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Temperature-Controlled Syntheses of Substituted 1,2,4-Triazolelead(II) Complexes: Active Lone Pair and N—H···X (X = Cl, Br, I) Hydrogen Bonds

Jian-Kai Cheng,[†,‡] Jian Zhang,[†] Pei-Xiu Yin,[†] Qi-Pu Lin,[†] Zhao-Ji Li,[†] and Yuan-Gen Yao*,[†]

[†]*The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and [‡]Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

Three isomorphous lead(II) complexes with a new {N₃SX}-coordinated (X = Cl, Br, I) mode have been synthesized and characterized by X-ray diffraction. The structural analyses reveal that the coordination environment around the center metal is distinctly influenced by the stereochemical $6s^2$ lone pair and N—H···X hydrogen bonds. Additionally, doubly deprotonated trzS²⁻ (HtrzSH = 1,2,4-triazole-3-thiol) generated in situ via deamination and dehydrazination of ahtrzS⁻ (ahtrzSH = 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) was first observed in a semiconducting three-dimensional coordination network at higher reaction temperature.

Lead, as an important industrial material, has been extensively used in paints, in the construction of storage batteries, and in the nuclear industry, although it is an environmental pollutant with severe toxic effects. In the past decades, an important issue frequently discussed in the field of coordination chemistry and stereochemistry of lead complexes is the "stereochemical activity" of valence-shell lone-electron pairs.[1] In particular, low-coordinate lead(II) complexes have attracted considerable interest because they provide a basis for a rather detailed analysis of the evidence for coordination-sphere distortions, which may be a consequence of the presence of the stereochemically active lone pair.[2] Such a lone pair of electrons can cause a nonspherical charge distribution around the Pb^II cation because it probably takes up more space on a specific region of the surface of the coordination sphere than a single bond does. As a result, the disposition of ligands around the Pb^II cation usually results in an identifiable gap, particularly in the lead(II) complexes

with low coordinate numbers (2−5). In a word, the nature and form of the coordination sphere in lead(II) complexes is generally determined by a number of factors including lone pair−bond pair repulsion and molecular interaction (hydrogen-bond, π−π, etc.) in the ligands, so that minor differences in ligand or in the crystal array can have quite remarkable effects on the coordination stereochemistry of lead complexes.

On the other hand, it has been shown that lead with a divalent oxidation state has a particularly high affinity for thiol groups in biological materials, such as nucleic acids, proteins, and cell membranes.[3] Therefore, the interaction of sulfur-containing ligands with lead(II) has been extensively investigated to understand and mimic physiologically relevant coordination environments.[2a] Recently, our interest focuses on the chemistry of ahtrzSH not only because of its structural versatility but also for its potential application in the probe to trace formaldehyde indoors.[4] Furthermore, the coordination chemistry of ahtrzSH remains very rare, although it possesses a great variety of coordination donors. As far as we are aware, no examples of crystal structures of metal complexes containing ahtrzSH have been reported to date. Besides, it is potentially a good building block to construct a supramolecule because of its rich hydrogen-bond donors and acceptors. Herein, we report three isomorphous ahtrzSHPb^II complexes with stereochemical lone pairs and N—H···X hydrogen bonds, as well as a trzS²⁻-Pb^II complex with ligand in situ transformed from ahtrzS⁻ via deamination and dehydrazination at higher reaction temperature.

The solvothermal reaction of ahtrzSH with PbX₂ (X = Cl, Br, I) in a mixed MeOH/DMF solution with a molar ratio of

*To whom correspondence should be addressed. E-mail: yyg@fjirsm.ac.cn.
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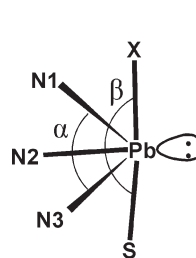(4) Shiraishi, F.; Ohkubo, D.; Toyoda, K.; Yamaguchi, S. *Chem. Eng. J.* **2005**, *114*, 153.
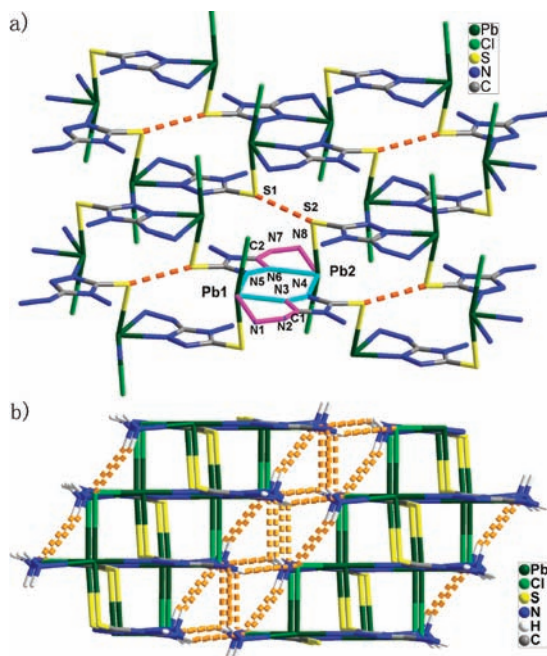
Figure 1. (a) Layered structure of **1** with S···S interactions. (b) Three-dimensional supramolecular network with N−H···X and N−H···N hydrogen bonds.

Scheme 1

Scheme 2

1:1 at 120 °C for 72 h afforded three isomorphous complexes, $[Pb(ahtrzS)X]_n$ [X = Cl (**1**), Br (**2**), I (**3**)].[5] Complex **1** was selected for its detailed structural description. It features a two-dimensional ladderlike coordination network, in which a coplanar $[Pb(ahtrzS)Cl]_2$ dimer, acting as a secondary building unit, is further connected by the pillared Pb−S bonds (Figure 1a). Each lead atom is in a hemidirected trigonal-bipyramidal or square-pyramidal environment {N₃SCl}, which is defined by one halogen atom, one sulfur atom, one hydrazine nitrogen atom, and two triazole nitrogen atoms from the adjacent five-membered heterocycles. This coordinative behavior gives rise to two five-membered rings (Pb1−N1−N2−C1−N3 and Pb2−N6−C2−N7−N8) and a six-membered ring (Pb1−N3−N4−Pb2−N5−N6), which confers stability to the coplanar system (Figure 1a). Each four-coplanar unit was further linked to a macrocycle through the Pb−S bonds. The S···S separations of 3.2339(28), 3.3093(49), and 3.3980(29) Å in complexes **1**−**3** are much shorter than the sum of the van der Waals radii (∼3.6 Å) and than those in Mo_3S_4 systems,[6] indicating strong S···S interaction, which is similar to girders on a building and further reinforces the macrocycles. Another prominent

structural feature of the three conplexes is that two-dimensional ladderlike layers are further connected to form a three-dimensional supramolecular network by N−H···X and N−H···N hydrogen bonds (Figure 1b).

As shown in Scheme 1, the arrangement of the donor atoms around the Pb^II atom suggests a clear gap in the coordination sphere, occupied by a stereochemically active lone pair of electrons on Pb^II. In the case of lead(II) complexes with coordination number 5, most of them show hemidirected trigonal-bipyramidal or square-pyramidal coordination geometries,[1,2] and there are few exceptions to this rule. According to the definition by Addison et al.,[7] the geometric parameter $\tau = (\beta - \alpha)/60$ (Scheme 1) is applicable to five-coordinate structures as an index of the degree of trigonality, within the structural continuum between trigonal-bipyramidal and rectangular-pyramidal. The values of τ in complexes **1**−**3** are 0.258, 0.277, and 0.321, respectively, indicating that the coordination geometries in the three compounds are inclined to a rectangular pyramid. Although the Pb−X bond distances in complex **1**−**3** are a little longer than those in the corresponding lead(II) halides,[8] they can also be considered as bonding interactions. In addition, it is interesting that the Pb−S bond distances and the S−Pb−X angles (Scheme 1) gradually increase in the order of complexes **1** < **2** < **3**, which is exactly in the reverse order of the electronegativity of the halogen atoms.

When the reaction temperature rises from 120 to 150 °C, a new three-dimensional coordination network, $[Pb(trzS)]_n$ (**4**),[9] was obtained instead of complexes **1**−**3** (Scheme 2). Of particular interest about this complex is that ahtrzSH

(5) Crystal data for **1**: $C_2H_5ClN_6PbS$, $M_r = 387.82$, monoclinic, space group $P2(1)/c$, $a = 9.577(4)$ Å, $b = 11.411(4)$ Å, $c = 7.492(3)$ Å, $\beta = 106.476(5)°$, $V = 785.1(5)$ Å³, $Z = 4$, $T = 293(2)$ K, $D_c = 3.281$ g·cm⁻³, $R_{int} = 0.0470$, 5892 reflections collected, R1 (wR2) = 0.0273 (0.0584) and $S = 1.019$ for 1742 reflections with $I > 2\sigma(I)$. Crystal data for **2**: $C_2H_5BrN_6PbS$, $M_r = 432.28$, monoclinic, space group $P2(1)/c$, $a = 9.8181(13)$ Å, $b = 11.4995(11)$ Å, $c = 7.5819(10)$ Å, $\beta = 106.222(7)°$, $V = 821.94(17)$ Å³, $Z = 4$, $T = 293(2)$ K, $D_c = 3.493$ g·cm⁻³, $R_{int} = 0.0895$, 6191 reflections collected, R1 (wR2) = 0.0437 (0.1001) and $S = 1.000$ for 1871 reflections with $I > 2\sigma(I)$. Crystal data for **3**: $C_2H_5IN_6PbS$, $M_r = 479.29$, monoclinic, space group $P2(1)/c$, $a = 10.1757(11)$ Å, $b = 11.6551(7)$ Å, $c = 7.7629(8)$ Å, $\beta = 106.443(6)°$, $V = 883.02(14)$ Å³, $Z = 4$, $T = 293(2)$ K, $D_c = 3.605$ g·cm⁻³, $R_{int} = 0.0558$, 6619 reflections collected, R1 (wR2) = 0.0351 (0.0793) and $S = 1.008$ for 1990 reflections with $I > 2\sigma(I)$.
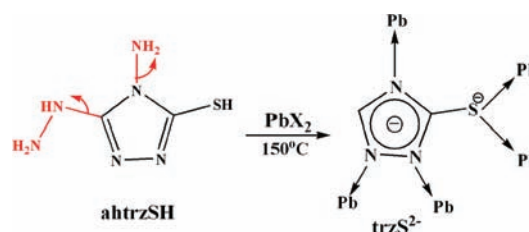
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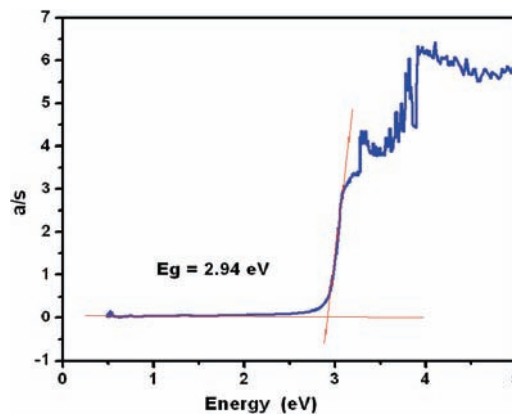
(9) Crystal data for **4**: C_2HN_3PbS, $M_r = 306.33$, orthorhombic, space group *Pbca*, $a = 8.8582(13)$ Å, $b = 8.4826(9)$ Å, $c = 13.0291(15)$ Å, $V = 979.0(2)$ Å³, $Z = 8$, $T = 296(2)$ K, $D_c = 4.157$ g·cm⁻³, $R_{int} = 0.1099$, 6923 reflections collected, R1 (wR2) = 0.0465 (0.1272) and $S = 1.064$ for 1012 reflections with $I > 2\sigma(I)$.
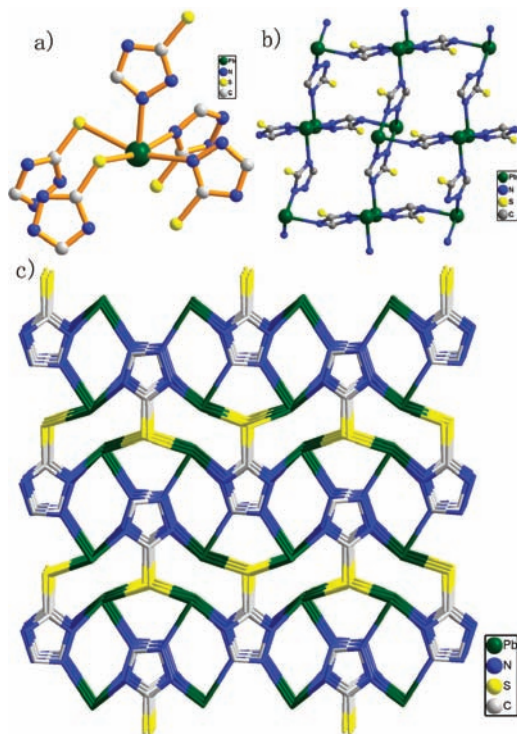
Figure 2. (a) Coordination environment of lead(II). (b) Two-dimensional layer structure of **4**. (c) Three-dimensional structure of **4**.

undergoes deamination and dehydrazination to give doubly deprotonated trzS^{2-}, which exhibits an unprecedented μ_5-bridging coordination mode (Scheme 2). As shown in Figure 2a, each Pb^{II} atom is in a hemidirected square-pyramidal (τ = 0.019) environment {N$_3$S$_2$}, commonly observed in the five-coordinated lead(II) complexes.[1,2] Such a coordination geometry is certainly caused by the stereochemically active lone pair, which is similar to that in complexes **1**−**3**. The prominent structural feature of **4** is that each lead atom is linked by three nitrogen donors to a two-dimensional layer (Figure 2b), which is further connected in a dense three-dimensional network through the pillared Pb−S bonds from the adjacent layers (Figure 2c). The structure of **4** is comparable with that of [Cd(trzS)$_2$]$_n$ reported previously by our group.[10] However, no stereochemical lone pairs are observed in [Cd(trzS)$_2$]$_n$. Each cadmium atom displays a distorted tetrahedral coordination geometry with no identifiable coordination gap around the center metal cations.

Thermogravimetric analyses (TGA) of complexes **1**−**4** were performed under an air atmosphere (Figures S1 and S2 in the Supporting Information). The TGA curves of **1**−**3** show that the three isomorphous compounds have thermal stability analogous to that of its TGA curve, unchanged up to about 200 °C. In comparison with the above three complexes, complex **4** displays much higher thermal stability than its TGA curve, unchanged up to 400 °C, which may be contributed to its dense three-dimensional structure and the

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Figure 3. Optical diffuse-reflectance spectra for **4**.

conjugated trzS^{2-}. In addition, TGA−quadrupole mass spectrometry analysis of **4** reveals that strong ion current signals m/z 26 and 52 (650−800 °C) are detected (Figure S2 in the Supporting Information), which may be assigned to CN$^+$ and (CN)$_2$$^+$ from the decomposition of trzS^{2-}. This further proves complex **4** has high thermal stability.

The UV absorption spectrum of complex **4** indicates that it is transparent in the range of 400−1100 nm (Figure S5 in the Supporting Information). From 400 to 200 nm, the absorption increases quickly with decreasing wavelength. An optical diffuse-reflectance study of **4** reveals an optical band gap of 2.94 eV, suggesting that it is a wide-band-gap semiconductor (Figure 3). Although PbS is a small-band-gap semiconductor (E_g = 0.37 eV),[11] semiconducting lead−sulfur−organic network solids remain very rare.[12]

In summary, we have successfully prepared a series of extended lead−sulfur−triazole networks and investigated in detail the influence of stereochemical lone pairs and hydrogen bonds on the coordination geometry of lead(II). Additionally, the results reported here have an important significance not only for revealing the deamination and dehydrazination of ahtrzSH into trzS^{2-} for the first time but also for offering new examples to understand the relationship between the structure and property, such as thermal stability and semiconductivity.

Supporting Information Available: X-ray crystallographic files in CIF format, IR spectra and TGA curves of complexes **1**−**4**, and a UV absorption spectrum of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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