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Synthesis, Characterization, and Crystal Structure of the New Schiff-Bases derived from 1,2,4-Triazole and the Structure of $[(PPh_3)_2Cu(AMTT)]NO_3\cdot EtOH$

(AMTT = 4-Amino-5-methyl-2H-1,2,4-triazole-3(4H)-thione)

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Abstract. The reactions of 4-amino-5-methyl-2H-1,2,4-triazole-3(4H)-thione (AMTT, **L1**) with 2-thiophen carbaldehyde, salicylaldehyde and 2-nitrobenzaldehyde in methanol led to the corresponding Schiff-bases (**L1a-c**). The reaction of **L1** with $[(PPh_3)_2Cu]NO_3$ in ethanol gave the ionic complex $[(PPh_3)_2Cu(L1)]NO_3\cdot EtOH$ (**2**) All compounds were characterized by infrared spectroscopy, elemental analyses as well as by X-ray diffraction studies. Crystal data for **L1a** at 20 °C: space group $P2_1/n$ with $a = 439.6(2)$, $b = 2074.0(9)$, $c = 1112.8(4)$ pm, $\beta = 93.51(3)^\circ$, $Z = 4$, $R_1 = 0.0406$, **L1b** at −80 °C: space group $P2_1/n$ with $a = 1268.9(2)$, $b = 739.3(1)$, $c = 1272.5(1)$ pm, $\beta = 117.97(1)^\circ$, $Z = 4$, $R_1 = 0.0361$, **L1c** at −80 °C: space group $P2_1/n$ with $a = 847.8(1)$, $b = 1502.9(2)$, $c = 981.5(2)$ pm, $\beta = 110.34(1)^\circ$, $Z = 4$, $R_1 = 0.0376$ and for **2** at −80 °C: space group $P\bar{1}$ with $a = 1247.8(1)$, $b = 1270.3(1)$, $c = 1387.5(1)$ pm, $\alpha = 84.32(1)^\circ$, $\beta = 84.71(1)^\circ$, $\gamma = 63.12(1)^\circ$, $Z = 2$, $R_1 = 0.0539$.

Keywords: 1,2,4-Triazole; Schiff bases; Copper; Crystal structures

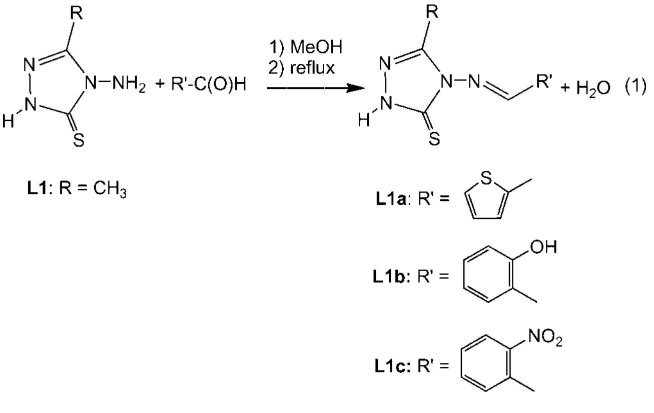
1 Introduction

In our ongoing interest in the study of the coordination chemistry of heterocyclic ligands containing nitrogen and sulfur atoms, such as AMTTO and its Schiff-bases, we have reported that the AMTTO acts as a unidentate ligand via its sulfur atom with a weak Ag···N interaction, which leads to a 2+2 coordination on the silver(I) atom [1]. We have also found that the 2-thiophene-Schiff-base based on AMTTO reacts with silver ion *via* its sulfur atoms in a molar ratio of 2:1 and the additional coordination of the thiophene heterocycle caused 2+1 coordination around the metal atom [2]. In addition, we have shown that the ligand AMTTO acts as a monodentate ligand in a molar ratio 2:1 with Cu(I) ion, while it reacts with Cu(II) as a bidentate one in a molar ratio 1:1 [3]. We have also reported the reaction of ATT with silver(I) and copper(I) including their molecular structures [4].

In this communication, we wish to report the synthesis and characterization of new Schiff-bases derived from 1,2,4-triazole and the Cu(I)-complex of AMTT.

2 Syntheses and Characterization of L1a-c and 2

Treatment of **1** with 2-thiophen carbaldehyde, salicylaldehyde and 2-nitrobenz-aldehyde in methanol and in presence of HCl under reflux conditions led to the corresponding iminic compounds **L1a-c** in high yields (eq. (1)).



Compound **2** can be obtained by the reaction of **L1** with $[(PPh_3)_2Cu]NO_3$ in the molar ratio 1:1 in ethanol according to equation (2).

$$\mathbf{L1} + [(Ph_3P)_2Cu]NO_3 \xrightarrow{EtOH} \underset{\mathbf{2}}{[(Ph_3P)_2Cu(L1)]NO_3\cdot EtOH} \qquad (2)$$

All synthesized compounds are air-stable colorless solid materials. The IR absorptions *ν*CuS and *ν*CuCl of complex **2** can be observed at 350 and 228 cm^{-1} [5]. The C=N functions cause two vibrations at 1617 and 1497 cm^{-1}, the first value is for the endocyclic C=N group and the latter can be assigned to the iminic group. P-C vibrations of the

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moiety PPh_3 are found in the range 747-695 cm^{-1}. For the N-H stretching vibrations absorption bands could be found at 3333 w, 3228 s, 3192 w, and 3120 w cm^{-1}.

3 Results and Discussion

Compounds L1a-c *and complex* 2

Table 1 shows the crystallographic data of **L1a-c** and **2**. Selected bond distances and angles are given in Table 2. Compounds **L1a-c** crystallize in the monoclinic space group $P2_1/n$. The basic five-membered ring skeleton in all compounds is planar, while the dihedral angle between the best planes through the triazole ring and the aldehyde rest is 6° for **L1a** (Fig. 1), 2° for **L1b** (Fig. 2) and 5° for **L1c** (Fig. 3), The bond distances in the triazole five-membered heterocycles are in well agreement with those observed in iminic derivatives of 1,2,4-triazole such as 4-(4-methoxybenzylideneamino)-5-methyl-2H-1,2,4-triazole-3(4H)-thione and 4-(3-methoxybenzylideneamino)-5-methyl-2H-1,2,4-triazole -3(4H)-thione [6].

In all compounds, the S1-C1 bond lengths of mean 168.04 pm is significant for a high double bond character, such as observed in AMTT [7]. The iminic C-N bond distance with mean 129.04 pm lies in the range observed in similar compounds such as 2-acetylthiophene thiosemicarbazone (129.2(3) pm) and 2-acetyl thiophene 4-phenyl thiosemicarbazone (128.2(3) pm) [8].

In all compounds an intermolecular weak hydrogen bonding links the sulfur atom of one molecule to the NH-group of the adjacent one (N4-H1···S1a: 331.0(2) pm (**L1a**), N3-H1···S1a: 326.3(2) pm (**L1b**), N4-H1···S1a: 324.0(2) pm (**L1c**) and is responsible for the centrosymmetric structure of the compounds. In addition, there is an intramolecular hydrogen bonding in **L1a** (C4-H41···S1: 318.7(3) pm) and **L1b** (O1-H2···N2: 267.9(2) pm.

Complex **2** consists of ionic molecules $[Cu(PPh_3)_2(L1)]NO_3{\cdot}C_2H_5OH$ (Fig. 4) and show a similar molecular structure as observed in Cu(I) complex with the modified AMTTO ligand, $C_4H_4N_3SON(=CMe_2)$ [9]. In molecules of **2**, the metal atom displays a distorted tetrahedral environment with crystallographic C_1 site position. The coordination sphere around the copper atom in **2** is occupied with two P atoms of the phosphane molecules, the S atom of the triazole heterocycle and the nitrogen atom of the hydrazine moiety. This arrangement is considerable distorted since the P angle at the metal site, P1-Cu1-P2 with a value of 124.29(4)° is close to Cu(I) complexes with trigonally coordinated copper atoms. The three other selected angles in the CuP_2NS group with P2-Cu1-S1: 102.27(3)°, S1-Cu1-N2: 86.24(7)° and P1-Cu1-N2: 108.05(8)° are nearly to those of a regular tetrahedron.

The tetrahedral distortion is due to steric hindrance of the bulky phosphane ligands and was observed in a series of analogous complexes [10]. The Cu-P bond distances for **2**, 224.86(8) and 229.12(9) pm are similar to the observed

Table 1 Crystallographic data for **L1a-c** and **2**.

Compound	**L1a**	**L1b**	**L1c**	**2**
Empirical formula	$C_8H_8N_4S_2$	$C_{10}H_{10}N_4OS$	$C_{10}H_9N_5O_2S$	$C_{41}H_{42}CuN_5O_4P_2S$
Formula mass	448.60	234.28	263.27	826.37
Crystal size/mm	0.65 × 0.09 × 0.09	0.4 × 0.28 × 0.09	0.28 × 0.25 × 0.2	0.39 × 0.31 × 0.06
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/pm	439.6(2)	1268.9(2)	847.8(1)	1247.8(1)
b/pm	2074.0(9)	739.3(1)	1502.9(2)	1270.3(1)
c/pm	1112.8(4)	1272.5(1)	981.5(2)	1387.5(1)
α/°	–	–	–	84.32(1)
β/°	93.51(3)	117.97(1)	110.34(1)	84.71(1)
γ/°	–		–	63.12(1)
Volume/$pm^3{\cdot}10^6$	1012.7(7)	1054.3(2)	1172.6(3)	1949.3(3)
Z	4	4	4	2
$d_{calcd.}/g{\cdot}cm^{-3}$	1.471	1.476	1.491	1.408
Absorption correction	numerical	numerical	numerical	numerical
μ/cm^{-1}	4.9	2.9	2.8	7.4
Temperature/K	293	193	193	193
$2\theta_{max}/°$	52.77	52.5	52.73	52.55
Index range h	−5→5	−15→15	−10→10	−15→15
k	−25→25	−9→9	−18→18	−15→15
l	−13→13	−15→15	−12→12	−17→17
Reflections collected	8766	14831	16880	28587
Unique reflections	2036	2131	2373	7848
(R_{int})	(0.0568)	(0.0532)	(0.0615)	(0.1155)
Reflections with $F_o > 4\sigma(F_o)$	1629	1668	1834	5670
Parameters	159	185	199	506
R_1	0.0406	0.0361	0.0376	0.0539
wR_2 (all data)	0.1179[a)]	0.0956[b)]	0.1046[c)]	0.1482[d)]
Max. residual electron density/$[(e{\cdot}pm^{-3}){\cdot}10^{-6}]$	0.21	0.28	0.23	0.96

[a)] $w = 1/[\sigma^2(F_o)^2+(0.0815{\cdot}P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [b)] $w = 1/[\sigma^2(F_o)^2+(0.0649{\cdot}P)^2]$. [c)] $w = 1/[\sigma^2(F_o)^2+(0.0721{\cdot}P)^2]$. [d)] $w = 1/[\sigma^2(F_o)^2+(0.1017{\cdot}P)^2]$.

Table 2 Selected bond lengths/pm and bond angles/°.[a)]

L1a		L1b		L1c		2	
S1−C1	167.9(2)	S1−C1	167.9(2)	S1−C1	167.9(2)	Cu1−N2	220.0(3)
C1−N4	134.3(3)	C1−N3	133.7(2)	C1−N4	133.3(2)	Cu1−S1	237.90(9)
N4−N3	137.3(3)	N3−N4	137.7(2)	N4−N3	137.2(2)	Cu1−P1	224.86(8)
N3−C2	130.2(3)	N4−C2	129.7(2)	N3−C2	129.3(2)	Cu1−P2	229.12(9)
C2−N1	138.5(6)	C2−N1	138.5(2)	C2−N1	138.5(2)	S1−C1	167.2(4)
N1−N2	139.7(2)	N1−N2	139.2(2)	N1−N2	138.8(2)	C1−N4	134.3(4)
N2−C4	127.4(3)	N2−C4	128.4(2)	N2−C4	127.2(2)	C1−N1	137.4(4)
C4−C5	144.4(3)	C4−C5	145.2(2)	C4−C5	147.3(2)	N1−C2	138.0(4)
C5−S2	171.1(2)	C10−O1	135.5(2)	C6−N5	146.9(2)	C2−N3	129.3(5)
S2−C8	170.7(2)	C2−C3	147.6(2)	N5−O1	122.1(2)	N3−N4	137.7(4)
				N5−O2	122.5(2)	N5−O1	120.6(4)
						N5−O2	124.8(4)
						N5−O3	127.3(4)
S1−C1−N1	130.8(2)	S1−C1−N3	126.1(1)	S1−C1−N4	126.7(1)	N2−Cu1−S1	86.24(7)
C1−N4−N3	115.0(2)	C1−N3−N4	114.5(1)	C1−N4−N3	114.3(2)	S1−Cu1−P2	102.27(3)
N4−N3−C2	103.6(2)	N3−N4−C2	103.7(2)	N4−N3−C2	104.2(2)	P2−Cu1−P1	124.29(4)
N3−C2−N1	110.7(2)	N4−C2−N1	110.9(2)	N3−C2−N1	110.8(2)	P1−Cu1−N2	108.05(8)
C2−N1−C1	108.9(2)	C2−N1−C1	108.3(1)	C2−N1−C1	107.9(1)	Cu1−S1−C1	92.6(1)
C1−N1−N2	132.6(2)	C1−N1−N2	132.9(2)	C1−N1−N2	133.1(1)	Cu1−N2−N1	107.3(2)
N1−N2−C4	119.5(2)	N1−N2−C4	119.2(1)	N1−N2−C4	119.2(1)	S1−C1−N1	127.3(2)
N2−C4−C5	120.5(2)	N2−C4−C5	120.7(2)	N2−C4−C5	117.1(2)	S1−C1−N4	129.7(3)
C4−C5−S2	122.1(2)	C5−C10−O1	122.9(2)	C6−N5−O1	117.7(2)	C1−N1−C2	108.4(3)
				C6−N5−O2	118.4(2)	C1−N4−N3	113.4(3)
				O1−N5−O2	123.8(2)	N1−C2−N3	110.8(3)
						O1−N5−O2	123.0(4)
						O2−N5−O3	116.8(3)
						O1−N5−O3	120.2(4)
						O1−N5−O2	123.0(4)
						O2−N5−O3	116.8(3)
						O1−N5−O3	120.2(4)

[a)] Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax.: (internat.) +44 (0)1223 336033; E-mail: **deposit@ccdc.cam.ac.uk**] quoting the depository numbers CCDC 632480 (**L1a**), 632481 (**L1b**), 632482 (**L1c**), and 632483 (**2**).

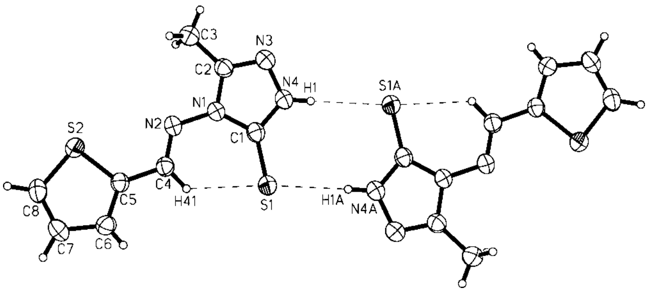

Figure 1 Centrosymmetrical dimer of **L1a** (thermal ellipsoids at the 30 % probability level).

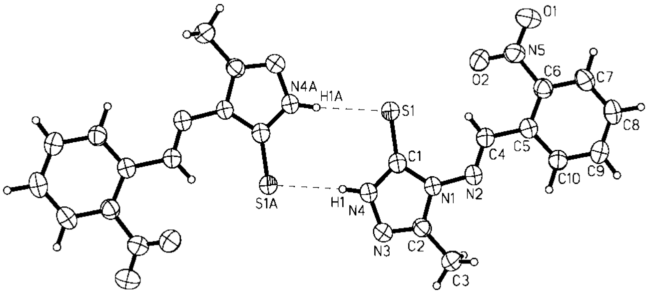

Figure 3 Centrosymmetrical dimer of **L1c** (thermal ellipsoids at the 50 % probability level).

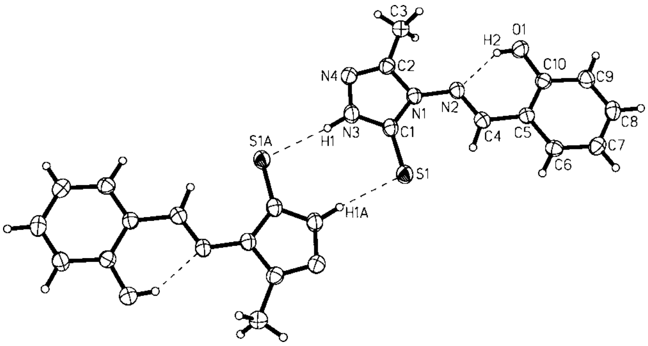

Figure 2 Centrosymmetrical dimer of **L1b** (thermal ellipsoids at the 40 % probability level).

distances in [$(C_4H_4N_3SON\{=CMe_2\})Cu(PPh_3)_2Cl$] (mean 229.2 pm) and in [$(AMTTO)Cu(PPh_3)_2Cl$] (mean 227.7 pm) [3, 9].

In **2** the nitrate ion and the ethanol solvate molecule act as bridging agents and link the cations *via* hydrogen bondings (N2-H1···O4, N2···O4: 293.5(5) pm, N2-H2···O3a, N2···O3a: 286.5(4) pm, N4-H3···O3, N4···O3: 276.6(4) pm and O4-H4···O2a, O4···O2a: 295.8(5) pm) and are responsible for the building of chains along [001], which are shielded by the phenyl rings (Fig. 5 and 6). The Cu1-S1 bond distance is 237.90(9) pm and lies in the range observed for complexes with tetrahedral coordinated Cu(I) atoms [11, 12]. The dihedral angle between the "best planes" (S1/N1/N2/N3/N4/C1/ C2 and Cu1/S1/N2) is 21° (Fig. 5).

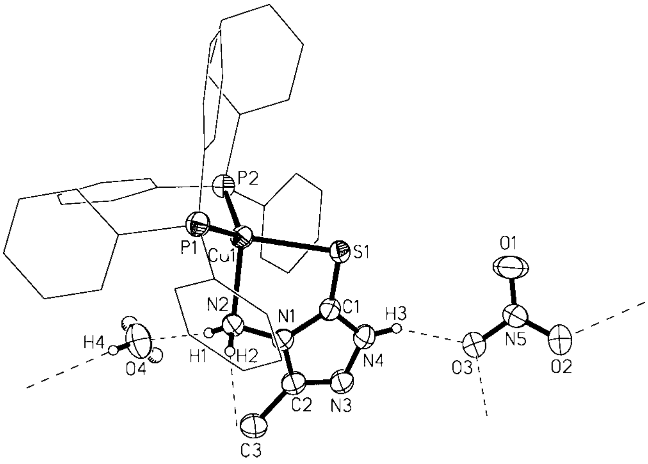

Figure 4 Structure of **2** (thermal ellipsoids at the 40 % probability level). The phenyl rings are represented as thin lines. Most of the hydrogen atoms are omitted for clarity.

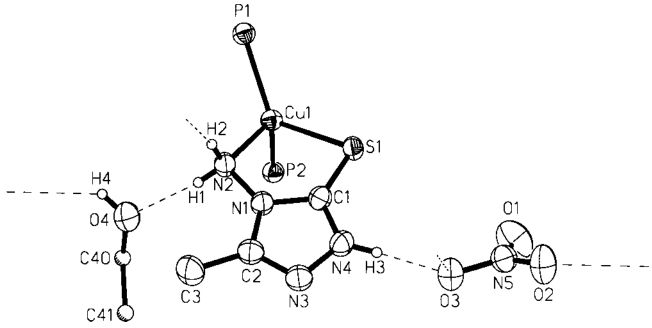

Figure 5 Perspective view of the unit cell of **2**. The ions and the ethanol molecule of **2** are arranged in the direction [001].

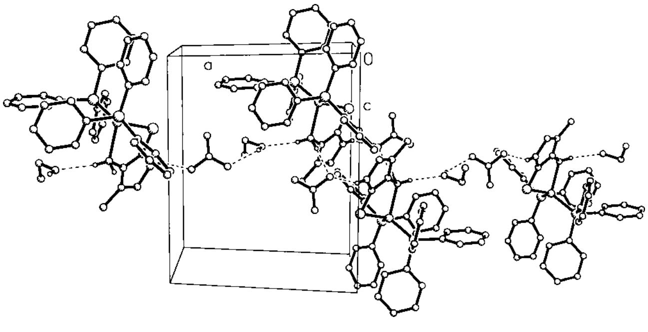

Figure 6 Second view of **2**. The phenyl rings and most of the hydrogen atoms are omitted for clarity.

4 Experimental Section

AMTT (**L1**) was prepared according to the literature procedure [13]. IR spectra were recorded on a Shimadzu spectrometer 470 (KBr pellets 4000−400 cm^{-1} and CsI pellets 4000-200 cm^{-1}). ^{1}H NMR spectra were recorded on the Bruker-AQS advance 300 MHz. Standard was TMS (external) with $\delta = 0.0$ ppm. Mass spectra were recorded on a GC mass QP 1100 EX spectrometer. Elemental analyses were performed by the following methods: C, H, N analyses; combustion method; sulfur analyses: combustion and titration with $Ba(ClO_4)_2$; Phosphorus: decomposition with $HClO_4$ and photometric analysis of the molybdophosphate. The following chemicals were purchased from Merck and Fluka and used without further purification: copper(I) nitrate, triphenylphosphane, 2-thiophen carbaldehyde, salicylaldehyde and 2-nitrobenzaldehyde, methanol and ethanol.

Synthesis of **L1a-c**. General procedure.
A solution of AMTT (1 mmol) in methanol (40 mL) was treated with corresponding aldehyde (1.5 mmol) and was refluxed for 6 h. The progress of the reaction was monitored by TLC using ethyl acetate: petroleum ether (1:2) as eluent. After completion of the reaction, the solvent was evaporated to 20 mL, the solid crude was filtered and washed with cold methanol (2 x 5 mL). The clear filtrate was kept at 4 °C to give the colorless single crystals of the corresponding Schiff bases **L1a-c**.

Selected data for L1a.

Used amounts for **L1**: 0.14 g (1 mmol); 2-thiophene carbaldehyde: 0.16 (1.5 mmol).
Yield: 0.20 g (90 %).
Anal. Calc. for $C_8H_8N_4S_2$ (224.31): C 42.82 (calcd. 42.84); H 3.50 (3.59); N 24.88 (24.98); S 28.50 (28.59) %.

IR (KBr disc, cm^{-1}): 3418 w (νNH), 3109 s, 3108 s (νCH, Ar), 2954 s, 1597 vs (νN=C, imine), 1582 s (νN=C, triazole), 1532 m, 1499 m (νC=C), 1427 s, 1407 m, 1316 s (νC=S), 1274 s, 740 s, 632 m, 606 m, 572 m, 549 w.
MS (70 eV) *m/z* (%): 448 (11) $(2M)^+$, 224 (100) M^+, 155 (30), 117 (31), 115 (95), 109 (85), 56 (53), 39 (32), 45 (35), 27 (19), 42 (27).
^{1}H NMR (DMSO-d_6): $\delta = 2.37$ (s, 3 H, Me), 7.08, 7.11 (dd, 1 H, H-thiophen), 7.48, 7.51 (dd, 2 H, H-thiophene), 10.52 (s, 1 H, CH=N).

Selected data for L1b.

Used amounts of **L1**: 0.14 g (1 mmol); salicylaldehyde: 0.18 g (1.5 mmol).
Yield: 2.1 g (93 %).
Anal. Calc. for $C_{10}H_{10}N_4OS$ (234.28): C 50.99 (calcd. 51.27); H 4.28 (4.30); N 23.88 (23.91); S 13.66 (13.69) %.

IR (KBr disc, cm^{-1}): 3433 w (νNH), 3105 s (νOH), 3068 m, 2936 s, 2759 s, 1603 vs (νN=C, imine), 1599 s (νN=C, triazole), 1504 m, 1488 m, 1412 s, 1346 m, 1315 s (νC=S), 1293 s, 1264 (νC-N, thioamide), 772 s, 613 m, 564 s, 479 w, 447 m.
MS (70 eV) *m/z* (%) 235 (31) $(M+1)^+$, 234 (47) (M^+), 137 (28), 121 (26), 119 (99), 115 (98), 102 (39), 102 (39), 91 (98), 74 (49), 64 (99), 56 (100), 42 (67), 39 968).
^{1}H NMR (DMSO-d_6): $\delta = 2.42$ (s, 3 H, Me), 7.01-7.11 (m, 4 H, Ar), 10.23 (s, 1 H, CH=N imine), 10.43 (s, 1 H, Ph).

Selected data for L1c.

Used amounts of **L1**: 0.14 g (1 mmol); 2-nitrobenzaldehyde: 0.22 g (1.5 mmol).
Yield: 0.24 g (94 %).
Anal. Calc. for $C_{10}H_9N_5O_2S$ (263.27): C 45.56 (calcd. 45.62); H 3.39 (3.45); N 26.57 (26.60); S 12.09 (12.18) %.

IR (KBr disc, cm^{-1}): 3441 w (νNH), 3068 s (νCH, Ar), 2936 s, 2762 m, 1600 vs (νC=C, Ar), 1591 s (νN=C, imine), 1525 (νN=C, triazole) 1506 m, 1404 m, 1378 m, 1344 m (νNO), 1315 s (νC=S), 1281 s, 1178 s, 1049 s, 798 s, 746 m, 603 m, 573 m, 550 s, 518 m, 472 m.
MS (70 eV) *m/z* (%): 264 (34) $(M+1)^+$, 263 (38) (M^+), 217 (34), 149 (35), 115 (99), 102 (47), 74 (100), 63 (35), 56 (98), 50 (81), 42 (35), 27 (32).

^{1}H NMR (DMSO-d_6): $\delta = 2.4$ (s, 3 H, Me), 7.91 (m, 1 H, H-benzyl ring), 7.97 (dd, 1 H, H-phenyl), 8.19 (dd, 2 H, phenyl), 11.0 (s, 1 H, H-imine), 13.8 (s, 1 H, NH-thione)

Synthesis of Complex 2. A solution of AMTT (0.13 g, 1 mmol) in 20 ml ethanol was added to a suspension of $[(PPh_3)_2Cu]NO_3$ (0.65 g, 1 mmol) (prepared in situ from $CuNO_3$ and PPh_3 in a molar ratio 1:2 in ethanol) and stirred for 5h at room temperature. After completion of reaction, which was monitored by TLC using petroleum ether/ ethyl acetate (2/1) as eluent, the crude product was filtered and washed with cold methanol (2 x 15 mL). The filtrate was kept at 4 °C and colorless crystals of **2** were obtained after few days.
Yield: 0.70 g (85 %); mp.: 190 °C.
Anal. Calc. for $C_{41}H_{42}CuN_5O_4P_2S$ (826.37): C 59.29 (calcd. 59.59); H 5.08 (5.12); N 8.46 (8.47); S 3.79 (3.88); Cu 7.53 (7.69) %.

IR (KBr disc, cm^{-1}): 3333 w (νNH_2), 3228 s (νNH_2), 3192 w, 3120 w (νNH), 3061 w, 2936 m, 1687 w, 1639 s (νC=N, imine), 1601 m, 1584 m, 1497 s (νC=N, triazole), 1387 m ($\nu_{as}NO_3$), 1350 m, 1328 s (νC=S), 1200 m, 1182 m, 1169 m, 1158 m, 1120 m, 1088 s, 1072 sh w, 995 m, 930 m, 882 m, 817 m, 745 w (νPPh_3), 723 m (νPPh_3), 695 m (νPPh_3), 420 m (νCuN), 380 s (νCuS), 338 s (νCuP), 247 s , 240 w, 234 sh m, 223 m, 215 m.
^{31}P NMR (DMSO): $\delta = 26.1$.

Crystal structure analyses of L1a-c and 2

The crystals of **L1a-c** and **2** were covered with perfluorinated oil and mounted on the top of a glass capillary. In addition, **L1b-c** and **2** were hold under a flow of cold gaseous nitrogen. The orientation matrix and unit cell dimensions were determined from *ca.* 5000 (**L1a**, **L1b**, Stoe IPDS II), *ca.* 7000 (**L1c**, Stoe IPDS II), and from *ca.* 10000 (**2**; Stoe IPDS II) reflections (graphite-monochromated Mo-Kα radiation, $\lambda = 71.073$ pm). The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for **L1a-c** and **2** (numerical). The structures were solved by direct methods for **L1a-c** (SHELXS-97) and for **2** (SIR-92) and refined against F^2 by full-matrix least-squares using the program SHELXL-97. The position of carbon bonded hydrogen atoms (except H1) in **2** were calculated for ideal positions and refined with a common displacement parameter. H1 atoms in **2** were included with a free refinement. All hydrogen atoms in **L1a-c** were freely refined. Programs used were SHELXS-97 [14], SIR-92 [15], SHELXL-97 [16], SHELXTL-Plus [17], and PLATON [18].

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