II) complex [17] but, the mode of its coordination in the nickel(II) complex was different from that observed in the present zinc(II) complex. In the dimeric nickel(II) complex, the pyridine nitrogen donor atom of the ligand was found to bridge two nickel(II) ions giving a six-coordinate octahedral arrangement of donor atoms around a nickel(II) ion. However, in the present zinc(II) complex, the ligand exhibits a different mode of coordination with the pyridine nitrogen atoms forming normal two-centre two-electron coordinate bonds instead of three-centre two-electron bonds. The stereochemistry around the zinc(II) is also different,

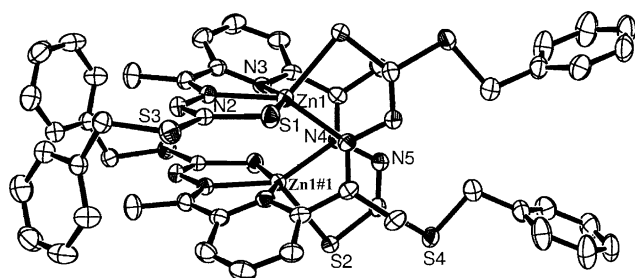


Fig. 2. The structure of  $[\text{Zn}_2(\text{SNNNS})_2]$ .

being five-coordinate compared to a six-coordinate geometry observed in the nickel(II) complex.

An inspection of the bond length data in Table 3 shows that the two Zn– $\text{N}_{\text{py}}$  bonds in the complex are considerably longer than the two Zn– $\text{N}_{\text{imine}}$  bonds. Similar differences in the two Zn–N bonds have also been observed in other five- and six-coordinate zinc(II) complexes of related ligands [30,37–40]. The Zn–S bond distances are longer in the present complex than those found in other related complexes indicating that the Zn–S bonds are weaker here than in other complexes. The C–S bond distances {1.720(2) and 1.727(2) Å} are longer than those reported for free thiosemicarbazones {1.684(4) Å in methyl pyruvate thiosemicarbazone [41]}, { $1.678 \pm 0.002$  Å in 4-formylthiosemi-carbazone [42]} and 1.652(6) Å in methylpyruvate Schiff base of *S*-methylthiocarbazate [43], being intermediate between 1.82 Å for a single bond and 1.56 Å for a double bond. The lengthening of the C–S bond can be attributed to the enethiolization process that occurs during complex formation of the ligand with the zinc(II) ion. A comparison of zinc(II)-donor atom distances in some five- and six-coordinate zinc(II) complexes of thiosemicarbazone and dithiocarbazate ligands (Table 4) shows that the bond lengths in the present complex are, more or less, comparable with those in other zinc(II) complexes despite differences in the nature of the ligands and different stereochemistry adopted by the zinc(II) ion.

The stereochemistry adopted by each zinc(II) ion in the  $\text{Zn}_2(\text{SNNNS})_2$  dimer is intermediate between a square-pyramid (SPY) and a trigonal-bipyramid (TBPY). Illustration of this point can be made by considering distortion from an idealized TBPY geometry. Thus, taking S(1) and N(3) as the axial donor atoms, an angle of  $154.93(5)^\circ$  is subtended at the zinc(II) ion {viz. the S(1)–Zn(1)–N(3) angle} which is much smaller than the theoretical value of  $180^\circ$ . The angles between the axial donors and the three equatorial donors N(2), N(4)#1 and S(2) range from  $146.79(7)^\circ$  for N(2)–Zn(1)–N(4)#1 to  $85.16(16)^\circ$  for N(4)#1–Zn(1)–S(2)#1 showing marked difference from the ideal value of  $120^\circ$ . A similar comparison can also be made for an idealized SPY geometry taking S(2)#1 as the apical donor and S(2), N(2), N(3) and N(4)#1 as the basal plane. Also, using Addison's formula,  $\tau = [(\beta - \alpha)/60] \times 100$  [44], where  $\beta$  and  $\alpha$  are the two biggest angles subtended at each zinc(II) ion, the value of  $\tau$  is found to be 32.5% which further supports the fact the stereochemistry adopted by each zinc(II) ion is between a SPY than a TBPY, but closer to SPY than TBPY. The deviation from an ideal SPY or TBPY geometry may be attributed to the restricted bite angles of the ligand.

Despite repeated attempts, we were unable to obtain the cadmium(II) complex in a suitable crystalline form for X-ray study. However, in view of its very low solubility in most of the common polar and non-polar organic

Table 3  
Selected bond lengths (Å) and angles (°) for [Zn<sub>2</sub>(SNNNS)<sub>2</sub>]

<i>Bond lengths</i>			
Zn(1)–S(1)	2.3860(15)	C(1)–S(3)	1.751(2)
Zn(1)–S(2)#1	2.3324(8)	C(2)–N(2)	1.293(3)
Zn(1)–N(4)#1	2.0846(17)	C(2)–C(17)	1.496(3)
Zn(1)–N(2)	2.0760(18)	N(4)–N(5)	1.394(2)
Zn(1)–N(3)	2.372(2)	C(8)–N(4)	1.293(3)
C(10)–S(3)	1.803(3)	N(1)–N(2)	1.388(3)
C(9)–N(5)	1.300(3)	C(9)–S(4)	1.760(2)
C(1)–N(1)	1.299(3)	C(9)–S(2)	1.727(2)
C(1)–S(1)	1.720(2)	C(19)–S(4)	1.813(3)
<i>Bond angles</i>			
N(2)–Zn(1)–N(4)#1	146.79(7)	S(2)#1–Zn(1)–N(3)	91.03(5)
N(2)–Zn(1)–S(2)#1	127.28(5)	N(2)–Zn(1)–S(1)	82.06(5)
N(4)#1–Zn(1)–S(2)#1	85.16(6)	N(4)#1–Zn(1)–S(1)	95.92(5)
S(2)#1–Zn(1)–S(1)	107.22(4)	N(2)–Zn(1)–N(3)	102.77(7)

Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, y, -z + 3/2$ .

Table 4  
Comparison of bond distances in some zinc(II) complexes of NS donor ligands

Compound <sup>a</sup>	C.N.[kernel]	Zn–S	Zn–N <sub>azom</sub>	Zn–N <sub>py</sub>	Ref.
Zn <sub>2</sub> (daptsc) <sub>2</sub> · MeOH · H <sub>2</sub> O	4[ZnN <sub>2</sub> S <sub>2</sub> ] <sup>+</sup> 6[ZnN <sub>4</sub> S <sub>2</sub> ]	2.317(3) 2.327(4)	2.07(1) 2.07(1)		[27]
[Zn <sub>2</sub> (daptsc) <sub>2</sub> ] · 2DMF	6[ZnN <sub>4</sub> S <sub>2</sub> ]	2.345(2) 2.370(2)	2.095(4) 2.102(4)	2.571(4) 2.705(5)	[27]
[Zn <sub>2</sub> (daptsc) <sub>2</sub> ] · MeOH · H <sub>2</sub> O	6[ZnN <sub>4</sub> S <sub>2</sub> ]	2.405(4) 2.436(4)	2.10(1) 2.12(1)	2.266(9) 2.46(1)	[27]
[Zn(H <sub>2</sub> daptsc)(H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	7[ZnN <sub>3</sub> O <sub>2</sub> S <sub>2</sub> ]	2.573(15) 2.586(3)	2.213(7)	2.344(9) 2.348(9)	[27]
[Zn <sub>2</sub> (SNNNS) <sub>2</sub> ]	5[ZnN <sub>3</sub> S <sub>2</sub> ]	2.3860(15) 2.3324(8)	2.0760(18) 2.0846(17)	2.372(2) 2.372(2)	this work
[Zn(BPA)(PhS) <sub>2</sub> ]	5[ZnN <sub>3</sub> S <sub>2</sub> ]	2.313(1) 2.3324(8)	2.175(3) 2.299(3)	2.229(3)	[40]
[Zn(BMAP)]	5[ZnN <sub>3</sub> S <sub>2</sub> ]	2.30(1) 2.31(1)	2.00(2) 2.32(2)	2.23(2)	[40]
[Zn(smfmtdc) <sub>2</sub> ]	4[ZnN <sub>2</sub> S <sub>2</sub> ]	2.3027(16) 2.3037(15)	2.050(4) 2.061(4)		[22]

<sup>a</sup> BPA, anionic form of bis(2-pyridylmethyl)amine; BMAP, anionic form of 2,6-bis(((2-mercaptophenyl)amino)methyl)pyridine; smfmtdc, anionic form of *S*-methyl-β-*N*-(2-furylmethyl)methylenedithiocarbazate.

solvents a monomeric five-coordinate geometry for [Cd(SNNNS)] is very unlikely. Because of the tendency of the cadmium(II) ion to form six-coordinate complexes, it is likely that the complex has a pyridine-nitrogen-bridged dimeric structure, similar to the previously reported nickel(II) complex [17] or it may have a mercapto sulfur-bridged dimeric structure.

#### 4. Conclusions

The 2,6-diacetylpyridine Schiff base of *S*-benzylidithiocarbazate, like other Schiff bases derived from *S*-alkyl- and *S*-aryl esters of dithiocarbazic acid, exists in

the thione form, both in the solid state and in solution but, in the presence of zinc(II) and cadmium(II) ions, it quickly converts to the thiol tautomeric form with the concomitant formation of neutral zinc(II) and cadmium(II) complexes containing the deprotonated thiolate forms of the ligand. Like the dimeric nickel(II) complex previously reported by us [17], the present zinc(II) complex is also a dimer but the mode of coordination of the ligand in the present zinc complex is entirely different from that found in the dimeric nickel(II) complex. The cadmium(II) complex is also probably dimeric, but in the absence of X-ray structure determination, a definite structure can not be assigned to this complex.

## 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204488. A copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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