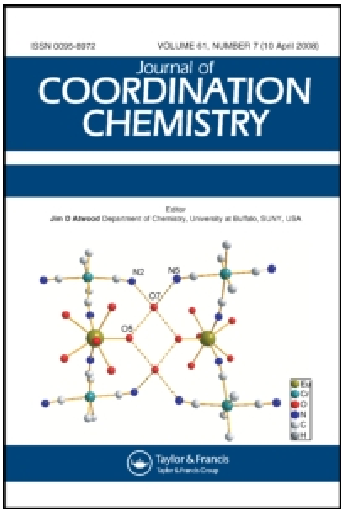

Journal of Coordination Chemistry

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

Synthesis and thermal, fluorescence and structural studies of mixed-ligand lead(II) complexes with 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazole

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First published on: 20 November 2010

To cite this Article Hosseinian, Akram and Mahjoub, Ali Reza(2010) 'Synthesis and thermal, fluorescence and structural studies of mixed-ligand lead(II) complexes with 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazole', Journal of Coordination Chemistry, 63: 24, 4245 — 4258, First published on: 20 November 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.533763

URL: http://dx.doi.org/10.1080/00958972.2010.533763

Journal of Coordination Chemistry
Vol. 63, No. 24, 20 December 2010, 4245–4258

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Synthesis and thermal, fluorescence and structural studies of mixed-ligand lead(II) complexes with 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole

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(*Received 30 May 2010; in final form 13 September 2010*)

The synthesized ligand (DADMBTZ = 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole) is used for preparing these two new 1 : 2 adducts of $[Pb(DADMBTZ)_2(NO_3)X]$ $X = CH_3COO^-$ (**1**) and $X = ClO_4^-$ (**2**) complexes. Characterization was done by IR, ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, and single crystal X-ray determination. UV-Vis and fluorescence spectra were studied. Thermal stabilities of **1** and **2** were studied by thermal gravimetric (TG) and differential thermal analysis (DTA). The coordination number of Pb in **1** is seven (four by the chelating DADMBTZ, two oxygens of acetate and one oxygen of nitrate), whereas in **2** it is five (four by the chelating DADMBTZ and one oxygen of nitrate). Coordination geometries of **1** and **2** show a possible vacant site around Pb(II), occupied possibly by a stereoactive lone pair of electrons on lead(II); coordination around lead is hemidirected with a significant gap *trans* to chelating DADMBTZ, nitrate, and acetate. Both **1** and **2** make 3-D networks *via* N–H $\cdots$ O and N–H $\cdots$ N hydrogen bonds; O–H $\cdots$ O hydrogen bonds are found in the network for **1**.

Keywords: X-ray; Fluorescence; Thermal; Coordination; Bithiazole; Hemidirected

1. Introduction

Coordination chemistry of Pb(II) has long been of interest for many reasons, including understanding of toxicity of lead compounds [1–3], though there are certainly more positive features [4, 5]. A fundamental aspect that has attracted considerable attention is whether or not the coordination geometry about Pb(II) reflects repulsive effects due to a 'stereochemistry active' lone pair [6], usually considered to be the $6s^2$ electrons [7, 8].

Recent structural studies on Pb^{II} compounds [9, 10] have provided a detailed analysis of coordination-sphere distortions as a consequence of the presence of such lone pairs. Stereochemical activity of the lone pair in divalent Pb compounds has been discussed by Shimoni-Livny *et al.* based on a thorough review of crystal data available from the

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.533763

Cambridge Structural Database (*CSD*) and by means of *ab initio* calculations. These authors classified lead coordination as '*holodirected*' when the bonds to ligands are directed throughout the surface of an encompassing sphere, and as '*hemidirected*' in cases where the bonds are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to ligands. The latter case, present in all Pb^{II} complexes with coordination numbers 2–5, is also quite common in Pb^{II} complexes with coordination numbers 6, 7, and 8, but has not been found in those with higher coordination numbers, where holodirected geometry is the rule. The lone-pair activity can also depend on: (1) hard or soft ligands, (2) attractive or repulsive interactions among ligands, (3) the *p* character of lone pairs, and (4) the number of electrons (charge) transferred from the ligands to the metal [10, 11].

Mixed ligand complexes whose difference is only in one part of the coordination sphere are interesting. The importance of this type of lead(II) complex is due to the influence of different ligands on the structure and lone pair activity of the complexes. Reports of the crystal structures of mixed ligand 1 : 1 adducts $[Pb(phen)(O_2CCH_3)X]$ $X = NCS^-$, NO_3^-, ClO_4^- [12] and $[Pb(bpy)(O_2CCH_3)X]$ $X = I^-$, NO_3^-, ClO_4^- and 1 : 2 adducts of $[Pb(phen)_2(O_2CCH_3)X]$ $X = NCS^-$, NO_3^-, ClO_4^- complexes described the presence of bridging acetate and its influence on the coordination stereochemistry of lead(II) and also on their structures. The coordination chemistry of lead(II) with N- and O-donors has been frequently discussed in regard to the coordination and stereoactivity of the valence shell lone electron pairs [13–17].

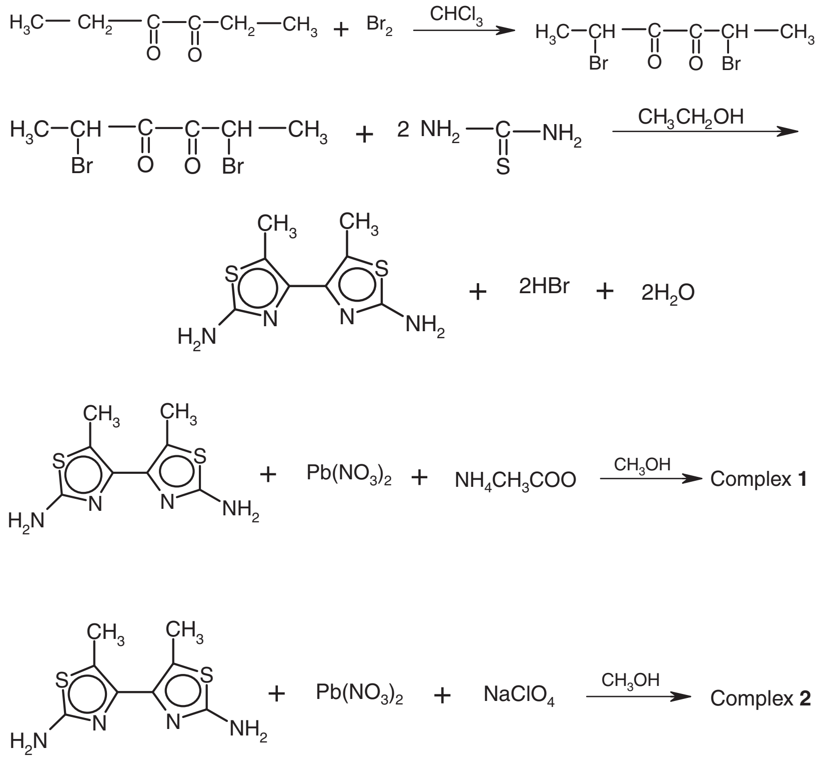
Aromatic heterocyclic polymers containing bithiazole rings are good ligands because two nitrogens in the bithiazole rings are able to chelate metal ions to form stable five-membered rings. In addition, transition metal complexes of bithiazole ligands have found increasing applications. For instance, Ni and Co complexes of 2,2′-diamino-4,4′-bithiazole are effective inhibitors of DNA synthesis in tumor cells [18–25] and Fe(II), Fe(III), and Cu(II) complexes have found application in soft magnetic materials [26–30].

Following our previous study on bithiazole derivatives and their complexes, the crystal structure of 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazolium dibromide mono hydrate was reported [31–33]. In this article, we report the synthesis and characterization of two new lead(II) complexes containing nitrate $[Pb(DADMBTZ)_2(NO_3)X]$ ($X = CH_3COO^-$, ClO_4^-).

2. Experimental

2.1. *Preparation of 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole*

In this study, 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazolium dibromide mono hydrate was neutralized with NaOH solution ($1\,mol\,L^{-1}$) giving 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole which was then recrystallized from $CHCl_3$; 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole was prepared by the procedure described previously. Reaction of 2,5-dibromo-3,4-hexadione and thiourea leads to 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazolium dibromide mono hydrate. Neutralization with NaOH solution ($1\,mol\,L^{-1}$) produces a bright yellow solid which was characterized as DADMBTZ (scheme 1).



Scheme 1. Synthesis of complexes **1** and **2**.

Analysis for $C_8H_{10}N_4S_2$ (226): C, 42.50 (Calcd C, 42.47); H, 4.25 (4.42); and N, 24.70 (24.77)%. IR (KBr, cm^{-1}): ν(N–H) 3305 (s), 3420 (m), $\nu(C–H)_{al}$ 2905 (m), ν(C=C) 1683 (m), ν(C=N) 1523 (vs), ν(C–S–C) 753 (m), ν(C=S) 627 (w). ^{1}H-NMR ([D6]DMSO, 25°C, TMS) δ: 6.5 (4H, $2NH_2$), 2.2 (6H, $2CH_3$). ^{13}C-NMR ([D6]DMSO, 25°C, TMS) δ: 164.1, 117.6, 114.1, and 11.83. UV-Vis in DMSO (λ_{max}, nm): 229.5, 229 ($\varepsilon = 25{,}500\ mol\ L^{-1}\ cm^{-1}$).

2.2. *Preparation of [Pb(DADMBTZ)$_2$(NO$_3$)(CH$_3$COO)]•H$_2$O (1)*

In this study, **1** was prepared by reaction of a methanolic solution of $Pb(NO_3)_2$ (0.1656 g, 0.5 mmol) with a methanolic solution of 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole (0.226 g, 1 mmol) and excess of $[NH_4][CH_3COO]$. After standing for 12 days at room temperature, colorless crystals were obtained, filtered, washed with methanol and cold ether, and dried invacuum. The complex is soluble in DMSO and insoluble in water, methanol, and $CHCl_3$ (0.519 g, Yield: 65%).

Analysis for $C_{18}H_{25}N_9O_6PbS_4$ (798.90): C, 27.00 (Calcd 27.03), H, 3.14 (3.12), and N, 15.71 (15.77)%. IR data (KBr, cm^{-1}): ν(N–H) 3355 (s) – 3170 (s), $\nu(C–H)_{al}$ 2965 (w), ν(C=C) 1623 (m), ν(C=N) 1509 (s), ν(Skeletal vibration) 1379 (w) and 1343 (s), $\nu_{as}(COO^-)$ 1509 (s), $\nu_s(COO^-)$ 1379 (w), $\nu(NO_3^-)$ 1379, 1343, and 1108, ν(C–S–C) 746 (w), ν(C=S) 655 (m), ν(Pb–N) 501 (m). ^{1}H-NMR ([D6]DMSO, 25°C, TMS) δ: 7.0

(4H, $2NH_2$), 2.2 (6H, $2CH_3$), and 1.8 (6H, $2CH_3$). ^{13}C-NMR ([D6]DMSO, 25°C, TMS) δ: 179.28, 166.33, 140.55, 117.47, 27.18, and 12.38. UV-Vis in DMSO (λ_{max}, nm): 232.5. 232 ($\varepsilon = 24{,}670\,\mathrm{mol\,L^{-1}\,cm^{-1}}$).

2.3. *Preparation of [Pb(DADMBTZ)$_2$(NO$_3$)(ClO$_4$)] (2)*

In this study, **2** was prepared by reacting a methanolic solution of $Pb(NO_3)_2$ (0.1656 g, 0.5 mmol) with a methanolic solution of 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole (0.226 g, 1 mmol) and excess of $NaClO_4$. After standing 15 days at room temperature, yellow crystals were obtained, filtered, washed with methanol and cold ether, and dried in vacuum. The complex is soluble in DMSO and insoluble in water, methanol, and $CHCl_3$ (0.55 g, Yield: 67%).

Analysis for $C_{16}H_{20}ClN_9O_7PbS_4$ (821.29): C, 23.32 (Calcd C, 23.37); H, 2.45 (2.43); and N, 15.29 (15.34)%. IR data (cm^{-1}): ν(N–H) 3425 (s) – 3195 (s), $\nu(C–H)_{al}$ 2940 (m), ν(C=C) 1615 (s), ν(C=N) 1507 (s), ν(Skeletal vibration) 1420 (s) and 1339 (w), ν(Cl–O) 1153 (w), 1103 (s), and 1029 (w), $\nu(NO_3^-)$ 1383, 1339, and 1029, ν(C–S–C) 757 (w), ν(C=S) 616 (m), ν(Pb–N) 459 (w). ^{1}H-NMR ([D6]DMSO, 25°C, TMS) δ ppm: 7.0 (4H, $2NH_2$), 2.4 (6H, $2CH_3$). ^{13}C-NMR ([D6]DMSO, 25°C, TMS) δ ppm: 170.9, 117.1, 114.0, and 12.6. UV-Vis in DMSO (λ_{max}, nm): 276 ($\varepsilon = 25{,}700\,\mathrm{mol\,L^{-1}\,cm^{-1}}$).

2.4. *Instrumental procedures*

Carbon, hydrogen, and nitrogen analyses were performed by microanalytical methods using a Heraeus CHN–O–RAPID apparatus. ^{1}H-NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H chemical shifts were determined relative to internal TMS. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer from KBr pellets (4000–370 cm^{-1}). Electronic absorption spectra were recorded on a Shimadzu UV-Vis 2100 recording spectrophotometer. Emission and excitation spectra of complexes were determined in DMSO using a Shimadzu RS-5000 fluorescence spectrophotometer at room temperature. The measurements were performed using a PL-STA 1500 Thermal/Sciences in static air, in a ceramic crucible with α-Al_2O_3 as the reference compound, at a heating rate of 5 K min^{-1}; 200-mg samples were used.

2.5. *Crystal structure determinations*

Crystallographic data of $[Pb(DADMBTZ)_2(NO_3)(CH_3COO)] \cdot H_2O$ (**1**) and $[Pb(DADMBTZ)_2(NO_3)(ClO_4)]$ (**2**) are given in table 1. X-ray diffraction measurements were performed at 120 K using a CAD4 Enraf-Nonius diffractometer (**1**) and Bruker APEX2 CCD area detector diffractometer (**2**), equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the φ–ω scan technique. Empirical absorption corrections were applied using SADABS.

The structures were solved by direct methods and subsequent Fourier difference maps and refined with anisotropic displacement parameters. Hydrogens attached to carbon and nitrogen were positioned geometrically, with U_{iso} values derived from the

Table 1. Crystallographic data and structure refinement for [Pb(DADMBTZ)$_2$(NO$_3$)(CH$_3$COO)]$\cdot$H$_2$O (**1**) and [Pb(DADMBTZ)$_2$(NO$_3$)(ClO$_4$)] (**2**).

Empirical formula	$C_{18}H_{25}N_9O_6S_4Pb$ (**1**)	$C_{16}H_{20}ClN_9O_7PbS_4$ (**2**)
Formula weight	798.90	821.29
Temperature (K)	566(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pbca
Unit cell dimensions (Å, °)		
a	21.541(4)	13.392(2)
b	15.357(3)	15.922(2)
c	19.109(4)	25.227(4)
α	90	90
β	118.51(3)	90
γ	90	90
Volume (Å^3), Z	5554.7(19), 8	5379.1(14), 8
Calculated density (Mg m^{-3})	1.911	2.028
Absorption coefficient (mm^{-1})	6.427	6.738
$F(000)$	3120	3184
Crystal size (mm^3)	$0.19 \times 0.17 \times 0.14$	$0.45 \times 0.35 \times 0.22$
θ range for data collection (°)	1.71–25.99	2.22–29.00
Limiting indices	$-26 \leq h \leq 0$; $-18 \leq k \leq 0$; $-20 \leq l \leq 23$	$-18 \leq h \leq 18$; $-21 \leq k \leq 21$; $-34 \leq l \leq 34$
Reflections collected	5546	60494
Independence reflection	5405 [R(int) = 0.0619]	70,000 [R(int) = 0.1017]
Completeness to θ (%)	99.0	97.8
Absorption correction	Pci-scan	Semi-empirical from equivalents
Max. and min. transmission	0.403 and 0.308	0.3187 and 0.1514
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5405/0/347	7000/52/424
Goodness-of-fit on F^2	1.063	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0350$, $wR_2 = 0.0814$ $R_1 = 0.0678$, $wR_2 = 0.0896$	$R_1 = 0.0534$, $wR_2 = 0.0881$ $R_1 = 0.1163$, $wR_2 = 0.1097$
Largest difference peak and hole (e Å^{-3})	1.151 and −1.160	1.556 and −0.858

corresponding carbon and nitrogen. The structures of the title compounds were refined with SHELXL-97 [34–36].

3. Results and discussion

3.1. *Synthesis*

Reaction of Pb(NO$_3$)$_2$ with DADMBTZ in 1 : 2 ratio in the presence of an excess of ammonium acetate or sodium perchlorate leads to **1** and **2**, respectively (scheme 1).

The IR spectrum of **1** shows bands at 1379 and 1343 cm^{-1} for skeletal vibrations of bithiazole ring suggesting that coordination occurred through the ring nitrogen of bithiazole. Complex **2** similarly shows bands at 1339 and 1420 cm^{-1}. Comparison of skeletal vibrations between complexes and free ligand provides evidence of coordination through the bithiazole ring nitrogens.

Table 2. Absorption (λ_{abs}), emission (λ_{em}) band maxima[a] of **1–4**.

Compound	$\lambda^{-1}_{abs\,nm}$	$\lambda^{-1}_{em\,nm}$ (298 K)
$[(C_4H_6N_2S)_2]$	229.5	360
$[Pb(DADMBTZ)_2(NO_3)(CH_3COO)]$ (**1**)	232.5	363.2
$[Pb(DADMBTZ)_2(NO_3)(ClO_4)]$ (**2**)	276	363.2

[a]Solvent: DMSO.

The carboxylato is a multifunction ligand with a number of binding geometries: monodentate and bidentate either by chelating, or by forming a bridge. Many complexes containing carboxylates play a key role in biochemical systems containing mono- or polymetallic sites [37]. The nature of carboxylate coordination can be determined by IR spectroscopy [38]. The $\Delta\nu$ value (ν_{as}–ν_{sym}) in **1** is 130 cm^{-1}, indicating that the carboxylate coordinates bidentate [39–41]. This is confirmed by the crystal structure.

Nitrate could be mono and bidentate chelated and also could be bridged. One oxygen of this anion is linked to two different hydrogens. In IR spectra of all nitrate complexes, the region associated with the NO stretches shows many bands, the most intense at 1379, 1343, and 1108 cm^{-1} in **1** and 1383, 1339, and 1029, which clearly identify these species as containing coordinate nitrate [42, 43]. Complexity of these bands suggests the presence of mono and bidentate nitrate, confirmed by X-ray diffraction studies of **1** and **2**. The strong absorption bands at 1153, 1103, and 1029 cm^{-1} are assigned to $\nu(ClO_4^-)$ in **2**. The IR spectra of **1** and **2** are in agreement with the X-ray structural data.

Comparison of ^{1}H-NMR spectra in free ligand with the complexes shows a shift for the amine from 6.5 for the ligand to 7.0 for **1** and **2**.

^{13}C-NMR spectrum shows two singlets with chemical shifts at 27.18 and 179.28 ppm for methyl and carbonyl groups of acetate in **1**.

Comparison of ^{13}C-NMR spectra of **1**, **2** and the free ligand shows carbon in the thiazole rings, the donor nitrogen, sulfur, and amine group shifts downfield from 164.1 ppm in free ligand to 166.33 ppm in **1** and 170.9 ppm in **2**.

UV-Vis spectra in DMSO display intense absorption bands at 229 for free ligand, 232 and 276 nm for **1** and **2**, respectively (table 2), ascribed to the bithiazole π–π* and n–π* transitions [44, 45] (figure 1).

3.2. *Structural descriptions*

Complex **1** contains $[Pb(DADMBTZ)_2]^{2+}$ (figure 2), two NO_3^- and CH_3COO^-. The Pb has an unsymmetrical seven-coordinate geometry, surrounded by four nitrogens of two DADMBTZ and three oxygens of nitrate and acetate in a N4O3 coordination sphere. Two ligands in **1** are bidentate in five-membered chelate rings, with internal angles 63.88(2)° and 66.15(2)° for N(1)–Pb(1)–N(3), N(5)–Pb(1)–N(7) (table 3). The Pb–N bond lengths are in the range 2.447(5)–2.767(5) Å and the Pb–O bond lengths are in the range 2.596(5)–2.919(5) Å.

Arrangement of DADMBTZ, acetate, and nitrate suggests a gap or hole in the coordination geometry around lead (the N(5)–Pb–N(3) angle is 151.41°), occupied probably by a stereoactive lone pair of electrons on lead(II). The observed shortening of

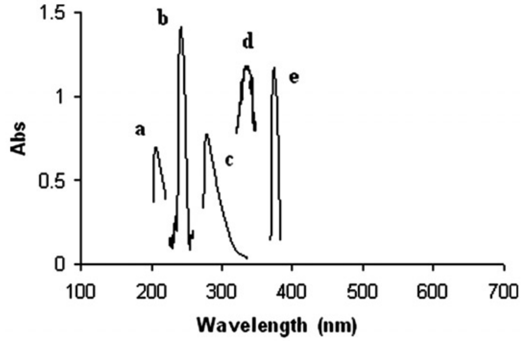


Figure 1. Electronic absorption of ligand DADMBTZ (a), Electronic absorption of complex **1**(b), Electronic absorption of complex **2** (c); Absorption: $c = 1.36 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, DMSO, $d = 1\,\mathrm{cm}$ for ligand and complexes **1** and **2**. The fluorescence spectra of ligand (d) and both complexes (e) in DMSO solution. Room temperature, $\lambda_{\mathrm{exc}} = 250$.

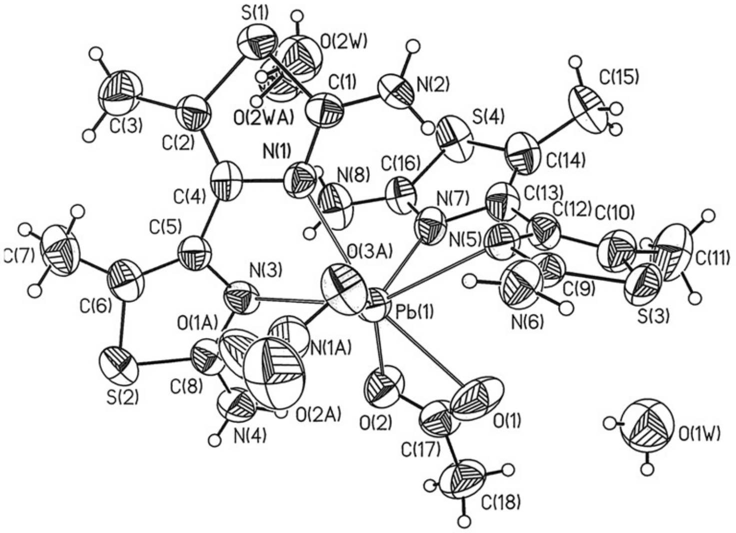


Figure 2. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

the Pb–N bonds opposite to the putative lone pair 2.447 Å compared with 2.767 Å for the adjacent bond supports the presence of this feature. Hence, the geometry of the nearest coordination environment of every lead atom is likely to be caused by the geometrical constraints of DADMBTZ, acetate, and nitrate and by the influence of a stereochemically active lone pair. There is no additional interaction between oxygens of acetate and neighboring leads in 2 : 1 adducts of $[\mathrm{Pb(DADMBTZ)_2(NO_3)(CH_3COO)}] \cdot \mathrm{H_2O}$, and **1** is a monomer.

There are eight types of N–H $\cdots$ O, O–H $\cdots$ O, and N–H $\cdots$ N intermolecular hydrogen bonds in the 3-D network between $[\mathrm{Pb(DADMBTZ)_2}]^{2+}$, two different anions, and an uncoordinated water. Unit cell packing of **1** is given in figure 3.

Table 3. Selected bond lengths (Å) and angles (°) for $[Pb(DADMBTZ)_2(NO_3)(CH_3COO)] \cdot H_2O$ (**1**).

Pb(1)–N(1)	2.604(5)	N(3)–C(8)	1.313(7)
Pb(1)–N(3)	2.767(5)	N(6)–C(9)	1.349(9)
Pb(1)–N(5)	2.649(5)	N(3)–C(5)	1.408(7)
Pb(1)–N(7)	2.447(5)	N(5)–C(9)	1.305(7)
Pb(1)–O(1)	2.648(6)	N(4)–C(8)	1.341(8)
Pb(1)–O(2)	2.596(5)	N(8)–C(16)	1.347(7)
Pb(1)–O(3A)	2.919(5)	N(5)–C(12)	1.408(8)
C(2)–C(4)	1.362(8)	N(7)–C(16)	1.307(7)
N(2)–C(1)	1.354(7)	N(7)–C(13)	1.414(8)
N(1)–C(1)	1.305(7)	N(1)–C(4)	1.386(7)
N(1A)–O(1A)	1.237(7)	N(1A)–O(2A)	1.216(8)
N(1A)–O(3A)	1.236(7)	O(1A)–N(1A)–O(2A)	119.2(7)
O(3A)–N(1A)–O(2A)	121.9(7)	O(1A)–N(1A)–O(3A)	118.8(6)
N(1)–Pb(1)–N(5)	91.81(2)	N(7)–Pb(1)–O(2)	78.54(2)
N(1)–Pb(1)–N(7)	75.82(2)	N(1)–Pb(1)–O(2)	129.01(2)
N(7)–Pb(1)–N(5)	66.16(2)	N(7)–Pb(1)–O(1)	84.83(2)
N(7)–Pb(1)–N(3)	92.09(2)	N(1)–Pb(1)–O(1)	160.09(2)
N(1)–Pb(1)–N(3)	63.89(2)	O(2)–Pb(1)–O(1)	48.95(2)
N(1)–Pb(1)–N(5)	91.81(2)	N(5)–Pb(1)–O(1)	75.93(2)
N(3)–Pb(1)–N(5)	151.42(2)	N(3)–Pb(1)–O(1)	122.34(2)

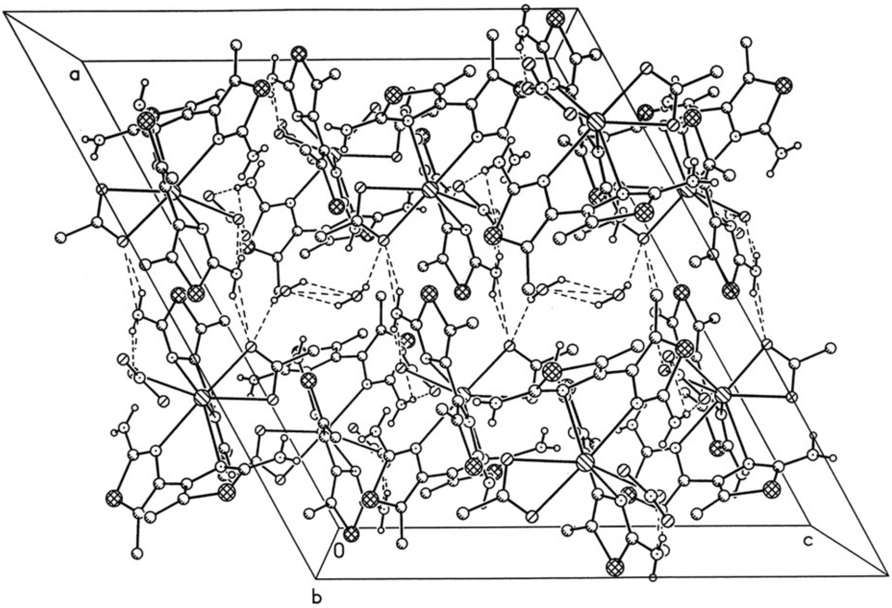


Figure 3. The unit cell of **1** showing intermolecular hydrogen bonding.

Complex **2** with its metal geometry (being bound to four nitrogens of two bidentate bithiazole ligands and one oxygen of nitrate) is five coordinate (figure 4). In each ligand, the two nitrogens coordinated to Pb(II) have different bond lengths (2.455(6)–2.593(6) Å). The two DADMBTZ ligands in **2** are bidentate in five-membered chelate rings, with different internal angles 67.67(2)° and 68.78(2) for N(1)–Pb(1)–N(3),

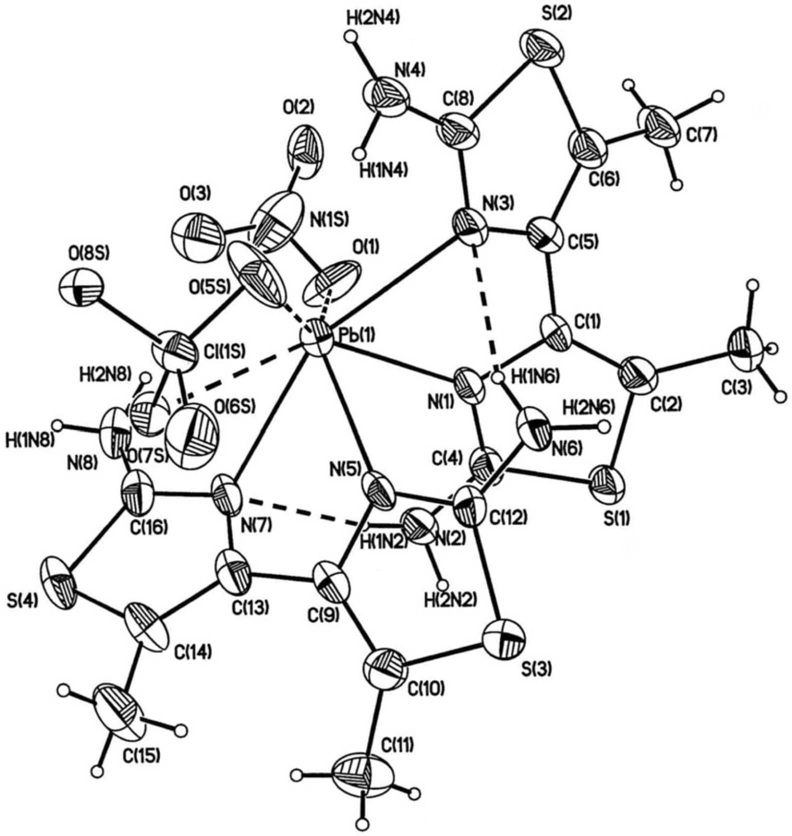


Figure 4. ORTEP drawing of **2** showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

N(5)–Pb(1)–N(7), respectively. The Pb–O (NO_3) bond length is 2.822(5) Å. The most relevant bond lengths and angles are given in table 4. Unit cell packing of **2** is shown in figure 5.

There are 19 types of N–H ··· O and N–H ··· N inter- and intramolecular hydrogen bonds in a 3-D network between $[Pb(DADMBTZ)_2]^{2+}$ and two different anions (figure 6).

The arrangement of the DADMBTZ ligands and nitrates suggests a gap or hole in the coordination geometry around lead [the N(7)–Pb–N(3) angle is 156.5°], occupied probably by a stereoactive lone pair of electrons on lead(II). The observed shortening of the Pb–N bonds opposite to the putative lone pair (2.455 Å compared with 2.593 Å for the adjacent bond) supports the presence of this feature. For the structures described here, coordination around lead is hemidirected with a significant gap *trans* to DADMBTZ. The π–π stacking interactions are not found in **1** and **2** because π–π stacking interactions are rarely observed in complexes with a ligand–metal ratio of 2 : 1.

Interestingly, if a limit of 2.83 Å were to be placed upon Pb(II)-donor separations regarded as involving coordinate bonding, only one oxygen of nitrate would be considered bound and perchlorate would be considered uncoordinated. If, however, the

Table 4. Selected bond lengths (Å) and angles (°) for [Pb(DADMBTZ)$_2$(NO$_3$)(ClO$_4$)] (**2**).

Pb(1)–N(1)	2.455(6)	N(3)–C(8)	1.313(9)
Pb(1)–N(3)	2.564(6)	N(6)–C(12)	1.361(9)
Pb(1)–N(5)	2.466(6)	N(3)–C(5)	1.405(9)
Pb(1)–N(7)	2.593(6)	N(5)–C(9)	1.392(8)
Pb(1)–O(1A)	2.73(3)	N(4)–C(8)	1.332(9)
C(2)–C(1)	1.350(2)	N(8)–C(16)	1.327(2)
C(1)–C(5)	1.470(9)	N(5)–C(12)	1.312(8)
C(2)–C(3)	1.508(2)	N(7)–C(16)	1.337(9)
N(2)–C(4)	1.338(9)	N(7)–C(13)	1.400(2)
N(1)–C(1)	1.400(8)	N(1)–C(4)	1.302(9)
N(1S)–O(1)	1.218(7)	N(1S)–O(2)	1.206(8)
N(1S)–O(3)	1.210(7)	O(1)–N(1S)–O(2)	120(3)
O(3)–N(1S)–O(2)	129(3)	O(1)–N(1S)–O(3)	110(3)
N(7)–Pb(1)–N(5)	68.78(2)	N(1)–Pb(1)–O(1A)	73.0(7)
N(7)–Pb(1)–N(3)	156.5(2)	N(1)–Pb(1)–N(5)	75.3(2)
N(1)–Pb(1)–N(3)	67.66(2)	N(1)–Pb(1)–N(7)	92.24(2)

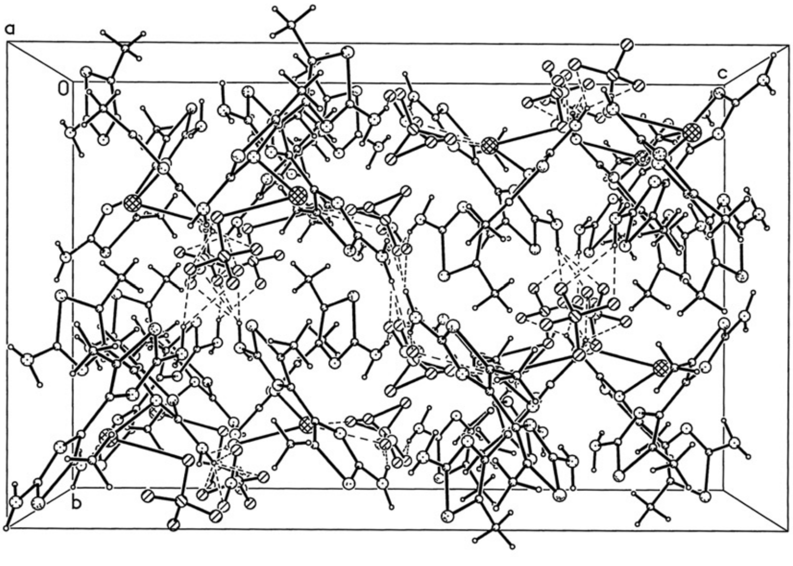


Figure 5. A view of unit cell of **2** showing intermolecular hydrogen bonding.

bonding limit is extended to 3 Å, the nitrate and perchlorate attached to Pb all become (asymmetric) chelating entities, leading to seven-coordinate Pb in a very strongly 'hemidirected' array, evidently consistent with the presence of a lone pair in the apparent coordination-sphere vacancy remote from the bound atoms. Such an environment leaves space for Pb···O bond with the oxygen atoms of perchlorate. Each Pb atom in this structure forms two 'weak' Pb···O bonds (2.913 and 2.987 Å).

The presence of a lone pair on lead is apparently the reason that bridging interactions cannot occur in the two structures and the large space not occupied by ligand. If the

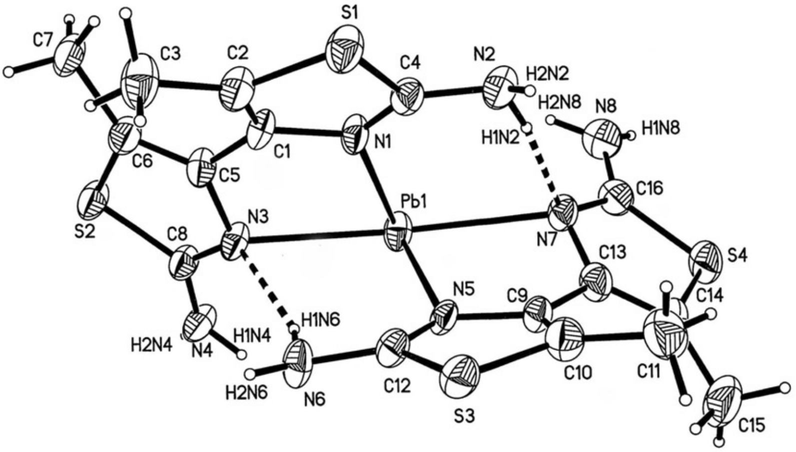


Figure 6. Intramolecular hydrogen bonding of **2**.

stereochemically active lone pair is not present, it might create more interactions between bridging atoms of lead(II) with oxygens of counter-ions. Consequently, this phenomenon could lead to inability of the complex to adopt higher symmetry in **1** and **2**.

Three N–O bond lengths and also three ONO bond angles of nitrate in **1** [N–O = 1.216(8), 1.236(7), and 1.237(7) Å and ONO angle = 118.8(6), 119.2 (7), and 121.9(7)°] and **2** are different [N–O = 1.206(8), 1.210(7), and 1.218(7) Å and ONO angle = 110(3), 120(3), and 129(3)°], and consequently the O–O distances are different. This point shows that the nitrate anion is highly distorted by the bridging.

Comparison of free ligand with that in two complexes represents the effect of coordination, for example the range of C–N distances in **1** is 1.305(7)–1.414(8) Å, and in **2**, 1.302(8)–1.405(9) Å, shorter than those in free ligand (1.393(4)–1.399(4) Å); also C(4)–C(5) = 1.472(8)–1.474(8) Å in **1** and C(1)–C(5) = 1.469(2)–1.470 Å in **2** are shorter than those of free ligand (1.481(4)–1.485(4) Å).

The distances between the two bithiazole nitrogens in free ligands is almost 3.079 Å (two nitrogens are *trans* with each other), whereas in **1** these distances are about 2.788–2.845 Å and in **2**, 2.797–2.859 Å in two DADMBTZ ligands (two nitrogens are *cis*).

The torsion angle of DADMBTZ in free ligand, ∠N(3)–C(4)–C(4′)–N(3′), is about 59.6(4)°, and in **1**, ∠N(1)–C(4)–C(5)–N(3) = −43.5(7), ∠N(5)–C(12)–C(13)–N(7) = −36.3(7) and in **2**, ∠N(1)–C(1)–C(5)–N(3) = 36.2(2), ∠N(5)–C(9)–C(13)–N(7) = 40.6(2), which shows that a deviation from planarity is formed by the two thiazole rings of bithiazoles.

The C–N bond length in the bithiazole rings in free ligand are at the range 1.393(4)–1.399(4) Å, and the title complexes 1.302(3)–1.474(3) Å, which are shorter than the single bond length of 1.48 Å and longer than the typical C=N distances of 1.28 Å, indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle.

On the other hand, the bond length range of N(2)–C(4) = 1.338(9) Å, N(4)–C(8) = 1.332(9) Å, N(8)–C(16) = 1.326(9) Å, and N(6)–C(12) = 1.361(9) Å in **1** and N(2)–C(1) = 1.354(7) Å, N(4)–C(8) = 1.341(8), N(8)–C(16) = 1.347(7) Å, and

N(6)–C(9) = 1.349(9) Å in **2** are shorter than that of normal C–N single bond, which confirms that the nitrogen of amido is involved in the delocalization system.

3.3. *Luminescence properties*

Luminescence spectra of **1** and **2** in DMSO exhibit an emission at 298 K upon excitation at 250 nm (figure 1). The intense emission bands observed (table 4), 360 for free ligand and 363 nm for **1** and **2**, are tentatively assigned to the bithiazole π–π^* and n–π^* transitions [44, 45].

3.4. *Thermal studies*

The thermal stabilities of $[Pb(DADMBTZ)_2(NO_3)(CH_3COO) \cdot H_2O$ and $[Pb(DADMBTZ)_2(NO_3)(ClO_4)]$ were investigated in static air from ambient to 700°C and studied by thermal gravimetric (TG) and differential thermal analysis (DTA) (Supplementary material). Compound **1** does not melt and it is stable up to 176°C. The TG curve of **1** indicates release of one water up to 177.8°C with an endothermic effect to give water-free $[Pb(DADMBTZ)_2(NO_3)(CH_3COO)]$, which is stable to 270°C. Decomposing of acetate and nitrate takes place at 274°C with an exothermic effect (observed 14.25%, Calcd 15.14%). The weight loss of 55% is equivalent to loss of two coordinated ligands DADMBTZ (Calcd 56.57%) with one exothermic effect at 530.17°C. The solid residue formed at 615°C is suggested to be PbO (observed 27.75%, Calcd 27.93%).

Compound **2** begins to decompose at 267°C. Decomposing of perchlorate takes place at 283.6°C with mass loss of 9.8% consistent with the calculated value 10% for elimination of one Cl and three oxygens with one exothermic effect (observed 27.75%, Calcd 27.93%). The release of nitrate takes place at 302°C with a slightly exothermic effect to give PbL_2 at 470°C (observed 6.9%, Calcd 7.54%).

The weight loss of 53.5% from 250°C to 650°Cis equivalent to the loss of two coordinated DADMBTZ molecules (Calcd 55%) with one exothermic effect at 511°C. The solid residue formed at 614°C is suggested to be PbO.

4. Conclusion

Two different coordination complexes arise from reaction of bithiazole with Pb(II). The coordination geometries of the complexes show a possible vacant site around Pb(II), occupied possibly by a stereoactive lone pair of electrons making coordination around lead hemidirected. This study demonstrates lead is capable to form compounds with different coordination numbers deeply influenced by the counter-ions. We anticipate that this property of lead(II) will result in a variety of new coordination polymers and supramolecular complexes with novel patterns and interesting physical properties.

Supplementary material

Complete bond lengths and angles, coordinates, and displacement parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 289427 for $[Pb(DADMBTZ)_2(NO_3)(CH_3COO)] \cdot H_2O$ (**1**) and 629103 for $[Pb(DADMBTZ)_2(NO_3)(ClO_4)]$ (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@cdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

The University of Tehran and Tarbiat Modares University Research Council supported this study. We thank the Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure by X-ray crystallography.

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