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Diorganotin(IV) Complexes of 2,5-Dithiobiurea (H_2dtbu). The Crystal Structures of Me_2Sn(dtbu) and Ph_2Sn(dtbu)

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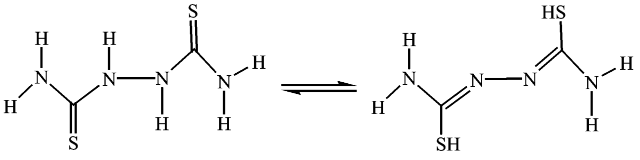
ABSTRACT: *The diorganotin(IV) complexes, R_2Sn(dtbu) (R = Me* **1***, n-Bu* **2***, Ph* **3***, $PhCH_2$* **4***; H_2dtbu = 2,5-dithiobiurea), have been synthesized and characterized by IR, ^1H, and ^{119}Sn NMR spectroscopy. The structures of* **1** *and* **3** *have been determined by X-ray crystallography. Crystal structures show that both complexes* **1** *and* **3** *consist of molecules in which the bideprotonated ligand is N,S,S-bonded, and the tin atom exhibits distorted pentacoordination with small differences between the methyl and phenyl derivatives in bond distances and bond angles. The unusual coordination mode of the $dtbu^{2-}$ anion creates four- and five-membered chelate rings. Moreover, the packing of complexes* **1** *and* **3** *are stabilized by the hydrogen bonding.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:93–98, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20173

INTRODUCTION

Metal thiolato complexes have been extensively studied because of their ability to adopt various structures and their relevance in biology, since they form the inorganic part of the biologically active centers of some metalloproteins and enzymes [1–3]. Recently, attention has been paid to the coordination chemistry of ligands containing nitrogen and thiol/thione donors, which can give potential access to new compounds with unusual structures and reactivities [4]. For example, triazyl- and tetrazolethiol organometallic derivatives have been reported. A related class of such compounds are thiosemicarbazones in which the structure unit HS—C=N—N or S=C—NH—N can bond to metal ions through S or N or both atoms [5–8].


H_2dtbu

As a result of our continuing interest in the coordination of main group metal with polydentate S, N ligands [9–11], here we report on the syntheses and characterizations of four diorganotin(IV) complexes with 2,5-dithiobiurea (H_2dtbu) of the type R_2Sn(dtbu) (R = Me **1**, *n*-Bu **2**, Ph **3**, $PhCH_2$ **4**). All the complexes **1–4** have been characterized by IR, ^1H, and ^{119}Sn NMR spectroscopy. The structures of **1** and **3** have been determined by X-ray crystallography. Crystal structures show that both complexes **1** and

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3 consist of molecules in which the bideprotonated ligand is N,S,S-bonded, and the tin atom exhibits distorted pentacoordination with small differences between the methyl and phenyl derivatives in bond distances and bond angles. The unusual coordination mode of the dtbu^{2-} anion creates four- and five-membered chelate rings. Moreover, the packing of complexes **1** and **3** are stabilized by the hydrogen bonding.

EXPERIMENTAL

Materials and Measurements

Dimethyltin dichloride, di-*n*-butyltin dichloride, diphenyltin dichloride, and 2,5-dithiobiurea were commercially available, and they were used without further purification. Dibenzyltin dichloride was prepared by a standard method reported in the literature [12]. The melting points were obtained with Kofler micromelting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr disks and sodium chloride optics. ^{1}H NMR spectra were obtained on a JEOL-FX-90Q spectrometer; chemical shifts were given in ppm relative to Me_4Si in $CDCl_3$ solvent. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses of the Complexes **1–4**

Me_2Sn(dtbu) **1**. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. The H_2dtbu (0.150 g, 1 mmol) was added to the solution of ethanol (20 mL) with sodium ethoxide (0.136 g, 2 mmol); the mixture was stirred for 10 min, and then added Me_2SnCl_2 (0.220 g, 1 mmol) to the mixture, continuing the reaction for 12 h at 60°C. After cooling down to the room temperature, the solution was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ethanol, and pale yellow crystals were formed. mp 182–184°C. Yield (0.226 g, 0.76 mmol), 76%. Anal. Calcd for $C_4H_{10}N_4S_2Sn$: C, 16.18; H, 3.39; N, 18.86. Found: C, 16.37; H, 3.64; N, 18.75%. IR (KBr, cm^{-1}): $\nu(NH_2)$ 3401 m, 3345, ν(C=N) 1600s, ν_{as}(Sn–C) 565 m, ν_s(Sn–C) 493 m. ^{1}H NMR ($CDCl_3$): δ 7.83 (s, 2H, N(1)H_2), 6.42 (s, 2H, N(4)H_2), 1.11 (s, 6H, Sn–CH_3) ppm. ^{119}Sn NMR ($CDCl_3$, ppm): $\delta = -79.4$.

n-Bu_2Sn(dtbu) **2**. The procedure is similar to that of complex **1**. H_2dtbu (0.150 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and *n*-Bu_2SnCl_2 (0.304 g, 1 mmol) were added to the solution of ethanol (20 mL), continuing the reaction for 12 h at 60°C. The solid was recrystallized from ethanol, and pale yellow crystals were formed. mp 155–157°C. Yield (0.278 g, 0.73 mmol), 73%. Anal. Calcd for $C_{10}H_{22}N_4S_2Sn$: C, 31.51; H, 5.82; N, 14.70. Found: C, 31.80; H, 5.77; N, 14.85%. IR (KBr, cm^{-1}): $\nu(NH_2)$ 3396m, 3304, ν(C=N) 1601s, ν_{as}(Sn–C) 523m, ν_s(Sn–C) 497m. ^{1}H NMR ($CDCl_3$): δ 7.84 (s, 2H, N(1)H_2), 6.39 (s, 2H, N(4)H_2), 0.86–2.10 (m, 18H, Sn–C_4H_9) ppm. ^{119}Sn NMR ($CDCl_3$, ppm): $\delta = -90.6$.

Ph_2Sn(dtbu) **3**. The procedure is similar to that of complex **1**. H_2dtbu (0.150 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Ph_2SnCl_2 (0.344 g, 1 mmol) were added to the solution of ethanol (20 mL), continuing the reaction for 12 h at 60°C. The solid was recrystallized from ethanol, and pale yellow crystals were formed. mp 202–204°C. Yield (0.337 g, 0.80 mmol), 80%. Anal. Calcd for $C_{14}H_{14}N_4S_2Sn$: C, 39.93; H, 3.35; N, 13.30. Found: C, 39.71; H, 3.02; N, 13.38%. IR (KBr, cm^{-1}): $\nu(NH_2)$ 3382m, 3258, ν(C=N) 1602s, ν_{as}(Sn–C) 440m, ν_s(Sn–C) 413m. ^{1}H NMR ($CDCl_3$): δ 7.89(s, 2H, N(1)H_2), 6.42 (s, 2H, N(4)H_2), 7.47–7.79 (m, 10H, Sn–C_6H_5) ppm. ^{119}Sn NMR ($CDCl_3$, ppm): $\delta = -82.5$.

$(PhCH_2)_2Sn$(dtbu) **4**. The procedure is similar to that of complex **1**. H_2dtbu (0.150 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and $(PhCH_2)_2SnCl_2$ (0.372 g, 1 mmol) were added to the solution of ethanol (20 mL), continuing the reaction for 12 h at 60°C. The solid was recrystallized from ethanol, and pale yellow crystals were formed. mp 142–143°C. Yield (0.368 g, 0.83 mmol), 82%. Anal. Calcd for $C_{16}H_{18}N_4S_2Sn$: C, 42.78; H, 4.04; N, 12.47. Found: C, 42.89; H, 4.10; N, 12.47%. IR (KBr, cm^{-1}): $\nu(NH_2)$ 3389m, 3250, ν(C=N) 1599s, ν_{as}(Sn–C) 442m, ν_s(Sn–C) 421m. ^{1}H NMR ($CDCl_3$): δ 7.87 (s, 2H, N(1)H_2), 6.45 (s, 2H, N(4)H_2), 6.84–7.23 (m, 10H, Sn–$CH_2C_6H_5$), 3.47 (s, 4H, Sn–$CH_2C_6H_5$) ppm. ^{119}Sn NMR ($CDCl_3$, ppm): $\delta = -85.2$.

X-ray Crystallography

Data were collected at 298 K on a Bruker SMART CCD 1000 diffractometer fitted with Mo Kα radiation. The structures were solved by direct-methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All non-hydrogen atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Crystal data and experimental details of the structure determinations are listed in Table 1.

TABLE 1 Crystal Data and Refinement Details for Complexes **1** and **3**

Complexes	**1**	**3**
Empirical formula	$C_4H_{10}N_4S_2Sn$	$C_{14}H_{14}N_4S_2Sn$
Formula weight	296.97	421.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	7.621(2)	14.387(3)
b (Å)	16.817(3)	12.823(2)
c (Å)	8.243(3)	9.1884(10)
α(°)	90	90
β(°)	109.325(2)	101.302(2)
γ(°)	90	90
V (Å^3)	996.9(5)	1662.2(5)
Z	4	4
D_c (mg m^{-3})	1.979	1.683
Absorption coefficient (mm^{-1})	2.931	1.786
F(0 0 0)	576	832
Crystal size (mm)	0.58 × 0.47 × 0.42	0.38 × 0.27 × 0.16
θ range (°)	2.42–25.02	2.15–25.02
Reflections collected	5115	8477
Independent reflections	1756 ($R_{int} = 0.0515$)	2923 ($R_{int} = 0.0321$)
Data/restraints/parameters	1756/0/100	2923/0/190
Goodness-of-fit on F^2	1.079	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0323$, $wR_2 = 0.0834$	$R_1 = 0.0346$, $wR_2 = 0.0737$
R indices (all data)	$R_1 = 0.0375$, $wR_2 = 0.0869$	$R_1 = 0.0597$, $wR_2 = 0.0885$

RESULTS AND DISCUSSION

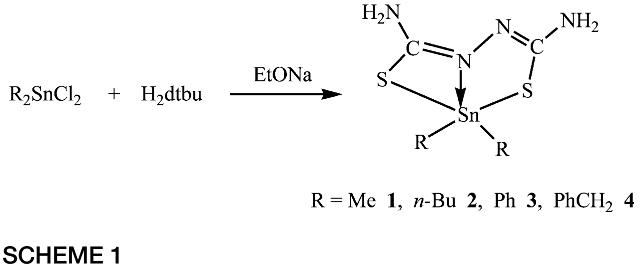
Syntheses of the Complexes **1–4**

The synthesis procedure is shown in the following Scheme 1:

IR Spectroscopic Studies of the Complexes **1–4**

The most significant IR bands are listed in the Experimental. The proposed assignment is based on previous studies of thiosemicarbazone and imidazole ligands in metal complexes [13–15]. The data suggest that the coordination mode of dtbu is same in all the complexes as was shown for the methyl and phenyl derivatives by the X-ray diffraction study.

The three high frequency bands of the free ligand, centered at 3354, 3273, and 3166 cm^{-1}, were attributed to ν(N–H) stretching. The spectra of both complexes lack bands located at about 3166 cm^{-1}, as a result of the ligand deprotonation, indicating that this absorption refer to the $\nu(N_{hydrazinic}–H)$ vibration. In organotin compounds, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [16]. In the case of our complexes, two bands were assigned to asymmetric and symmetric Sn–C vibrations; thus suggesting nonlinear SnC_2 units for all complexes.



SCHEME 1

^{1}H NMR Data of the Complexes **1–4**

The NH proton signals of the ligand H_2dtbu was not observed in the ^{1}H NMR spectra of the complexes due to the double deprotonation of H_2dtbu. Nevertheless, the most prominent feature of these spectra is behavior of the NH_2 groups. The sharp resonances appear at 7.83–7.89 ppm and 6.39–6.45 ppm in all complexes **1–4** indicating existence of the NH_2 groups. All the information accords well with what the IR data have revealed.

^{119}Sn NMR Data of the Complexes **1–4**

The ^{119}Sn NMR chemical shift is very sensitive to complexation and usually greatly shifted downfield or upfield on bonding to a Lewis base. The upfield chemical shift values of −79.6, −90.6, −82.5, and −85.2 ppm observed for complexes **1–4**, respectively, are indicative of five-coordination of the Sn(IV) nucleus [17].

TABLE 2 Selected Bond Lengths (A) and Bond Angels (°) for **1**

	Bond lengths		
Sn(1)–N(2)	2.106 (3)	N(3)–C(2)	1.294 (5)
Sn(1)–C(4)	2.115 (5)	N(2)–C(1)	1.316 (5)
Sn(1)–C(3)	2.122 (5)	S(1)–C(1)	1.747 (4)
Sn(1)–S(2)	2.5231 (14)	S(2)–C(2)	1.722 (4)
Sn(1)–S(1)	2.8716 (13)	N(2)–N(3)	1.398 (4)
	Bond angles		
N(2)–Sn(1)–C(4)	115.57 (19)	C(3)–Sn(1)–S(2)	103.87 (15)
N(2)–Sn(1)–C(3)	111.93 (18)	N(2)–Sn(1)–S(1)	59.76 (9)
C(4)–Sn(1)–C(3)	128.9 (2)	C(4)–Sn(1)–S(1)	91.60 (14)
N(2)–Sn(1)–S(2)	76.62 (9)	C(3)–Sn(1)–S(1)	96.54 (15)
C(4)–Sn(1)–S(2)	104.25 (14)	S(2)–Sn(1)–S(1)	136.17 (4)
C(1)–N(2)–N(3)	119.6 (3)	C(1)–N(2)–Sn(1)	112.5 (3)
N(3)–N(2)–Sn(1)	127.2 (2)		

TABLE 3 Selected Bond Lengths (Å) and Bond Angels (°) for **3**

	Bond lengths		
Sn(1)–N(2)	2.080 (4)	N(2)–C(1)	1.320 (6)
Sn(1)–C(9)	2.125 (4)	N(3)–C(2)	1.306 (7)
Sn(1)–C(3)	2.137 (5)	S(1)–C(1)	1.700 (6)
Sn(1)–S(2)	2.5179 (15)	S(2)–C(2)	1.748 (6)
Sn(1)–S(1)	2.7251 (15)	N(2)–N(3)	1.361 (6)
	Bond angles		
N(2)–Sn(1)–C(9)	118.22 (16)	C(3)–Sn(1)–S(2)	103.72 (16)
N(2)–Sn(1)–C(3)	119.47 (17)	N(2)–Sn(1)–S(1)	61.88 (13)
C(9)–Sn(1)–C(3)	120.41 (18)	C(9)–Sn(1)–S(1)	96.92 (14)
N(2)–Sn(1)–S(2)	77.54 (13)	C(3)–Sn(1)–S(1)	97.15 (16)
C(9)–Sn(1)–S(2)	101.71 (14)	S(2)–Sn(1)–S(1)	139.42 (5)
C(1)–N(2)–N(3)	122.2 (5)	C(1)–N(2)–Sn(1)	109.7 (4)
N(3)–N(2)–Sn(1)	128.1 (4)		

Crystal Structures of Complexes **1** *and* **3**

Selected bond lengths and bond angles for **1** and **3** are shown in Tables 2 and 3, respectively. The crystal structures of **1** and **3** are shown in Figs. 1 and 2, respectively.

In both complexes **1** and **3**, the ligand is tridentate via its S, N, and S atoms, giving a coordination polyhedron around the Sn atom that can be described as a distorted trigonal bipyramid with the ligand occupying the two axial positions and one equatorial position.

As in other complexes of tridentate thiosemicarbazones [13–15,18], the main distortion from regular bipyramidal geometry comes from the stereochemical limitations of the ligand, which reduce the S–Sn–S angle from the ideal value of 180° to the values of 136.17(4)° and 139.42(5)° observed in **1** and **3**, respectively, contributing to the distortion. The Sn(1)–N(2) distance (2.106(3) Å for **1**, 2.080(4) Å for **3**) is close to the low degree of planarity of the ligand in the complexes, also the sum of the nonpolar covalent radii (2.15 Å) [19] but largely shorter than in [Sn(CH$_3$)$_2$(aptsc)Cl]

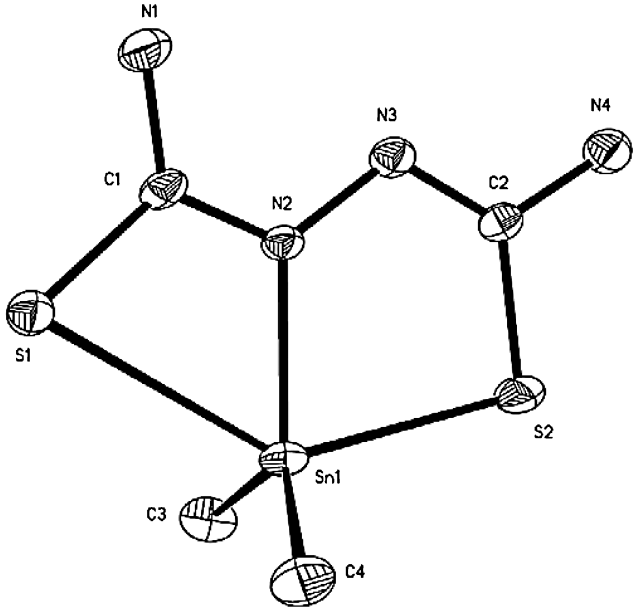


FIGURE 1 The molecular structure of complex **1**.

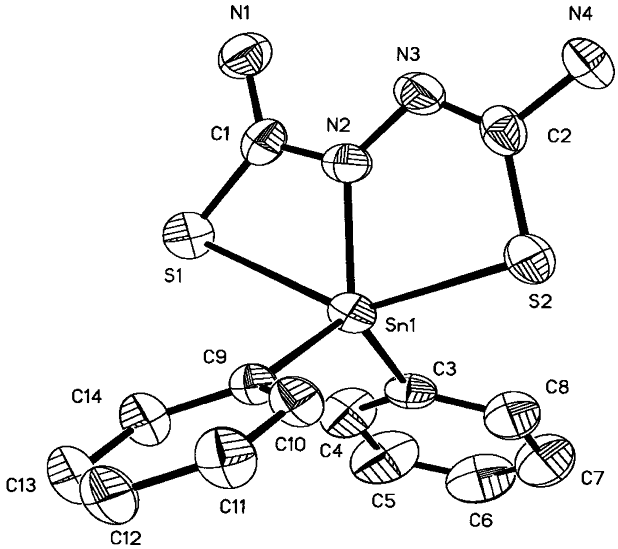


FIGURE 2 The molecular structure of complex **3**.

(2.328(2) Å) and $[Sn(CH_3)_2(aptsc)Br]$ (2.359(2) Å) [20], indicating strong bonds. The Sn(1)–S(2) distance (2.5231(14) Å for **1**, 2.5179(15) Å for **3**), though little longer than the sum of the nonpolar covalent radii (2.42 Å) [19] and the Sn–S distance in the organotin(IV) derivatives from heterocyclic thionates containing nitrogen atom(s) [9–11], is considerably shorter than the sum of the van der Waals radii (4.0 Å) [21], suggesting a fairly strong bond. The Sn(1)–S(1) distance (2.8716(13) Å for **1**, 2.7251(15) Å for **3**), though shorter than the sum of the van der Waals radii (4.0 Å), is slightly longer than Sn(1)–S(2) distance in **1** and **3**, respectively and Sn–S bond distances in $[Sn(CH_3)_2(aptsc)Cl]$ (2.4192(8) Å) and $[Sn(CH_3)_2(aptsc)Br]$ (2.4467(7) Å) [20], indicating a secondary coordinated bond. The Sn–C distances are unremarkable.

Even though the coordination scheme is basically the same in both complexes **1** and **3**, a closer look at the bond distances and bond angles (Tables 2 and 3) shows certain differences. In the phenyl derivative, the Sn–N and Sn–S distances are slightly shorter than in the methyl complex. Also, the angle N–Sn–S is slightly larger in the phenyl complex.

The main changes in the free ligand structure [22] under coordination can be described as follows: (1) a 180° rotation about N(3)–C(2) that switches the N(4) and S(2) and thereby allows the S atom to form a five-membered chelate ring with the Sn and N(2); (2) modifications in bond distances and bond angles in thiocarbamide group, namely the lengthening of C(1)–S(1) and C(2)–S(2), shortening of C(1)–N(2) and C(2)–N(3), widening of S(2)–C(2)–N(3), and narrowing of the other two angles at C(2). In addition, the changes of bond distances of C(1)–S(1) and C(1)–N(2) are smaller than those of C(2)–S(2) and C(2)–N(3), suggesting the coordination modes of two S atoms are different.

In the complex **1**, the hydrogen bonding between the amido of ligand and sulfur or nitrogen atom's adjacent molecule (N(1)–H(1A)···S(1) 3.409 Å, N(1)–H(1A)–S(1) 147.94°, N(1)–H(1B)···N(4) 3.224 Å, N(1)–H(1B)–N(4) 135.09°, and N(4)–H(4B)···S(1) 3.729 Å, N(4)–H(4B)–S(1) 173.96°) is recognized, which contributes to construct the 3D network of **1** (Fig. 3). As for **3**, the hydrogen bonds are also found (N(1)–H(1B)···N(4) 3.154 Å, N(1)–H(1B)–N(4)

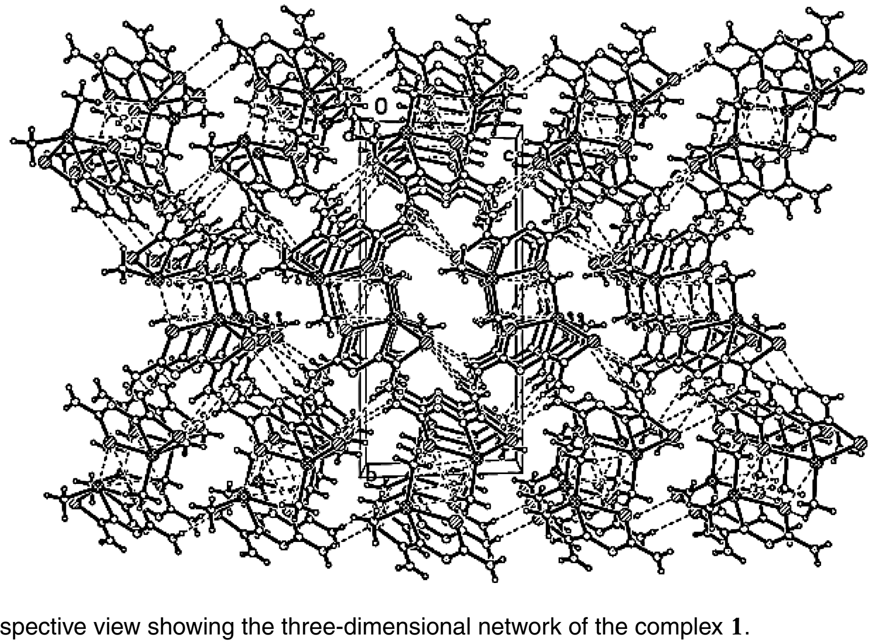


FIGURE 3 Perspective view showing the three-dimensional network of the complex **1**.

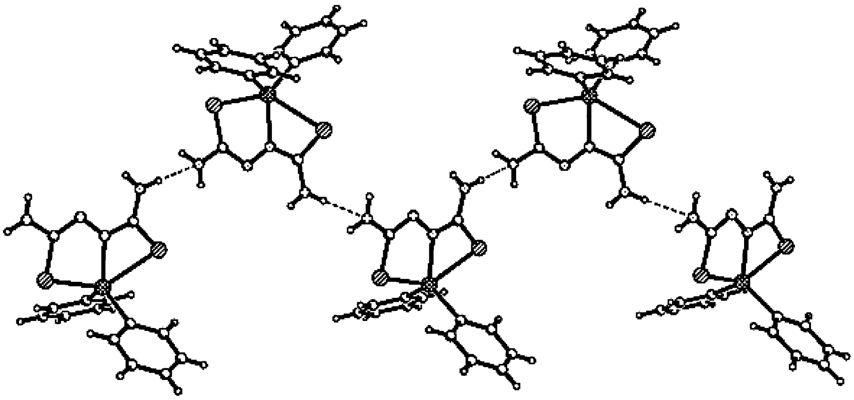


FIGURE 4 Perspective view showing the one-dimensional network of the complex **3**.

163.77°) and its discrete molecules are connected to a 1D chain through hydrogen bonding (Fig. 4).

SUPPLEMENTARY DATA

Atomic coordinates, thermal parameters, and bond lengths and angles for complexes **1** and **3** have been deposited in the Cambridge Crystallographic Data Center, CCDC nos. CCDC 274953, 274954. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK on request (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or URL: http://www.ccdc.cam.ac.uk), quoting the deposition numbers for **1** and **3**.

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