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

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

The new cyclic 5-ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione ligand (HTa3T-Et) has been obtained by an intramolecular cyclization reaction of α -diphenylethanedione bis(4-ethylthiosemicarbazone) (H₂BbTSC-Et). The cyclization may be promoted either by hydroxylic solvents or by Zn^{II} ions. Thus, the reaction of H₂BbTSC-Et with ZnCl₂ led to the formation of [Zn(HTa3T-Et)₂Cl₂] containing not the ligand H₂BbTSC-Et but the cyclic HTa3T-Et ligand that forms during the reaction. On the other hand, crystallization of H₂BbTSC-Et from DMSO/EtOH produces a cocrys-

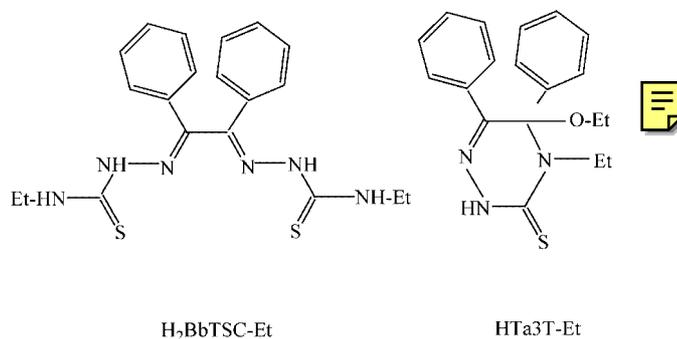
tal containing the open-chain H₂BbTSC-Et ligand together with the cyclic HTa3T-Et molecules, which are linked to a DMSO molecule by hydrogen bonds. However, reaction of the cocrystal with Pd^{II} ions yields a planar tetracoordinate complex in which only the H₂BbTSC-Et ligand, in the deprotonated form, 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]



Scheme 1. Structures for the open-chain H₂BbTSC-ET and the cyclic HTa3T-Et ligands.

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 α -diphenylethanedione bis(thiosemicarbazone) derivatives. In all compounds studied there, the ligands unambiguously show the bis(thiosemicarbazone) form.^[12] To extend

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our studies, particularly with respect to the coordination properties of $\text{H}_2\text{BbTSC-Et}$ 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 $\text{H}_2\text{BbTSC-Et}$ ligand, to obtain good quality crystals suitable for X-ray analysis from DMSO/EtOH solution. These proved to be cocrystals containing, together with $\text{H}_2\text{BbTSC-Et}$, 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 cyclized form as single crystals. Interestingly, the reaction of the new cocrystal isolated with palladium(II) ions gave the mononuclear N_2S_2 -tetracoordinate bis(thiosemicarbazone) complex instead the binuclear CNS_2 -tetracoordinate complex recently reported by us.^[12]

Some of the different routes published that undergo the cyclization of thiosemicarbazones use a metallic salt (Zn^{2+} , Cu^{2+} and Fe^{3+}). On this basis and in order to search for novel cyclized compounds, we also report here the reaction of $\text{H}_2\text{BbTSC-Et}$ with ZnCl_2 . 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-2*H*-[1,2,4]-triazine-3-thione (HTa3T-Et , see Scheme 1).

Results and Discussion

Synthesis of the Ligands

The preparation of crude $\text{H}_2\text{BbTSC-Et}$ was carried out according to ref.^[12] Analytical and spectroscopic properties are consistent with those reported.

Attempted slow recrystallization of $\text{H}_2\text{BbTSC-Et}$ from DMSO/EtOH resulted in the isolation of a cocrystal $\text{H}_2\text{BbTSC-Et/HTa3T-Et}$ in a 1:1 ratio that also contains DMSO molecules. The structural data suggests that some $\text{H}_2\text{BbTSC-Et}$ 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 hydroxylic 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 $\text{H}_2\text{BbTSC-Et/HTa3T-Et}$ consists of one $\text{H}_2\text{BbTSC-Et}$ 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.

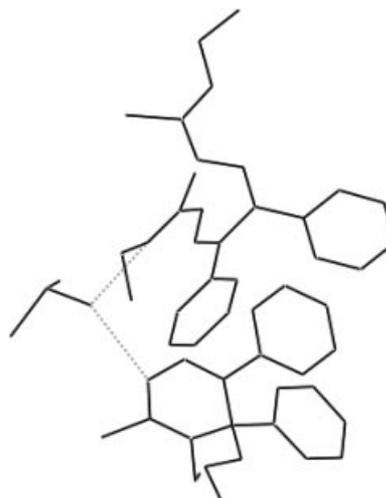


Figure 1. Structure of the cocrystal $\text{H}_2\text{BbTSC-Et/HTa3T-Et}$.

Table 1. Selected bond lengths [Å] for $\text{H}_2\text{BbTSC-Et}$ and $\text{H}_2\text{BbTSC-Et/HTa3T-Et}$.

$\text{H}_2\text{BbTSC-Et}$		$\text{H}_2\text{BbTSC-Et/HTa3T-Et}$	
S1–C3	1.678(2)	S1–C3	1.681(3)
S2–C6	1.676(2)	S2–C6	1.689(3)
N1–C2	1.459(3)	N1–C2	1.467(4)
N1–C3	1.317(3)	N1–C3	1.313(4)
N2–N3	1.356(2)	N2–N3	1.362(4)
N2–C3	1.369(3)	N2–C3	1.371(4)
N3–C4	1.286(3)	N3–C4	1.290(3)
N4–C5	1.291(3)	N4–C5	1.294(4)
N4–N5	1.360(2)	N4–N5	1.360(3)
N5–C6	1.368(3)	N5–C6	1.375(4)
N6–C6	1.317(3)	N6–C6	1.325(4)
N6–C7	1.456(3)	N6–C7	1.460(4)
		S3–C23	1.679(3)
		N7–C22	1.470(4)
		N7–C23	1.344(4)
		N7–C25	1.490(4)
		N8–N9	1.359(4)
		N8–C23	1.354(4)
		N9–C24	1.281(4)

The crystal and molecular structures with the numbering schemes of the $\text{H}_2\text{BbTSC-Et}$ and HTa3T-Et molecules are shown in Figure 2.

The $\text{H}_2\text{BbTSC-Et}$ 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 C_3N_3 ring is close to planar [torsional angles: C25–N7–C23–N8 10.0(4)°, N9–N8–C23–N7 1.5(4)°, N8–N9–C24–C25 –0.4(4)°]. Although

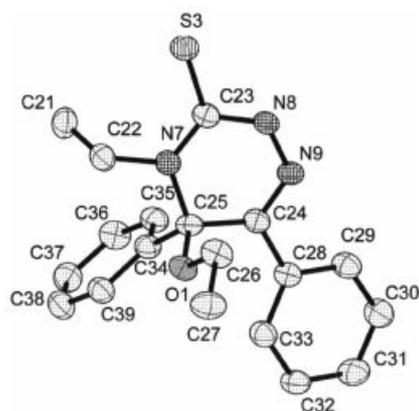
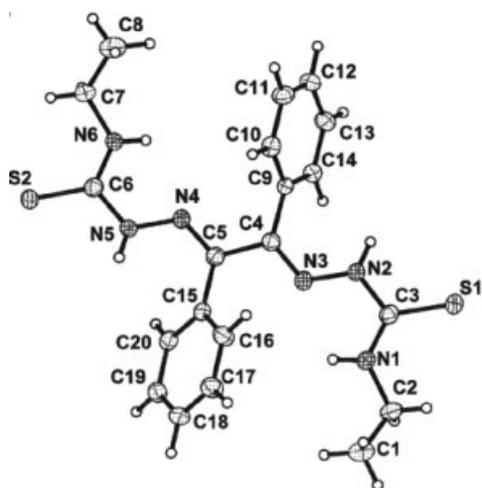


Figure 2. Molecular structure of the H₂BbTSC-Et (top) and HTa3T-Et (below) molecules, which shows the atom numbering scheme (H atoms were omitted for clarity).

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 pal-

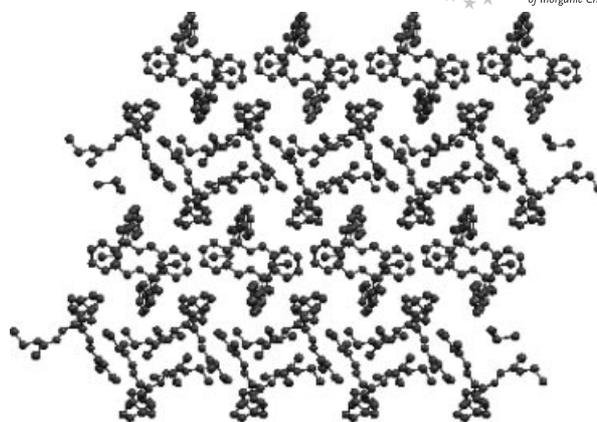


Figure 3. View of cocrystal H₂BbTSC-Et/HTa3T-Et along the *b* axis.

ladium(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 formulae.

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 Pd^{II} complex crystallizes in the monoclinic *C2/c* space group with *Z* = 4 as discrete C₂₀H₂₂N₆S₂Pd·DMSO molecules.

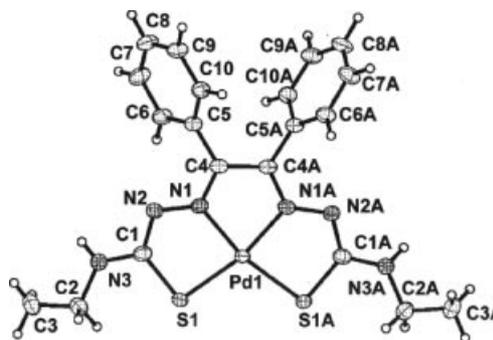


Figure 4. Molecular structure of [Pd(BbTSC)].

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 PdNNCS).

A careful examination of the bond length data shows that the Pd–N_{iminic} and Pd–S distances are comparable with those reported for other thiosemicarbazone palladium(II) complexes with strong Pd–N coordination.^[9] Since the Pd–S bonds are significantly longer than the Pd–N bonds, the coordination geometry around the metal ion is more trape-

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

[Zn(HTa3T-Et) ₂ Cl ₂]		[Pd(BbTSC)]	
S1–C1	1.7113(19)	S1–C1	1.771(3)
N1–C1	1.329(2)	N1–C4	1.325(4)
N1–C2	1.490(2)	N2–C1	1.332(4)
N2–C1	1.342(2)	N3–C1	1.334(4)
N3–C3	1.281(3)	N3–C2	1.462(4)
N2–N3	1.376(2)	N1–N2	1.351(4)
Zn1–Cl1	2.2380(5)	Pd1–N1	1.982(3)
Zn1–Cl1A	2.2379(5)	Pd1–N1A	1.982(3)
Zn1–S1	2.3694(5)	Pd1–S1	2.2792(8)
Zn1–S1A	2.3693(5)	Pd1–S1A	2.2792(8)
Cl1A–Zn1–Cl1	124.74(3)	N1A–Pd1–N1	82.38(15)
Cl1A–Zn1–S1A	111.374(17)	N1–Pd1–S1A	166.84(8)
Cl1A–Zn1–S1	102.003(17)	N1–Pd1–S1	84.47(8)
Cl1–Zn1–S1	111.376(17)	N1A–Pd1–S1A	84.46(8)
Cl1–Zn1–S1A	102.000(17)	N1A–Pd1–S1	166.84(8)
S1A–Zn1–S1	103.79(3)	S1A–Pd1–S1	108.69(4)

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)°.

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 5-ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione (HTa3T-Et) during the complexation reaction. An analogous cyclization of 2-pyridinformamide 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.

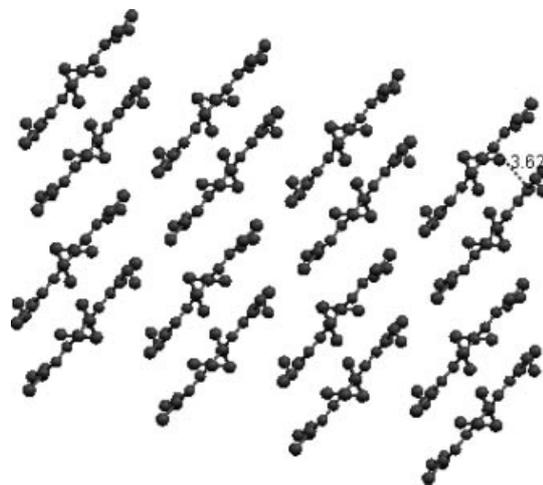


Figure 5. Side view of H₂BbTSC-Et, which shows the parallel disposition of the molecules as a result of π – π stacking.

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.

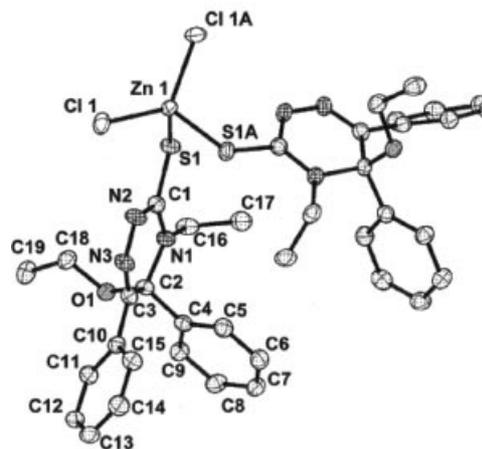


Figure 6. Molecular structure of [Zn(HTa3T-Et)₂Cl₂] (H atoms were omitted for clarity).

This neutral complex crystallizes in the orthorhombic *Fdd2* space group with *Z* = 8. The zinc atom is tetraordinated 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–Zn–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.^[17] The Zn–S and C–S distances [2.369 and 1.711 Å, respectively] are similar to those found in other complexes with thiocarbonyl sulfur atoms.^[18] 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.^[19,20] 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 cyclization, 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) ■■ ((=>Author: Is this change okay?)) ■■ .

The intramolecular cyclization reaction may also be promoted by the presence of the salt ZnCl₂. Thus, we have achieved the isolation of a Zn^{II}-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 stereochemical effects, as do the solvent and the counterion of the metal.

However, reaction of the cocrystal with Li₂PdCl₄ yields a planar tetracoordinate complex in which the bis(4-ethylthiosemicarbazone) ligand in the deprotonated form is present. In this case, the clear preference for a planar environment of the Pd^{II} 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 hydroxylic solvents, 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 ⁴N 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.^[11]. Yield: 0.35 g (77%). 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, which is composed of a 1:1 ratio of H₂BbTSC-Et and cyclic HTa3T-Et according to its crystal and molecular structure.

[Zn(HTa3T-Et)₂Cl₂]: 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)₂Cl₂] 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): $\tilde{\nu}$ = 3252 (s, NH), 1574 (s, CN), 854 (w, CS-thioamide IV band). ¹H NMR ([D₆]DMSO): δ = 9.72 (s, 1 H, ²NH), 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), 1.20–1.15 (t, ■■ ((=>Author: Please add coupling constant)) ■■ 2 H, OCH₂CH₃) ppm. After filtering the Zn^{II} 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.^[11]

[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%). C₂₀H₂₂N₆S₂Pd·DMSO (595.08): calcd. C 44.40, H 4.70, N 14.10, S 16.15; found C 44.00, H 5.00, N 13.50, S 15.40%. IR (KBr): $\tilde{\nu}$ = 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)) ■■ 1 H, 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

Table 3. Crystal data and structure refinement for H₂BbTSC-Et, H₂BbTSC-Et/HTa3T-Et, [Zn(HTa3T-Et)₂Cl₂] and [Pd(BbTSC)].

	H ₂ BbTSC-Et	H ₂ BbTSC-Et/HTa3T-Et	[Zn(HTa3T-Et) ₂ Cl ₂]	[Pd(BbTSC)]
Formula	C ₂₀ H ₂₄ N ₆ S ₂	C ₄₁ H ₅₁ N ₉ O ₂ S ₄	C ₃₈ H ₄₂ Cl ₂ N ₆ O ₂ S ₂ Zn	C ₂₂ H ₂₈ N ₆ OPdS ₃
<i>M</i>	412.57	830.15	815.17	595.08
System	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>F</i> dd2	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	9.5938(11)	19.1014(9)	22.1376(5)	12.3451(6)
<i>b</i> [Å]	9.8145(12)	11.3471(5)	28.2782(8)	22.2996(11)
<i>c</i> [Å]	12.0817(15)	20.9504(10)	12.6602(2)	9.1162(5)
<i>a</i> [°]	98.752(4)	90	90	90
<i>β</i> [°]	106.338(4)	105.820(3)	90	95.758(3)
<i>γ</i> [°]	96.281(4)	90	90	90
<i>V</i> [Å ³]	1065.0(2)	4368.9(4)	7925.4(3)	2496(2)
<i>λ</i> [Å]	1.54178	1.54178	1.54178	1.54178
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
<i>Z</i>	2	4	8	4
<i>D</i> _c [g cm ⁻³]	1.287	1.262	1.366	1.583
<i>F</i> (000)	436	1760	3392	1216
<i>μ</i> [mm ⁻¹]	2.402	2.359	3.412	8.562
<i>R</i> ₁ (all data)	0.0535	0.0829	0.0254	0.0401
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0425	0.0503	0.0251	0.0315
<i>wR</i> ₂ (all data)	0.1215	0.1327	0.0645	0.0806
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1104	0.1166	0.0642	0.0760
GOF	1.036	1.019	1.122	1.023

measurements were obtained from the Servicio Interdepartamental de Investigación (SIDI) of the Universidad Autónoma de Madrid. Infrared spectra (KBr discs) were recorded with a Bomem–Michelson spectrophotometer (4000–400 cm⁻¹).

X-ray Crystallographic Studies: A summary of the crystal data, experimental details and refinement results is listed in Table 3. The X-ray measurement was performed on a Bruker SMART 6 K CCD area-detector three-circle diffractometer with a rotating anode generator (Cu-*K*_α radiation, *λ* = 1.54178 Å) equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected at 100 K. The software package SHELXTL version 6.10 was used for space group determination, structure solution and refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares techniques against *F*² by using SHELXL-97.

CCDC-649679 (ligand H₂BbTSC-Et), -649677 (cocrystal H₂BbTSC-Et/HTa3T-Et), -649678 {compound [Zn(HTa3T-Et)₂-Cl₂]} and -634275 {compound [Pd(BbTSC-Et)]} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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