Syntheses, Characterization and X-Ray Structures of the first Copper(I) and Silver(I) Complexes with ATT (ATT = 6-Aza-2-thiothymine)

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Abstract. The reaction of copper(I) chloride with 6-aza-2-thiothymine (ATT, **1**) and triphenylphosphane in methanol/chloroform gives $[(ATT)CuCl(PPh_3)]$ (**2**) as a neutral complex. $[(ATT)Ag(NO_3)(PPh_3)_2]\cdot MeOH$ (**3**) can be obtained by the reaction of **1** with silver(I) nitrate and triphenylphosphane in methanol/chloroform in excellent yields and the single crystals of **3** can be obtained from acetonitril solution.

Both complexes were characterized by infrared spectroscopy, elemental analyses as well as by X-ray diffraction studies. Crystal data for **2** at −80°C: space group I2/a with a = 1859.3(1), b = 1143.2(1), c = 2208.2(1) pm, β = 104.84(1)°, Z = 8, R_1 = 0.0355 and for **3** at −80°C: space group $P2_1/c$ with a = 1344.1(1), b = 1553.6(1), c = 1977,3(3) pm, β = 105.26(1)°, Z = 4, R_1 = 0.0436.

Keywords: Copper; Silver; Thiothymine complexes; Crystal structures

Synthesen und Bestimmung der ersten Kupfer(I)- and Silber(I)-Komplexe mit ATT (ATT = 6-Aza-2-thiothymin)

Inhaltsübersicht. Die Reaktion von Kupfer(I)chlorid mit 6-Aza-2-thiothymin (ATT, **1**) und Triphenylphosphan in Methanol/Chloroform ergibt den Neutralkomplex $[(ATT)CuCl(PPh_3)]$ (**2**). $[(ATT)Ag(NO_3)(PPh_3)_2]\cdot MeOH$ (**3**) kann in sehr guter Ausbeute erhalten werden, wenn Silber(I)nitrat mit ATT und Triphenylphosphan in Methanol/Chloroform umgesetzt wird. Geeignete Einkristalle für die Röntgenstrukturanalyse wurden aus der Acetonitril-Lösung von **3** erhalten. Die Komplexe wurden mittels IR-Spektroskopie, Elementaranalysen und Röntgenstrukturanalysen charakterisiert. Kristalldaten für **2** bei −80°C: Raumgruppe I2/a mit a = 1859,3(1), b = 1143,2(1), c = 2208,2(1) pm, β = 104,84(1)°, Z = 8, R_1 = 0,0355 und für **3** at − 80°C: Raumgruppe $P2_1/c$ mit a = 1344,1(1), b = 1553,6(1), c = 1977,3(3) pm, β = 105,26(1)°, Z = 4, R_1 = 0,0436.

1 Introduction

There is considerable interest in the coordination chemistry of chelating ligands containing mixed functionalities [1]. Our group has previously synthesized and characterized the AMTTO-complexes of Pd^{II}-, Pt^{II}-, Ag^{I}-, Cu^{I}- and Cu^{II}-ions (AMTTO = 4-amino-6-methyl-1,2,4-triazin-thione-5-one). In our investigations in the coordination chemistry of hydrazine family, we have shown that the AMTTO reacts with palladium(II) halides such as chloride, bromide and iodide as a S,N-chelating ligand [2] and with silver(I) nitrate according to the "*Pearson* Principles" [3] as a unidentate one *via* its sulfur atom with a weak Ag···N interaction, which leads to a 2+2 coordination on the silver atom [4]. We have also studied the behavior of the AMTTO to the homologous Cu^{I} and Cu^{II} ions and found that the AMTTO reacts with Cu^{I} as a monodetate in ratio 2:1, while it reacts with Cu^{II} as a bidentate one in a ratio of 1:1. In the latter complex the ligand occupied two equatorial positions in the *Jahn-Teller* distorted stretched octahedron [4c]. We have studied also the behavior of the synthesized complexes against the nucleophile PPh_3. As part of our continuing interest in the syntheses and characterization of heterocyclic thione complexes of transition metals, specially silver(I), we reported on further thione argentanacycles [5].

In this communication we wish to report the synthesis, characterization and crystal structure of copper(I) and silver(I) complexes containing another representative of hydrazine family, namely ATT.

2 Syntheses and Characterization of 2 and 3

2 can be prepared by the reaction of CuCl, PPh_3 and **1** in a molar ratio 1:1:1 in methanol/chloroform according to equation (1).

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$$\mathbf{1} + \mathrm{CuCl} + \mathrm{PPh_3} \xrightarrow{\mathrm{MeOH/CHCl_3}} \underset{\mathbf{2}}{[(\mathrm{ATT})\mathrm{CuCl}(\mathrm{PPh_3})]} \qquad (1)$$

3 can be obtained by the reaction of $AgNO_3$, PPh_3 and **1** in a molar ratio 1:2:1 in methanol/chloroform [eq. (2)].

$$\mathbf{1} + \mathrm{AgNO_3} + 2\,\mathrm{PPh_3} \xrightarrow{\mathrm{MeOH/CHCl_3}} \underset{\mathbf{3}}{[(\mathrm{ATT})\mathrm{Ag}(\mathrm{PPh_3})_2(\mathrm{NO_3})]} \qquad (2)$$

Both complexes are colorless compounds. The absorptions νCuS and νCuCl of complex **2** can be observed at 340 and 284 cm^{-1}, respectively. In the IR spectra of **3** a band at 295 and 322 cm^{-1} can be assigned to νAgS and νAgO [6]. The C=O and C=N functions cause two vibrations at 1687 and 1543 cm^{-1} for **2** and 1684 and 1552 cm^{-1} for **3**, respectively. P−C vibrations of the moiety PPh_3 are found in the range 748−696 cm^{-1} for **2** and at 761−696 cm^{-1} for **3**. The NO_3^--moiety presents its N−O asymmetric stretching mode at 1378 cm^{-1}. For N−H stretching vibrations two broad weak absorptions could be found at 3477 (**2**) and 3490 (**3**) cm^{-1}, a result of hydrogen bonding. Consistent with the structures of **2** and **3**, only one sharp singlet resonance at −3.14 ppm and at 8.6 ppm were observed in each of the $^{31}P\{^1H\}$ NMR spectra. The value for **2** is in good agreement with the resonances of $[Cu(PPh_3)_2Cl]$ (−3.7 ppm) [7] and $[Cu(PPh_3)_3][NO_3]$ (−2.9 ppm) [8]. In general, the coordination of the triphenylphosphane to copper(I) causes no large shifts of the signal of the uncoordinated phosphane at −6.0 ppm.[9]

3 Results and Discussion

The copper(I) complex consists of neutral molecules (Fig. 1). The molecule of **2** posseses C_1-symmetry. The coordination around the metal atom is distorted trigonal planar with one P atom of the phosphane molecule, one S atom of the thione and one Cl atom. This arrangement is considerable distorted since the angle P1−Cu1−Cl1 with a value of 127.02(3)° is somewhat larger than the trigonally coordinated Cu^I, which caused a reduction of the other two selected angles at the metal site with 114.86(3)° (P1−Cu1−S1) and 117.62(3)° (S1−Cu1−Cl1).

The Cu−P bond distance with 220.42(6) pm is shorter than those observed in $[(Ph_3P)_2CuCl]\cdot 0.5THF$ (average 226.2 pm) [7] and $[(Ph_3P)_2CuCl]\cdot 0.5C_6H_6$ [average 226.6 pm] [10] and is slightly longer than those observed in the binuclear Cu^I complex $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ containing three and four coordinated copper moieties. (Cu−P: C.N. 3: 218.1(1) pm) and is shorter than those in four coordinated copper in the same complex (average 223.55 pm) [7].

Similar Cu−Cl distances, here 223.32(6) pm, have been observed in complexes with three coordinated Cu^I such as $[(Ph_3P)_2CuCl]\cdot 0.5THF$ (221.4(1) pm) and $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ (225.0(1) pm) [7] and it is slightly shorter than the distances observed in the complexes with four coordinated copper complexes like $[Cu(AMTTO)_2(PPh_3)_2Cl]$ (236.7(2) pm) and $[(C_4H_4N_3SON(=CMe_2)Cu(PPh_3)_2Cl]$ (238.0(1) pm) [4b, 4c].

The Cu−S bond distance of 226.50(6) pm is consistent with the distances usually found for trigonally coordinated copper(I) ions containing S-donor ligands.

The complexes in **2** are connected by strong hydrogen bonds (N1−H1···O1a): 282.0(2) pm) to each other, forming centrosymmetrical dimers. In addition, a medium strong intramolecular hydrogen bonding links the NH group to the halide atom (N3−H2···Cl1: 311.3(2) pm). The dihedral angle between the "best planes" of the ligand and the CuClPS-moiety is 17° (see Fig 1).

The silver complex, **3**, consists in contrast to the similar silver complex containing AMTTO, which is an ionic complex $[(AMTTO)Ag(PPh_3)_2]NO_3$ [11], of neutral molecules and possesses only C_1-symmetry (Fig. 2). The ATT ligand acts here as monodentate one and coordinates to the silver atom through its sulfur atom. The silver atom is also surrounded by two triphenylphosphane molecules and the coordination of the nitrate ion completes the distorted tetrahedral coordination around it. This arrangement is considerable distorted since the P angle at the metal site, P1−Ag1−P2 with a value of 128.24(3)°, is close to trig-

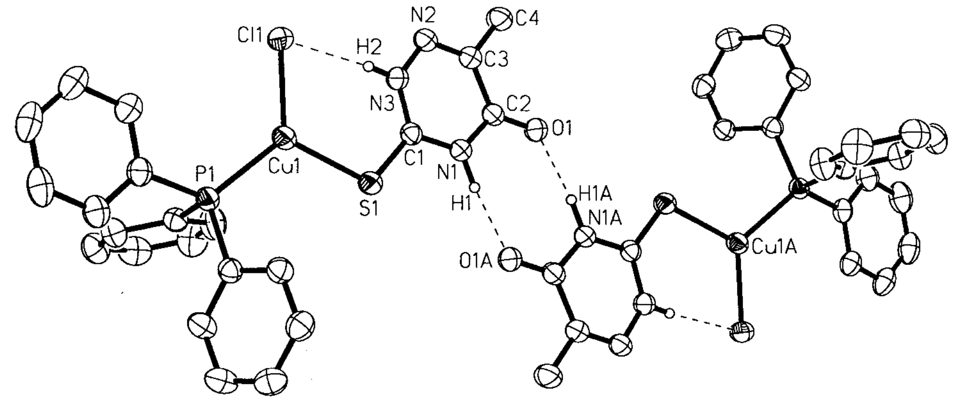

Fig. 1 Structure of two molecules of **2** dimerized by hydrogen bonds (most of the H atoms are omitted for clarity; thermal ellipsoids 40% probability).

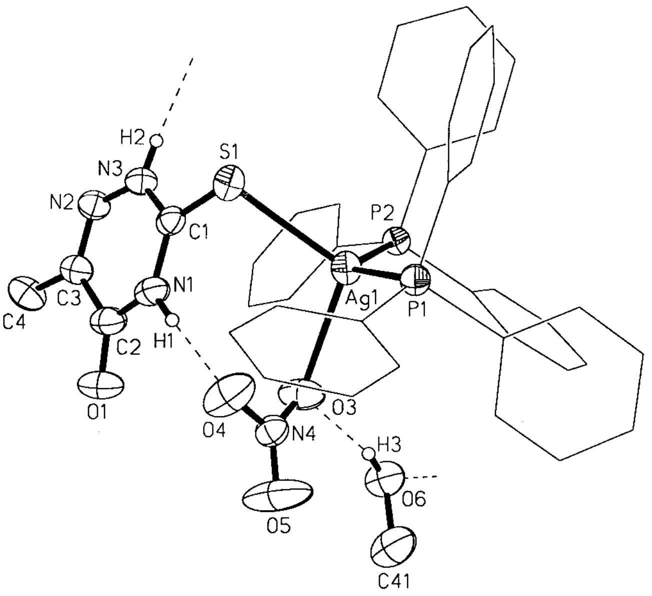

Fig. 2 Molecular structure of **3** (most of the H atoms are omitted for clarity; the phenyl rings are representated as thin lines only; thermal ellipsoids 40% probability).

onally coordinated Ag^I, while three other selected angles in the AgP_2SN group with 108.97(8)°(S1−Ag1−O3), 109.47(3)°(S1−Ag1−P2) and 108.2(1)°(P1−Ag1−O3) are nearly to those of a regular tetrahedron. The tetrahedral distortion can be accounted for the steric hindrance induced by the two bulky phosphane molecules and was observed in analogous silver complexes such as $[(AMTTO)Ag(PPh_3)_2]NO_3{\cdot}0.5MeOH{\cdot}0.5H_2O$ [P1−Ag1−P2: 126.95(3)°] [11] and $[(C_4H_4N_3SON({=}CMe_2)Ag(PPh_3)_2]$-$NO_3$ (P1−Ag1−P2: 124.33(6)°) [4b]. The Ag−P distances mean 244.75 pm, are within the range observed in complexes with four coordinated Ag^I containing two phosphanes (242.6−250.4 pm) [12]. The Ag−S bond lengths of 262.11(9) pm is significantly longer than the distance found in $[(AMTTO)_2Ag]NO_3$ (243.50(8) pm], possessing a 2+2 coordination around the Ag^+ center and lies in the range observed in $[(AMTTO)Ag(PPh_3)_2]NO_3{\cdot}0.5MeOH{\cdot}0.5H_2O$ (264.40(8) pm) [11] and $[(C_4H_4N_3SON({=}CMe_2)Ag(PPh_3)_2]$-$NO_3{\cdot}0.5MeOH$ (262.9(2) pm) with four coordinated silver atoms [4b]. The Ag−O distance of 256.0(3) pm lies in the range observed in $[Ag_2(NO_3)_2(Ph_2AsCH_2CH_2AsPh_2)]$ [13].

The existence of a medium strong intramolecular hydrogen bond between the NH-group of the ligand and an oxygen atom of the nitrate moiety [N1···O4: 285.0(5) pm] and an intermolecular hydrogen bond between the other oxygen atom of the nitrate molecule and the coordinated solvate molecule (MeOH) [O3···O6: 277.7(4) pm)] also contribute to the angular distortion about the silver atom and the nitrogen atom of the nitrate moiety. There is also a medium strong intermolecular hydrogen bond between the NH-group of the ligand and the oxygen atom of the solvate molecule leading to chains along [010].

4 Experimental Section

The following chemicals were purchased and used without further purification: CuCl, $AgNO_3$, MeOH, $CHCl_3$ and PPh_3. **1** was prepared according to the literature procedures [14]. The IR spectra were obtained on a Bruker IFS-88 (nujol mulls: CsI discs of the range 4000−500 cm^{-1}; polyethylen discs for the range 500−100 cm^{-1}).

The ^{31}P NMR spectrum was measured on a Bruker instrument AX-200 with 85% aqueous H_3PO_4 (external) as standard (δ = 0.0 ppm)

[(ATT)CuCl(PPh$_3$)] (2). Copper(I) chloride (0.12 g, 1 mmol) was added to a solution of **1** (0.14 g, 1 mmol) in 10 mL of methanol and stirred for 5 hrs at room temperature. To this solution was added a solution of triphenylphosphane (0.26 g, 1 mmol) in 5 mL of chloroform and stirred for further 2 hrs at room temperature. The resulted crude was filtered and washed with cold methanol and chloroform. Suitable single crystals for X-ray diffraction could be obtained from the acetonitril solution of **2**.

Yield: 0.45 g (90%)

Elemental analysis: $C_{22}H_{20}ClCuN_3OPS$ (504.44): calcd C 52.38, H 3.99, N 8.33, Cu 12.59, P 6.13, S 6.35; found C 51.98, H 3.88, N 8.30, Cu 12.33, P 6.01, S 6.28%.

IR (Nujol; cm^{-1}): 3477 vw (νNH, br), 1716 s, 1687 s (νC=O), 1605 s, 1543 s (νC=N, triazine), 1478 m, 1434 s, 1378 m, 1326 m, 1270 w, 1226 s, 1096 s, 748 s (νPPh_3), 695 s (νPPh_3), 579 s, 521 s, 502 s, 416 s, 340 s (νCuS), 285 s, 200 m (νCuCl), 175 (νCuP) m, 134 m.

^{31}P NMR (d_6-DMSO): −3.14 ppm.

[(ATT)Ag(NO$_3$)(PPh$_3$)$_2$]·MeOH (3). Silver nitrate (0.17 g, 1 mmol) was added to a solution of **1** (0.14 g, 1 mmol) in 10 mL of methanol and stirred for 3 hrs at room temperature. A solution of triphenylphosphane (0.52 g, 2 mmol) in 10 mL of chloroform was added dropwise to the reaction mixture and stirred for further 5 hrs at room temperature. The solvent was evaporated to a small volume, the formed crude was filtered and washed with cold methanol. The clear solution was kept at 4°C to give colorless crystals of **3**.

Yield: 0.71 g (85%)

Elemental analysis: $C_{41}H_{39}AgN_4O_5P_2S$ (869.64): calcd C 56.62, H 4.52, N 6.44, Ag 12.40, P 7.12, S 3.68; found C 55.89, H 4.43, N 6.35, Ag 12.29, P 7.00, S 3.59%.

IR (Nujol; cm^{-1}): 3490 vw (νNH, br), 3183 s, 3132 s, 1717 s, 1684 s (νC=O), 1601 s, 1552 s (νC=N, triazine), 1453 m, 1426 s, 1378 m, 1347 m, 1269 w, 1133 s, 1038 s, 791 s, 767 s (νPPh_3), 721 s (νPPh_3), 694 s (νPPh_3), 582 s, 551 s, 446 s, 417 s, 409 s, 322 s (νAgO), 295 s (νAgS), 277 s.

^{31}P NMR (d_6-DMSO): 8.6 ppm.

Crystal structure analyses of **2** *and* **3**

The crystals of **2** and **3** were covered with a perfluorinated oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from ca. 1000 (**2**, **3**; Stoe IPDS) reflections (graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) for both complexes. The final cell parameters were determined from 15000 for **2** and from 20000 for **3**. The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for **2** and **3** (numerical). The structures were solved by the direct methods for **2** and **3** (SHELXS-97 [15]) and refined against F^2 by full-matrix least-squares using the program SHELXL-97 [16]. The hydrogen atoms (C−H) in **2** and **3** were cal-

Table 1 Crystallographic data for **2** and **3**

Compound	2	3
Empirical formula	$C_{22}H_{20}ClCuN_3OPS$	$C_{41}H_{39}AgN_4O_5P_2S$
Formula mass	504.46	869.66
Crystal size (mm)	0.43 × 0.21 × 0.15	0.48 × 0.3 × 0.21
Crystal system	monoclinic	monoclinic
Space group	I2/a	$P2_1/c$
a/pm	1159.3(1)	1344.1(1)
b/pm	1143.2(1)	1553.6(1)
c/pm	2208.2(1)	1977,3(3)
β/°	104.84(1)	105.26(1)
Volume/$pm^3 \cdot 10^6$	4537.1(5)	2330.7(4)
Z	8	4
d_{calcd}/$g \cdot cm^{-3}$	1.477	1.45
Absorption correction	numerical	numerical
μ/cm^{-1}	12.6 (Mo-Kα)	6.9 (Mo-Kα)
Temperature/K	193	193
$2\theta_{max}$/°	52.58	52.61
Index range *h*	−23 → 22	−16 → 16
k	−14 → 14	−19 → 19
l	−27 → 27	−24 → 24
Reflections collected	32256	57206
Unique reflections (R_{int})	4571 (0.0606)	8043 (0.0711)
Reflections with $F_o > 4\,\sigma(F_o)$	3735	6097
Parameters	282	503
R_1	0.0355	0.0436
wR_2 (all data)	0.0959[a]	0.1214[b]
Max. electron density /$(e \cdot pm^{-3}) \cdot 10^{-6}$	0.51	0.98

[a] $w = 1/[\sigma^2(F_o)^2 + (0.0657 \cdot P)^2 + (4.39 \cdot P)]$, [b] $w = 1/[\sigma^2(F_o)^2 + (0.0847 \cdot P)2]$; $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$

Table 2 Selected bond lengths/pm and angles/° of **2** and **3**

2			
Cu1−Cl1	222.32(6)	Cl1−Cu1−S1	117.62(3)
Cu1−S1	226.50(6)	Cl1−Cu1−P1	127.02(3)
Cu1−P1	220.42(6)	S1−Cu1−P1	114.86(3)
S1−C1	168.2(2)	Cu1−S1−C1	108.21(8)
C1−N1	136.3(3)	N3−C1−N1	115.6(2)
N1−C2	137.2(3)		
C1−N3	133.0(3)		
N3−N2	136.7(3)		
C2−O1	122.1(3)		
3			
Ag1−S1	262.11(9)	S1−Ag1−P1	106.55(3)
Ag1−P1	244.35(8)	S1−Ag1−P2	109.47(3)
Ag1−P2	245.16(8)	S1−Ag1−O3	108.97(8)
Ag1−O3	256.0(3)	O3−Ag1−P1	108.2(1)
S1−C1	168.5(3)	Ag1−S1−C1	101.3(1)
C1−N1	134.4(4)	P1−Ag1−P2	128.24(3)
C1−N3	133.0(4)	N1−C1−N3	115.7(3)
N1−C2	137.5(5)	O3−N4−O4	115.3(3)
N3−N2	137.3(4)	O3−N4−O5	125.3(4)
C2−O1	121.9(4)	O4−N4−O5	119.3(4)

culated in ideal positions (C−H: 95 pm; refinement with a common displacement parameter for all H atoms except for H1, H2 and H3 in **2** and H1 and H2 in **3**). Programs used were SHELXTL-Plus [17], SHELXL-97 [16], ORTEP [18], and PLATON [19, 20].

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[20] Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposite@ccdc.cam.ac.uk] quoting the depository nos. CCDC 224103 (**2**) and CCDC 224104 (**3**).