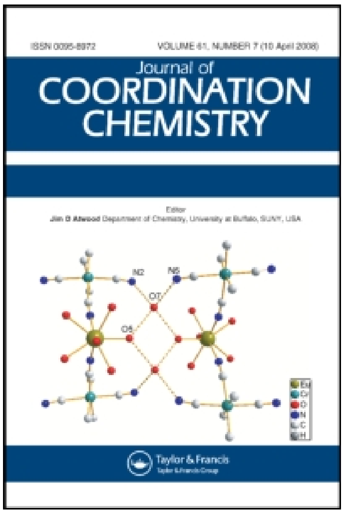

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Lead(II) complexes of 2,2′-diamino-4,4′-bithiazole (DABTZ) including crystal structure of a novel 1D chain polymer, [PB(DABTZ)(μ-SCN)(μ-NO$_3$)]$_n$

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Three new 2,2′-diamino-4,4′-bithiazole (DABTZ) lead(II) complexes were synthesized and characterized by elemental analyses, IR-, ^{1}H-NMR-, and ^{13}C-NMR-spectroscopy. The single crystal X-ray structural analysis of [Pb(DABTZ)(μ-SCN)(μ-NO$_3$)]$_n$ shows the complex to be a 1D chain polymer as a result of sequential thiocyanate and nitrate bridging. The Pb atoms are seven-coordinated by two nitrogen atoms of the 2,2′-diamino-4,4′-bithiazole, three nitrate and two thiocyanate ligands. The arrangement of the 2,2′-diamino-4,4′-bithiazole, nitrate and thiocyanate ligands does not suggest a gap in the coordination around the Pb^{II} ion, caused by a stereo-active lone pair of electrons on lead(II) where the coordination around the lead atoms is the less common holodirected.

Keywords: Lead, π–π stacking; Crystal structure; 2,2′-diamino-4,4′-bithiazole; Lone pair

1. Introduction

The effects of cobalt(II) and nickel(II) complexes with 2,2′-diamino-4,4′-bithiazole on the DNA synthesis of sarcoma 180 tumour cells has been investigated by the technique of isotopic liquid scintillation. The results indicated that the complexes inhibit DNA synthesis of the tumour cells [1]. In our current studies, we reported the preparation and characterization of a series of lead(II) and bismuth(III) complexes of 4,4′-bithiazole, [Pb(BTZ)(NCS)$_2$]$_n$, [Pb(BTZ)$_2$(NO$_3$)$_2$] [2], [Pb$_2$(BTZ)$_4$(NO$_3$)(H$_2$O)](ClO$_4$)$_3$ [3] and [Bi(BTZ)$_2$(NO$_3$)$_3$] (BTZ = bithiazole) [4]. Some complexes of diphenyl (DPBTZ)

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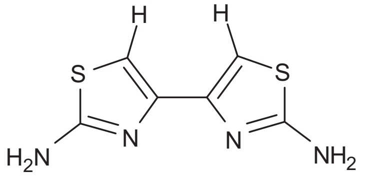
and diamine derivatives of bithiazole have recently been reported [5–9]. The introduction of the amine groups changes both the electronic and steric properties of the ligand and the metal complexes.



DABTZ

In relation to work on different metal ions [1, 7–9], we became interested in DABTZ complexes with Pb^{II}. In this paper, we report the syntheses and characterization of coordination compounds formed between the DABTZ ligand and lead(II) salts and a 1D chain polymer involving sequentially bridging thiocyanate and nitrate anions, $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$.

2. Experimental

2.1. *Physical measurements*

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. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

2.1.1. Preparation of the 2,2′-diamino-4,4′-bithiazole (DABTZ). The 2,2′-diamino-4,4′-bithiazole ligand was prepared from 1,4-dibromobutane-2,3-dione and thiourea by the method of Erlenmeyer and Ueberwasser [10].

2.1.2. Preparation of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$. The complex was prepared by dissolving lead(II) nitrate (0.33 g, 1 mmol) and potassium thiocyanate (0.097 g, 1 mmol) in distilled water (15 mL) and adding an alcoholic solution of 2,2′-diamino-4,4′-bithiazole (DABTZ) (0.198 g, 1 mmol). The resulting solution was stirred for 5 h at room temperature, and then allowed to stand for 2–3 days in a refrigerator (ca. 6°C). Brown powder precipitated, was filtered off, washed with acetone and ether, and air dried (d.p. 210°C). Yield: 0.210 g, 40%. Anal. Calcd for $C_7H_6N_6O_3PbS_3$ (525.55): C, 15.98; H, 1.14; N, 10.65. Found: C, 15.70; H, 1.40; N, 10.90. IR (film) selected bands: $\nu = 719$(m), 974(w), 1341(vs), 1377(vs), 1502(vs), 1602(vs), 2035(s), 3085(w), 3255(s) and 3365(s) cm^{-1}. ^1H NMR (DMSO): $\delta = 6.53$(s, 2H), 7.250(s, 4H). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 102.711$, 146.121, and 169.516.

2.1.3. Preparation of $Pb(DABTZ)I_2$. The complex was prepared by dissolving lead(II) acetate (0.36 g, 1 mmol) and potassium iodide (0.332 g, 2 mmol) in distilled water

(15 mL) and adding an alcoholic solution of 2,2′-diamino-4,4′-bithiazole (DABTZ) (0.198 g, 1 mmol). The resulting solution was stirred for 5 h at room temperature, and then allowed to stand for 2–3 days in a refrigerator (ca. 6°C). Brown powder of the desired product precipitated, was filtered off, washed with acetone and ether and air-dried (m.p. 244°C). Yield: 0.363 g, 55%. Anal. Calcd for $C_6H_6N_4S_2PbI_2$ (660): C, 10.90; H, 0.91; N, 8.84. Found: C, 10.50; H, 1.05; N, 8.70. IR (film) selected bands: $\nu = 689$(m), 1013(w), 1290(s), 1448(w), 1515(vs), 1588(vs), 3100(w), 3270(m) and 3420(s) cm^{-1}. ^{1}H NMR (DMSO): $\delta = 6.50$(s, 2H), 7.255(s, 4H). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 102.712$, 146.125, and 169.510.

2.1.4. Preparation of Pb(DABTZ)($CH_3COO)_2$. The complex was prepared by dissolving lead(II) acetate (0.36 g, 1 mmol) in distilled water (15 mL) and adding an alcoholic solution of 2,2′-diamino-4,4′-bithiazole (DABTZ) (0.198 g, 1 mmol). The resulting solution was stirred for 5 h at room temperature, and allowed to stand for 2–3 days in a refrigerator (ca. 6°C). Brown powder of the desired product precipitated, was filtered off, washed with acetone and ether and air-dried (d.p. 186°C and m.p. 218°C). Yield: 0.235 g, 45%. Anal. Calcd for $C_{10}H_{12}N_4O_4S_2Pb$ (524): C, 22.90; H, 2.29; N, 10.68. Found: C, 22.60; H, 2.15; N, 10.70. IR (film) selected bands: $\nu = 690$(m), 773(m), 1036(w), 1262(s), 1338(s), 1398(s), 1502(vs), 1603(vs), 1627(s), 2890(w), 3110(w), 3260(m) and 3365(s) cm^{-1}. ^{1}H NMR (DMSO): $\delta = 1.729$(s, 6H), 6.50(s, 2H), 7.255(s, 4H). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 27.536$ ($^{13}CH_3$–COO), 178.817 (CH_3–^{13}COO), 102.712, 146.125, and 169.510.

2.2. *X-ray structure determination*

The intensity data of the title complex were collected using a STOE IPDS 2 diffractometer (Mo–Kα radiation, $\lambda = 0.71073$ Å) at 193 K. The structure was solved by using the programs SIR97 [11], SHELXL-97 [12] and WinGX [13]. The molecular plots were prepared by using ORTEP III [14]. The details of the data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Syntheses*

Reaction between 2,2′-diamino-4,4′-bithiazole (DABTZ) and lead(II) acetate, and mixtures of lead(II) nitrate with potassium thiocyanate, provided crystalline $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$ and Pb(DABTZ)($CH_3COO)_2$. Also reaction between 2,2′-diamino-4,4′-bithiazole (DABTZ) and mixtures of lead(II) acetate and potassium iodide provided crystalline Pb(DABTZ)I_2.

The IR spectra of all three complexes show absorption bands resulting from skeletal vibrations of aromatic rings in the 1400–1600 cm^{-1} range. The IR spectrum of the $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$ complex shows $\nu(NO_3)$ at ca. 1377 cm^{-1}, and ν(SCN) at ca. 2035 cm^{-1}. The absorption bands of the NH_2 groups in the three complexes are observed as a strong band centered at 3255 and 3420 cm^{-1}, and are significantly shifted to the lower frequency region compared to the free ligand (3257 and 3430 cm^{-1}). The relatively low frequency is indicative of hydrogen bonding.

Table 1. Crystal data and structure refinement for $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$.

Complex	$[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$
Empirical formula	$C_7H_6N_6O_3PbS_3$
Molecular weight	525.55
Temperature [K]	193(2)
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	7.0570(11)
b[Å]	9.8170(14)
c [Å]	10.4970(17)
α [°]	115.776(13)
β [°]	94.697(13)
γ [°]	94.751(13)
V [Å^3]	646.95(17)
Z	2
D_{calcd} [g cm^{-3}]	2.698
μ [mm^{-1}]	13.539
$F(000)$	488
Crystal size [mm^3]	$0.43 \times 0.33 \times 0.17$
θ Range [°]	2.17 to 25.66
Index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-12 \le l \le 12$
Reflections collected	8574
Independent reflections (R_{int})	2439 (0.0985)
Reflections observed (>2σ)	2407
Absorption correction	Numerical
Max. and min. transmissions	0.093 and 0.377
Data/restraints/parameters	2439/0/197
Goodness-of-fit on F^2	1.157
R [$I > 2\sigma(I)$]	$R1 = 0.0324$, $wR2 = 0.0858$
R (all data)	$R1 = 0.0328$, $wR2 = 0.0862$
Largest diff. Peak and hole (e Å^{-3})	3.502 and −2.047

The relatively weak band at 2890 cm^{-1} is assigned to the $\nu(CH_3)$ of the methyl group of acetate and the relatively weak bands around 3100 cm^{-1} are assigned to the ν(CH) mode of the aromatic bithiazole rings in the three complexes. The characteristic bands of the carboxylate group in the $Pb(DABTZ)(CH_3COO)_2$ complex appear about $1502\nu_{as(C\text{–}O)}$ and $1398\nu_{sym(C\text{–}O)}$ cm^{-1}. The $\Delta\nu$ value ($\nu_{as} - \nu_{sym}$) of 104 cm^{-1} indicates that the carboxylate group is bidentate [15–19].

The ^{1}H NMR spectrum of the DMSO solution of the three complexes displays two distinct absorption bands at 6.50(s, 2H) and 7.255(s, 4H) ppm assigned to the aromatic and amino protons, respectively. In $Pb(DABTZ)(CH_3COO)_2$, a band at 1.729 (s, 6H) is assigned to methyl protons of acetate. The ^{13}C NMR spectrum of the DMSO solution of the three complexes displays three distinct absorption bands at 102.712, 146.125, and 169.510 ppm, assigned to the aromatic carbons. In Pb(DABTZ) $(CH_3COO)_2$, bands at 27.536 ($^{13}CH_3$–COO) and 178.817 (CH_3–^{13}COO) assigned to carbons of acetate.

3.1.1. Crystal structure of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$. An ORTEP drawing of the title complex is shown in figure 1, while selected bond distances and angles are listed in table 2. The crystal structure of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$ consists of one-dimensional polymeric units with the basic repeating dimeric $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]$ moiety; the structure may be considered

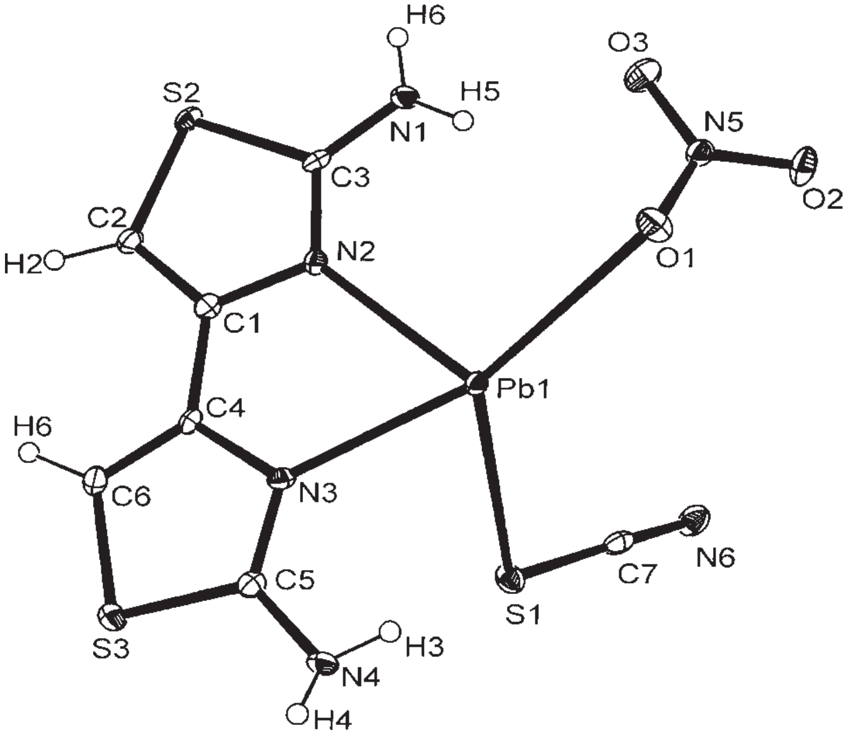


Figure 1. ORTEP diagram of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$ with ellipsoids (30% probability).

Table 2. Bond lengths [Å] and angles [°] for $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$.

Pb1–N2	2.552(5)	N3–Pb1–N6#	119.4(2)
Pb1–N3	2.527(5)	N3–Pb1–N2	66.43(18)
Pb1–N6	2.547(6)	N6–Pb1–N2#	76.83(19)
Pb1–S1	2.9336(18)	N3–Pb1–S1#	75.36(12)
Pb1–O2	2.829(6)	N6–Pb1–S1#	79.08(15)
Pb1–O1	2.851(6)	N2–Pb1–S1	114.89(12)
Pb1–O1#	2.985(5)	N6–C7–S1	178.7(7)
		N3–Pb1–O2	85.69(12)
		N3–Pb1–O1	156.14(14)
		N3–Pb1–O1#	124.72(12)
		N6–Pb1–O2	135.14(12)
		N6–Pb1–O1	76.60(13)
		N6–Pb1–O1#	94.63(12)
		N2–Pb1–O2	146.76(12)
		N2–Pb1–O1	103.89(11)
		N2–Pb1–O1#	168.71(12)
		O2–Pb1–O1	94.41(12)
		O2–Pb1–S1	72.03(12)
		O2–Pb1–O1#	43.52 (14)
		O1–Pb1–S1	127.35(12)
		O1–Pb1–O1#	66.52(12)
		S1–Pb1–O1	69.84(13)

Symmetry operations: (#) $2-x$, $1-y$, $-z$.

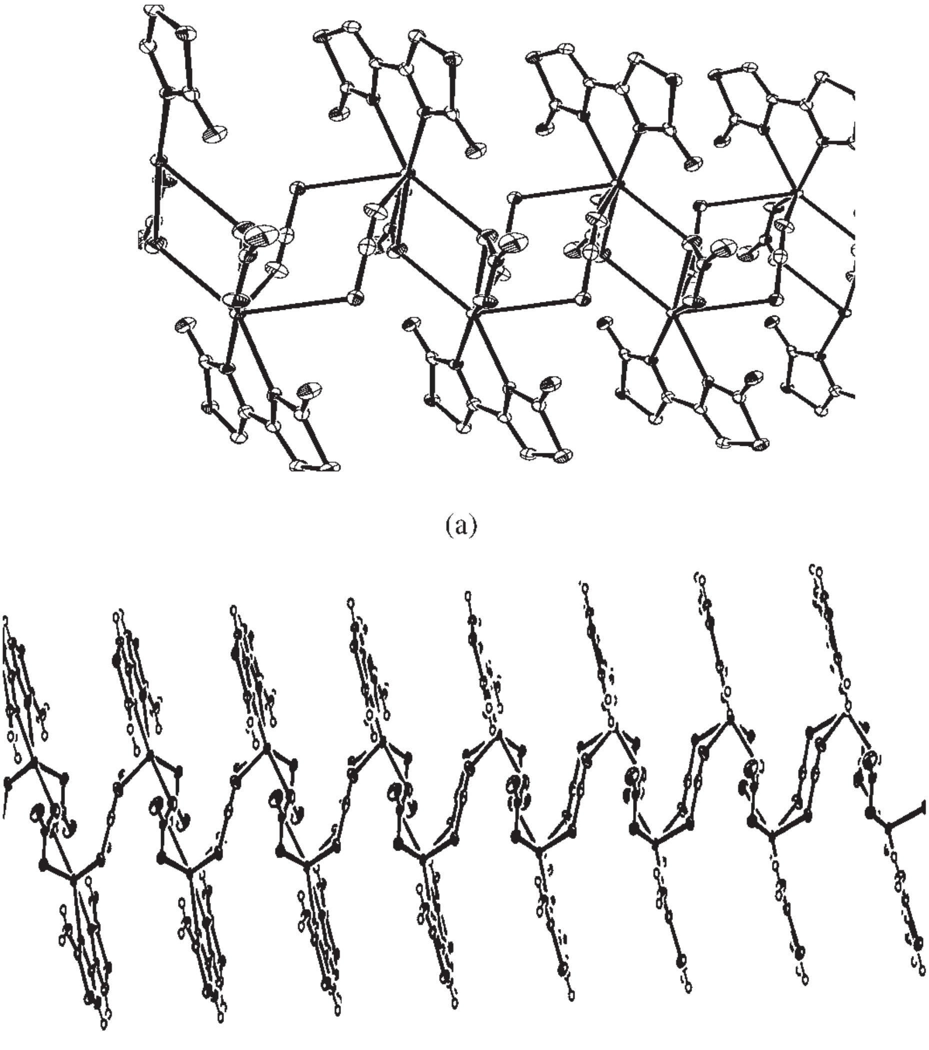


Figure 2. (a) A view of the Pb_2O_2 rhomb forming the basic link of the repeating polymeric units of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$; (b) a view of [001] layer, showing a one-dimensional chain polymer.

a one-dimensional coordination polymer of lead(II) consisting of linear chains formed by bridging thiocyanate and nitrate ligands. Two SCN^- anions bridge two lead(II) ions *via* the S and N atoms and the $Pb–N_{bridging\ NCS}$ and $Pb–S_{bridging\ SCN}$ distances are 2.547(6) and 2.9336(18) Å, respectively. The two NO_3^- anions adopt bidentate chelating, and bridging coordination modes. The NO_3^- ligand coordinates to Pb1 as a bidentate ligand with bond distances Pb1–O2 = 2.829(6) and Pb1–O1 = 2.851(6) Å; O1 of NO_3^- ligand also bridges two adjacent lead(II) ions with a bond distance of $Pb1–O1_{bridging}$ = 2.985(5) Å. The repeating unit in the linear chains is $[Pb(NO_3)(SCN)]$. The individual polymeric chains are almost parallel to each other and further coordinated by the DABTZ ligands through two N atoms behaving as a bidentate ligand with Pb–N distances of 2.552(5) and 2.527(5) Å.

The coordination number in this lead(II) complex is seven with a PbN_3O_3S chromophore (two SCN^-, three NO_3^- and two of DABTZ ligands) and the lead atoms are sequentially bridged by SCN^- and NO_3^- ligands to produce polymer units in solid state. The NO_3^- ligand acts as a bidentate, and bridging group (totally tridentate) in a μ-1, 3 mode where two oxygen atoms of the nitrate group coordinate to a lead(II) ion and also one bridges the two adjacent lead(II), yielding the Pb_2O_2 rhomb. The thiocyanate anions are coordinated both sulfur and nitrogen atoms and act as a bridging group (totally bidentate), yielding the $Pb_2(NCS)_2$ rhomb (figure 2a).

The structure of $[Pb(DABTZ)(\mu\text{-}SCN)(\mu\text{-}NO_3)]_n$ is interesting in several aspects. It is a new 1D framework type with two ligands simultaneously bridging in its crystal structure. Coordination around the lead atoms is holodirected and the arrangement of DABTZ, nitrate and thiocyanate ligands do not suggest any gap or hole in coordination geometry around the metal, indicating that the lone pair of electrons on lead(II) is inactive. The lone pair in most lead(II) complexes is active, particularly with seven coordinate [20]. The present, somewhat fortuitous, determination of the structure of mixed-anion, nitrate and thiocyanate, Pb(II) complex of DABTZ ligand indicates the situation in the coordination polymers to be somewhat more complicated and the spontaneous aggregation of several bridging ligands may cause the gap to disappear and the lead(II) to take a less common holodirected geometry [20].

Supplementary material

Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-249989. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 36033; email: deposit@ccdc.cam.ac.uk).

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