Research Article

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Synthesis and crystal structure of N, N'-bis(4chlorophenyl)thiourea N,N-dimethylformamide

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Abstract: This study is about the synthesis of *N*,*N*'-bis(4chlorophenyl)thiourea N,N-dimethylformamide (C₁₆H₁₇Cl₂N₃OS) compound. Single crystals of the compound were obtained by slow evaporation of *N*,*N*'-bis(4-chlorophenyl)thiourea (C₁₃H₁₀Cl₂N₂S) in *N*,*N*-dimethylformamide (C₃H₇NO; DMF) through recrystallization under mild condition. Important classical N-H…O links the two molecules together. Results revealed that C₁₆H₁₇Cl₂N₃OS crystallized in the monoclinic space group $P2_1/c$ with the respective cell parameters of a = 92,360 (4) Å, b = 7.2232 (3) Å, 25.2555 (11) Å, $\beta = 91.376$ (3), $\alpha = \gamma = 90^{\circ}$, V = 1684.40 (12) Å³, T = 119.94 (13) K and Z = 4 and Z' = 1.

Keywords: thiourea, dimethylformamide, crystal structure, monoclinic

1 Introduction

Thiourea belongs to the class of organic compounds containing sulphur [1]. It is a broad-spectrum compound used in synthetic chemistry [2]. Thiourea belongs to the thioamide class of compounds. The structure is similar to urea and has a general formula of $(R_1R_2N)(R_3R_4N)C=S$ [1]. Thiourea is also referred to as thiocarbamide and sulphourea. The International Union of Pure and Applied

Chemistry name is 2-thiourea, while the atomic formula for thiourea is CS(NH₂)₂ [1]. Thiourea has numerous applications in agriculture, health and metallurgy [1]. Thiourea derivatives are useful anticancer agents [1,3].

Several ways of synthesizing thiourea have been reported [1,2]. Methods reported to synthesize thiourea involve intermediaries, such as carbon disulphide and ammonium thiocyanate isomerization, cyanamide, cyanamide-hydrogen sulphide, lime nitrogen, urea-calcium cyanamide and urea-cyanamide [4-6].

The synthetic method to yield thiourea from ureacyanamide involves dehydrated urea under normal pressure from the reaction of ammonia and carbon(IV) oxide to form cyanamide (H_2CN_2) [5]. The H_2CN_2 reaction with hydrogen sulphide forms thiourea. This method, which is of high production cost, usually gives a low yield of thiourea because of many side reactions which take place during the reaction process. Another demerit in this method is the difficulty encountered in the reaction because of carbon(IV) oxide inertness [5].

In the case of method involving urea-calcium cyanamide (Ca(OCN)₂) as intermediary, calcium cyanamide and calcium oxide are used as reactants to form the intermediate product, namely Ca(OCN)₂. The Ca(OCN)₂ reacts with H₂S to form thiourea. This method is also flawed with high production cost and low product yield. Additionally, the produced viscous Ca(OCN)₂ as intermediate during the reaction process cannot be removed from the subsequent reaction in the thiourea synthesis, due to the lack of supporting apparatus [5]. The by-product, calcium hydroxide (Ca(OH)₂), produced along with H₂S, has low solubility in water, which forms a thick agglomerate in the reaction vessel, and as a result affects reaction progress.

The method involving carbon(IV) sulphide (CS₂) uses CS₂ and ammonia (NH₃) as reactants, as the same reactants apply to the synthesis of dithiocarbamate [5,7]. The decomposition reaction between both reactants gives ammonium thiocyanate, which is isomerized to form thiourea, and H₂S as by-product [5]. This method also gives a low yield because of ammonium thiocyanate

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isomerization as well as properties of both ammonium thiocyanate and thiourea. Additionally, no efficient separation method was used in the synthesis due to the reaction vessel's neck. The method involving ammonium thiocyanate isomerization uses ammonium thiocyanate as the reactant to obtain thiourea. The reaction's demerits are high production cost and low yield. The method involving lime nitrogen uses calcium oxide and water as reactants to produce lime milk, which absorbs hydrogen sulphide to obtain calcium hydrosulphide with a better yield [5].

Synthesis of thiourea through cyanamide–hydrogen sulphide uses cyanamide and a catalyst (as an improved atmospheric molecular sieve) in the urea atmospheric pressure dehydration stage, which is accomplished in an ammonia atmosphere to form cyanamide. The thiourea is then synthesized in a concentrated cyanamide solution and hydrogen sulphide gas. It gives a low reaction product of thiourea [5,7]. Among the aforementioned methods, the CS_2 method was applicable to this study because of the availabilities and accessibilities of the reactants [7].

However, in an attempt to synthesize chloroaniline dithiocarbamate (C₇H₆ClN₂S₂NH₄), a new crystalline compound of thiourea $(C_{13}H_{10}Cl_2N_2S)$ was formed. The thiourea was formed from a mixture of chloroaniline, carbon(IV) sulphide and ammonia solution in methanol at a temperature of less than 4°C [5]. In order to confirm the structure, crystal growth by slow evaporation at room temperature was carried out on a quantity of the product (solid white precipitate) in N,N-dimethylformamide (DMF). The structural determination was carried out with single crystal X-ray diffraction characterization technique. In this article, we present the crystal structure of C₁₆H₁₇Cl₂N₃OS. Specific intermolecular interactions are halogen bonds, orthogonal multipolar interactions, halogen and aromatic rings, hydrophobic interaction and hydrogen bonds (Scheiner 2016). Existence of specific interaction, such as NH-O between two partner molecules, has made molecular recognition to rely on it for stability and strength [8,9].

2 Experimental

2.1 Materials

P-Chloroaniline and ammonia solution were purchased from BDH Laboratory Reagents (England), while carbon(IV) sulphide was supplied by Associated Chemical Enterprises (Pty) Ltd (South Africa). *N*,*N*-DMF was purchased from Merck (Germany). All chemicals and reagents were used as received without further purification.

2.2 Synthesis of C₁₃H₁₀Cl₂N₃S

The methods used were in line with Azizi et al. and Maddani and Prabhu methods, though with some modifications [10,11]. To a methanolic solution containing *para*-chloroaniline (1 mmol) and cold carbon(IV) sulphide (6.00 mL, 1 mmol), ammonia solution (4.00 mL) was added dropwise. Reaction temperature was less than 4°C with continuous stirring for 3 h at room temperature (298 K), which gave a product of white precipitates. The product was filtered, washed several times with diethyl ether solvent to remove unreacted reactants [7] and dried *in vacuo* over silica gel. Yield was high to give 84% of the product. The chemical reaction is shown in Scheme 1.

2.3 Formation of C₁₆H₁₇Cl₂N₃OS crystals

The $C_{13}H_{10}Cl_2N_2S$ (50 mg, 0.11 mmol) was placed in a 100mL conical flask. Methanol (7 mL) and DMF (5 mL) were added to $C_{13}H_{10}Cl_2N_2S$ in the 100 mL conical flask. This was stirred on a magnetic stirrer until all the solute dissolved in the solvent mixture to give a clear solution. The flask was covered with punched aluminium foil and kept in a fume cupboard. The reaction vessel was allowed to evaporate slowly at room temperature. Filtration method was used to collect single, large and white polygon crystals, which were dried over silica gel in a desiccator. The percentage yield obtained was 84%.

2.4 Study of C₁₆H₁₇Cl₂N₃OS

A suitable crystal $0.17 \text{ mm}^3 \times 0.12 \text{ mm}^3 \times 0.10 \text{ mm}^3$ was selected and mounted on a tip of a glass fibre with a small quantity of silicon grease and later placed on a goniometer head [12]. Data were collected on a Xcalibur, AtlasS2, Gemini ultra diffractometer (Agilent Technologies XRD)

 $2C_6H_4CINH_{2(aq)} + CS_{2(l)} + 2NH_{3(l)} \rightarrow C_{13}H_{10}Cl_2N_2S_{(s)} + 3H_{2(g)} + H_2S_{(g)} + N_{2(g)}$

Scheme 1: Synthesis of N, N'-bis(4-chlorophenyl)thiourea.

Products, Oxfordshire, United Kingdom) with graphite-monochromatized Mo-Kα radiation at 150 K. The crystal was kept at T = 119.94 (13) K during data collection. CrysAlisPro software package was used to refine, reduce and integrate the data for Lorentz polarization. Corrections for the absorption (multi-scan) were also performed using CrysAlisPro 1.171.39.12b [13]. Empirical absorption correction using spherical harmonics was implemented in SCALE3 ABSPACK scaling algorithm. Coordinates of bulk non-hydrogen atoms were established by direct methods using CrysAlisPro [13]. Locations of the outstanding non-hydrogen bonding were positioned with a combination of least-square refinement in CrysAlisPro program. Other hydrogen atoms were positioned in geometrically calculated locations. The model was refined with version 2017/1 of olex2.refine [14] using Gauss-Newton minimization. Crystal data and refinement parameters are shown in Table 1.

Ethical approval: The conducted research is not related to either human or animal use.

3 Result and discussion

The title compound was synthesized, and the crystal structure is reported here. Related structure can be seen in Ghorab et al. [15]. The standard bond-length data can be seen in Allen et al. [16]. For bond lengths, other substituted thioureas can be seen in Rauf et al. and Saeed et al. [17,18]. For earlier reported C=S distances, bond distances can be seen in Bailey et al. [19].

3.1 Structural description and tabular results of C₁₆H₁₇Cl₂N₃OS

The compound of $C_{16}H_{17}Cl_2N_3OS$ crystallized in monoclinic system, space group $P2_1/c$, and the crystallographic independent unit has a twin chlorophenyl azanide ring linked to a carbon monosulphide bond at the basal (Figure 1). Intrinsic phasing using the ShelXT structure solution program was used to solve the structure [20], while Gauss–Newton version 2017/1 of olex2 was used to refine the structure [14]. All non-hydrogen atoms were anisotropically refined with CrysAlisPro 1.171.39.12b [21]. Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for $C_{16}H_{17}Cl_2N_3OS$ are summarized in Table S1, while the anisotropic displacement parameters (×10⁴) for $C_{16}H_{17}Cl_2N_3OS$ are summarized in **Table 1:** Single-crystal X-ray diffraction analysis of $C_{16}H_{17}Cl_2N_3OS$ and its structural refinement parameters

| Crystal data | |
|---|--------------------------------|
| Empirical formula | |
| Formula weight $(M_{\rm e})$ | 370.30 |
| Crystal colour | White |
| Crystal size (mm) | $0.17 \times 0.12 \times 0.10$ |
| Crystal system | Monoclinic |
| Snace group | $P_{2_1/c}$ |
| Shane | Polygon |
| a/Å | 9 2360 (4) |
| h/Å | 7 2232 (3) |
| c/Å | 25 2555 (11) |
| $\alpha/^{\circ}$ | 90 |
| а, В/° | 91 376 (3) |
| γ/° | 90 |
| V/Å ³ | 1684 40 (12) |
| 7 | и И |
| - 7' | 1 |
| Т/К | - 119.94 (13) |
| $D_{\rm role}$ /g cm ⁻¹ | 1 4601 |
| $C_{\rm H}$ -Kg radiation λ (Å) | 1 54184 |
| μ/mm^{-1} | 4.684 |
| θ | 67.61° |
| GoF | 1.0403 |
| Data collection | |
| Excalibur Gemini ultra- | Single source at offset |
| diffractometer (Atlas) | 5 |
| Absorption correction | Multi-scan Gaussian |
| | Jana 2006 |
| Radiation source | X-ray tube |
| T _{min} | 0.199 |
| T _{max} | 1 |
| Refinement | |
| Restraints | 0 |
| Measured reflections | 2,991 |
| Independent reflections | 2,989 |
| Reflections used | 2,642 |
| R _{int} | 0.0000 |
| Parameters | 276 |
| Largest peak | 0.3145 |
| Deepest hole | -0.3414 |
| wR_2 (all data) | 0.0991 |
| WR_2 | 0.0938 |
| R ₁ (all data) | 0.0389 |
| R_1 | 0.0336 |

Table S2. Bond lengths in Å and bond angles in ° for $C_{16}H_{17}Cl_2N_3OS$ are given in Tables S3 and S4, respectively. On the other hand, the hydrogen fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for $C_{16}H_{17}Cl_2N_3OS$ are given in Table S5, and hydrogen bond information is given in Table S6. The



Figure 1: Crystalline structure of C₁₆H₁₇Cl₂N₃OS.

crystalline compound is an isomer of 2-[(2,6-dichlorophenyl) methyl]-*N*-piperidin-1-yl-1,3-thiazole 4-carboxamide. The difference between it and the isomer is the positioning of the chloro group [22].

3.2 Interpretation of significant thiourea DMF solvate

Single-crystal X-ray diffraction method was used to determine and confirm the structure of the synthesized $C_{16}H_{17}Cl_2N_3OS$ compound. In the compound, two Cl atoms are coplanar with the C2–C7 and C11–C10 rings, respectively [23,24]. The C8–C2–N2–O1 and C14–C11–N3–O1 torsion angles are set up by aromatic ring. Inside the thiourea moiety, the geometry of C1 atom is preferably planar with a sum of bond angle of 490 (2). Result varies from bond angle reported by Binzet et al. [25], probably due to hydrogen bonding [25]. The S1 atom is out of the plane of the N–C–N thiourea. The thiourea moiety is almost vertical to two benzene rings [24].

The geometry around the nitrogen atom is distorted and cannot be estimated on hybridization origin. The distortion can simply be drawn by the contribution of lone pair of electrons on nitrogen in the delocalization phenomenon with the π electrons of C—S moiety [26]. The bond distances of C1–N2 (1.357 Å) and C1–N3 (1.360 Å) are shorter than the average C–N single-bond distance (1.499 Å) and likewise that of C—S bond distance (1.680 Å) is longer than the average distance (1.599 Å) as stated in literature [26,27]. The elongation of C—S bond might be due to the presence of intermolecular hydrogen bonding (data given in Table S5).

In $C_{16}H_{17}Cl_2N_3OS$, two benzene rings enclose a dihedral angle of 111.05 (18)°, while the corresponding angle from the carbonyl groups of the DMF is 124.9 (2)° in N4–C9–O1. The thiourea molecule in its thione form includes C=S and C–N bond lengths [28]. In the crystal, N–H…O hydrogen bonds can be found between the thiourea and carbonyl groups of the DMF. The DMF molecule forms a hydrogen bond with two N atoms of the thiourea group [28].

The N–C bonds in Figure 1 differ from one another as also reported by Li and Hou [28]. They are shorter in comparison with the conventional value for an N–C single bond (1.479 Å). The adjacent C=S bond length (1.680 (1) Å) is shorter than the earlier reported C=S distance (1.710 (7) Å) [19], because of the introduced C=O electron-acceptor group. These distances are similar to those normally found in substituted thioureas [23,29]. Intramolecular and intermolecular N–H···O hydrogen bonds occur between the thiourea N–H atoms and carbonyl-O atom of the DMF solvate molecule, which also has a hydrogen bond between the two N atoms of the thiourea groups (2.880 (2) and 2.8802 (2); Figure 2, Table S6) [28].

The solid-state crystal packing and intermolecular interactions are shown in Figure 2. The $C_{16}H_{17}Cl_2N_3OS$ molecules are structured and held together with the help of intermolecular N–H···O hydrogen bonding with an average distance of 2.880 (2) Å. Their *a*, *b* and *c* axes are shown in Figure 2. The $C_{16}H_{17}Cl_2N_3OS$ molecules are arranged and structured with the assistance of N–H···O hydrogen bonding, with an average distance of 2.841 Å, which is in the expected range, reported for analogues' compounds, that is, 2.87 Å [16,26].

The packing contains parallel networks formed by intermolecular bonding [27]. The crystal packing is intermolecular hydrogen bonding through $N(3)\cdots H(3)\cdots O(1)$ and intramolecular hydrogen bonding through $N(2)\cdots H(2)\cdots O(1)$, where the two-dimensional hydrogen bonding network could be observed. The NH group of $C_{16}H_{17}Cl_2N_3OS$ ligand was arranged to enable the formation of intra- and intermolecular hydrogen bonds, which entails the two chloro atoms as acceptors [27].

3.3 Crystal packing

The crystal packing for $C_{16}H_{17}Cl_2N_3OS$ in *a*, *b* and *c* axes is shown in Figure 2.



Figure 2: (a) Crystalline structure of $C_{16}H_{17}Cl_2N_3OS$ along *a* axis. (b) Crystalline structure of $C_{16}H_{17}Cl_2N_3OS$ along *b* axis. (c) Crystalline structure of $C_{16}H_{17}Cl_2N_3OS$ along *c* axis.

4 Conclusion and future direction

Characterization technique of single crystal diffraction confirmed the crystalline structure of N,N'-bis(4-chloropenyl)thiourea N,N-DMF.

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Supplementary materials: Supplementary data and figures for this study are available from the International Union of Crystallography (IUCr) electronic archives (Reference: CCDC 1579588).

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