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Synthesis, Characterization and X-ray Structures of \{\alpha\text{-Diphenylethanedione Bis(4-ethylthiosemicarbazonato)}\}palladium(II) and 1,2,4-Triazine-3-thione–Zinc(II) Complexes Obtained by Metal-Induced Cyclization

Ana I. Matesanz,[a] Cesar Pastor,[b] and Pilar Souza* [a]

Keywords: Thiosemicarbazones / Cocrystals / Palladium(II) / Zinc(II) / X-ray diffraction

The new cyclic 5-ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2H[1,2,4]-triazine-3-thione ligand (HTa3T-Et) has been obtained by an intramolecular cyclization reaction of \(\alpha\text{-diphenylethanedione bis(4-ethylthiosemicarbazone)}\) (H\(_2\)BbTSC-Et). The cyclization may be promoted either by hydroxylic solvents or by Zn\(^{II}\) ions. Thus, the reaction of H\(_2\)BbTSC-Et with ZnCl\(_2\) led to the formation of [Zn(HTa3T-Et)\(_2\)Cl\(_2\)] containing not the ligand H\(_2\)BbTSC-Et but the cyclic HTa3T-Et ligand that forms during the reaction. On the other hand, crystallization of H\(_2\)BbTSC-Et from DMSO/EtOH produces a cocrystal containing the open-chain H\(_2\)BbTSC-Et ligand together with the cyclic HTa3T-Et molecules, which are linked to a DMSO molecule by hydrogen bonds. However, reaction of the cocrystal with Pd\(^{II}\) ions yields a planar tetracoordinate complex in which only the H\(_2\)BbTSC-Et ligand, in the deprotonated form, is present. The preparation and molecular structures of these compounds are discussed.

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Introduction

Thiosemicarbazones (TSCs) are a versatile type of ligand because of the number of donor atoms they possess, among which sulfur is of paramount importance in the metal–ligand linkage; moreover, their configurational flexibility creates the possibility of a variety of coordination modes.[1–3] Thiosemicarbazone derivatives have raised considerable interest in chemistry and biology because of the antibacterial, antiviral and antitumor activity that many of them have shown.[4,5] In some cases, the highest activity is associated with a metal complex rather than the free thiosemicarbazone.[6]

It is well known that thiosemicarbazones derived from 1,2-dicarbonyl compounds easily cyclize during the synthesis process, especially when hydroxylic solvents are used or when solutions in such solvents are allowed to crystallize over several days.[7] In all cases, this cyclization leads to 1,2,4-triazine-3-thione ligands (Scheme 1); these ligands are very versatile and are able to form mono-, di- and polynuclear metal complexes as a result of two different coordination modes: as a monodentate, neutral ligand with coordination through the sulfur atom or as an anionic bidentate ligand with coordination through the sulfur and nitrogen atoms.[8]

Compounds containing the 1,2,4-triazine moiety have been found in natural products and some of these have important applications in various fields. For example, 1,2,4-triazine-3,5-diones represent aza analogues of pyrimidine nucleic acid bases, some neutral antibiotics are derivatives of pyrimido[5,4-e]-1,2,4-triazine, and 4-amino-6-tert-butyl-3-methylthio-1,2,4-triazine-5-one and 4-amino-3-methyl-6-phenyl-1,2,4-triazine-5-one are used as agricultural chemicals.[9]

As part of our systematic investigation on the coordination chemistry of thiosemicarbazone derivatives,[10,11] we recently reported a paper that focuses on the structure–antitumor activity relationships of a series of palladium and platinum \(\alpha\text{-diphenylethanedione bis(thiosemicarbazone)}\) derivatives. In all compounds studied there, the ligands unambiguously show the bis(thiosemicarbazone) form.[12] To extend...
our studies, particularly with respect to the coordination properties of H₂BbTSC-Et and the stereochemistry and molecular structure of the complexes, we planned to synthesize new metal derivatives. It was possible, after numerous attempts at crystallization of the H₂BbTSC-Et ligand, to obtain good quality crystals suitable for X-ray analysis from DMSO/EtOH solution. These proved to be cocrystals containing, together with H₂BbTSC-Et, the cyclic derivative formed by an intramolecular cyclization reaction. To the best of our knowledge, this is the first report of the isolation of a bis(thiosemicarbazone) molecule and the cyclic form as single crystals. Interestingly, the reaction of the new cocrystal isolated with palladium(II) ions gave the mononuclear N₂S₂-tetracoordinate bis(thiosemicarbazone) complex instead the binuclear CNS₂-tetracoordinate bis(thiosemicarbazone) recently reported by us.[12]

Some of the different routes published that undergo the cyclization of thiosemicarbazones use a metallic salt (Zn²⁺, Cu²⁺ and Fe³⁺). On this basis and in order to search for novel cyclized compounds, we also report here the reaction of H₂BbTSC-Et with ZnCl₂. The reaction yields a new zinc(II) compound containing, in neutral form, the cyclic ligand 5-ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione (HTa₃T-Et, see Scheme 1).

Results and Discussion

Synthesis of the Ligands

The preparation of crude H₂BbTSC-Et was carried out according to ref.[12] Analytical and spectroscopic properties are consistent with those reported.

Attempted slow recrystallization of H₂BbTSC-Et from DMSO/EtOH resulted in the isolation of a cocrystal H₂BbTSC-Et/HTa₃T-Et in a 1:1 ratio that also contains DMSO molecules. The structural data suggests that some H₂BbTSC-Et molecules may be transformed into the final 1,2,4-triazine-3-thione ligand by an intramolecular cyclization reaction, similar to that described by Alsop et al.[13] The cyclization with concomitant insertion of ethanol and elimination of 4-ethylthiosemicarbazide seems to be favoured when hydroxyl solvents are used or when solutions in such solvents are allowed to crystallize over several days.

Structures of the Ligands

The structure of the cocrystal H₂BbTSC-Et/HTa₃T-Et consists of one H₂BbTSC-Et molecule and one cyclic triazine molecule HTa₃T-Et together with one dimethylsulfoxide molecule of crystallization (Figure 1). Selected bond lengths and angles are given in Table 1.

![Figure 1. Structure of the cocrystal H₂BbTSC-Et/HTa₃T-Et.](image)

Table 1. Selected bond lengths [Å] for H₂BbTSC-Et and H₂BbTSC-Et/HTa₃T-Et.

<table>
<thead>
<tr>
<th>Bond</th>
<th>H₂BbTSC-Et</th>
<th>H₂BbTSC-Et/HTa₃T-Et</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1–C3</td>
<td>1.678(2)</td>
<td>1.681(3)</td>
</tr>
<tr>
<td>S2–C6</td>
<td>1.676(2)</td>
<td>1.689(3)</td>
</tr>
<tr>
<td>N1–C2</td>
<td>1.459(3)</td>
<td>1.467(4)</td>
</tr>
<tr>
<td>N1–C3</td>
<td>1.317(3)</td>
<td>1.313(4)</td>
</tr>
<tr>
<td>N2–N3</td>
<td>1.356(2)</td>
<td>1.362(4)</td>
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<td>N2–C3</td>
<td>1.369(3)</td>
<td>1.371(4)</td>
</tr>
<tr>
<td>N3–C4</td>
<td>1.286(3)</td>
<td>1.290(3)</td>
</tr>
<tr>
<td>N4–C5</td>
<td>1.291(3)</td>
<td>1.294(4)</td>
</tr>
<tr>
<td>N4–N5</td>
<td>1.360(2)</td>
<td>1.360(3)</td>
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<tr>
<td>N5–C6</td>
<td>1.368(3)</td>
<td>1.375(4)</td>
</tr>
<tr>
<td>N6–C6</td>
<td>1.317(3)</td>
<td>1.325(4)</td>
</tr>
<tr>
<td>N6–C7</td>
<td>1.456(3)</td>
<td>1.460(4)</td>
</tr>
<tr>
<td>N7–C22</td>
<td>1.470(4)</td>
<td></td>
</tr>
<tr>
<td>N7–C23</td>
<td>1.470(4)</td>
<td></td>
</tr>
<tr>
<td>N8–N9</td>
<td>1.359(4)</td>
<td></td>
</tr>
<tr>
<td>N8–C23</td>
<td>1.354(4)</td>
<td></td>
</tr>
<tr>
<td>N9–C24</td>
<td>1.281(4)</td>
<td></td>
</tr>
</tbody>
</table>

The crystal and molecular structures with the numbering schemes of the H₂BbTSC-Et and HTa₃T-Et molecules are shown in Figure 2.

The H₂BbTSC-Et molecule consists of two distinct essentially planar sections, which are pivoted about the C₅–C₄ “backbone” of the ligand, with a C₁₅–C₅–C₄–C₉ torsion angle of 79.4(3)°. Within each planar section, the C–N and N–N bond lengths, intermediate between the ideal values of corresponding single and double bonds, are indicative of a delocalized system. The existence of the thiosemicarbazone groups in the thione form, in the solid state, is evidenced by the C–S bond lengths of 1.681(3) and 1.689(3) Å, which are close to a formal C=S bond length.[13]

The HTa₃T-Et molecule is a triazine-thione formed from an intramolecular reaction during the recrystallization process. This six-membered heterocyclic C₅N₃ ring is close to planar [torsional angles: C₂₅–N₇–C₂₃–N₈ 10.0(4)°, N₉–N₈–C₂₃–N₇ 15.5(4)°, N₈–N₉–C₂₄–C₂₅ 0.4(4)°]. Although
Synthesis of Thiosemicarbazone Complexes by Metal-Induced Cyclization

Figure 2. Molecular structure of the H2BbTSC-Et (top) and HTa3T-Et (below) molecules, which shows the atom numbering scheme (H atoms were omitted for clarity).

Figure 3. View of cocrystal H2BbTSC-Et/HTa3T-Et along the b axis.

Figure 4. Molecular structure of [Pd(BbTSC)].

the C–S bond length of 1.679(3) Å is in the range of a C=S bond, some electronic delocalization occurs in the ring formed. Thus, while the bond length for N9–C24 of 1.281(4) Å is consistent with a C=N bond, both N8–C23 and N7–C23 bonds [1.354(4) and 1.344(4) Å, respectively] are considerably shorter than the predicted length of 1.47 Å for a C–N bond. Further, the N8–N9 bond with a length of 1.359(4) Å is significantly shorter than the predicted N–N bond length of 1.45 Å. On the other hand, the N7–C25 bond [1.490(4) Å] is slightly longer than the predicted C–N bond, and the C24–C25 bond [1.523(4) Å] is slightly shorter than the predicted length 1.54 Å for a C–C bond.14

Within the crystal, the two independent molecules are linked to a DMSO molecule by N–H···O bonds. The crystal packing along the b axis (Figure 3) shows parallel alternating lines of H2BbTSC-Et and HTa3T-Et molecules.

Synthesis and Structure of the Complex [Pd(BbTSC)]

We have recently verified that the reaction of crude H2BbTSC-Et with Li2PdCl4 in methanol undergoes orthometallation to give a dinuclear bis(thiosemicarbazone) complex.12 Thus, we decided to investigate the coordinating properties of the cocrystal H2BbTSC-Et/HTa3T-Et to palladium(II). The analytical and spectroscopic data of the isolated compound are in agreement with the formula [Pd(BbTSC)], in which the H2BbTSC ligand is in the doubly deprotonated form. Green single crystals were obtained on recrystallization from DMSO, and the X-ray diffraction study confirmed the proposed formula.

An ORTEP representation of [Pd(BbTSC)] together with the atom labelling scheme is shown in Figure 4, and selected bond lengths and angles are given in Table 2. This neutral PdII complex crystallizes in the monoclinic C2/c space group with Z = 4 as discrete C20H22N6S2Pd·DMSO molecules.

On the basis of other α-diketone bis(thiosemicarbazones),15 the mode of coordination for this complex is as expected; two iminic nitrogen atoms and two thiolato sulfur atoms bond to Pd on the loss of the hydrogen atoms of N2 and N2A from both thiosemicarbazone moieties to give an approximately planar, four-coordinate complex. Thus, the coordination of the bis(thiosemicarbazone) results in the formation of three five-membered chelate rings (PdSCNN, PdNCCN and PdNNS).

A careful examination of the bond length data shows that the Pd–Nimine and Pd–S distances are comparable with those reported for other thiosemicarbazone palladium(II) complexes with strong Pd–N coordination.10 Since the Pd–S bonds are significantly longer than the Pd–N bonds, the coordination geometry around the metal ion is more trape-
zoid than square. The overall impression from the values of the bond lengths and angles in the vicinity of the palladium atom is that the ligand cavity is too small to accommodate the Pd²⁺ ion ideally. Thus, the N–Pd–N bond angles are less than 90°, and the sulfur ends of the ligand arms are pushed outwards beyond the natural position that would be adopted by the planar ligand, with S–Pd–S bond angles of ca. 109°.

The loss of the protons originally bonded to N2 and N2A atoms produces a negative charge delocalized in the ligand system, which is consistent with the C–N distances (intermediate between formal single and double bonds) and C–S distances (see Table 2). This substantiates the displacement of the tautomeric equilibrium to the thiol form in the ligand.

The terminal uncoordinated nitrogen atoms are involved in intermolecular hydrogen bonds with the oxygen atoms of the solvent molecules; the contact distances and angles are N3···O1 2.897(4) Å and N–H–O 162(4)°.

### Table 2. Selected bond lengths [Å] and angles [°] for [Zn(HTa3T-Et)2Cl2] and [Pd(BbTSC)].

<table>
<thead>
<tr>
<th></th>
<th>[Zn(HTa3T-Et)2Cl2]</th>
<th>[Pd(BbTSC)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1–C1</td>
<td>1.7113(19)</td>
<td>1.771(3)</td>
</tr>
<tr>
<td>N1–C1</td>
<td>1.329(2)</td>
<td>1.325(4)</td>
</tr>
<tr>
<td>N1–C2</td>
<td>1.490(2)</td>
<td>1.332(4)</td>
</tr>
<tr>
<td>N2–C1</td>
<td>1.342(2)</td>
<td>1.334(4)</td>
</tr>
<tr>
<td>N3–C3</td>
<td>1.281(3)</td>
<td>1.462(4)</td>
</tr>
<tr>
<td>N2–N3</td>
<td>1.376(2)</td>
<td>1.351(4)</td>
</tr>
<tr>
<td>Zn1–C1</td>
<td>2.2380(5)</td>
<td>1.982(3)</td>
</tr>
<tr>
<td>Zn1–C1A</td>
<td>2.2379(5)</td>
<td>1.982(3)</td>
</tr>
<tr>
<td>Zn1–S1</td>
<td>2.3694(5)</td>
<td>2.2792(8)</td>
</tr>
<tr>
<td>Zn1–S1A</td>
<td>2.3693(5)</td>
<td>2.2792(8)</td>
</tr>
<tr>
<td>Cl1A–Zn1–C1</td>
<td>124.74(3)</td>
<td>N1A–Pd1–N1</td>
</tr>
<tr>
<td>Cl1A–Zn1–S1A</td>
<td>111.374(17)</td>
<td>N1–Pd1–S1A</td>
</tr>
<tr>
<td>Cl1A–Zn1–S1</td>
<td>102.003(17)</td>
<td>N1–Pd1–S1</td>
</tr>
<tr>
<td>Cl1–Zn1–S1A</td>
<td>102.000(17)</td>
<td>N1A–Pd1–S1A</td>
</tr>
<tr>
<td>Cl1–Zn1–S1A</td>
<td>102.000(17)</td>
<td>N1–Pd1–S1</td>
</tr>
<tr>
<td>S1A–Zn1–S1</td>
<td>103.79(3)</td>
<td>S1A–Pd1–S1</td>
</tr>
</tbody>
</table>

### Synthesis and Structure of the Complex [Zn(HTa3T-Et)2Cl2]

The reaction of crude H₂BbTSC-Et ligand with ZnCl₂ in ethanol led to the formation of the crystalline yellow [Zn(HTa3T-Et)2Cl2] complex. The analytical, spectroscopic, and X-ray diffraction data (see Experimental Section) revealed that H₂BbTSC-Et is transformed into cyclic ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione (HTa3T-Et) during the complexation reaction. An analogous cyclization of 2-pyridiformamide 4-ethylthiosemicarbazone that is promoted by the presence of silver(I) ions was reported recently by Castiñeiras et al.[16]

The mother liquor was allowed to stand at 4 °C. After several days, crystalline pale yellow needles were isolated, which were identified as the free ligand H₂BbTSC-Et by X-ray diffraction analysis. Its molecular structure essentially shows the same structural characteristics as that of the open-chain molecule in the cocrystal H₂BbTSC-Et/HTa3T-Et. Selected bond lengths and angles are given in Table 1.

The crystal packing (Figure 5) shows parallel pseudochains of molecules, and the absence of any solvent of crystallization indicates possible existence of noncovalent interactions between the individual bis(thiosemicarbazone) molecules. A closer look reveals π–π stacking interactions between successive thiosemicarbazone moieties (3.62 Å). These extended intermolecular interactions are responsible for holding the crystal together.

![Figure 5. Side view of H₂BbTSC-Et, which shows the parallel disposition of the molecules as a result of π–π stacking.](image)

An ORTEP representation of [Zn(HTa3T-Et)2Cl₂] together with the atom labelling scheme is shown in Figure 6, and selected bond lengths and angles are given in Table 2.

![Figure 6. Molecular structure of Zn(HTa3T-Et)2Cl₂ (H atoms were omitted for clarity).](image)

This neutral complex crystallizes in the orthorhombic Fdd₂ space group with Z = 8. The zinc atom is tetracoordinated by two chlorido ligands and two sulfur atoms from the neutral monodentate ligands HTa3T-Et. The largest angular distortion from ideal tetrahedral geometry is shown by Cl1A–Zn1–Cl1 [124.74(3)°]. Although the chlorido ligands participate in the hydrogen bonding, the distances Zn–Cl [2.238 Å] fall in the range of the shortest lengths for...
terminal Zn-Cl bonds. The Zn-S and C-S distances [2.369 and 1.711 Å, respectively] are similar to those found in other complexes with thioะcarbynyl sulfur atoms. The 4-ethyl substituent on the N1 atom reduces the possibilities for hydrogen bonding. Thus, only two intramolecular N2-H···Cl bonds are present in the complex.

An analysis of the relative disposition of the complex molecules in the crystal structure highlights the importance of aromatic-aromatic edge-to-face interactions in the packing that takes place when the crystal is formed. The perpendicular (ca. 96°) distance between C–H and the plane of π system is ca. 2.88 Å.

Conclusions

The investigations show that the synthesis of bis(thiosemicarbazone) derivatives from α-diketones with alkyl substituents can be complicated by the formation of cyclized products. Typically, the α-bis(thiosemicarbazones) are made by heating a thiosemicarbazide under reflux with an α-diketone in an alcoholic solvent with an acid catalyst. Although it is well known that such solvents favour cyclisation, we have not found the cyclic 1,2,4-triazine-3-thione form in our previous studies. However, slow recrystallization of the H2BbTSC-Et from DMSO/EtOH affords a cocrystal composed of a 1:1 ratio of open-chain H2BbTSC-Et and cyclic 1,2,4-triazine-3-thione. The formation of the cocrystal could be favoured by the presence of DMSO molecules since they each form two hydrogen bonds with the terminal nitrogen atom of one thiosemicarbazone moiety (hindering the cyclization) and with the hydrazinic nitrogen atom of the other thiosemicarbazone moiety (favouring the cyclization). The intramolecular cyclization reaction may also be promoted by the presence of the salt ZnCl2. Thus, we have achieved the isolation of a ZnII-1,2,4-triazine-3-thione complex in which the zinc atom is tetracoordinated by two chlorido ligands and two sulfur atoms from the neutral monodentate cyclic ligands. Although the different steps involved in this process are not completely understood, it has been assumed that the metal ion plays an important role in this process, probably because of both inductive and steric reasons, as do the solvent and the counterion of the metal.

However, reaction of the cocrystal with Li3PdCl4 yields a planar tetracoordinate complex in which the bis(4-ethyl-thiosemicarbazone) ligand in the deprotonated form is present. In this case, the clear preference for a planar environment of the PdII ion assists the stabilization of the bis(thiosemicarbazone) form.

In summary, the conversion of H2BbTSC-Et to the cyclic 1,2,4-triazine-3-thione form is relatively rapid in hydroxylsolvants, and when a metallic salt is present, the formation of the metal complex stabilizes one of the forms according to its structural preferences. Thus, the cyclization of the H2BbTSC-Et ligand can be controlled by selection of the appropriate metal salt and reaction conditions. Moreover, in this case, the presence of either the phenyl rings, which allow extensive delocalization, or the N1 substitution appears to facilitate the cyclization of the H2BbTSC-Et ligand.

Experimental Section

Materials: Solvents were purified and dried according to standard procedures. 4-Ethylthiosemicarbazide, 1,2-diphenylethanedione, lithium chloride, palladium(II) chloride and zinc chloride were commercially available from Aldrich.

Preparation of the Ligands: H2BbTSC-Et was synthesized according to ref. The reaction of cocrystal H2BbTSC-Et/HTa3T-Et from DMSO/EtOH resulted in the isolation of a cocrystal, which is composed of a 1:1 ratio of H2BbTSC-Et and cyclic HTa3T-Et according to its crystal and molecular structure. The reaction of ZnCl2 (0.3 mmol) in ethanol (40 mL) with H2BbTSC-Et (0.3 mmol), over 5 h whilst stirring and refluxing, led to the formation of a yellow solution, which was filtered and allowed to evaporate at room temperature overnight to give a yellow crystalline solid. The product was identified as the [Zn(HTa3T-Et)Cl2] complex, which does not contain the H2BbTSC-Et ligand but the cyclic HTa3T-Et molecule. Single prismatic crystals suitable for X-ray diffraction were selected directly from the reaction vessel. Yield: 0.17 g (71%). MS (FAB+ with mNBA matrix): m/z (%): 816.1 [M + H]+, 340.1 (100) [HTa3T–Et + H]+. IR (KBr): μ = 3252 (s, NH), 1574 (s, CN), 854 (w, CS-thioamide IV band). 1H NMR ([D6]DMSO): δ = 9.72 (s, 1 H, 3NH), 7.72–7.20 (m, 6 H, Ph), 3.64–3.59 (m, 3 H, CH2CH3), 3.35–3.33 (m, 3 H, OCH2CH3), 1.30–1.25 (t, ((<Author: Please add coupling constant)) 2 H, CH2CH3). After filtering the ZnII complex, the mother liquor was allowed to stand at 4°C, and after several days, pale yellow needles of the free ligand H2BbTSC-Et suitable for X-ray analysis were obtained. Analytical and spectroscopic properties are consistent with those previously reported.

[Pd(BbTSC-Et)]: The reaction of cocrystal H2BbTSC-Et/HTa3T-Et (1 mmol) with a methanol solution of lithium tetrachloropalladate prepared in situ from palladium(II) chloride (1.2 mmol) and lithium chloride (4.4 mmol), over 5 h at room temperature while stirring, led to a dark green solution, which was filtered. From the solution, a dark green solid was isolated by slow evaporation of the solvent, which could then be recrystallized from DMSO to give green crystals suitable for X-ray analysis. On the basis of the molecular structure of [Pd(BbTSC-Et)], the coordinated doubly deprotonated ligand was unambiguously identified as H2BbTSC-Et. Yield: 0.15 g (30%). C28H22N4S2Pd-DMSO (595.08) calculated: C 44.40, H 4.70, N 14.10, S 16.15; found C 44.00, H 5.00, N 14.50, S 15.40%. IR (KBr): μ = 3237, 3187 (s, NH), 1547 (s, CN), 842 (w, CS-thioamide IV band) cm−1. 1H NMR ([D6]DMSO): δ = 8.10 (t, ((<Author: Please add coupling constant)) 1H, 4NH), 7.17–7.11 (m, 6 H, Ph), 3.26 (m, 2 H, CH2CH3), 1.23 (m, 3 H, CH2CH3).

Physical Measurements: Elemental analyses were performed on a LECO CHNS-932 microanalyzer. Fast atom bombardment (FAB) mass spectra were performed with a VG AutoSpec spectrometer (nitrobenzyl alcohol matrix). 1H NMR spectra ([D6]DMSO) were recorded with BRUKER AMX-300 spectrometer. All cited physical
Fourier syntheses, and refined with full-matrix least-squares techniques. Structures were solved by direct methods, completed with difference space group determination, structure solution and refinement. The experimental details and refinement results are listed in Table 3. The data are obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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