Syntheses and Characterization of New Copper Complexes with the Heterocyclic Thione, AMTTO. X-Ray Structures of [Cu(AMTTO)Cl$_2$], [Cu(AMTTO)$_2$]Cl, and [Cu(AMTTO)(PPh$_3$)$_2$Cl]

(AMTTO = 4-Amino-6-methyl-1,2,4-triazine-3-thione-5-one)

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Received May 27th, 2002.

Abstract. The complexes [Cu(AMTTO)Cl$_2$] (**2**), [Cu(AMTTO)$_2$]Cl (**3**), and [Cu(AMTTO)(PPh$_3$)$_2$Cl] (**4**) have been prepared and characterized by IR spectroscopy and elemental analyses. Also single-crystal X-ray diffraction studies on compound **2**, **3** and **4** revealed that AMTTO acts in **2** as a bidentate ligand via nitrogen and sulfur atoms, in **3** and **4** as a monodentate via sulfur atoms. Complex **3** was already mentioned in literature, but the structure was not described in detail. The molecules in **2** form infinite chains through additional weak Cu−S interactions along [010] indicating the Jahn-Teller distortion of the d^9 ion Cu^{2+}. The infinite chains are connected by hydrogen bonding along [100]. Crystal data for **2** at −80°C: monoclinic, space group P2$_1$/m, a = 666.7(1), b = 609.4(1), c = 1132.6(2) pm, b = 95.46(2)°, Z = 2, R$_1$ = 0.0365; for **3** at −80°C: orthorhombic, space group Pbcn, a = 1291.2(2), b = 1146.5(1), c = 1000.5(1) pm, Z = 4, R$_1$ = 0.0315; for **4** at −80°C: monoclinic, space group, P2$_1$/n, a = 879.4(1), b = 1849.3(2), c = 2293.8(3) pm, β = 92.38(1)°, Z = 4, R$_1$ = 0.0688.

Keywords: Copper; Triazine; Metallacycles

Synthesen and Charakterisierung von neuen Kupfer-Komplexen des heterocyclischen Thions AMTTO. Die Kristallstrukturen von [Cu(AMTTO)Cl$_2$], [Cu(AMTTO)$_2$]Cl und [Cu(AMTTO)(PPh$_3$)$_2$Cl]

(AMTTO = 4-Amino-6-methyl-1,2,4-triazin-3-thion-5-on)

Inhaltsübersicht. Über die Darstellung der Komplexe [Cu(AMTTO)Cl$_2$] (**2**), [Cu(AMTTO)$_2$]Cl (**3**) sowie [Cu(AMTTO)(PPh$_3$)$_2$Cl] (**4**) und deren Charakterisierung mittels IR-Spektroskopie and Elementaranalysen wird berichtet. Die zusätzlich an **2**, **3** und **4** durchgeführten Röntgenstrukturanalysen ergaben, daß der Ligand AMTTO in **2** als zweizähniger Ligand über Stickstoff- und Schwefelatome koordiniert, dagegen in **3** und **4** nur als einzähniger Ligand über die Schwefelatome fungiert. Komplex **3** wurde bereits in der Literatur erwähnt, jedoch wurde der dreidimensionale Aufbau dort nicht ausführlich beschrieben. Die Moleküle von **2** bilden durch zusätzliche schwache Cu−S-Kontakte unendliche Ketten entlang [010], was die Jahn-Teller-Verzerrung des d^9-Ions Cu^{2+} belegt. Diese Polymerstränge sind untereinander durch Wasserstoffbrücken-Bindungen entlang [100] verknüpft.Strukturparameter für **2** bei −80°C: monoklin, Raumgruppe P2$_1$/m, a = 666,7(1), b = 609,4(1), c = 1132,6(2) pm, β = 95,46(2)°, Z = 2, R$_1$ = 0,0365; für **3** bei −80°C: orthorhombisch, Raumgruppe Pbcn, a = 1291,2(2), b = 1146,5(1), c = 1000,5(1) pm, Z = 4, R$_1$ = 0,0315; für **4** bei −80°C: monoklin, Raumgruppe P2$_1$/n, a = 879,4(1), b = 1849,3(2), c = 2293,8(3) pm, β = 92,38(1)°, Z = 4, R$_1$ = 0,0688.

1 Introduction

Thiosemicarbazone and thiosemicarbazide derivatives like heterocyclic thiones as ligand in metal complexes exhibit important biological properties [1a]. The antitumoral, antiviral and antibacterial activities of a number of complexes derived from heterocyclic thiones have also been reported

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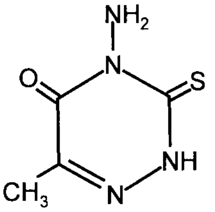
[1b−d]. These ligands show in their coordination different geometries such as neutal S-monodentate, N-monodentate, S-bridge, N,S-chelate etc. [2]. From a bio-inorganic point of view, thiolate complexes are of great importance, mainly due to the presence of thiolate donors in the coordination sphere of many metal ions in very diverse metallaproteins [3].

On the other hand, there is a long standing interest in the preparation and study of Cu^I complexes with sulfur-containing ligands with the awareness of the significance of copper-sulfur interactions in biological systems [4].

Many attention has been paid to copper(I) complexes because of their participation in certain biochemical redox reactions [5] and provide suitable models for the representation of several enzymatic sites [6]. Although copper definitely is an essential element of many life processes in higher organisms, but its biological relevance and prevalence was recognized when the bio-inorganic chemistry have been developed [7]. In our investigation, we have shown that the heterocyclic thione ligand AMTTO (**1**) reacts with silver [8a, b], copper [8b−d] and palladium [8e−g] as a monodentate ligand or bidentate chelating agent. In this paper we wish to report on the behaviour of **1** against copper(I) and copper(II) ions.



Scheme 1 Graphic representation of a molecule AMTTO

2 Results and Discussion

2.1 Synthesis and characterization of 2, 3, and 4

Complex **2** can be observed by the addition of equimolar amount of **1** to $CuCl_2$ in methanol/hydrochloric acid solution as a green solid at room temperature [eq (1)].

$$\mathbf{1} + CuCl_2 \xrightarrow{MeOH/HCl} \underset{\mathbf{2}}{[(AMTTO)CuCl_2]} \qquad (1)$$

The reaction of **1** with CuCl in a 2:1 molar ratio in methanol/hydrochloric acid solution leads to the complex **3** at room temperature [eq (2)]. **3** was already published independently by others, using a known literature route [8d, h]. We decided to synthesize **3**, because it is an important starting compound for further investigations [see eq (4)].

$$2\,\mathbf{1} + CuCl \xrightarrow{MeOH/HCl} \underset{\mathbf{3}}{[(AMTTO)_2Cu]Cl} \qquad (2)$$

4 can be prepared by the reaction of **1**, copper(I) chloride and triphenylphosphane in a molar ratio 1:2 in chloroform/acetonitrile under reflux conditions [eq (3)].

$$\mathbf{1} + CuCl + 2\,PPh_3 \xrightarrow{MeOH/MeCN} \underset{\mathbf{4}}{[(AMTTO)Cu(PPh_3)_2Cl]} \qquad (3)$$

This complex can also be obtained by the reaction of **3** with PPh_3 in a molar ratio 1:2 under reflux conditions [eq (4)].

$$\mathbf{3} + 2\,PPh_3 \xrightarrow{CHCl_3/MeCN;\ \Delta} \underset{\mathbf{4}}{[(AMTTO)Cu(PPh_3)_2Cl]} + AMTTO \qquad (4)$$

All of the complexes are air-stable crystalline solids. In the IR spectra of **2**−**4**, the νCuS absorptions were found at 347, 352 and 345 cm^{-1} and the absorption bands of the Cu−N streching vibrations at 462 cm^{-1} for **2** and 457 cm^{-1} for **3**. The band at 271 cm^{-1} for **2** and at 237 cm^{-1} for **4** can be assigned to νCuCl. νCuP_2 of **4** was observed at 159 cm^{-1}. Characteristic for the AMTTO ligand are the C=O and $N{=}C_{ring}$ vibrations at 1702 and 1609 cm^{-1} for **2**, at 1712 and 1603 cm^{-1} for **3** and 1689 and 1593 cm^{-1} for **4**. Because of the two NH-containing functions in AMTTO two absorptions νNH or νNH_2, respectively, could be verified in **2**−**4**. Measured values are 3231 and 3179 cm^{-1} for **2**, 3229 and 3126 cm^{-1} for **3**, and 3297 as well as 3210 cm^{-1} in **4**. The P-C vibrations as well as the δ-CH vibrations of the moiety PPh_3 are found in the range of 690−750 cm^{-1}. Consistent with the structure of **4**, only a sharp singlet resonance at 32.6 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum.

2.2 Crystal Structures of 2−4

Complex 2

The crystal structure of **2** consists of neutral complex molecules $[(AMTTO)CuCl_2]$ (Fig. 1). AMTTO acts as a bidentate ligand and occupies two equatorial positions in the Jahn-Teller distorted stretched octahedron. The sites *trans* to nitrogen and sulfur atoms, respectively, are occupied by the chloride ligands. This approximately square planar arrangement around Cu^{II} is completed to a distorted octahedron by additional weak Cu−S contacts using the S atoms of molecules above and below. The Cu1−S1 and Cu1−S1a bond lengths are 231.1(3) and 304.7(3) pm, respectively. The Cu−S distance observed in similar complexes with square planar coordination, lies in the range of 228.4−229.2 pm [9a−c] (Cu^{II}) and for tetrahedral coordination in the range of 232.6−244.4 pm (Cu^I) [5b, 9g].

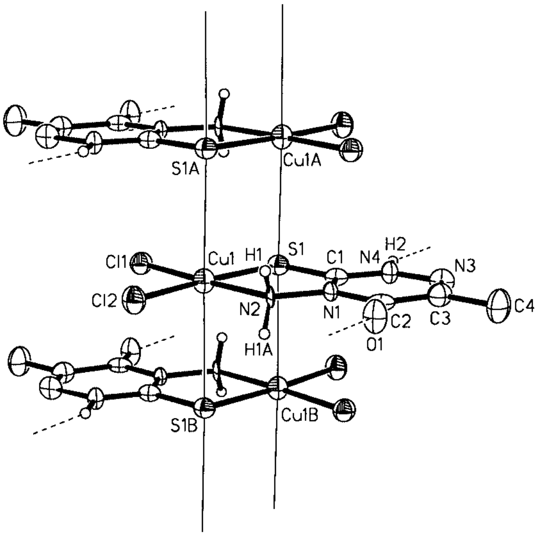


Fig. 1 Molecular structure of three molecules of **2** (view approximately perpendicular to string direction [010]; most of the H atoms are omitted for clarity; thermal ellipsoids 40% probability)

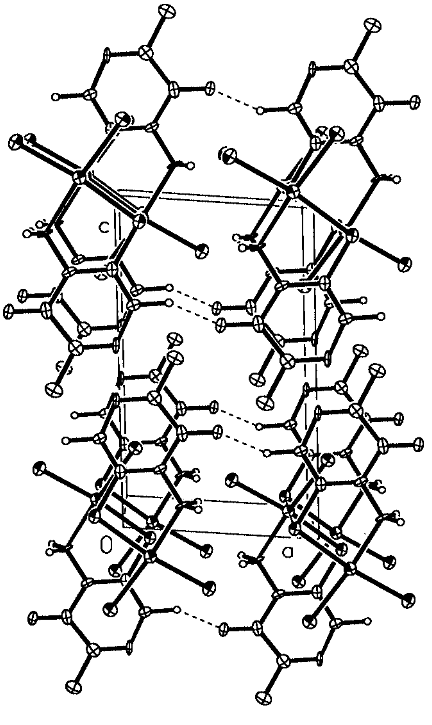


Fig. 2 View of the unit cell of **2** in direction [010].

The Cu1−Cl1, Cu1−Cl2 and Cu1−N2 bond lengths are 224.5(3), 225(3) and 203.5(9) pm. Similar Cu^{II} complexes have Cu−N distances of 196.0−203.5 pm [9b, 9c, 9f] and Cu−Cl distances of 220.0−230.1 pm [9b,c]. **2** is stacked along [010] by the additional Cu−S contacts and the formed columns are connected by hydrogen bonds, which extent along [100] (Fig. 2). The N···O distance in N4−H2···O1a of 281(1) pm indicates a medium strong hydrogen bridge. Additional weak hydrogen bonds were formed in N2−H1···Cl2a with a distance of 351.3(5) pm for N2···Cl2a.

Table 1 Selected bond lengths/pm and bond angles/° in **2**−**4**[a)]

			2		
Cu1...S1a	304.7(3)	S1a−Cu1−S1b	178.09(9)	Cl1−Cu1−Cl2	97.3(1)
Cu1−Cl1	224.6(3)	Cl1−Cu1−Cl2	97.3(1)	Cl1−Cu1−S1	89.7(1)
Cu1−Cl2	225.2(3)	Cl1−Cu1−N2	174.8(3)	Cl2−Cu2−S1	173.0(1)
Cu1−S1	231.1(3)	Cl2−Cu1−N2	87.9(3)	S1−Cu1−N2	85.1(3)
Cu1−N2	203.7(9)	Cu1−S1−C1	97.1(4)		
S1−C1	173(1)				
O1−C2	118(2)				
			3		
Cu1−S1	225.28(8)	S1−Cu1−N2	84.93(8)	S1−Cu1−S1a	143.28(4)
Cu1−N2	217.9(4)	S1−Cu1−N2a	120.22(8)	N2−Cu1−N2a	97.6(1)
S1−C1	168.1(4)	Cu1−S1−C1	98.8(1)	Cu1−N2−N1	112.0(2)
O1−C2	121.1(4)				
			4		
Cu1−Cl1	236.7(2)	Cl1−Cu1−S1	104.69(6)	Cl1−Cu1−P1	115.07(6)
Cu1−S1	242.6(2)	Cl1−Cu1−P2	105.25(6)	S1−Cu1−P1	97.10(6)
Cu1−P1	225.9(2)	S1−Cu1−P2	106.83(6)	P1−Cu1−P2	125.43(7)
Cu1−P2	229.5(2)	Cu1−S1−C1	108.5(2)	Cu1−P1−C5	118.1(2)
S1−C1	168.1(6)	Cu1−P1−C6	114.0(2)	Cu1−P1−C7	110.2(2)
O1−C2	122.2(7)	Cu1−P2−C8	118.9(2)	Cu1−P2−C9	120.1(2)
P1−C5	181.7(6)	Cu1−P2−C10	107.1(2)		
P1−C6	182.6(6)				
P1−C7	181.4(6)				
P2−C8	182.6(6)				
P2−C9	183.7(6)				
P2−C10	181.6(6)				

[a)] Crystallographic data (excluding structure factors) for the crystal structures have been deposited at the Cambridge Crystallographic Data Center with the numbers CCDC 181959 (**2**), CCDC 181960 (**3**) and CCDC 181961 (**4**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

Complex 3

3 consists of $[Cu(AMTTO)_2]^+$ ions and Cl^- ions (Fig. 3). Cu^+ and Cl^- ions lie on identical twofold axes. The copper(I) ion is surrounded by two AMTTO ligands quite similar to the $[Ag(AMTTO)_2]^+$ ion [8a]. This means a 2+2 coordination of Cu1 by S1and S1a (225.28(8) pm) as well as by N2 and N2a (217.9(7) pm). Important for the characterization of the coordination sphere in **3** are the angles S1−Cu1−S1a (143.28(4)°) and N2−Cu1−N2a (97.6(1)°). Therefore, the structure of **3** can be described either as distorted linear or distorted tetrahedral [8d, 10e]. The Cu−S distance lies in the range of values, found for Cu(I) complexes with tetrahedral arrangment (224.4−230.0 pm) [5b, 6c, 10a−c]. The Cu−N bonds are rather weak, indicated by the distances of reference complexes [10c, d], exhibiting values of 198.1−210.7 pm. The dihedral angle between the "best planes" of the five-membered chelate rings in the cation $[Cu(AMTTO)_2]^+$ is 103° (see Fig. 4). The chelate rings possess a slight distinct envelope conformation, recognizable by the angle Cu1/S1/N2//S1C1/N1/N2 of 11°. The cations in **3** are connected by strong hydrogen bonds

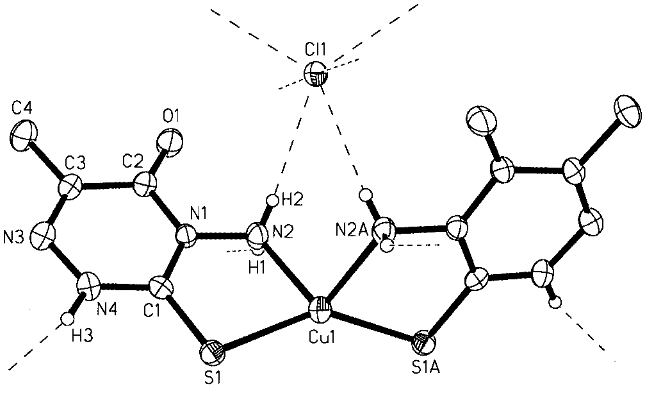


Fig. 3 Structure of one unit of **3** (most of the H atoms are omitted for clarity; thermal ellipsoids 40% probability; only the H···Cl hydrogen bonds are given)

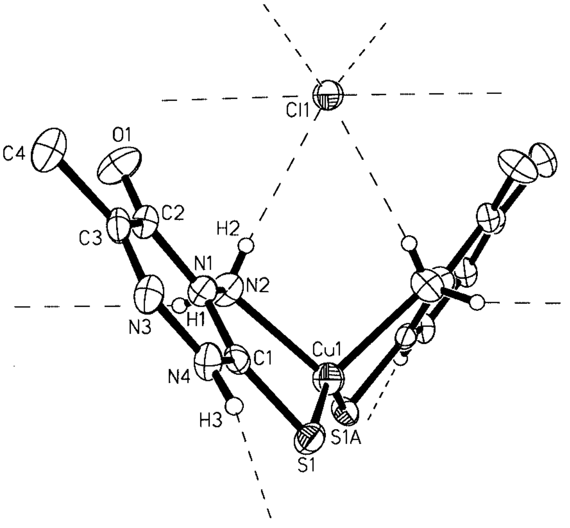


Fig. 4 Side view of the salt **3** in the direction S1−Cu1−S1a with H···Cl hydrogen bridges.

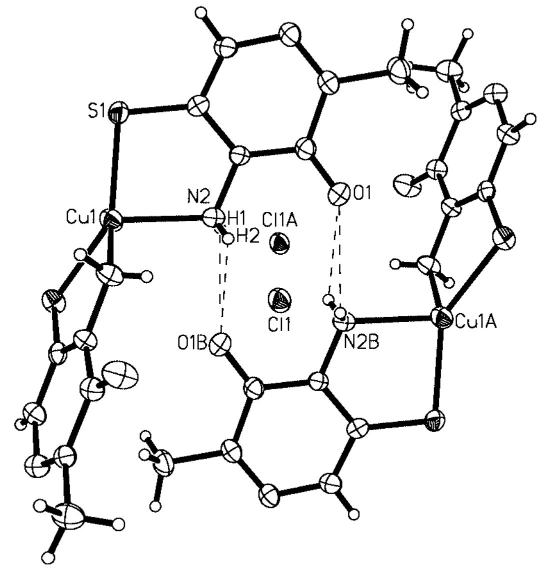


Fig. 5 Two molecules of **3** forming a centrosymmetrical dimer by H···O hydrogen bridges.

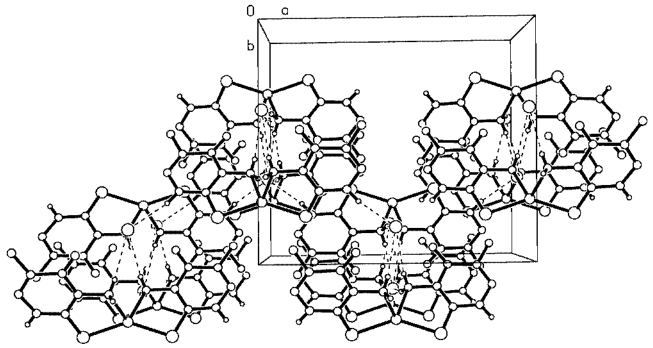


Fig. 6 View of the unit cell of **3** along the direction [001].

(N2−H1···O1b: 279.7(4); N2−H2···O1b: 279.8(4) pm) to each other, forming centrosymmetrical dimers (see Fig. 5). The chloride ion is coordinated via six hydrogen bondings to four cations, leading to a 3d-network of cations and anions (Fig. 6).

Complex 4

The copper(I) ion in **4** is surrounded by two triphenyl phosphine molecules, one AMTTO ligand and one chloride ion (Fig. 7). In **4**, compound **1** acts as a monodentate ligand through its sulfur atom. The Cu1−S1 bond length is 242.6(2) pm and lies in the range observed in similar complexes with tetrahedral Cu(I) centers [5b, 6c, 10a−c]. This shows again the 2+2 character of the coordination sphere in **3** (Cu−S: 225.28(8) pm!). The atom distances Cu1−Cl1 (236.7(2) pm), Cu1−P1 (225.9(2) pm) and Cu1−P2 (229.5(2) pm) are close to those found in literature (Cu−P: 224.7−230.7 pm [5b, 6c, 8b]; Cu−Cl: 230.8−241.0 pm [5b, 6c, 8b, 11a]). The Cu−P bond lengthening of ca. 3.5 pm reflects the sterical influence of the AMTTO ligand caused by the orientation through the hydrogen bond network. Because of the sterical repulsion the angle S1−Cu1−P1 is smaller (97.10(6)°) than the angle S1−Cu1−P2 (106.83(6)°). The other strong sterical repulsion was observed between the two phosphane ligands, indicated by the expansion of the angle P1−Cu1−P2 to 125.43(7)° [6c, 10a, 11a, b]. We reported a second Cu(I) complex (**5**) with Cl^- and PPh_3 ligands but with a modified AMTTO ligand, $C_4H_4N_3SON(=CMe_2)$ [8b] which is also bound as monodentate ligand via S function. **4** possesses three intramolecular hydrogen bondings (N2−H1···O1, N2···O1: 262.2(6) pm; N2-H2···S1, N2···S1: 295.3(6); N4−H1···Cl1, N4···Cl1: 311.7(6) pm) and one intermolecular hydrogen bridge (N2−H1···Cl1, N2···Cl1: 333.2(6) pm), leading to chains along [100].

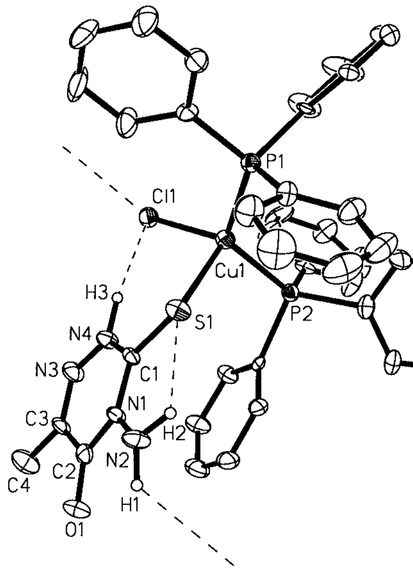


Fig. 7 Molecular structure of **4** (most of the H atoms are omitted for clarity; thermal ellipsoids 40% probability).

3 Experimental Section

General Remarks: All chemicals and solvents were purchased from Merck and Fluka and were used without further purification or drying. **1** was prepared according to literature [12]. The IR spectra were obtained on a Bruker IFS-88 (nujol mulls, CsI disks for the range 4000−500 cm^{-1} and polyethylene disks for the range 500−100 cm^{-1}). The ^{31}P NMR spectrum was measured on a Bruker instrument ARX-200 with 85% aqueous H_3PO_4 as standard ($\delta = 0.0$ ppm).

[Cu(AMTTO)Cl$_2$] (2): A methanolic solution (15 mL) of **1** (0.22 g, 1.4 mmol) was added to an aqueous solution (10 mL) of $CuCl_2$ (0.18 g, 1.4 mmol) and 15% hydrochloric acid (3 mL) and was stirred for 1 h at 20°C. A green precipitate was obtained very fast and was filtered. The filtrate was kept at 20°C for one week to give green crystals of **2**. The crystalline material was washed with methanol and dried on air.
Yield: 0.40 g (95%).
Elemental analysis: $C_4H_6Cl_2CuN_4OS$ (292.62): C 16.32 (calc. 16.42), H 2.01 (2.07), N 19.19 (19.15), Cl 24.18 (24.23), Cu 21.82 (21.71), S 10.89 (10.96)%.

IR (nujol; cm^{-1}): 3231 w (νNH), 3179 w (νNH), 2724 w, 1720 s (νC=O), 1609 m (νC=N), 1589 m, 1526 m, 1314 m, 1244 m, 1165, 1113 vw, 1050 vw, 972 vw, 936 vw, 766 w, 748 m, 735 w, 645 m, 595 w, 516 m, 462 m (νCuN), 412 m, 348 m, 311 m (νCuS), 271 m (νCuCl), 237 vw, 178 m (br), 139 vw.

[Cu(AMTTO)$_2$]Cl (3): 0.14 g (1.4 mmol) of CuCl in 10 mL of H_2O and 0.44 g (2.8 mmol) of **1** in 17 mL 15% hydrochloric acid/MeOH (2 mL/15 mL) were added under stirring at 20°C. The reaction mixture was stirred for 45 min and a yellow shiny microcrystalline solid precipitated. The mixture was filtered and dried on air. Suitable crystals for X-ray structure determination were obtained by recrystallization from EtOH/$CHCl_3$/MeCN (1:1:1) at 4°C after several days.
Yield: 0.58 g (92%).
Elemental analysis: $C_8H_{12}ClCuN_8O_2S_2$ (415.35): C 23.09 (calc. 23.13), H 2.86 (2.91), N 26.91 (26.98), Cl 8.59 (8.53), Cu 15.21 (15.30), S 15.52 (15.44)%.

IR (nujol; cm^{-1}) 3229 m (νNH), 3126 w (νNH), 2853 vs,1712 s (νC=O), 1603 m (νC=N), 1509 m, 1297 m, 1168 m, 1139 m, 1080 vw, 932 w, 749 w, 641 m, 587 w, 504 m, 457 m (νCuN), 436 w, 412 m, 352 m (νCuS), 313 vw, 272 w, 223 vw, 171 w, 136 m, 114 m.

[Cu(AMTTO)(PPh$_3$)$_2$Cl] (4): A solution of **1** (0.22 g; 1.4 mmol) in MeCN (15 mL) was added to a solution of CuCl (0.14, 1.4 mmol)

Table 2 Crystallographic data of **2**−**4**.

Compound	**2**	**3**	**4**
Instrument	IPDS I (Stoe)	IPDS I (Stoe)	CAD4 (Enraf-Nonius)
Radiation	Mo-Kα (λ = 71.073 pm)	Mo-Kα	Mo-Kα
Empirical formula	$C_4H_6Cl_2CuN_4OS$	$C_8H_{12}ClCuN_8O_2S_2$	$C_{40}H_{36}ClCuN_4OP_2S$
Formula mass/g·mol^{-1}	261.63	415.35	781.76
Crystal size/mm	0.32x0.09x0.03	0.38x0.07x0.04	0.37x0.11x0.08
Crystal system	monoclinic	orthorhombic	monoclinic
Space group (no. [18])	$P2_1/m$ (11)	Pbcn (60)	$P2_1/n$ (14)
a/pm	666.7(1)	1291.2(2)	879.4(1)
b/pm	609.4(1)	1146.5(1)	1849.3(2)
c/pm	1132.6(2)	1000.5(1)	2293.8(3)
β/°	95.46(2)		92.38(1)
Volume/pm^3·10^6	458.1(1)	1481.0(3)	3727.1(8)
Z	2	4	4
d_{calc}/g·cm^{-3}	2.122	1.863	1.393
Absorption correction	numerical	numerical	empirical
μ/cm^{-1}	31.6	19.6	8.4
Temperature/K	193	193	193
$2\theta_{max}$	51.99	52.09	50.0
h	−8 → 8	−15 → 15	−10 → 0
k	−13 → 13	−11 → 11	−21 → 0
l	−7 → 7	−14 → 14	−27 → 27
reflection collected	2797	11008	7237
Unique reflections (R_{int})	981 (0.083)	139 (0.0636)	6540 (0.067)
Reflections with F_o>4s>(F_o)	560	775	3326
Parameters	87	114	462
R_1 (F_o<4s>(F_o))	0.0365	0.0315	0.0688
wR_2 (all data)	0.0904[a)]	0.0781[b)]	0.1093[c)]
Largest diff. peak and hole /[(e·pm^{-3})·10^{-6}]	0.46/−0.44	0.52/−0.47	0.44/−0.43

[a)] $w = 1/[\sigma^2(F_o)^2 + (0.0387 \cdot P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.[b)] $w = 1/[\sigma^2(F_o)^2 + (0.0461 \cdot P)^2]$. [c)] $w = 1/[\sigma^2(F_o)^2 + (0.0234 \cdot P)^2]$.

and PPh_3 (0.73 g, 2.8 mmol) in $CHCl_3$ (30 mL). The yellow solution was stirred for 3 h and then concentrated to a volume of 10 mL. Colorless crystals were obtained at 20°C after several days, washed with methanol and dried on air.
Yield: 1.09 g (95%).
Elemental analyses: $C_{40}H_{36}ClCuN_4OP_2S$ (781.76): C 61.39 (calc. 61.46), H 4.71 (4.64), N 7.21 (7.19), Cl 4.58 (4.50), Cu 8.09 (8.13), P 7.88 (7.92), S 4.07 (4.10)%.

IR (nujol; cm^{-1}): 3298 w (νNH), 3210 w (νNH), 3120 vw, 3049 w, 1689 s (νC=O), 1592 m-w (νN=C), 1524 s, 1436 s, 1405 m, 1311 m, 1250 m, 1218 m, 1181 w, 1093 m, 1066 m, 1026 w, 995 m, 904 w, 856 vw, 829 vw, 743 s, 694 s, 619 vw, 580 vw, 510 s, 482 m, 429 m, 413 w, 390 vw, 366 m, 343 w, 315 m (νCuS), 295 w, 271 m, 237 m (νCuCl), 216 m, 190 m, 159 m, 143 m, 111 m.
$^{31}P\{^{1}H\}$ NMR (MeOH): 32.6 ppm (s).

Crystal Structure Analyses of 2−4

The crystals of **2**, **3** and **4** were covered with a perfluorinated polyether and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen (−80°C; intruments and graphite monochromated radiation see Table 2). The orientation matrix and preliminary unit cell dimensions were determined from 1000 (**2**), 1000 (**3**) and 15 (**4**) reflections. The final cell parameters were determined from 2000 (**2**), 8000 (**3**) and 25 (**4**) reflections. The intensities were corrected for Lorentz and polarization effects. Used programs: SIR-92 [13], SHELXS-97 [14], SHELXL-97 [15], SHELXTL [16] and PLATON-98 [17].
H-Atoms: **2**, **3**: Free refinement of N-H; ideal positions for C−H and refinement with common displacement parameter. **4**: Free refinement of N−H in positions; ideal positions for C−H; refinement with common displacement parameter for all H atoms.

Acknowledgments. The work was financially supported by the Deutsche Forschungsgemeinschaft and the Adolf-Haeuser Foundation (Marburg).

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