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Synthesis and characterization of new AMTTO-imine-ligands and their silver(I) complexes: crystal structures of TAMTTO, $[Ag_2(TAMMTO)_4](NO_3)_2 \cdot 4MeOH$, $[Ag(TAMTTO)(PPh_3)_2]NO_3 \cdot 1.5THF$, $[Ag(FAMTTO)(PPh_3)_2]NO_3$

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Abstract

Reaction of 4-amino-6-methyl-1,2,4-triazin-thione-5-one (AMTTO, **1**) with 2-thiophenecarboxaldehyde and 2-furaldehyde led to the corresponding iminic compounds 6-methyl-4-[thiophene-2-yl-methylene-amino]-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2H)-5-one (TAMTTO, **2**) and 4-[furan-2-yl-methylene-amino]-6-methyl-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2H)-5-one (FAMTTO, **3**). Treatment of **2** with $AgNO_3$ gave the complex $[Ag_2(TAMMTO)_4](NO_3)_2 \cdot 4MeOH$ (**4**) and of **2** and **3** with $[Ag(PPh_3)_2]NO_3$ gave the complexes $[Ag(TAMTTO)(PPh_3)_2]NO_3 \cdot 1.5THF$ (**5**) and $[Ag(FAMTTO)(PPh_3)_2]NO_3$ (**6**), respectively. All the compounds have been characterized by elemental analyses, IR spectroscopy and mass spectrometry. Compound **2** and all the complexes have been characterized by X-ray diffraction studies, respectively. In addition, **5** and **6** have been characterized by ^{31}P NMR spectroscopy. Crystal data for **2** at −80 °C: monoclinic, space group $C2/c$, $a = 2319.6(2)$, $b = 609.8(1)$, $c = 1673.6(2)$ pm, $\beta = 106.14(1)°$, $Z = 8$, $R_1 = 0.0523$; for **4** at −80 °C: triclinic, space group $P\bar{1}$, $a = 877.6(1)$, $b = 1085.2(1)$, $c = 1557.7(2)$ pm, $\alpha = 77.14(1)°$, $\beta = 80.87(1)°$, $\gamma = 78.18(1)°$, $Z = 1$, $R_1 = 0.0407$; for **5** at 20 °C: triclinic, space group $P\bar{1}$, $a = 1151.1(2)$, $b = 1225.1(2)$, $c = 1887.4(3)$ pm, $\alpha = 78.04(1)°$, $\beta = 86.20(1)°$, $\gamma = 76.03(1)°$, $Z = 2$, $R_1 = 0.0662$; for **6** at −80 °C: triclinic, space group $P\bar{1}$, $a = 1189.7(2)$, $b = 1387.8(2)$, $c = 1410.9(2)$ pm, $\alpha = 94.74(2)°$, $\beta = 95.12(2)°$, $\gamma = 112.41(2)°$, $Z = 2$, $R_1 = 0.0511$.

Keywords: Triazines; S-ligands; Silver; Self-assembly; Crystal structure

1. Introduction

Metal complexes of sulfur–nitrogen chelating agents were reviewed in 1974 [1] and the particular features of sulfur as a donor atom have been discussed in some detail in an earlier review [2].

1,2,4-Triazines are well-known heterocyclic thiones derived from thiocarbo-hydrazide, which some of their derivatives exhibit biological activity and have been used for various purposes such as herbicides, neutral antibiotics, antibacterial, etc. The heterocyclic thione exists in two thione and thiole tautomeric forms and there has been considerable interest in the coordination properties of both the neutral thione and of the deprotonated thiol ligand [3].

It has been found that the thione coordinates exclusively via S atom [3b], while the thiolate shows a variety of possibilities, namely (I) S-unidentate, (ii) S,N-chelating [3b,4,5], (iii) S,N-bridging [4,6] and (iv) S-unidentate (with a weak M···N interaction) [7].

In our investigations, we have shown that the AMTTO reacts with palladium(II) halides such as chloride,

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bromide and iodide as a S,N-chelating ligand [8] and with silver(I) nitrate according to the "Pearson Principles" [9] 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 [10]. 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 monodentate in a 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 streched octahedron [10c]. We have also studied 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 wish to report on further thione argentanacycles.

2. Experimental

2.1. General remarks

AMTTO (**1**) was prepared according to the literature procedure [11]. Solvents were purified by standard methods [12]. IR spectra were recorded on a Perkin–Elmer spectrometer 883 (KBr pellets, Nujol mulls, 4000–250 cm^{-1}) or on a Bruker IFS 88 instrument (CsBr discs, 4000–400 cm^{-1}; polyethylene discs, 500–100 cm^{-1}; Nujol mulls). ^{1}H, ^{13}C and ^{31}P NMR were recorded on a Bruker AC 200 spectrometer using TMS and 85% aqueous H_3PO_4 as an external standard. 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; silver: decomposition with $HClO_4$ and X-ray fluorescence analysis. The following chemicals were purchased from Merck and Fluka and used without further purification: silver nitrate, furfural-2-carboxaldehyde, 2-thiophenecarboxaldehyde, methanol, triphenylphosphane.

2.2. Synthesis of the ligands and complexes

2.2.1. Synthesis of TAMTTO (2)

A solution of **1** (0.95 g, 6 mmol) in MeOH (40 mL) was treated with 2-thiophenencarboxaldehyde (2.01 g, 18 mmol) and the resulting mixture was acidified with 10 drops of hydrochloric acid (37.5%). The reaction mixture was refluxed for 9 h. The white precipitate formed was filtered off and was recrystallized from EtOH/THF. Yield: 1.21 g (80%). mp.: 231°. *Anal.* Calc. for $C_9H_8N_4OS_2$ (252.31): C, 42.84; H, 3.20; N, 22.20. Found: C, 43.05; H, 3.68; N, 21.98%. IR (Nujol): $\tilde{\upsilon} = 3146$ [(NH)], 2923, 2854 (C–Ar), 1670 (νC=O), 1617 (C=N, imine), 1593 (C–N, thioamide), 1520 (C=N, triazine), 1462, 1377, 1324 (C–N, thioamide), 1272, 1045 (νC=S), 935, 854, 793, 771, 732, 720, 629, 588, 569, 514. MS (70 eV) *m/z* (%): 252(31)[M^+], 253(13)[M^++1], 143(40), 110(55), 102(48), 96(44), 83(14), 70(34), 69(100), 59(35), 56(18), 45(23), 42(34), 39(32), 27(22). ^{1}H NMR (DMSO-d_6): $\delta = 2.19$ (s, 3H, CH_3), 7.14–7.18 (dd, 1H, H-2), 7.58–7.61 (dd, 1H, H-3), 7.74 (dd, 1H, H-1), 8.61 (d, 1H, H-imine), 12.65 (bs, 1H, NH-thione). ^{13}C NMR (DMSO-d_6): $\delta = 16.55$ (CH_3), 128.29 (C-2), 133.32(C-1), 135.48(C-3), 136.17(C-4), 146.90 (CH=N, imine), 149.60 (C=N, triazine), 166.41 (C=O), 170.50 (C=S).

2.2.2. Synthesis of FAMTTO (3)

Compound **3** was synthesized by a similar procedure used for **2** using the following amounts: **1** (0.95 g, 6 mmol), furfural-2-carboxaldehyde (1.73 g, 18 mmol, 1.50 mL), 10 drops HCl in MeOH, refluxing time 7.5 h. Yield: 1.16 g (81%). mp.: 186.8°, *Anal.* Calc. for $C_9H_8N_4O_2S$ (236.25): C, 45.75; H, 3.41; N, 23.71; S, 13.57. Found: C, 45.54; H, 3.45; N, 22.95; S, 12.64%. IR (Nujol): $\tilde{\upsilon} = 3232$, 3092 [(NH)], 2982 (C–Ar), 1702 (C=O), 1671, 1613 (C=N, imine), 1547 (C–N, thioamide), 1500 (C=N, triazine), 1477, 1427, 1407, 1378, 1338 (C–N, thioamide), 1287, 1261, 1018 (C=S), 935, 757 (C=S), 730, 436, 407, 354, 333, 313, 270, 238, 214, 186, 113. MS (70 eV) *m/z* (%): 236(78)[M^+], 237(18)[M^+ + 1], 143 (35), 110(9), 102(83), 96(54), 93(37), 69(100), 59(22), 52(45), 42(43), 39(34), 29(9), 27(17). ^{1}H NMR (DMSO-d_6): $\delta = 2.25$ (s, 3H, CH_3), 7.08 (m, 1H, H-2), 7.12 (d, 1H, H-3), 7.51 (d, 1H, H-1), 8.24 (s, 1H, H-imine).

2.2.3. Synthesis of $[Ag_2(TAMMTO)_4](NO_3)_2 \cdot 4MeOH$ (4)

A solution of **2** (0.50 g, 2 mmol) in dry methanol (25 mL) was treated with silver nitrate (0.17 g, 1 mmol) and the yellow reaction mixture was stirred at 25 °C for 2 h and refluxed for further 6 h. The yellow precipitate was filtered off and washed with cold dry methanol (10 mL). The clear solution was kept at 4 °C to give colorless crystals of **4**.

Yield: 1.21 g (91%). *Anal.* Calc. for $C_{36}H_{32}Ag_2N_{18}O_{10}S_8$ (1349.01): C, 32.05; H, 2.39; N, 18.68; S, 19.01. Found: C, 31.98; H, 2.41; N, 18.99; S, 18.88%. IR (Nujol): $\tilde{\upsilon} = 3072$ [ν(NH)], 2922 (C–Ar), 1673 (νC=O), 1625 (νC=N, imine), 1575 (νC–N, thioamide), 1518 (νC=N, triazine), 1460, 1376 (νNO_3), 1298 (νC–N, thioamide), 1281, 1203, 1178, 1079 (νC=S), 865 (C–S–C, thiophene), 802 (νNO_3), 741 (C=S), 724, 480, 435, 404, 343 (νAg–S), 301 (νAg–S), 262, 195, 166, 139. ^{1}H NMR (DMSO-d_6): $\delta = 2.14$ (s, 3H, CH_3), 7.22–7.24 (dd, 1H, H-2), 7.78–7.80 (d, 1H, H-3), 7.94–7.99 (d, 1H, H-1), 8.77 (s, 1H, H-imine), 9.88(s, 1H, NH-thione).

2.2.4. Synthesis of $[Ag(TAMMTO)(PPh_3)_2](NO_3) \cdot 1.5THF$ (5)

A solution of **2** (0.23 g, 1 mmol) in dry methanol (40 mL) was treated with $[Ag(PPh_3)_2]NO_3$ (produced in situ from silver nitrate (0.17 g, 1 mmol) and triphenyl phosphane (0.52 g, 2 mmol) in dry methanol (20 mL)) and the reaction mixture was stirred at 25 °C for 1 h and refluxed for further 5 h. The yellowish precipitate was filtered off and washed with cold dry MeOH (15 mL) and dried in vacuo. Single crystals of **5** suitable for X-ray diffraction can be obtained from the solution of solid in THF. Yield: 1.21 g (91%). *Anal.* Calc. for $C_{45}H_{38}AgN_5O_4P_2S_2$ (946.76): C, 57.07; H, 4.04; N, 7.39; S, 6.77; Ag, 11.39. Found: C, 56.80; H, 4.18; N, 7.27; S, 6.68; Ag, 10.90%. IR (Nujol): $\tilde{\upsilon} = 3052$ [s, ν(NH)], 1700 [s, ν(C═O)], 1674 (w), 1608 [w, ν(C═N, imine)], 1581 [s, ν(C–N, thioamide)], 1529 [m, νC═N, triazine)], 1479 (s), 1434 (m), 1410 (m), 1379 [w, (νNO_3), E'], 1298 [w, δ(C–N, thioamide)], 1094 [s, ν(C═S)], 1027 (w), 996 (w), 850 (w), 823 [s, $\nu(NO_3)$, A_2''], 748 [s, ν(P–C)], 694 [s, ν(C–P)], 618 (vw), 514(s), 503 (vw), 489 (w), 440 (s), 347 (w), 311 (s), 272 [m, ν(Ag–N)], 215 [m, ν(Ag–S)], 192 (m), 159 (w), 130 [m, $\nu(AgP_2)$]. ^{31}P NMR (THF): $\delta = 12.8$.

2.2.5. Synthesis of $[Ag(FAMMTO)(PPh_3)_2](NO_3)$ (**6**)

A solution of **3** (0.25 g, 1 mmol) in dry dichloromethane was treated with $[Ag(PPh_3)_2]NO_3$ (produced in situ from silver nitrate (0.17 g, 1 mmol) and triphenyl phosphane (0.52 g, 2 mmol) in dry dichloromethane) and the reaction mixture was stirred at 25 °C for 1 h. The yellowish precipitate was filtered off and washed with cold dry methanol (10 mL) and dried in vacuo. Suitable single crystals for X-ray diffraction can be obtained from a methanolic solution of **6** at 4 °C. Yield: 0.78 g (84%). *Anal.* Calc. for $C_{45}H_{38}AgN_5O_5P_2S$ (930.70): C, 58.07; H, 4.11; N, 7.52; S, 3.44; Ag, 11.58. Found: C, 57.94; H, 4.18; N, 7.38; S, 3.37; Ag, 11.34%. IR (Nujol): $\tilde{\upsilon} = 3138$ [(NH)], 3052, 2987 (C–Ar), 1705 (C═O), 1612 (C═N, imine), 1578 (C–N, thioamide), 1537 (C═N, triazine), 1479, 1434, 1401, 1378 (νNO_3), 1344 (C–N, thioamide), 1283, 1094 (C═S), 1027, 823 (NO_3), 770, 749 (C═S), 725, 695 (C–P, PPh_3), 586, 516 (C–P, PPh_3), 502 (C–P, PPh_3), 488, 439, 406, 360, 322, 264 (Ag–N), 216 (Ag–S), 128 (Ag–P). ^{31}P NMR (THF): $\delta = 13.5$.

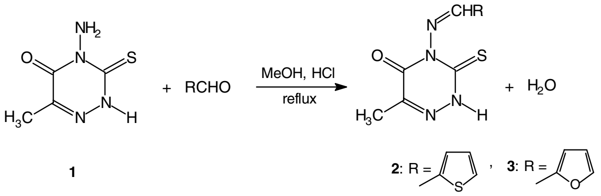
2.3. Crystal structure analyses of **2**, **4**–**6** (Tables 1 and 2)

The selected crystals of **2**, **4**–**6** were covered with a perfluorinated oil and mounted on the tip of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 2000 (**2**, Stoe IPDS), 2000 (**4**, Stoe IPDS), 15 (**5**, Enraf-Nonius CAD 4) and 2000 (**6**, Stoe IPDS) reflections (graphite-monochromated Mo Kα radiation in all cases; $\lambda = 71.073$ pm). The final cell parameters were determined from 8000 for **2**, from 10 000 for **4**, from 25 for **5** and from 8000 for **6**. The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for **2**, **4** and **6** (numerical) and for **5** (empirical, 10 psi-scans). The structures were solved by the direct methods for **2** (SHELXS-97 [13]), for **4** and **5** (SIR-92 [14]) and by Patterson method for **6** (SHELXTL-Plus [15]) and refined against F^2 by full-matrix least-squares using the program SHELXL-97 [16]. The hydrogen atoms (C–H) in **4**–**6** were calculated in ideal positions (refinement with a common displacement parameter). The hydrogen atoms of NH- and OH-groups were fixed at 85 pm (**4**) or freely refined (**2**, **5** and **6**). Programs used were SHELXTL-Plus, SHELXL-97, SHELXS, ORTEP [17], and PLATON [18]. [1]

3. Results and discussion

3.1. Syntheses and characterization of **2**–**6**

Treatment of **1** with 2-thiophenecarboxaldehyde and 2-furaldehyde in dry methanol under reflux conditions gave the corresponding iminic compounds **2** and **3**



(1)

Compound **4** can be obtained by the reaction of **2** with $AgNO_3$ in the molar ratio 2:1 in dry MeOH at 50°

$$4\,\mathbf{2} + 2\,AgNO_3 \xrightarrow{\text{dry MeOH}} \underset{\mathbf{4}}{[Ag_2(TAMTTO)_4](NO_3)_2} \cdot 4\,MeOH \qquad (2)$$

Treatment of $[Ag(PPh_3)_2]NO_3$ with **2** and **3** in a molar ratio of 1:1 led to the complexes **5** and **6**

$$\mathbf{2} + [Ag(PPh_3)_2]NO_3 \xrightarrow{\text{dry MeOH/THF}} \underset{\mathbf{5}}{[(TAMTTO)Ag(PPh_3)_2]NO_3} \cdot 1.5\,THF \qquad (3)$$

$$\mathbf{3} + [Ag(PPh_3)_2]NO_3 \xrightarrow{\text{dry MeOH}} \underset{\mathbf{6}}{[(FAMTTO)Ag(PPh_3)_2]NO_3} \qquad (4)$$

All synthesized compounds are colorless crystalline solids and are air-stable.

IR spectra of **4**–**6** show the bands for νNH and νC═O at 3072, 3053 and 3138 cm^{-1} and 1673, 1700 and 1705 cm^{-1} [19].

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[1] Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposite@ccdc.cam.ac.uk] quoting the depository CCDC nos. 231184 (2), 231186 (4), 231185 (5) and 231187 (6).

Two absorption bands at 301 and 347 cm^{-1} for **4** and two absorption bands at 311 and 323 cm^{-1} for **5** and **6** can be assigned to ν(AgS). The P–C vibrations as well as the δ-CH vibrations of the PPh_3 moiety are seen in the range 748–694 cm^{-1} for **5** and in the range 749–695 cm^{-1} for **6**. The NO_3^- anions in **4**–**6** present their N–O asymmetric streching mode (E') at 1374, 1379 and 1378 cm^{-1} and their out-of-plane absorptions (A_2'') at 865, 823 and 823 cm^{-1}. Consistently, with the structure of **5** and **6** only a sharp singlet resonance at 12.8 ppm and 13.5 were observed in the $^{31}P\{^1H\}$ NMR spectra.

3.2. X-ray structures

3.2.1. Compound 2

Table 1 shows the crystallographic data of **2**, **4**–**6**. Selected bond lengths and angles are given in Table 2. Compound **2** crystallizes in the monoclinic space group $C2/c$. The basic six-membered ring skeleton is planar, while the dihedral angle between the best planes through the six-membered ring and the thioheterocycle is 62° (Fig. 1). The distances between the six-membered ring atoms exhibit a delocalization of π-electrons. The 142.0(3) pm for C1–N1 is the highest, 128.0(3) pm for C3–N3 is the lowest value inside the ring and the ring atoms possess a planar coordination geometry. The bond lengths 166.4(2) pm for S1–C1 and 120.1(3) pm for O1–C2 are significant for a high double bond character. The similar distances are observed in **1** [8a]. The bond length C5–N2 with 126.7(3) pm lies in the range observed in similar compounds such as 2-acetylthiophene thiosemicarbazone (129.2(3) pm) and 2-acetylthiophene 4-phenyl thiosemicarbazone (128.2(3) pm) [20].

A weak hydrogen bonding links the sulfur atom of one molecule to the NH-group of the adjacent one (N4–H1···S1 332.2(2) pm) and is responsible for the centrosymmetric geometry of **2**.

3.2.2. Complex 4

The Ag atom in the cation is coordinated to the sulfur atoms of the two ligands and the sulfur atom of the thiofural hetero ring of the adjacent complex, which is responsible for the dimer complex (Fig. 2).

Table 1
Crystallographic data for **2**, **4**–**6**

Compound	**2**	**4**	**5**	**6**
Empirical formula	$C_9H_8N_4OS_2$	$C_{40}H_{48}Ag_2N_{18}O_{14}S_8$	$C_{51}H_{50}AgN_5O_{5.5}P_2S_2$	$C_{45}H_{38}AgN_5O_5P_2S$
Formula mass	252.31	1477.15	1054.92	930.70
Crystal size (mm)	0.65 × 0.4 × 0.4	0.36 × 0.26 × 0.1	0.45 × 0.45 × 0.2	0.53 × 0.54 × 0.26
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (pm)	2319.6(2)	877.6(1)	1151.1(2)	1189.7(2)
b (pm)	609.8(1)	1085.2(1)	1225.1(2)	1387.8(2)
c (pm)	1673.6(2)	1557.7(2)	1887.4(3)	1410.9(2)
α (°)	90	77.14(1)	78.04(1)	94.74(2)
β (°)	106.14(1)	80.87(1)	86.20(1)	95.12(2)
γ (°)	90	78.18(1)	76.03(1)	112.41(2)
Volume ($pm^3 \times 10^6$)	2274.0(5)	1405.7(3)	2526.5(7)	2127.7(6)
Z	8	1	2	2
$D_{calcd.}$ ($g\,cm^{-3}$)	1.474	1.745	1.387	1.453
Absorption correction	numerical	numerical	empirical	numerical
Mo Kα (cm^{-1})	4.5	10.7	6.0	6.5
Temperature (K)	193	193	293	193
2θ range	51.81	52.49	50.02	51.90
Index range				
h	$-28 \rightarrow 28$	$-10 \rightarrow 10$	$-13 \rightarrow 13$	$-14 \rightarrow 14$
k	$-7 \rightarrow 7$	$-13 \rightarrow 13$	$0 \rightarrow 14$	$-17 \rightarrow 17$
l	$-20 \rightarrow 20$	$-19 \rightarrow 19$	$-21 \rightarrow 21$	$-17 \rightarrow 17$
Reflections collected	10 598	20 589	10 276	20 973
Unique reflections (R_{int})	2116 (0.0481)	5646 (0.0792)	8826(0.0751)	7721(0.063)
Reflections with $F_o > 4\sigma(F_o)$	1647	4604	5129	5524
Parameters	177	391	552	511
R_1	0.0523	0.0407	0.0662	0.0511
wR_2 (all data)	0.1311[a]	0.1130[b]	0.1777[c]	0.1351[d]
Largest difference peak and hole (($e\,pm^{-3}$) · 10^{-6})	0.43	0.77	0.46	1.09

[a] $w = 1/[\sigma^2(F_o^2) + (0.1001P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[b] $w = 1/[\sigma^2(F_o^2) + (0.0772P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[c] $w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + (4.57P)]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[d] $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2
Selected bond lengths (pm) and bond angles (°) in **2**, **4**–**6**

2		**4**				**5**		**6**	
S1–C1	166.4(2)	Ag1–S1	248.64(9)	N6–C14	129.6(4)	Ag1–S1	259.2(2)	Ag1–S1	263.9(1)
C1–N1	137.0(3)	Ag1–S3	246.69(9)	C14–C15	143.3(4)	Ag1–P1	245.8(2)	Ag1–P1	243.6(1)
C1–N4	134.5(3)	S1–C1	168.8(3)	C15–S4	170.8(3)	Ag1–P2	250.7(2)	Ag1–P2	244.9(1)
N1–N2	142.0(3)	S3–C10	168.9(3)	S4–C18	168.7(4)	Ag1···N2	267.5(6)	Ag1–N2	250.4(4)
N2–C5	126.7(3)	C1–N1	136.7(4)	Ag1···Ag1a	314.77(7)	S1–C1	168.1(7)	S1–C1	167.6(5)
C5–C6	143.7(3)	N1–N2	142.5(3)	N9–O3	125.6(4)	C1–N1	135.2(8)	C1–N1	137.6(5)
C6–S2	171.9(3)	N2–C5	129.1(4)	N9–O4	122.8(4)	N1–N2	143.4(7)	N1–N2	143.3(4)
S2–C9	171.0(3)	C5–C6	143.4(4)	N9–O5	120.9(4)	N2–C5	128.9(8)	N2–C5	125.6(6)
C2–O1	120.1(3)	C6–S2	172.5(3)	O6–C19	141.9(5)	C5–C6	144.3(9)	C5–C6	143.7(6)
		S2–C9	170.9(3)	O7–C20	141.0(5)	C6–S2	171.3(7)	C6–O2	136.8(6)
		C10–N5	136.9(4)	Ag1–S2A	287.92(8)	S2–C9	170.6(8)	O2–C9	136.0(5)
		N5–N6	141.8(4)			N5–O2	122.1(9)	N5–O3	127.7(6)
						N5–O3	122.2(9)	N5–O4	123.0(5)
						N5–O4	118.9(9)	N5–O5	120.3(6)
S1–C1–N1	123.7(2)	S1–Ag1–S3	159.88(3)	S3–C10–N5	124.4(2)	P1–Ag1–P2	123.72(6)	P1–Ag1–P2	131.59(4)
S1–C1–N4	121.8(2)	S2A–Ag–S3	104.58(3)	C10–N5–N6	117.4(2)	P2–Ag1–S1	108.99(6)	P2–Ag1–S1	111.69(4)
C1–N1–N2	115.9(2)	S2A–Ag–S1	95.51(3)	N5–N6–C14	113.1(3)	S1–Ag1–P1	122.37(7)	S1–Ag1–P1	109.59(4)
N1–N2–C5	114.4(2)	Ag1–S1–C1	96.6(1)	N6–C14–C15	119.8(3)	Ag1–S1–C1	98.9(3)	Ag1–S1–C1	98.9(1)
N2–C5–C6	121.0(2)	Ag1–S3–C10	97.2(1)	C14–C15–S4	121.7(3)	C1–N1–N2	118.3(5)	C1–N1–N2	118.2(2)
C6–S2–C9	91.2(2)	S1–C1–N1	124.0(2)	C15–S4–C18	91.4(2)	N1–N2–C5	109.4(5)	N1–N2–C5	113.0(4)
C1–N4–N3	127.6(2)	C1–N1–N2	117.3(2)	C19–O6–H3	113(3)	N2–C5–C6	121.8(7)	N2–C5–C6	122.1(4)
N1–C2–O1	122.2(2)	N1–N2–C5	111.8(2)	C20–O7–H4	103(3)	C6–S2–C9	91.2(4)	C6–O2–C9	105.7(4)
		N2–C5–C6	120.5(3)	O3–N9–O4	118.3(3)	O2–N5–O3	121.9(8)	O3–N5–O4	119.6(5)
		C5–C6–S2	123.5(2)	O3–N9–O5	118.2(3)	O3–N5–O4	115.3(8)	O4–N5–O5	119.1(5)
		C6–S2–C9	91.4(2)	O4–N9–O5	123.5(4)	O4–N5–O2	122.8(8)	O5–N5–O3	121.2(7)

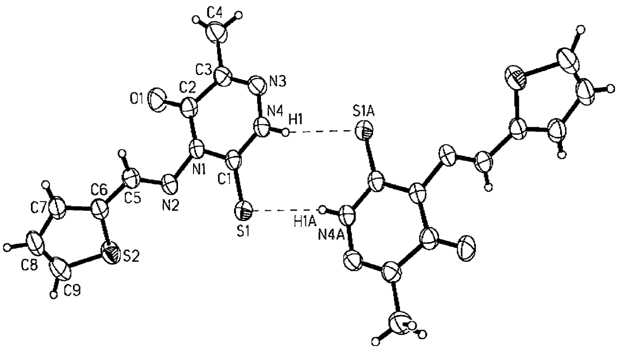

Fig. 1. Molecular structure of **2**.

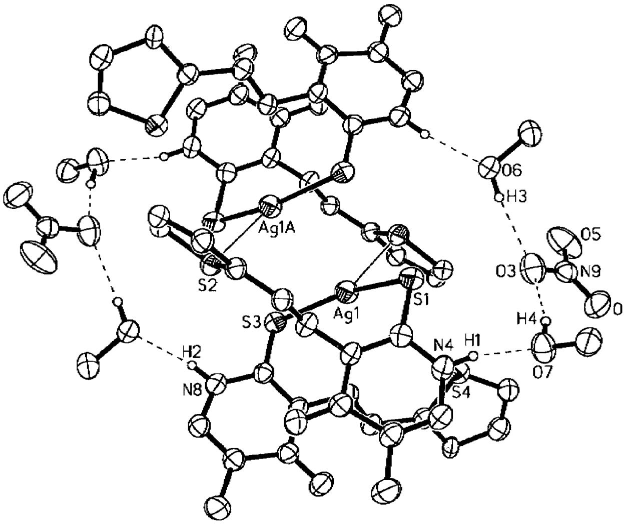

Fig. 2. Molecular structure of **4**.

The S1–Ag1–S3-pseudoaxis with an S–Ag–S angle of 159.88° is characteristic for a distorted linear coordination sphere, caused by additional Ag–S contact. The sum of the angles around metal atom is 360° and the complex is planar. The Ag–S bond distances of 246.69(9) and 248.64(9) pm are significantly longer than the Ag–S distances found in silver complexes with coordination number two (236.2–241.8 pm) [21] and lie within the range expected for c.n. three (246.4–253.4 pm) [22].

The other Ag–S distances of 287.92(8) and 374.2(1) pm are longer than the maximum atom distance generally accepted for Ag(I)–S bonds of 261 pm [23] and the latter is clearly longer than the sum of van der Waals radii of silver and sulfur (170 + 180 = 350 pm) [24], indicating a 2 + 1 coordination sphere for the metal centers in **4**. The Ag···Ag distance is 314.77(7) pm and is shorter than the sum of the van der Waals radii of 340 pm, but there is no interaction between the silver atoms, due to the planar environment of the Ag^+ ions.

Medium strong hydrogen bonds link the NO_3^- anion over oxygen atoms of the methanol molecules to the NH-groups of the adjacent ligands. The contacts N4···O7 (272.7(4) pm), N8···O6a (278.6(4) pm), O6···O3 (299.4(4) pm), O6···O5 (322.5(5) pm) and

O7···O3 (290.7 pm) are responsible for an interesting aureole (ring) around the cation via self assembly.

The dihedral angles formed by the planes of the ligands (A: N5–N7–N8–C10–C11–C12 and B: S4–C15–C16–C17–C18) and (C: N1–N3–N4–C1–C2–C3 and D: S2–C6–C7–C8–C9) are 66° and 75°. The latter is significantly wider than the angle observed in the ligand. The other observed dihydral angles between the planes (C,D) and (E,A) are 44° and 52°.

3.2.3. *Complex* **5**

In the cation of **5**, the ligand is coordinated to the silver atom through its sulfur atom (Fig. 3). Two PPh_3 molecules are also bound to the central atom and complete the trigonal coordination around the silver atom. The sum of the angles around the central atom is 355° and it shows a slightly pyramidalization of the trigonal coordination.

The Ag–S bond lengths of 259.2(2) pm are longer than the Ag–S distances found in complexes with c.n. three (246.4–253.4 pm) [22] and lies in the range of c.n. four silver complexes [21]. It is slightly shorter than the Ag–S distance obtained in the acetone complex [262.9(2) pm], where a distorted tetrahedral coordination around the Ag^+ center was observed [10b]. The Ag–N distance is 267.5(6) pm and is longer than the generally as typical accepted Ag–N distance of 224 pm and the Ag–N distance of 245.9(2) pm observed in similar acetone complex [10b] and 250.4(3) pm in the AMTTO-complex [10a], but it is clearly shorter than the sum of van der Waals radii of silver and nitrogen ($170 + 155 = 325$ pm) [24]. Therefore, the coordination around silver atom is 3 + 1.

The Ag–S bond distances of 246.69(9) and 248.64(9) pm are significantly longer than in silver complexes with coordination number two (236.2–241.8 pm) [21] and lie within the range expected for c.n. three complexes (246.4–253.4 pm) [22].

The dihedral angle formed from the planes S2–C6–C7–C8–C5 and N1–N3–N4–C1–C2–C3 is 67°. The Ag–P bond distances, 245.8(2) and 250.7(2) pm, agree well with the distances observed in the acetone complex $[(C_4H_4N_3SON({=}CMe_2)Ag(PPh_3)_2]NO_3$ (243.0(2) and 249.0(2) pm).

There are two weak hydrogen bondings between two oxygen atoms of the nitrate ion and the NH-group of the heterocycle (308.2(9) and 292.7(9) pm), which caused the reduction of the O–N–O angle to 115°.

3.2.4. *Complex* **6**

Complex **6** is an ionic compound which consists of the cation $[(FAMTTO)Ag(PPh_3)_2]^+$ and the anion NO_3^- (Fig. 4). The molecules of the cationic complexes possess only C_1-symmetry. In the cation of **6**, the ligand chelates the silver atom through its sulfur and iminic nitrogen atom forming a five-membered ring. The distorted tetrahedral coordination around the metal is completed by two P atoms of the phosphane molecules. The deviation from perfect tetrahedral coordination is best illustrated by the P1–Ag1–P2 angle of 131.59(4)° and can be accounted for the steric hindrance induced by the two phosphane molecules, consequently compressing the S1–Ag1–N2 angle to 71.3(1)°. The existence of a medium strong hydrogen bond between the NH-group of the ligand and an oxygen atom of the nitrate anion [N4···O3: 273.1(6) pm] contributes to the angular distortion about the silver atom. In contrast to **5**, where the sulfur-nitrogen ligand bound in a 3 + 1 fashion (strong Ag–S bond; weak and long Ag···N contact) to Ag^+, in **6** the ligand acts more bidentately. However, the Ag–N distance of 250.4(4)

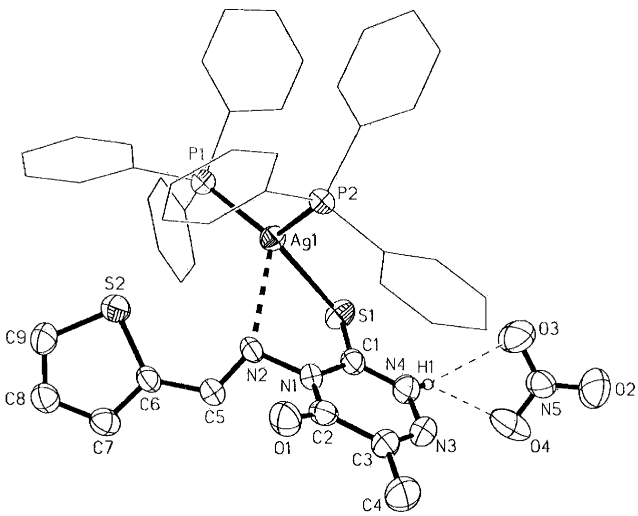

Fig. 3. Structure of **5**.

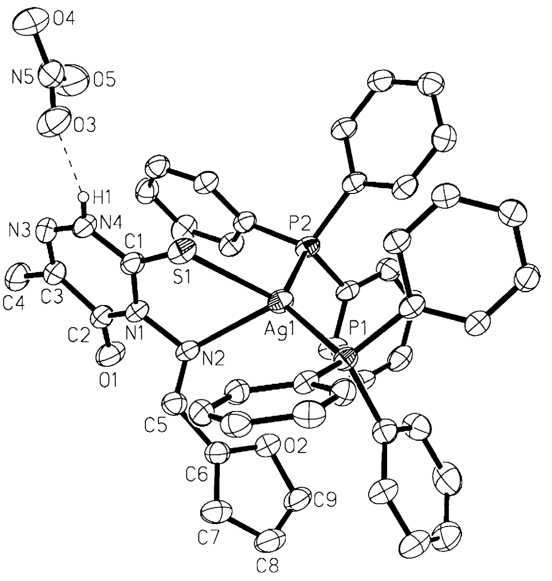

Fig. 4. Molecular structure of **6**.

pm indicates still a long and relatively weak bond, even if significantly shorter than 267.5(6) pm, as found in **5**. The 224 pm is generally accepted as typical Ag–N distance [23], but Ag1–N2 is clearly shorter than the sum of van der Waals radii of silver and nitrogen $(155 + 170 = 325$ pm) [24].

The Ag–P bond distances, 243.6(1) (Ag1–P1) and 244.9(1) pm (Ag1–P2), agree well with the values 242.6–250.4 pm measured for a number of complexes containing silver atoms coordinated by two phosphanes [21b,17]. The Ag–S bond lengths of 263.9(1) pm are slightly longer than the distance found in **5** [259.2(2) pm], where a $3 + 1$ coordination around the Ag^+ center was observed. Nevertheless, the value observed in the **6** lies in the range, which was found for Ag^I complexes with coordination number four [25].

In all complexes, the hydrogen bridges cause slightly different N–O bond lengths within the standard deviations in the strictly planar nitrate ion. So, the distances O3–N9 (125.6(4) pm) for **4** and the distances O3–N5 (127.7(6) pm) for **6**, including the oxygen atoms which participate in the H bridge are somewhat longer than the other N–O bonds in the both complexes (for **4**: O4–N9: 122.8(4) pm and O5–N9: 120.9(4), for **5**: N5–O2: 122.1(9) pm and for **6**: O4–N5: 123.0(5) pm and O5–N5: 120.3(6) pm). The bond angles of nitrate ions in **4** and **6** are very close to the ideal value of 120° and are nearly planar, whereas in **5** the O3–N5–O4 angle is 115.3(8)°, caused by the twice coordination to the cation (the environment of the N atom of this NO_3^- ion is also planar).

The distances C5=N2 of 129.2(4) and C14–N6 of 129.6(4) pm for **4**, C5=N2 of 128.9(8) pm for **5** and C5=N2 of 125.6(6) pm for **6** are characteristic for iminic compounds such as acetone thiosemicarbazones (C=N: 126.6(7) pm) and acetone semicarbazone (C=N: 127.8 pm) and are slightly longer than the distance observed in free ligand **2** [26].

4. Conclusion

According to the molecular structure of the synthesized complexes, we have found that in spite of the similarity of the used ligands, they show different coordination numbers in their complexes. In contrast to the parent compound AMTTO, which coordinated bidentately to the silver atom, TAMTTO acts as a monodentate one and coordinates through thione S-atom of its 6-membered ring heterocycle. In addition, there is only a weak intermolecular coordination to one of the thiophene units and the other one is non-coordinated. There is also no thiophene and furan coordination in the triphenylphosphine complexes of TAMTTO and FAMTTO; a possible vacant coordination site on a metal ion will always be occupied by the strong donor triphenylphosphane. These features make the above ligands interesting for further studies, espcecially in the absence of strong donor ligands like phosphanes.

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