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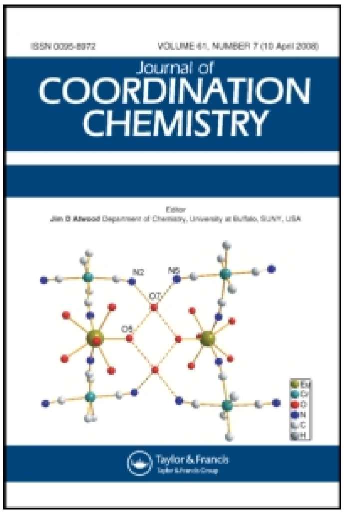

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Hg(II), Tl(III), Cu(I), and Pd(II) Complexes with 2,2'-Diphenyl-4,4'-Bithiazole (DPBTZ), Syntheses and X-Ray Crystal Structure of [Hg(DPBTZ)(SCN)$_2$]

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Hg(II), Tl(III), Cu(I), AND Pd(II) COMPLEXES WITH 2,2′-DIPHENYL-4,4′-BITHIAZOLE (DPBTZ), SYNTHESES AND X-RAY CRYSTAL STRUCTURE OF [Hg(DPBTZ)(SCN)$_2$]

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Reaction of the ligand 2,2′-diphenyl-4,4′-bithiazole (DPBTZ) with Hg(SCN)$_2$, Tl(NO$_3$)$_3$, CuCl, and PdCl$_2$ gives complexes with stoichiometry [Hg(DPBTZ)(SCN)$_2$], [Tl(DPBTZ)(NO$_3$)$_3$], [Cu(DPBTZ)(H$_2$O)Cl], and [Pd(DPBTZ)Cl$_2$]. The new complexes were characterized by elemental analyses and infrared spectroscopy. The crystal structure of [Hg(DPBTZ)(SCN)$_2$] determined by X-ray crystallography. The Hg atom in the title monomeric complex, (2,2′-diphenyl-4,4′-bithiazole)mercury(II)bisthiocyanate, [Hg(C$_{18}$H$_{12}$N$_2$S$_2$)(SCN)$_2$], is four-coordinate having an irregular tetrahedral geometry composed of two S atoms of thiocyanate ions [Hg–S 2.4025(15) and 2.4073(15) Å] and two N atoms of 2,2′-diphenyl-4,4′-bithiazole ligand [Hg–N 2.411(4) and 2.459(4) Å]. The bond angle S(3)–Hg(1)–S(4) of 147.46(5)° has the greatest derivation from ideal tetrahedral geometry. Intermolecular interaction between Hg(1) and two S atoms of two neighboring molecules, 3.9318(15) and 3.9640(18) Å, make the Hg(1) distort from a tetrahedron to a disordered octahedron. The attempts for preparation complexes of Tl(I), Pb(II), Bi(III), Cd(II) ions with 2,2′-diphenyl-4,4′-bithiazole ligand were not successful and also the attempts for preparation complexes of 4,4′,5,5′-tetraphenyl-2,2′-bithizole ligand with Cu(II), Ni(II), Co(II), Co(III), Mn(II), Mn(III), Fe(II), Fe(III), Cr(III), Zn(II), Tl(III), Pb(II), Hg(II), Cu(I), Pd(II) were not successful. This point can be regarded as the initial electron withdrawing of phenyl rings and also their spatial steric effects.

Keywords: Hg(II), Tl(III); Cu(I); Pd(II) complexes; Crystal structure; 2,2′-diphenyl-4,4′-bithiazole ligand

INTRODUCTION

The ability of mercury(II), thallium(III), copper(I) and palladium(II) salts to form a wide variety of 1 : 1 and 1 : 2 complexes, with neutral ligands has been known for some time [1–5]. The most common neutral donors are phosphine and amine derivatives. Most of these complexes contain halide ions and thiocyanate ion was rarely reported [6–8]. This ion is ambidentate and can be coordinated via both N atom and S atom. The coordination mode depends on the nature of the metal center,

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hence *N*-donor atoms are found in Zn complexes, while in mercury(II) complexes, the S atom is undoubtedly the expected ligating site [9]. In part one of our current study, we reported the preparation and characterization of a series of 1 : 1 and 1 : 2 lead(II), bismuth(III) complexes of 4,4′-bithiazole, $[Pb(BTZ)(NCS)_2]_n$, $[Pb(BTZ)_2(NO_3)_2]$ [10], $[Pb_2(BTZ)_4(NO_3)(H_2O)](ClO_4)_3$ [11] and $Bi(BTZ)_2(NO_3)_3$ [12]. Here, we want to show the nature of adducts formed between metal ions and bithiazole derivations [2,2′-diphenyl-4,4′-bithiazole (DPBTZ) and 4,4′,5,5′-tetraphenyl-2,2′-bithizole (TPBTZ)].

The incorporation of bithiazole groups with aromatic groups in the design of ligands and also preparation the complexes allow both the electronic and strict control of the properties of metal complexes. A five-member heterocycle like bithiazole and an aromatic compound like phenyl are thus directly linked in a single ligand system, thus the electronic communication between these two heterocycles can be avoided.

EXPERIMENTAL

Physical Measurment

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

Preparation of the 2,2′-Diphenyl-4,4′-bithiazole

The 2,2′-diphenyl-4,4′-bithiazole ligand was prepared from 1,4-dibromobutane-2,3-dione and thiobanzamide by method of Erlenmeyer and Ueberwasser [13] (m.p. 185°C).

Preparation of the 4,4′,5,5′-Tetraphenyl-2,2′-bithiazole

The 4,4′,5,5′-tetraphenyl-2,2′-bithiazole ligand was prepared from Dithioaxamid and Dezilebromide and recrystallized from $CHCl_3$ [14], (m.p.240°C).

Preparation of $Hg(DPBTZ)(SCN)_2$

The $Hg(DPBTZ)(SCN)_2$ compound was obtained by reacting 2,2′-diphenyl-4,4′-bithiazole ligand (0.64 g, 2 mmol) with mercury(II) thiocyanate (0.316 g, 1 mmol) in methanol (5 mL) at room temperature, with stirring, for 48 h. The white solid formed was filtered out and dried under vacuum. Yield: 0.445 g, 70%. m.p.: 230°C. Anal. Calc. for $C_{20}H_{12}N_4S_4Hg$: C, 37.37; H, 1.9; N, 8.8. Found: C, 37.99; H, 1.93; N, 8.82.

IR(cm^{-1}) selected bands: 1590(s), 1648(s), 2040(vs), 3140(w).

The crude product was dissolved in CH_3CN (10 mL), and Et_2O was diffused into it, forming a mixture of white precipitate and light yellow crystals.

Preparation of $Tl(DPBTZ)(NO_3)_2$

The complex $Tl(DPBTZ)(NO_3)_2$ was prepared by dissolving thallium(III) nitrate (0.320 g, 1 mmol) in distilled water and adding an alcoholic solution of 2,2′-diphenyl-4,4′-bithiazole (0.320 g, 1 mmol). The resulting solution was stirred for 5 h at room temperature, then it was allowed to stand for 2–3 days in a refrigerator (*ca.* 6°C). Yellow crystals of the desired product precipitated, which were filtered off, washed with acetone and ether and air dried (0.352 g yield 60%), m.p.: 275°C. Found C, 30.1; H, 1.7; N, 9.3: calculated for $C_{20}H_{12}N_5O_3$ S_4Tl; C, 30.65; H, 1.58; N, 9.32%.

IR(cm^{-1}) selected bands: 740(s), 1010(s), 1380(vs), 1590(s), 1618(s), 3040(w).

Preparation of [Cu(DPBTZ)(H_2O)Cl]

The complex [Cu(DPBTZ)(H_2O)Cl] was prepared by dissolving 0.1 g (1 mmol) copper(I)chloride in distillation water and adding mixture alcoholic solution of 2, 2′-diphenyl-4,4′-bithiazole (0.320 g, 1 mmol). The resulting solution was stirred for 2 h. at room temperature, and then it was allowed to stand for 3–4 days in a refrigerator. Red powder of the desired product precipitated, which were filtered off, and washed with acetone and ether and air dried (0.238 g, yield 60%), m.p.: 215°C.

Anal. Found: C, 54.28 H, 3.28 N, 6.93: Calc. for $C_{20}H_{14}ClN_2OS_2Cu$, C, 54.79; H, 3.1; N, 6.39%.

IR (KBr, cm^{-1}); ν(O–H) 3560; $\nu(C–H)_{ar}$ 3030; ν(C=C), ν(C=N) 1615, 1570; ν(Cu–N) 412; ν(Cu–Cl) 320; ν(Cu–N) 260.

Preparation of [Pd(DPBTZ)Cl_2]

The complex was prepared by dissolving $PdCl_2$ (0.266g, 1.5 mmol) and LiCl in distillation methanol (15 mL) and adding an alcoholic solution of 2,2′-diphenyl-4,4′-bithiazole, (0.480 g, 1.5 mmol). The resulting solution was stirred for 5 h at room temperature, then it was allowed to stand for 2–3 days in a refrigerator (*ca.* 6°C). Red powder of the desired product precipitated, which were filtered off, washed with acetone and ether and air dried (0.522 g yield 70%), m.p.: 225°C. Found C, 48.54; H, 2.25; N, 5.79: calculated for $C_{20}H_{12}Cl_2N_2S_2Pd$; C, 48.38; H, 2.42; N, 5.64%.

IR (KBr, cm^{-1}) , $\nu(C–H)_{ar}$ 3010(w); ν(C=C)(s), ν(C=N) 1610(s), 1580(s), ν(Pd–N) 412; ν(Pd–Cl) at *ca.* 340 and 290 cm^{-1}.

Crystallography

Crystal Data and Refinement Details

Hg(N-(2,2′-diphenyl-4,4′-bithiazole)(SCN)$_2$] $C_{20}H_{12}HgN_4S_4$, M=637.17, monoclinic, Space group $P2_1/n$, $a = 13.167(3)$, $b = 7.3032(15)$, $c = 22.474(8)$ Å, $\alpha = 90$, $\beta =$ 92.99(2), $\gamma = 90°$, $V = 2158.1(10)$ Å^3, Dc ($Z = 2$ f.u.) 1.961 mg/m^3, $F(000)$ 1216. Specimen: 0.30 × 0.30 × 0.20 mm; $T_{\max,\min}$ 0.974, 0.491, N 4441, N_0 4252, R 0.0268, R_w 0.0515.

Determination of the Structure

Crystallographic measurements were made at 293(2) K for Hg(*N*-(2,2′-diphenyl-4,4′-bithiazole)(SCN)$_2$] using a Siemens R3m/V diffractometer. The intensity data were collected within the range. $2.93 \leq \theta \leq 26.05°$ using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection was obtained from least-squares refinement. Intensities of 4441 unique reflections were measured, from which 2701 with $I > 2\sigma(I)$ were used in the refinement. The structure have been solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. R, R_w, with goodness-of-fit on F^2 0.812 are 0.0268, 0.0515. The final difference density map showed a maximum peak and hole of 0.569, $-0.530\,\mathrm{e}\,\text{Å}^{-3}$. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs were applied. All structural calculations were carried out with a PDP −11/23+ computer using the SDP-PLUS program package [15,16].

Crystal data and structure refinement and selected bond lengths and angles are given in Tables I and II. Anisotropy thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the

TABLE I Crystal data and structure refinement for DPBTZ

Identification code	DPBTZ
Empirical formula	$C_{20}H_{12}HgN_4S_4$
Formula weight	637.17
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 13.167(3)$ Å $\alpha = 90°$ $b = 7.3032(15)$ Å $\beta = 92.99(2)°$ $c = 22.474(8)$ Å $\gamma = 90°$
Volume	2158.1(10) Å^3
Z	4
Density (calculated)	1.961 mg/m^3
Absorption coefficient	7.533 mm^{-1}
$F(000)$	1216
Crystal size	$0.3 \times 0.3 \times 0.2$ mm^3
Theta range for data collection	2.93 to 26.05°.
Index ranges	$0 \Leftarrow h \Leftarrow 16$, $0 \Leftarrow k \Leftarrow 9$, $-27 \Leftarrow l \Leftarrow 27$
Reflections collected	4441
Independent reflections	4252 [R(int) = 0.02991]
Completeness to theta = 26.05°	99.6%
Absorption correction	Empirical
Max. and min. transmission	0.974 and 0.491
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4252/0/310
Goodness-of-fit on F^2	0.812
Final R indices [for 2701 rfln with $I > 2\sigma(I)$]	$R1 = 0.0268$, $wR2 = 0.0515$
R indices (all data)	$R1 = 0.0743$, $wR2 = 0.0552$
Largest diff. peak and hole	0.569 and −0.530 eÅ^{-3}

TABLE II Selected bond lengths and angles for the $Hg(DPBTZ)(SCN)_2$

Bond lengths (Å)		*Bond angles* (°)	
Hg(1)–S(3)	2.4025(15)	S(3)–Hg(1)–S(4)	147.46(5)
Hg(1)–S(4)	2.4073(15)	S(3)–Hg(1)–N(1)	108.14(9)
Hg(1)–N(1)	2.411(14)	S(4)–Hg(1)–N(1)	98.01(9)
Hg(1)–N(2)	2.459(4)	S(3)–Hg(1)–N(2)	99.71(10)
Hg(1)–S(4) #1	3.9318(15)	S(4)–Hg(1)–N(2)	107.32(9)
Hg(1)–S(3) #2	3.9640(18)	N(1)–Hg(1)–N(2)	70.10(13)

#1 $-x+1$, $-y+2$, $-z$; #2 $-x$, $-y+1$, $-z$.

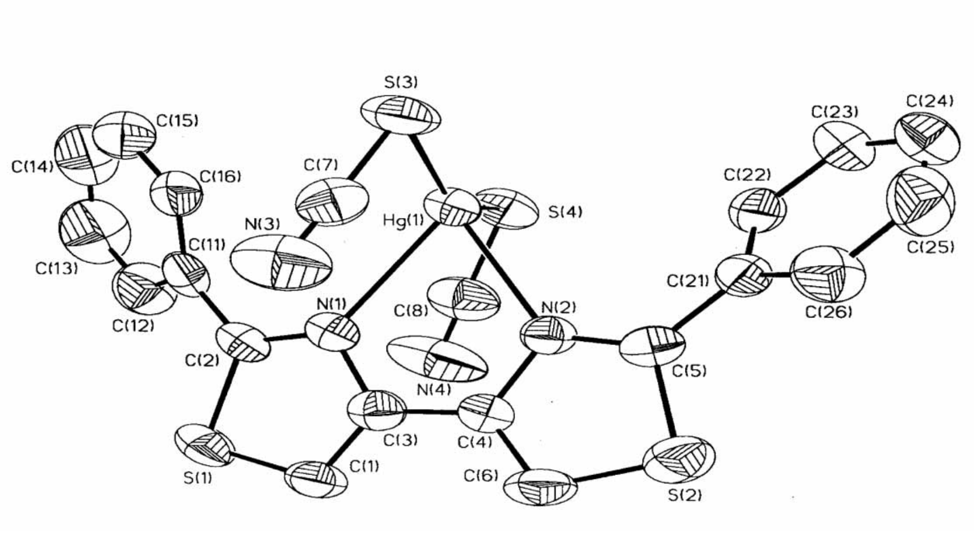

FIGURE 1 ORTEP diagram of $Hg(DPBTZ)(SCN)_2$.

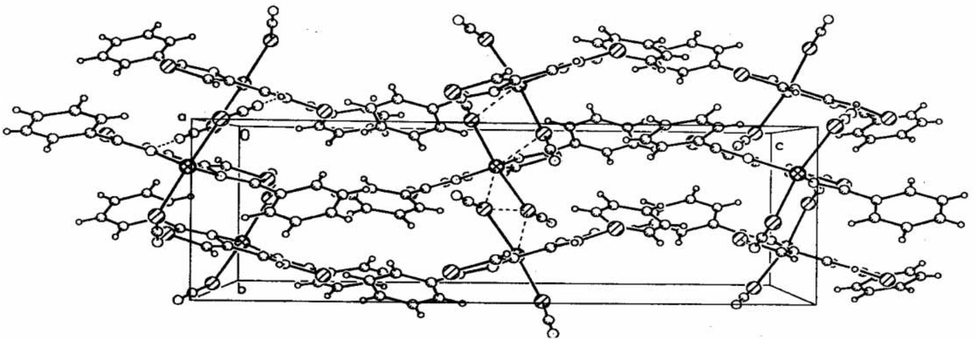

FIGURE 2 The unit cell and showing π–π stacking interaction in $Hg(DPBTZ)(SCN)_2$.

supplementary material available from A.R.M. ORTEP diagram and a perspective view of the packing in the unit cell are shown in Figs. 1 and 2.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Properties of the Complexes

Reaction between $Hg(SCN)_2$, $Tl(NO_3)_3$, CuCl, and $PdCl_2$ with 2,2′-diphenyl-4,4′-bithiazole ligand provided powder materials analyzing as $[Hg(DPBTZ)(SCN)_2]$, $[Tl(DPBTZ)(NO_3)_3]$, $[Cu(DPBTZ)(H_2O)Cl]$, and $[Pd(DPBTZ)Cl_2]$, respectively. The IR spectrum of the $[Hg(DPBTZ)(SCN)_2]$ complex shows ν(SCN) at 2100 cm^{-1} and $[Tl(DPBTZ)(NO_3)_3]$ complex shows $\nu(NO_3)$ at 1380 cm^{-1} and $[Cu(DPBTZ)(H_2O)Cl]$, and $[Pd(DPBTZ)Cl_2]$ complex shows ν(Cu–Cl) at *ca.* 320 and ν(Pd–Cl) at *ca.* 290, 340 cm^{-1}. Attempts to isolate $[Pd(DPBTZ)_2]Cl_2$, $[Cu(DPBTZ)_2]Cl$ were not successful, giving each time the 1 : 1 adduct. Also attempts to isolate a suitable single crystal of [Tl(DPBTZ)(NO_3)$_3$] for X-ray crystallography were not successful, only a powder was isolated. We tried to synthesize the complexes of Tl(I), Pb(II), Bi(III), Cd(II) ions with 2,2′-diphenyl-4,4′-bithiazole ligand but the complexes were not isolated. Preparation of complexes of 4,4′,5,5′-tetraphenyl-2,2′-bithizole ligand with Cu(II), Ni(II), Co(II), Co(III), Mn(II), Mn(III), Fe(II), Fe(III), Cr(III), Zn(II), Tl(III), Pb(II), Hg(II), Cu(I), Pd(II) were not successful. This point can be regarded as the initial electron withdrawing of phenyl rings and also their steric effects.

Crystal Structure of Hg(DPBTZ)(SCN)$_2$

A view of ORTEP diagram is shown in Fig. 1 and selected bond lengths and angles are given in Table II. The complex is built up of a monomeric Hg(SCN)$_2$ unit [Hg(1)–S(3) 2.4025(15) and Hg(1)–S(4) 2.4073(15) Å], with one 2,2′-diphenyl-4,4′-bithiazole ligand coordinated to the Hg via the two N atoms giving rise to a five-member chelate ring [Hg(1)–N(1) 2.411(4) Å and Hg(1)–N(2) 2.459(4) Å], in a distorted tetrahedral environment. The smallest and largest bond angles around the Hg atoms are S(3)–Hg(1)–S(4) 147.46(5)° and N(1)–Hg(1)–N(2) 70.10(13)°. Intermolecular interaction between Hg(1) and two S atoms of two neighboring molecules, Hg(1)–S(4) $\neq 1$, 3.9318(15) Å and Hg(1)–S(3) $\neq 2$, 3.9640(18) Å, make the Hg(1) distorted from a tetrahedron to a distorted pseudo-octahedral geometry. The intermolecular Hg(1)...S interaction links the molecules in chains along the *a*-axis (Fig. 2). However, the distances Hg(1)...S(4) $\neq 1$, 3.9318(15) Å ($\neq 1 = -x, y+2, -z$) and Hg(1)–S(3) $\neq 2$, 3.9640(18) Å ($\neq 2 = -x, -y+1, -z$) cannot be taken as indicative of additional weak interactions (both are larger than the sum of the Van der Waals radii, 3.53Å [17]). This is in contrast to the lead(II) complexes, in which the thiocyanate ion is coordinated via N atom [10,18,19]. In the present mercury complex the thiocyanate ions are coordinated via S atoms. This shows that Hg^{+2} ion is softer than the Pb^{+2} ion.

There are π–π stacking interactions (charge-transfer arrays) [20,21] between the parallel aromatic rings of adjacent chains, as shown in Fig. 2. The planar species with mean molecular planes close to parallel and separated by a distance of ~ 3.5 Å, are close to the planes in graphite.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road,Cambridge CB2 1EZ, UK on request, quoting the deposition number 169024.

Acknowledgments

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