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Studies on the crystal structure and characterization of

N-(4-acetylphenyl)-N'-(2-nitrobenzoyl)-thiourea

Jing-Han Hu^{*}, Jian-Bin Li, Jing Qi, You Sun

College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, P. R. China

*Corresponding author: J. H. Hu; E-mail: hujinghan62@163.com

Keywords

Aroylthiourea; Crystal structure; Biological activity; Recognition performance

N-(4-acetylphenyl)-N'-(2-nitrobenzoyl)-thiourea has been synthesized in high yield under PEG-400 as the phase-transfer catalyst and its the compound structure was determined by single crystal X-ray diffraction. The compound is also a considerable plant-growth regulator. In addition, the compound **L** exhibited selective recognition

for Hg^{2+} over other metals ions such as Ag^+ , Ca^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Mg^{2+} in DMSO solutions.



² ACCEPTED MANUSCRIPT

Introduction

Thiourea derivatives have been known for over a century and are easily synthesized in good yields. Thiourea derivatives have a long history as a ligand in coordination chemistry and coordinate to a metal via both sulfur and oxygen¹. These hard and soft donor atoms provide a multitude of bonding possibilities². Hydrogen bonding behaviors of some thioureas have been investigated and it is found that the intermolecular hydrogen bond between the sulfur and a hydrogen atom on N is common³.

Thiourea derivatives are extensively applied in various industries because of their unique molecular structure, good physical and chemical properties, and comprehensive biological activities. The literature shows that a number thiourea derivatives have been shown to posses antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties⁴. Thioureas serve as indispensable scaffolds in material chemistry pertaining to electroluminescent organic dyes^{5,6}. Also, thiourea along with its related molecules are important as structural components in agricultural and pharmaceutical chemistry^{7,8}. Furthermore, thiourea polymers possessing coordination sites can act as supports for immobilized catalysts⁹. In supramolecular chemistry, thiourea polymers are of interest due to their specific interactions with biologically important anions^{10,11}. Accordingly, thiourea-based materials are excellent candidates of advanced

technological significance in the fields of anion sensing, waste recovery of anions through solid-phase extraction and anion membrane transport for purification and synthesis purposes. Another promising aspect of these thiourea-based polymers is that they can act as coordinating resins for selective binding of heavy metal cations such as Hg(II) and Pb(II) from acidic as well as neutral solutions^{12,13}.

In continuation of our earlier work^{14,15}, we designed and synthesized the compound of N-(4-acetylphenyl)-N'-(2-nitrobenzoyl)-thiourea. The compound's structure was determined by single crystal X-ray diffraction. In addition, by investigating the biological activity of the title compound, we found that the compound has high plant growth regulating activity at low concentration (Table 1, Supplemental Materials) Moreover, sensing performance based on the compound **L** were demonstrated, which could be very useful for the compound of molecule recognition with fast and selective detection for mercury and ions.

Results and discussion

Structure Determination

In the molecule of the title compound, the crystal data and structure refinement details for $C_{16}H_{13}N_3O_4S$ are summarized in **Table 1**, is not planar, selected bond distances and angles are

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listed in **Table 2** and **Table S 2** (**Supplemental Materials**). The dihedral angle between the mean plane of the thiourea fragment and both benzene rings are $81.32(0.11)^\circ$ and $27.36(0.11)^\circ$. The molecular conformation is stabilized by an intramolecular N-H···O hydrogen bond. In the crystal structure, molecules are linked by intermolecular N-H···O hydrogen-bonding interactions into one-dimensional a ribbon chains along the a-axis direction. The O(2) atom of the -NO₂ group is disordered over two sites with refined occupancies of 0.36 and 0.64.

Crystal Structure

In the crystal structure (Figure 1) of the title compound is similar to those of N-(2-nitrophenyl)-N'-(methoxycarbonyl)-thiourea and

N-(4-nitrophenyl)-N'-(ethoxycarbonyl)-thiourea¹⁶. The molecule is not planar. The bond lengths of C=O are 1.216 (3)Å and 1.217 (4)Å while the bond length of C=S is 1.640 (3)Å. At the same time, in the torsion angle of C8-N2-C7-O3, C7-N2-C8-N3, C9-N3-C8-S1, C7-N2-C8-S1, C6-C7-N2-C8 and N2-C8-N3-C9 are -0.8 (6)°, 1.8 (5)°, 1.2 (6)°, -177.8 (3)°, 175.30 (0.30)° and -178.25 (0.30)°. In the crystal, each molecule is joined to an intramolecular N-H···O hydrogen bond and intermolecular N-H···O hydrogen bond which stabilizes the molecular conformation and leads to the crystal packing in a supramolecular one-dimensional a ribbon chains along the a-axis direction as shown in **Figure S 1 (Supplemental Materials**). A summary of important bond

lengths and angles are presented in Table 1.

Biological activity

We also investigated the plant growth regulation activity. Here, we adopted the method of plate culture. The compound was collected to the solution in concentration of 1 ppm, 0.1 ppm, 0.01 ppm, and coleseed was cultured in a 10 cm Petri dish with 10 mL different solution and a circular filter paper (for the experiment process and data see Supplemental Materials).

Cation recognition properties

To evaluate the recognition studies of ligand L, Hg^{2+} , Ag^+ , Ca^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Mg^{2+} ions were used to measure the selectivity and sensitivity of L (2×10⁻⁴ M) in DMSO, and absorption spectral were recorded upon the addition of 20 equiv. of each of these metal ions. Compared to other metal ions examined, changes in the spectral pattern were observed only in the presence of Hg^{2+} (4×10⁻³ M). No change in the spectral pattern for L in the presence of other cations suggested either a very weak or no interaction between these cations and the ligand L (**Figure 2**). As is well-known, for an ideal ion probe, only the target ion should induce drastic spectral changes, and the coexistence of other competing ions should not disturb the detection of

the target ion^{17,20}. Thus, competition behavior was checked to further elucidate whether the coexistence of competing metal cations interferes with the detection of Hg^{2+} . In the solutions of ligand **L**, upon addition of Hg^{2+} (4×10⁻³ M) together with other competing cations (4×10⁻³ M) (**Figure 3**), similar absorption weakened was clearly observed. Thus, the ligand **L** displays a good selectivity for Hg^{2+} over other competing metal ions in DMSO solution.

Uv-vis titrations were carried out in DMSO at a concentration of 2.0×10^{-5} M with the addition of different concentrations of Hg²⁺ (0.02 M). The strong new band with maximum absorbance peak at 287 nm was observed after adding of Hg²⁺, and then the absorbance peak at 325 nm decreased gradually. The isosbestic points at 312 nm can be clearly observed with increasing concentrations of Hg²⁺ (0-10 equiv.), indicating a new and stable complexation of ligand L with Hg²⁺ ion (**Figure S 2**).

The whole reaction process was shown in **Scheme 2**. This phenomenon may be attributed to the function of desulfurization of the ligand **L** toward Hg^{2+} (**Figures S 3 and S 4**) ²¹⁻²³.

Experimental

Synthesis and characterization

N-(4-acetylphenyl)-N'-(2-nitrobenzoyl)-thiourea was synthesized in high yield (**Scheme 1**). Potassium thiocyanate (7.5 mmol), 2-nitrobenzoyl chloride (5 mmol), PEG-400 (3% with respect

to ammonium thiocyanate) and dichloromethane (20 mL) were placed in a dried flask and stirred at room temperature for 1h, then 1-(4-aminophenyl)ethanone (5 mmol) was added. The mixture was stirred for 0.5h at room temperature and a precipitate was formed. This was filtered off, washed with water and dried. Yellow single crystals of the title compound were obtained slowly due to evaporation of an ethanol-dimethylformamide (1:1) solution. Yield, 80%; m.p. 162-164 °C ¹H NMR (600 MHz, cdcl₃) δ 12.45 (S, N–H), 12.25 (S, N–H), 8.24-7.81 (m, Ar–H), 3.34 (S, –CH₃). Anal. calcd. (%) for C₁₆H₁₃N₃O₄S (%): C, 5.97; H, 3.82; N, 12.24; O, 18.64; S, 9.34. Found (%): C, 5.98; H, 3.84, N, 12.21; O, 18.65; S, 9.36. IR (KBr) ν : 3450 cm⁻¹ (–OH), 3179 cm⁻¹, 1519 cm⁻¹ (–NH), 3032 cm⁻¹ (–CH₃), 1596 cm⁻¹ (–C=S), 1680 cm⁻¹ (–C=O). ESI-MS calcd for C₁₆H₁₃N₃O₄+H 344.06, found 344.16.

Investigation Techniques

The title compound was studied by various physicochemical methods: X-ray diffraction.

X-Ray Diffraction

A single crystal was carefully selected under a polarizing microscope in order to perform its structural analysis by X-ray diffraction. Data collection: Bruker APEX2; cell refinement: Bruker SAINT; data reduction: Bruker SAINT; program(s) used to solve structure: SHELXS97

(Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Bruker SHELXTL; software used to prepare material for publication: Bruker SHELXTL. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 2. Crystallographic data for the title compound L have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC reference numbers 1056740. These data can be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

Conclusions

In summary, we have designed and synthesized N-(4-acetylphenyl)-N'-(2-nitrobenzoyl)-thiourea in high yield. The crystal structure show that the intramolecular hydrogen bonding (N3-H3A···O3 and C10-H10···S1) between the amide-N and*p*-nitrobenzoyl-O atoms, and the acetylphenyl-C10 and the thiourea-S, respectively. Moreover, in the crystals, the compound were linked to a supramolecular one-dimensional a ribbon chains through the intermolecular hydrogen bonds. In addition, investigation of biological activity shows the compound show good plant-growth regulation activity and the ligand L demonstrated an

excellent property of molecule recognition with fast and selective detection for mercury.

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Figure 1. The crystal structure of the title compound.



Figure 2. UV-vis absorption of sensor L $(2.0 \times 10^{-4} \text{ M})$ in the presence of 20 equiv. various

cations in DMSO.



Figure 3. UV-vis absorption response of L (2×10^{-4} M) in the presence of various cations

 $(4 \times 10^{-3} \text{ M})$ in DMSO solution in response to Hg²⁺ $(4 \times 10^{-3} \text{ M})$



Scheme 1. Synthetic procedures for the title compound.



Scheme 2. Possible recognition mechanism.