

A new dinuclear lead(II) complex of 2,3-diphenyl-tetrazole-5-thione: synthesis and characterization

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The present work reports on the synthesis, crystal structure, fluorescence, electrochemical behavior, and thermogravimetric analysis of a new dinuclear lead(II) complex of 2,3-diphenyl-tetrazole-5-thione. Its structure was characterized by X-ray crystallography, IR spectroscopy, and elemental analysis. Each lead atom adopts a distorted octahedral geometry by coordinating to 2 sulfur atoms from 2 2,3-diphenyl-tetrazole-5-thione ligands and 4 oxygen atoms from 3 nitrates. The fluorescence spectrum shows that the title complex has 2 fluorescence emission peaks, at 412 nm and 433 nm. Cyclic voltammetry studies show that the title complex has only one reduction peak, at 0.309 V. The thermogravimetric analysis indicates that the title complex shows a thermal stability below 211 °C; it may decompose instantly above that temperature.

Key Words: Lead complex, tetrazole-5-thione. crystal structure, fluorescence, electrochemistry

Introduction

Many substituted tetrazoles show a variety of interesting properties. For instance, they exhibit certain types of physiological activity by affecting the nervous system in a number of ways.¹ They are also sensitive explosives, used in initiating devices such as primers and detonators for commercial and military applications.^{2,3} Tetrazole-5-thione can coordinate with metal ions through the sulfur atom and nitrogen atom. This potential metal-complexing ligand should have interesting properties that arise from the extensive electron delocalization in the tetrazole ring system and the exocyclic sulfur atom. Kozarek et al. reported a tetrazole-5-thione mercury complex in which the mercury atom coordinated to the sulfur atom.⁴ Jerry et al. synthesized a polypyridyl

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ruthenium complex in which the ruthenium atom coordinated to the sulfur atom.⁵ Bravo et al. reported a tetrazole-5-thione tin complex in which the tin atom coordinated to the sulfur atom and nitrogen atom.⁶

However, to the best of our knowledge, studies about tetrazole-5-thione are less reported. Our group had reported the synthesis and structures of diaryl tetrazole-5-thione compounds.⁷ We theoretically calculated the thermodynamic properties and charge distribution of these compounds.⁸ In the calculation, the exocyclic sulfur atom had a more negative charge than the nitrogen, suggesting that the sulfur atom was the most active site to coordinate with metal ions. In order to verify this, we synthesized a series of tetrazole-5-thione complexes with metal ions such as copper, silver, mercury, and lead, and obtained the crystal structure of a dinuclear lead nitrate complex. Here we report the synthesis, crystal structure, fluorescence, electrochemical behavior, and thermogravimetric analysis of this new dinuclear lead(II) complex containing 2,3-diphenyl-tetrazole-5-thione.

Experimental

Chemicals and measurement

All of the chemicals were analytical reagent grade and used without further purification. Elemental analysis was performed with a PerkinElmer (Massachusetts, USA) 1400C analyzer. Infrared spectra in the 4000–400 cm^{-1} range were recorded on a Nicolet 170SX spectrometer (Wisconsin, USA) using pressed KBr disks. Crystal structure determination by X-ray diffraction was performed on a Bruker-Nonius diffractometer with Kappa geometry attached with an APEX-CCD detector (Bruker, Germany). The fluorescence spectrum was observed on an F-4500 FL spectrophotometer with excitation and emission wavelengths of 200.0–900.0 nm, an interval of 10 nm, scan speed of 1200 nm min^{-1} , slit of 5.0 nm, and PMT voltage of 700 V. Thermogravimetry (TG) was recorded on an SDT 2980 simultaneously for approximately 10 mg samples under a nitrogen flush (150 mL min^{-1}) at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Electrochemical measurements were performed with an Autolab PGSTAT-30 digital potentiostat/galvanostat (EcoChemie, Utrecht, the Netherlands). A 3-electrode cell was used in the experiments. A glass carbon working electrode ($\varnothing = 2 \text{ mm}$) was used. A platinum wire was the counter electrode. The reference electrode was $\text{Ag}|\text{AgCl}, \text{KCl} (1 \text{ M})$, and all of the potentials reported in this work were measured relative to this electrode (236.3 mV SHE^{-1} at 25 $^{\circ}\text{C}$). DMF solution containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte. All of the measurements were performed at room temperature ($25 \pm 2 \text{ }^{\circ}\text{C}$).

Preparation and physical measurement of the title complex

The ligand 2,3-diphenyl-tetrazole-5-thione was obtained as described in the literature.^{1,7} 2,3-Diphenyl-tetrazole-5-thione (2.54 g, 10.0 mmol) and $\text{Pb}(\text{NO}_3)_2$ (1.655 g, 5 mmol) were dissolved in 50 mL of acetone. After stirring for 2 h, a yellow precipitate was obtained (yield: 1.763 g, 42%). Single crystals of dinuclear lead(II) complex were obtained by slow evaporation at room temperature from the DMF solution. The C, H, N, and S contents were determined by elemental analysis (Anal. calcd. for $\text{C}_{52}\text{H}_{40}\text{N}_{20}\text{O}_{12}\text{Pb}_2\text{S}_4$: C, 37.18%; H, 2.40%; N, 16.68%; S, 7.64%. Found: C, 37.21%; H, 2.38%; N, 16.73%; S, 7.58%).

The band in the IR spectrum at 3057 cm^{-1} is assigned to the C–H stretching vibration of the phenyl ring. Several bands in the 1627–1461 cm^{-1} range are assigned to $\nu(\text{N}=\text{N})$ modes and overlap with the stretching

vibrations of the phenyl ring. Strong bands at 1322 cm^{-1} and 1284 cm^{-1} are attributed to the C=S and C–N stretching vibrations of the tetrazole ring, respectively. In addition, there are 2 strong bands at 1384 cm^{-1} and 836 cm^{-1} ; the former is due to asymmetric stretching and the latter is attributed to symmetric stretching of nitrate.⁹

The crystal data collection was carried out by CCD. X-ray diffraction was measured at $20\text{ }^{\circ}\text{C}$ using Mo K_{α} radiation ($\lambda = 0.71073\text{ \AA}$) with a graphite monochromator. The structure of the title complex was solved by direct methods and refined by least squares on F_{obs}^2 by using the SHELXTL software package.¹⁰ All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.¹¹

Results and discussion

Crystal structure of the title complex

The structural unit of the title complex (Figure 1) was generated through inversion symmetry. Crystal and structure refinement data are listed in Table 1. The final position parameters of nonhydrogen atoms are given in Table 2. Selected bond distances and angles are listed in Table 3. The title complex forms a dinuclear complex with nitrate bridging. In each molecule, the central lead atoms adopt a distorted octahedral geometry by coordinating to 2 sulfur atoms from 2 2,3-diphenyl-tetrazole-5-thione ligands and 4 oxygen atoms from 3 nitrates. The 2 lead atoms and bridging nitrate ligands are arranged in an 8-membered ring with chair conformation. This double-bridging mode of the nitrate ion is the same as in the reports in the literature.^{12–15} The bond lengths of Pb(1)–S(2) [$2.784(2)\text{ \AA}$], Pb(1)–S(1) [$2.810(2)\text{ \AA}$] and Pb(1)–O(5) [$2.466(4)\text{ \AA}$], Pb(1)–O(4) [$2.722(5)\text{ \AA}$] are consistent with the corresponding values reported earlier.^{14–17} The S(1)–C(13) bond length is $1.724(5)\text{ \AA}$, which is intermediate between a single and double bond. The exocyclic sulfur atom and the tetrazole ring are almost planar with the largest deviation of 0.115 \AA from the least-squares plane. These phenomena indicate that there is considerable electron delocalization in the tetrazole ring and the exocyclic sulfur atom. The Pb(1)···Pb(1A) distance is 4.103 \AA , which is too long to include metal-metal interaction. The bond angles, O(5)–Pb(1)–O(4) $48.6(2)^{\circ}$, O(5)–Pb(1)–S(2) $75.1(2)^{\circ}$, O(4)–Pb(1)–S(2) $123.1(2)^{\circ}$, O(5)–Pb(1)–S(1) $80.0(2)^{\circ}$, S(2)–Pb(1)–S(1) $93.55(5)^{\circ}$, and C(13)–S(1)–Pb(1) $90.3(2)^{\circ}$, are comparable with the corresponding values in a similar complex.⁹ The equatorial plane of the title complex is defined by the Pb(1), O(1), O(3), and O(5) atoms. The dihedral angles between the tetrazole ring, [S(1), N(1), N(2), N(3), N(4), C(13)], and the ring [Pb(1), O(4), O(5), O(6), N(10)], the phenyl ring[C(7)~C(12)], are 35.69° and 68.27° , respectively. There are potentially weak C–H···O hydrogen-bond intermolecular interactions where the donor-acceptor distance for C(10)···O(6) is 3.25 \AA . The intermolecular interactions in the structure have stabilized the crystal structure.

Electrochemical characterization of the title complex

Cyclic voltammetry was employed to study the sulfur atom of the C=S bond coordinated to the lead atom. A comparison of the cyclic voltammograms (CVs) for the ligand and the title complex is shown in Figure 2. Curve

(a) is the cyclic voltammogram of 5.0×10^{-5} M ligand in DMF solution containing 0.1 M TBAP, and curve (b) is that of 5.0×10^{-5} M title complex. The ligand has a well-defined reduction peak at 0.365 V, whereas no oxidation peak appears. The reduction peak of the ligand may be the reduction of the C=S band. The title complex also has only one reduction peak, at 0.309 V; no new peak appears. This reduction peak also may be the reduction of the C=S band. Comparing curve (a) and curve (b), the potential difference of 56 mV may be due to the sulfur atom coordinated to the lead atom.

Table 1. Crystal data and structure refinement for the title complex.

Empirical formula	C ₅₂ H ₄₀ N ₂₀ O ₁₂ Pb ₂ S ₄
Formula weight	1679.72
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	9.348(2)
<i>b</i> (Å)	12.985(3)
<i>c</i> (Å)	14.278(3)
α (°)	113.14(3)
β (°)	92.05(3)
γ (°)	102.75(3)
Volume (Å ³)	1539.8(6)
<i>Z</i> , Calculated density (g cm ⁻³)	1, 1.811
Absorption coefficient (mm ⁻¹)	5.672
<i>F</i> (000)	816
Crystal size (mm)	0.15 × 0.20 × 0.25
Theta range for data collection (°)	1.57 to 26.97
Limiting indices	0 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 17
Reflections collected / unique	7057 / 6644 [<i>R</i> _(int) = 0.0249]
Completeness to $\theta = 26.97$	99.2%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4271 / 0 / 209
Goodness-of-fit on <i>F</i> ²	1.016
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0336, <i>wR</i> ₂ = 0.0784
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0561, <i>wR</i> ₂ = 0.0867
Extinction coefficient	0.0005(7)
Largest diff. peak and hole (e Å ⁻³)	1.504 and -1.312

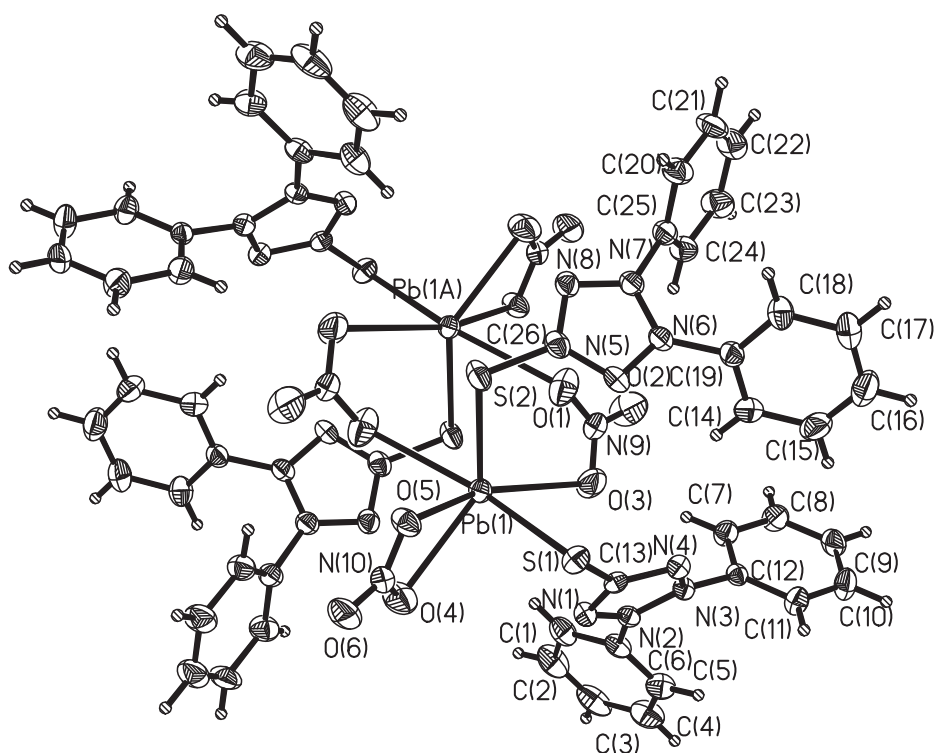
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for the title complex.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pb(1)	-125(1)	3261(1)	4304(1)	40(1)
S(1)	1130(2)	1520(1)	4393(1)	47(1)
S(2)	2573(2)	4634(2)	4221(1)	55(1)
O(4)	-1879(6)	1556(5)	2596(4)	80(2)
O(5)	325(5)	2363(4)	2503(3)	56(1)
N(1)	-1396(5)	1216(4)	5243(4)	41(1)
N(2)	-1735(4)	1297(4)	6148(3)	36(1)
N(3)	-498(4)	1549(4)	6790(3)	35(1)
N(4)	663(5)	1622(4)	6301(4)	36(1)
N(5)	3585(5)	4373(4)	5908(4)	46(1)
N(6)	4171(5)	5088(4)	6854(4)	43(1)
N(7)	4327(5)	6183(4)	6994(4)	44(1)
N(8)	3860(5)	6231(4)	6134(4)	44(1)
C(1)	-4145(7)	1635(6)	6066(5)	59(2)
C(2)	-5630(8)	1399(8)	6249(7)	77(2)
C(3)	-6107(7)	683(8)	6730(6)	77(3)
C(4)	-5173(8)	172(7)	7046(6)	73(2)
C(5)	-3690(7)	389(6)	6870(5)	56(2)
C(6)	-3239(6)	1108(5)	6393(5)	44(1)
C(7)	-768(7)	2877(5)	8486(5)	51(1)
C(8)	-598(8)	3218(6)	9547(5)	60(2)
C(9)	-84(7)	2562(6)	9961(5)	57(2)
C(10)	257(8)	1543(7)	9338(5)	63(2)
C(11)	122(7)	1196(6)	8286(5)	51(2)
C(12)	-402(5)	1866(5)	7888(4)	36(1)
C(13)	102(6)	1431(4)	5349(4)	35(1)
C(14)	3502(8)	3996(6)	7891(6)	62(2)
C(15)	3919(10)	3584(7)	8595(6)	77(2)
C(16)	5360(11)	3885(7)	9004(6)	79(2)
C(17)	6432(9)	4614(7)	8747(6)	66(2)
C(18)	6054(7)	5029(6)	8046(5)	56(2)
C(19)	4596(7)	4707(5)	7624(4)	44(1)
C(20)	6245(7)	7894(6)	8103(6)	59(2)
C(21)	6754(8)	8800(6)	9060(6)	70(2)
C(22)	5892(10)	8957(6)	9844(7)	73(2)
C(23)	4492(9)	8223(6)	9678(6)	71(2)
C(24)	3944(7)	7318(5)	8726(5)	54(2)

Table 2. Contunied.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(25)	4858(6)	7170(5)	7968(5)	47(1)
C(26)	3387(6)	5098(5)	5464(5)	47(1)
C(27)	-870(6)	1593(5)	2062(4)	37(1)
C(28)	-994(7)	955(5)	1187(4)	49(1)
N(9)	143(6)	4730(5)	7000(4)	49(1)
O(1)	886(5)	5266(6)	6517(5)	83(2)
O(2)	80(9)	5221(5)	7904(4)	107(2)
O(3)	-483(8)	3706(4)	6529(4)	92(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

**Figure 1.** The molecular structure of the title complex showing the atom labeling scheme.

Fluorescence studies

The fluorescence spectrum of the title complex, using an excitation frequency of 370 nm, is shown in Figure 3. The emission spectrum showed 2 fluorescence emission peaks at 412 nm and 433 nm, which may be ascribed to a ligand-to-metal charge transfer.^{16,17} However, the free ligand displayed no fluorescence emission under the same conditions. That is to say, 2,3-diphenyl-tetrazole-5-thione showed no fluorescence emission, while it showed a fluorescence emission when reacted to the lead atom by coordination. In order to investigate this

phenomenon, in our experiment, the metal complexes of the ligand, coordinated to other metal salts such as copper, silver, and mercury, were also synthesized (see Supplementary Material) and their fluorescence properties were studied. The results showed that those metal complexes all showed no fluorescence emission. At the same time, the metal complexes of the ligand, coordinated to other lead salts such as lead acetate and lead chloride, were also synthesized (see Supplementary Material) and their fluorescence properties were studied. Those metal complexes also showed no fluorescence emission. We can conclude that the 2,3-diphenyl-tetrazole-5-thione may be the fluorescent detection agent of lead nitrate, although the causes and mechanisms are not clear now.^{18,19}

Table 3. Selected bond lengths and angles of the title complex.

Bond lengths (Å)	Bond angles (°)
Pb(1)–O(5) 2.466(4)	O(5)–Pb(1)–O(4) 48.6(2)
Pb(1)–O(4) 2.722(5)	O(5)–Pb(1)–S(2) 75.1(2)
Pb(1)–S(2) 2.784(2)	O(4)–Pb(1)–S(2) 123.1(2)
Pb(1)–S(1) 2.810(2)	O(5)–Pb(1)–S(1) 80.0(2)
S(1)–C(13) 1.724(6)	O(4)–Pb(1)–S(1) 85.7(2)
S(2)–C(26) 1.718(6)	S(2)–Pb(1)–S(1) 93.55(5)
O(4)–N(10) 1.246(7)	C(13)–S(1)–Pb(1) 90.3(2)
O(5)–N(10) 1.272(6)	C(26)–S(2)–Pb(1) 99.3(2)
N(1)–N(2) 1.308(6)	N(10)–O(4)–Pb(1) 91.2(3)
N(1)–C(13) 1.357(6)	N(2)–N(1)–C(13) 104.5(4)

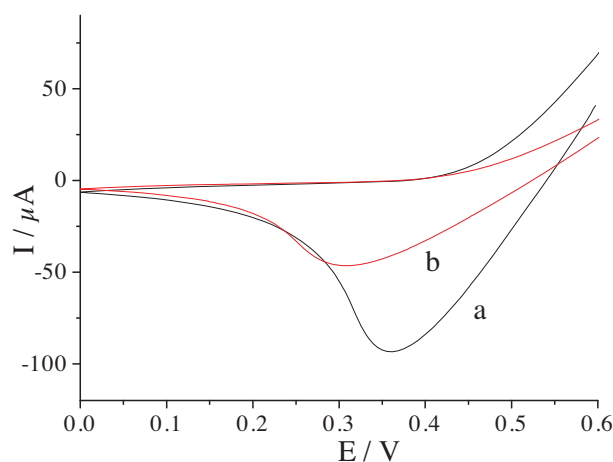


Figure 2. CVs of (a) 5.0×10^{-5} M ligand and (b) 5.0×10^{-5} M title complex in DMF solution containing 0.1 M TBAP with the scan rate of 0.10 V s^{-1} .

Thermal analysis

We investigated the thermal stability properties of the title complex. The thermogravimetric analysis under N_2 indicated that the complex was stable up to $211 \text{ }^\circ\text{C}$. There was only a one-step weight loss; decomposition took

place at 211–212 °C. The weight of the complex increased to 128% and then rapidly decreased to 9% when heated to 211–212 °C, which indicated that the title complex decomposed instantly. This phenomenon may be considered as an explosion. The residue may be Pb (found 6.74%, calculated 24.67%), and this conclusion was supported by quantitative analysis. The error was so large that it may be attributed to the explosion.

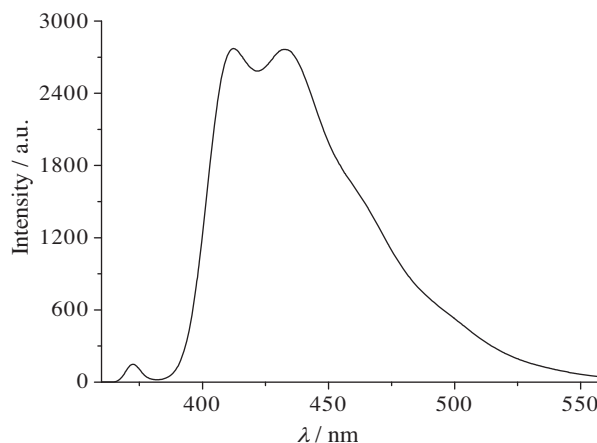


Figure 3. Fluorescence spectrum of 5.0×10^{-5} M title complex in DMF solution.

Conclusions

In summary, a new dinuclear lead(II) complex containing 2,3-diphenyl-tetrazole-5-thione was synthesized and its structure was characterized. The title complex forms a dinuclear complex with nitrate bridging. Each lead atom adopts a distorted octahedral geometry by coordinating to 2 sulfur atoms from 2 2,3-diphenyl-tetrazole-5-thione ligands and 4 oxygen atoms from 3 nitrates. In the metal complexes of 2,3-diphenyl-tetrazole-5-thione, the coordination to lead nitrate showed fluorescence emission in our experiment. The ligand of 2,3-diphenyl-tetrazole-5-thione may be the fluorescent detection agent for lead nitrate, although the causes and mechanisms are not clear now. The weight of the title complex increased to 128% and then rapidly decreased to 9% when heated to 211–212 °C, which indicated that the title complex decomposed instantly. The causes and mechanisms of the fluorescence emission and instant decomposing of the title complex are under further study.

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Supplementary Material

Crystallographic data of the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference number 667087. Copies of this information can be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; or <http://www.ccdc.cam.ac.uk>).

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