

Syntheses, characterization and crystal structures of new mono- and bis-Schiff base compounds derived from 1,2,4-triazine and the silver(I) complexes containing mono-Schiff base ligands

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Abstract Some new Schiff bases, (*Z*)-4-amino-3-((*E*)-(*R*-methoxybenzylidene)hydrazono)-6-methyl-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (*R* = 2 (**L2**), *R* = 3 (**L3**) and *R* = 4 (**L4**)), were synthesized by the condensation reactions of 4-amino-3-hydrazinyl-6-methyl-1,2,4-triazin-5(4*H*)-one (**L1**) and corresponding methoxybenzaldehyde in a molar ratio 1:1.5 in high yields. The reaction of **L2** and **L4** with an excess amount of the corresponding aldehydes gave the unsymmetrical bis-Schiff bases (*E*)-3-((*E*)-(*R*-methoxybenzylidene)hydrazono)-4-((*E*)-*R*-methoxybenzylideneamino)-6-methyl-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (*R* = 2 (**L22**) and *R* = 4 (**L44**)), respectively. Furthermore, the reaction of **L2–L4** with silver(I) nitrate in a molar ratio 2:1 led to the silver(I)-complexes with the general formula $[Ag(Lx)_2]NO_3$ (**Lx** = **L2** (**2**), **L3** (**3**) and **L4** (**4**)). All synthesized Schiff base compounds and complexes were characterized by a combination of IR-, ¹H-NMR spectroscopy, mass spectrometry and elemental analyses. In addition, the structures of **L2**, **L4**·CH₃CN, **L22**·CH₃OH and **L44**·CH₃OH and complexes **2** and **4** were determined by X-ray diffraction studies.

Keywords Mono- and bis-Schiff base compounds · 1,2,4-Triazine · Silver(I) complexes · Crystal structures

Introduction

The synthetic methodologies and reactivity of 1,2,4-triazine and its substituted derivatives have been widely studied and reviewed [1–4]. Compounds containing 1,2,4-triazine moiety are known to be endowed with a wide spectrum of biological activities. In particular, 1,2,4-triazin-5(2*H*)-one derivatives exhibit anticancer [5–8], antimicrobial [9–11], herbicidal [12, 13] and anti-HIV [14] activities. Numerous compounds containing 1,2,4-triazine moieties are well-known in natural materials and show interesting biological and antiviral properties [15, 16]. In addition to the mentioned properties and applications of 1,2,4-triazine and its substituted derivatives, the presence of three nitrogen atoms in the six-membered cycle combined with substituents of various nature allows one to produce metal complexes displaying different coordination modes. On the other hand, a number of Schiff bases have been studied due to their potent biological, physiological and pharmacological activities and they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [17–23]. The Schiff bases containing heterocycles with donor atoms such as nitrogen, oxygen, sulfur, etc., have been playing an important role in the development of coordination chemistry, giving metal complexes which serve as models for biological systems [24–28]. They also exhibit biological activities and have potential applications in many fields of chemistry, such as oxidation catalysis, electrochemistry, etc. [29–38]. It is also known that the existence of metal ions bonded to biologically active compounds may enhance their activities.

We have previously reported that heterocycles such as 1,2,4-triazoles and 1,2,4-triazines can be used as good stabilization agents for late transition metal ions such as copper(I), silver(I), palladium(II) and platinum(II) ion in

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their low oxidation states [39–44]. For instance, we have found that according to the molecular structures of silver(I) complexes containing 4-amino-6-methyl-1,2,4-triazin-3-thion-5-one (AMTTO), the heterocycle AMTTO act as S-monodentate ligand with a weak Ag...N interaction, which leads to 2 + 2 coordination with the silver(I) atom [39]. We have also reported that the sulfur atom of each 4-amino-6-methyl-1,2,4-triazol-3-thione (AMTT) moiety in its silver(I) complex acts simultaneously as S-monodentate one, as well as bridging agent between two metal centers forming the polymeric coordination complex $[\{Ag(AMTT)_2\}NO_3]_n$ [44]. We have also reported the synthesis and characterization of the silver(I) complex $[\{Ag(AETT)NO_3\}_2]_n$ (AETT = 4-amino-5-ethyl-2H-1,2,4-triazol-3(4H)-thione) with new coordination modes between silver(I) ions and the sulfur atoms of the 1,2,4-triazole-3-thione moieties. These coordination modes lead to the formation of a ten-membered Ag–S “mosaic” pattern and cause a two-dimensional endless framework [45]. Furthermore, we have synthesized and characterized several Schiff bases derived from AMTTO and AMTT using different aldehydes and studied their behavior toward late transition metals such as copper(I), silver(I) and palladium(II) ions [46–49].

In our ongoing interest in the study of the behavior of nitrogen-donor ligands toward late transition metals, this work focuses on the synthesis and characterization of new nitrogen-donor Schiff base compounds based on 1,2,4-triazine and their complexation ability toward silver(I) ion.

Experimental section

Chemicals and starting materials

All chemicals were purchased from Merck AG and Fluka and were used without further purification. **L1** was prepared according to the literature procedure [50]. Ethanol was purified and dried by the standard method.

Physical measurements

Infrared (IR) spectra were recorded on a Perkin-Elmer 883 spectrometer (KBr pellets 4,000–400 cm^{-1}). Melting points were recorded on a Büchi B545 melting point apparatus and are uncorrected. 1H NMR spectra were recorded on the Bruker-AQS AVANCE 300 using TMS ($\delta = 0.0$ ppm) as internal standard. Mass spectra were recorded on a Fisons Instruments Trio 1000 spectrometer in positive mode with EI (70 eV). Elemental analyses (C, H, and N) were performed on a Thermo Finnigan Flash EA 1112 series elemental analyzer and Costech ECS 4010 CHNS analyzer.

Synthesis of mono-Schiff bases **L2**, **L3** and **L4**—general procedure

A solution of **L1** (0.31 g, 2 mmol) in ethanol (40 mL) was treated with a solution of the corresponding methoxy-substituted benzaldehyde (0.40 g, 3 mmol) in the same solvent (10 mL) and was refluxed for 8 h. In the case of **L3**, the solution of the corresponding aldehyde was acidified with acetic acid (3 drops). The progress of the reaction was monitored by thin layer chromatography (TLC) using ethyl acetate:petroleum ether (1:2) as eluent. After completion of the reaction, the solvent was evaporated to 20 mL, and the solid crude was filtered and washed with hexane and cold water (2×5 mL). The clear filtrate was kept at 4 °C to give the colorless crystals of the corresponding Schiff bases **L2–L4**.

Selected data for **L2**: Yield: 0.52 g (95%), mp.: 185 °C. Elemental analysis for $C_{12}H_{14}N_6O_2$ (274.12), Calcd.: C, 52.55; H, 5.14; N, 30.64. Found: C, 52.35; H, 5.10; N 30.38; 1H -NMR (DMSO- d_6); δ , 2.08 (s, 3H, CH_3), 3.69 (s, 3H, O- CH_3), 5.36 (s, 2H, NH_2), 6.74–7.20 (d, 4H, Ar), 8.60 (s, 1H, H-imine), 11.03 (s, 1H, NH); IR $\tilde{\nu}$ (KBr disc, cm^{-1}): 3,319 (N–H, triazine), 3,226–3,153 (NH, NH_2), 1,689 (C=O), 1,633 (C=N, imine), 1,562 (C=N, triazine), 1,244, 1,024 (CH_3 –O–Ar); MS (70 eV): m/z : 276 [$M^+ + 2$], 275 [$M^+ + 1$], 274 [M^+], 243, 228, 217, 186, 167, 156, 141, 134, 119, 114, 104, 92, 91, 77, 42, 29.

Selected data for **L3**: Yield: 0.41 g (76%), mp.: 202 °C. Elemental analysis calculated for $C_{12}H_{14}N_6O_2$ (274.12): C, 52.55; H, 5.14; N, 30.64. Found: C, 52.14; H, 5.31; N, 30.12. 1H -NMR (DMSO- d_6); δ , 2.32 (s, 3H, CH_3), 3.91 (s, 3H, O- CH_3), 5.40 (s, 2H, NH_2), 6.99–7.38 (d, 2H, Ar), 8.41(s, 1H, H-imine), 10.03 (s, 1H, NH). IR $\tilde{\nu}$ (KBr disc, cm^{-1}): 3,286 (N–H, triazine), 3,143–3,211 (NH, NH_2), 1,695 (C=O), 1,630 (C=N, imine), 1,570 (C=N, triazine), 1,265, 1,033 (CH_3 –O–Ar). MS (70 eV) m/z : 275 [$M^+ + 1$], 274 [M^+], 168, 141, 134, 119, 114, 91, 77, 43, 32, 27.

Selected data for **L4**: Yield: 0.50 g (90%), mp.: 165 °C. Elemental analysis calculated for $C_{12}H_{14}N_6O_2$ (274.12): C, 52.55; H 5.14; N, 30.64. Found: C, 52.42; H, 5.12; N, 30.58. 1H -NMR (DMSO- d_6); δ , 2.31 (s, 3H, CH_3), 3.90 (s, 3H, O- CH_3), 5.38 (s, 2H, NH_2), 6.97–7.72 (d, 2H, Ar), 8.38 (s, 1H, H-imine), 10.00 (s, 1H, NH). IR $\tilde{\nu}$ (KBr disc, cm^{-1}): 3,286 (N–H, triazine), 3,199–3,213 (NH, NH_2), 1,689 (C=O), 1,635 (C=N, imine), 1,610 (C=N, triazine), 1,251, 1,026 (CH_3 –O–Ar). MS (70 eV); m/z : 276 [$M^+ + 2$], 275 [$M^+ + 1$], 274 [M^+], 259, 167, 156, 141, 134, 120, 91, 77, 43, 31.

Synthesis of bis-Schiff bases **L22** and **L44**: general procedure

A solution of mono-Schiff bases (**L2** or **L4**, 0.55 g, 2 mmol) in hot dry ethanol (25 mL) was treated with a

solution of corresponding aldehyde (0.41 g, 3 mmol) in the same solvent (10 mL). The reaction mixture was acidified with hydrochloric acid (pH 4.5–5) and refluxed for 15 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, and the solid crude was filtered and washed with hexane (2 × 5 mL). The clear filtrate was kept at 4 °C to give the yellowish crystals of the corresponding bis-Schiff base compounds **L22** and **L44**.

Selected data for **L22**: Yield: 0.47 g (60%), mp.: 189 °C. Elemental analysis calculated for C₂₀H₂₀N₆O₃ (392.16): C, 61.21; H, 5.14; N, 21.42. Found: C, 61.11; H, 5.12; N, 21.22. ¹H-NMR (DMSO-d₆): δ, 2.16 (s, 3H, CH₃), 3.80 (s, 3H, O-CH₃), 3.89 (s, 3H, O-CH₃), 6.98–8.35 (8H, Ar), 8.46 (s, 1H, H-imine), 8.88 (s, 1H, H-imine), 12.07 (s, 1H, NH). IR $\tilde{\nu}$ (KBr disc, cm⁻¹): 3,367 (N-H, triazine), 1,689 (C=O), 1,610 (C=N, imine), 1,246, 1,020 (CH₃-O-Ar). MS (70 eV); *m/z*: 392 [M⁺], 359, 259, 258, 229, 228, 215, 187, 133, 119, 104, 103, 92, 91, 85, 78, 27.

Selected data for **L44**: Yield: 0.43 g (55%), mp.: 180 °C. Elemental analysis calculated for C₂₀H₂₀N₆O₃ (392.16): C, 61.21; H, 5.14; N, 21.42. Found: C, 60.98; H, 5.22; N, 21.13. ¹H NMR (DMSO-d₆): δ, 2.16 (s, 3H, CH₃), 3.81 (s, 3H, O-CH₃), 3.87 (s, 3H, O-CH₃), 6.95–7.14 (d, 2H, Ar), 7.86–7.89 (d, 2H, Ar), 8.18 (s, 1H, H-imine), 8.57 (s, 1H, H-imine), 12.04 (s, 1H, NH). IR $\tilde{\nu}$ (KBr disc, cm⁻¹): 3,325 (N-H, triazine), 1,681 (C=O), 1,604 (C=N, imine), 1,577 (C=N, triazine), 1,242, 1,018 (CH₃-O-Ar). MS (70 eV); *m/z*: 394 [M⁺+2], 392 [M⁺], 274, 258, 228, 217, 187, 133, 119, 92, 77, 43, 27.

Synthesis of the complexes **2**, **3** and **4**: general procedure

A solution of mono-Schiff bases (**L2**, **L3** or **L4**, 0.27 g, 1 mmol) in methanol/acetonitrile (40 mL, 1/1) was treated with silver(I) nitrate (0.08 g, 0.5 mmol). The reaction mixture was stirred for 5 h at room temperature and was refluxed for a further 1 h. After completion of the reaction, which was monitored by TLC using ethyl acetate:petroleum ether (1:2) as eluent, the solid crude was filtered and washed with cold ethanol (2 × 5 mL). The clear filtrate was kept at 4 °C to give the colorless crystals of **2** and **4**.

Selected data for **2**: Yield: 0.22 g (62%), mp.: >290 °C (dec.). Elemental analysis calculated for C₂₄H₂₈AgN₁₃O₇ (718.43): C, 40.12; H, 3.93; N, 25.35. Found: C, 40.03; H, 3.88; N, 25.29. IR $\tilde{\nu}$ (KBr disc, cm⁻¹): 3,481 (N-H, triazine), 3,323, 3,238, 1,627 (C=O), 1,604 (C=N, imine), 1,589, 1,489 (C=N, triazine), 1,429, 1,409, 1,385, 1,301, 1,267, 1,186, 1,035 (CH₃-O-Ar), 974, 920, 830, 771, 692,

501. MS (70 eV); *m/z*: 276 [M⁺+2], 275 [M⁺], 274, 259, 244, 243, 228, 167, 133, 119, 91, 77, 42, 28.

Selected data for **3**: Yield: 0.21 g (60%), mp.: >290 °C (dec.). Elemental analysis calculated for C₂₄H₂₈AgN₁₃O₇ (718.43): C, 40.12; H, 3.93; N, 25.35. Found: C, 39.98; H, 3.95; N, 25.40. IR $\tilde{\nu}$ (KBr disc, cm⁻¹): 3,454 (N-H, triazine), 3,284, 1,695 (C=O), 1,629 (C=N, imine), 1,577 (C=N, triazine), 1,469, 1,386, 1,323, 1,265, 1,195, 1,033 (CH₃-O-Ar), 983, 941, 877, 837, 786, 732, 684, 567, 536, 503, 460, 412. MS (70 eV); *m/z*: 275 [M⁺], 274, 245, 244, 243, 215, 167, 141, 134, 119, 91, 77, 42, 28.

Selected data for **4**: Yield: 0.23 g (65%), mp.: >290 °C (dec.). Elemental analysis calculated for C₂₄H₂₈AgN₁₃O₇ (718.43): C, 40.12; H, 3.93; N, 25.35. Found: C, 40.03; H, 3.88; N, 25.29. IR $\tilde{\nu}$ (KBr disc, cm⁻¹): 3,491 (N-H, triazine), 3,286, 1,689 (C=O), 1,635, 1,608 (C=N, imine), 1,577 (C=N, triazine), 1,508, 1,463, 1,367, 1,317, 1,249, 1,168, 1,026, 975, 937, 898, 829, 773, 732, 665, 638, 592, 534, 503, 459, 414. MS (70 eV); *m/z*: 274, 264, 173, 167, 147, 133, 119, 103, 90, 77, 76, 64, 63, 38, 36.

Crystal structure analysis of **L2**, **L4**·CH₃CN, **L22**·CH₃OH, **L44**·CH₃OH and complexes **2** and **4**

Table 1 shows the crystallographic data of **L2**, **L4**·CH₃CN, **L22**·CH₃OH, **L44**·CH₃OH, **2** and **4**. The crystals of all compounds were covered with perfluorinated oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and unit cell dimensions were determined from ca. 6,000 (**L2**; Stoe IPDS I), 7,500 (**L4**·CH₃CN, Stoe IPDS I), 12,000 (**L22**·CH₃OH, Stoe, IPDS II), 5,500 (**L44**·CH₃OH, Stoe, IPDS I), 5,700 (**2**, Stoe, IPDS I) and from ca. 7,400 (**4**; Stoe IPDS I) reflections (graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) for all compounds. The intensities were corrected for Lorentz and polarization effects. In addition, absorption corrections were applied for **L4**·CH₃CN, **L22**·CH₃OH, **L44**·CH₃OH, **2** and **4** (numerical). The structures were solved by the direct methods for **L4**·CH₃CN and **L44**·CH₃OH (SHELXS-97), for **L2**, **L22**·CH₃OH and **2** (SIR-92) and by the Patterson method for **4** (SHELXTL-Plus). No absorption correction was used for **L2** and all data were refined against *F*² by full-matrix least-squares using the program SHELXL-97. The position of carbon bonded hydrogen atoms in all compounds except those in **L4**·CH₃CN, and those mentioned below were calculated for ideal positions and refined with a common displacement parameter. H1–H3 atoms for **L2**, **2** and **4** and H1 and H2 atoms for **L22**·CH₃OH and **L44**·CH₃OH were included with a free refinement, respectively. Programs used were SHELXS-97 [51], SIR-92 [52], SHELXL-97 [53], SHELXTL-Plus [54], ORTEP [55] and PLATON-98 [56].

Table 1 Crystallographic data of compounds and complexes

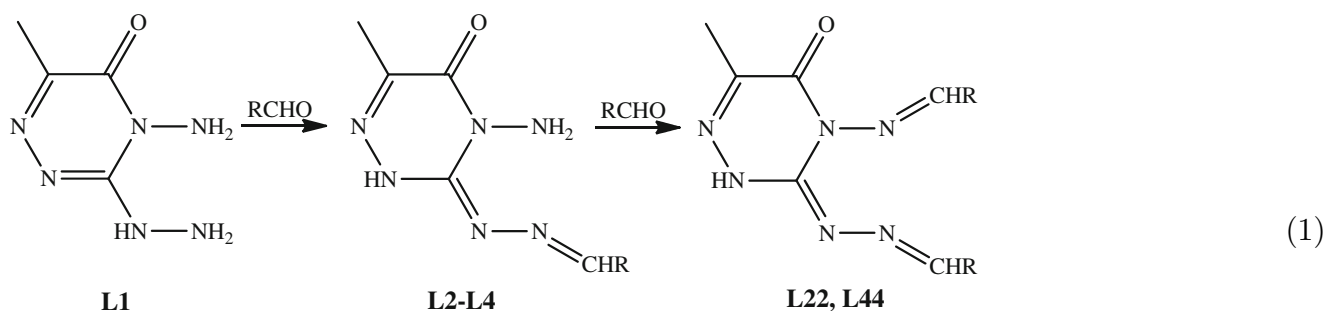
	L2	L4-CH₃CN	L22-CH₃OH	L44-CH₃OH	2	4
Instrument	IPDS I (Stoe)	IPDS I (Stoe)	IPDS II (Stoe)	IPDS I (Stoe)	IPDS I (Stoe)	IPDS I (Stoe)
Radiation	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α
Formula	C ₁₂ H ₁₄ N ₆ O ₂	C ₁₄ H ₁₇ N ₇ O ₂	C ₂₁ H ₂₄ N ₆ O ₄	C ₂₁ H ₂₄ N ₆ O ₄	C ₂₄ H ₂₈ AgN ₁₃ O ₇	C ₂₄ H ₂₈ AgN ₁₃ O ₇
Formula weight/g mol ⁻¹	274.31	315.39	424.46	424.46	718.48	718.50
Crystal size/mm	0.49 × 0.06 × 0.05	0.51 × 0.27 × 0.26	0.19 × 0.14 × 0.09	0.28 × 0.28 × 0.09	0.38 × 0.28 × 0.07	0.51 × 0.08 × 0.05
a/pm	1,789.5(1)	726.7(1)	1,170.7(1)	912.5(1)	756.3(1)	2,883.8(3)
b/pm	1,789.5(1)	1,352.1(1)	1,337.7(1)	1,013.6(1)	765.6(1)	732.2(1)
c/pm	1,599.7(1)	1,545.9(2)	1,326.6(1)	1,250.2(2)	1,271.7(2)	1,341.9(1)
α /°	90	90	90	91.91(2)	86.07(2)	90
β /°	90	90.54(2)	104.97(1)	99.85(2)	84.42(2)	94.94(1)
γ /°	90	90	90	111.12(2)	69.63(2)	90
Unit cell volume/pm ³	5,122.7(5) × 10 ⁶	1,518.9(3) × 10 ⁶	2,007.0(3) × 10 ⁶	1,057.1(2) × 10 ⁶	686.6(2) × 10 ⁶	2,822.9(5) × 10 ⁶
Z	16	4	4	2	1	4
dcalc/g cm ⁻³	1.423	1.379	1.405	1.334	1.738	1.691
Crystal system	tetragonal	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group (No.)	I4 ₁ /a	P2 ₁ /c	P2 ₁ /c	P-1	P-1	C2/c
Absorption correction	none	numerical	numerical	numerical	numerical	numerical
μ /cm ⁻¹	1.03	0.98	1.00	0.95	8.06	7.84
Temperature/K	193	193	100	193	193	193
2 θ /max/°	52.46	52.46	51.86	52.00	52.30	51.92
Index range						
<i>h</i>	-21 → 22	-8 → 8	-14 → 14	-11 → 11	-9 → 8	-35 → 34
<i>k</i>	-22 → 22	-16 → 16	-16 → 16	-12 → 12	-9 → 9	-8 → 8
<i>l</i>	-19 → 18	-18 → 19	-16 → 16	-15 → 15	-15 → 15	-16 → 16
Measured reflection	13,524	14,715	27,880	10,490	6,475	10,486
Unique reflections	2,535	2,988	3,897	3,851	2,516	2,748
<i>R</i> _{int}	0.0632	0.0504	0.1107	0.0338	0.071	0.0506
Reflections with <i>F</i> _o > 4 σ (<i>F</i> _o)	1,465	1,803	1,813	2,180	2,116	2,124
Parameter	196	276	292	295	234	261
<i>R</i> ₁	0.0343	0.0364	0.0323	0.0493	0.0484	0.0299
<i>wR</i> ₂ (all data)	0.0975 ^a	0.0907 ^b	0.0381 ^c	0.1327 ^d	0.1188 ^e	0.0683 ^f
Max. residual electron density/10 ⁻⁶ e pm ⁻³	0.23	0.186	0.152	0.69	1.048	0.786

^a $w = 1/[\sigma^2(F_o^2) + (0.0507 \cdot P)^2]$; $P = [\max(F_o^2, 0) + 2F_o^2]/3$ ^b $w = 1/[\sigma^2(F_o^2) + (0.0564 \cdot P)^2]$ ^c $w = 1/[\sigma^2(F_o^2)]$ ^d $w = 1/[\sigma^2(F_o^2) + (0.0822 \cdot P)^2]$ ^e $w = 1/[\sigma^2(F_o^2) + (0.009 \cdot P)^2]$ ^f $w = 1/[\sigma^2(F_o^2) + (0.0423 \cdot P)^2]$

Results and discussion

Syntheses and characterization

Mono-Schiff base compounds **L2**, **L3** and **L4** can be obtained as colorless solid materials by the treatment of **L1** with the corresponding *o*-, *m*- or *p*-methoxybenzaldehyde in molar ratio 1:1.5 in ethanol under reflux conditions in high yields. The reaction of **L2** and **L4** with an excess amount of the same methoxybenzaldehyde in dry methanol gave the bis-Schiff bases as yellowish crystalline solids in good yields according to Eq. (1).



R = *o*-MeO-Ph (**L2**), *m*-MeO-Ph (**L3**), *p*-MeO-Ph (**L4**)

R = *o*-MeO-Ph (**L22**), *p*-MeO-Ph (**L44**)

The complexes **2**, **3** and **4** can be prepared by the reaction of **L2**, **L3** and **L4** with silver(I) nitrate in a molar ratio 1:2 in methanol under reflux conditions in good yields according to Eq. (2).



All synthesized compounds are air stable. In IR spectra of the compounds **L2–L4**, **L22** and **L44**, the absorptions $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ of the triazine heterocycles were obtained at 1,689 and 1,562 cm^{-1} (**L2**), 1,695 and 1,570 cm^{-1} (**L3**), 1,689 and 1,610 cm^{-1} (**L4**), 1,689 and 1,610 cm^{-1} (**L22**) and 1,681 and 1,604 cm^{-1} (**L44**), and new absorption bands at 1,633 cm^{-1} (**L2**), 1,630 cm^{-1} (**L3**), 1,635 cm^{-1} (**L4**), 1,633 cm^{-1} (**L22**), 1,630 cm^{-1} (**L44**) could be assigned to $\nu(\text{C}=\text{N}, \text{iminic})$. The $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{N}$ (iminic) function cause vibrations at 1,627 and 1,604 cm^{-1} for **2**, at 1,695 and 1,629 cm^{-1} for **3**, and at 1,689 and 1,608 cm^{-1} for **4**. The NO_3^- anion in **2–4** presents its N–O asymmetric stretching mode (E') at

1,385 cm^{-1} (**2**), 1,386 cm^{-1} (**3**) and 1,367 cm^{-1} (**4**), and its out-of-plane absorptions (A_2'') at 830, 837 and 829 cm^{-1} , respectively. In $^1\text{H-NMR}$ of the ligands, the signals at 8.60 ppm (**L2**), 8.41 ppm (**L3**) and 8.38 ppm (**L4**) can be assigned to $\text{N}=\text{CH}$, and no signal at 4.36 ppm corresponding to NH_2 group of **L1** was observed. In $^1\text{H-NMR}$ spectra of diiminic compounds, the disappearance of the signals at 4.36 and 5.51 ppm corresponding to NH_2 groups of the **L1** and the presence of new signals at 8.46 and 8.88 ppm (**L22**) and 8.18 and 8.57 ppm (**L44**) confirm the formation of diiminic compounds. The highest fragment in the mass spectra of the ligands was observed at $m/z = 274$ for **L2–L4**

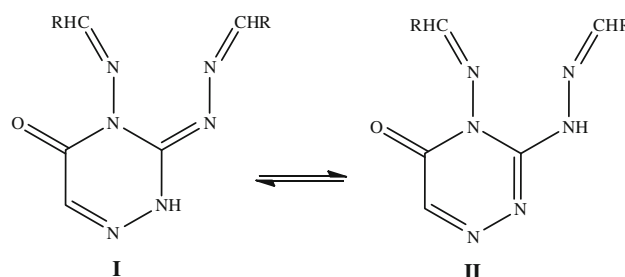
and at $m/z = 392$ for **L22** and **L44** and can be assigned to corresponding M^+ . The mass spectra of **2**, **3** and **4** show only the main peak of their corresponding ligands.

Table 1 shows the crystallographic data of all Schiff base compounds and the synthesized silver(I)-complexes.

Crystal structures of compounds and complexes

Crystal structures of compounds **L2**, **L4**· CH_3CN , **L22**· CH_3OH and **L44**· CH_3OH

The Schiff bases derived from **L1** can exist in two tautomeric forms I and II as shown in Scheme 1.



Scheme 1 Tautomeric forms in bis-Schiff base compounds

Due to the determined molecular structures of all synthesized mono- and bis-iminic compounds, the Schiff bases exist in the form I containing one endocyclic NH group and one exocyclic C=N moiety in the solid state. They exhibit no significant differences in their endocyclic-, exocyclic- and azomethine C=N bond distances (129.1(3), 130.4(2) and 128.7(2) pm in **L2** (Fig. 1), 128.8(2), 129.1(2) and 127.3(2) pm in **L4**·CH₃CN (Fig. 2), 128.5(2), 130.2(2), 128.0(2) and 127.7(2) pm in **L22**·CH₃OH (Fig. 3) and 129.2(3), 130.4(3), 128.5(3) and 123.5(3) pm in **L44**·CH₃OH (Fig. 4), respectively). The C=N bond lengths and the bond distances in the six-membered heterocycles compare well with those observed in previously reported 4-amino-6-methyl-3-thio-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (AMTTO) and its Schiff base derivatives [47, 48, 57].

L4·CH₃CN molecules are strictly planar, while the dihedral angle between the “best” planes through basic six-membered ring of 1,2,4-triazine moiety and the aldehyde rest in **L2** is 16°.

The dihedral angles between the “best” planes in the molecules of **L22**·CH₃OH (A: N1 N3 N4 C1 C2 C3, B: C6 C7 C8 C9 C10 C11 and C: C14 C15 C16 C17 C18 C19) are 6° (A, B) and 84° (A, C), and those observed in **L44**·CH₃OH (A: N1 C1 C2 N3 N4 C3, B: C6 C7 C8 C9 C10 C11 and C: C16 C17 C18 C19 C20 C21) are 101° (A, B) and 20° (A, C).

In **L2**, the molecules are arranged along the 4₁-axis and are associated via H bonds (Figs. 1, 5). The NH₂ group of each molecule acts as bridging agent between two adjacent molecules. It links the imine nitrogen atom of one ligand to the oxygen atom of the carbonyl group of the adjacent one via hydrogen bondings (N2–H1...N6a: 359.9(2) pm and

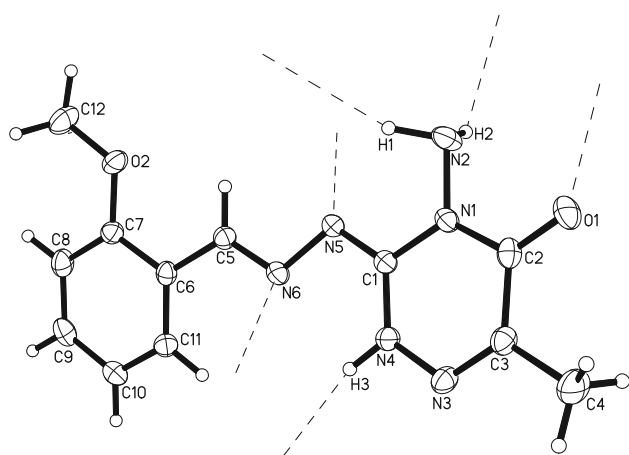


Fig. 1 Molecular structure and numbering scheme of **L2** (ORTEP plot at 40% probability level). Selected bond lengths [pm] and angles [°]: N1–C2 137.9(2), N1–C1 138.1(2), N1–N2 142.1(2), N3–C3 129.1(3), N3–N4 136.2(2), N4–C1 135.3(2), N5–C1 130.4(2), N5–N6 140.4(2), N6–C5 128.7(2), C2–C3 147.03, C3–C4 148.2(3), N5–C1–N4 125.9(2), N5–C1–N1 118.1(2), C5–N6–N5 111.8(2), C1–N5–N6 111.7(2)

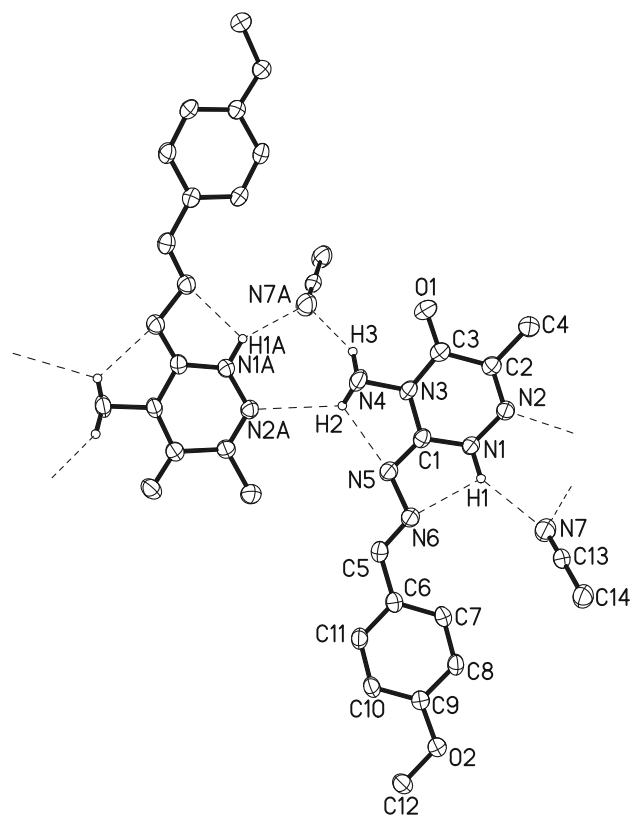


Fig. 2 Molecular structure and numbering scheme of **L4**·CH₃CN; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: N1–C1 136.4(2), N2–C2 128.8(2), N3–C1 137.6(2), N1–N2 135.7(2), N3–N4 141.9(2), N5–C1 129.1(2), N5–N6 140.6(2), N6–C5 127.3(2), C1–N5–N6 109.8(1), C5–N6–N5 113.3(1), N6–C5–C6 122.1(2)

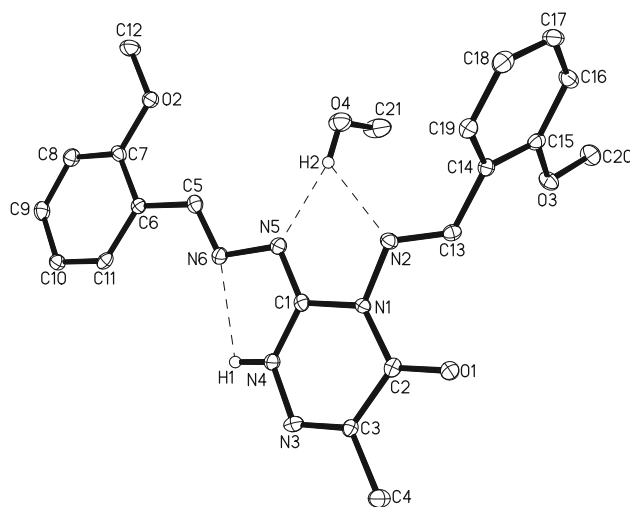


Fig. 3 Molecular structure and numbering scheme of **L22**·CH₃OH; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: N1–C1 138.0(2), N5–C1 130.2(2), C3–N3 128.5(3), N5–N6 141.1(2), N6–C5 128.0(2), N1–N2 142.1(2), N2–C13 127.7(2), C13–C14 1.471(2), N6–C5–C6 121.0(2), C5–N6–N5 113.3(1), C1–N5–N6 110.0(1), C13–N2–N1 114.2(2), N2–C13–C14 117.9(2)

$N2-H2\cdots O1a$: 318.9(2) pm). Another H bonding is formed between the endocyclic NH group of one ligand and the exocyclic imine nitrogen atom ($N4-H3\cdots N5a$: 289.2(2) pm).

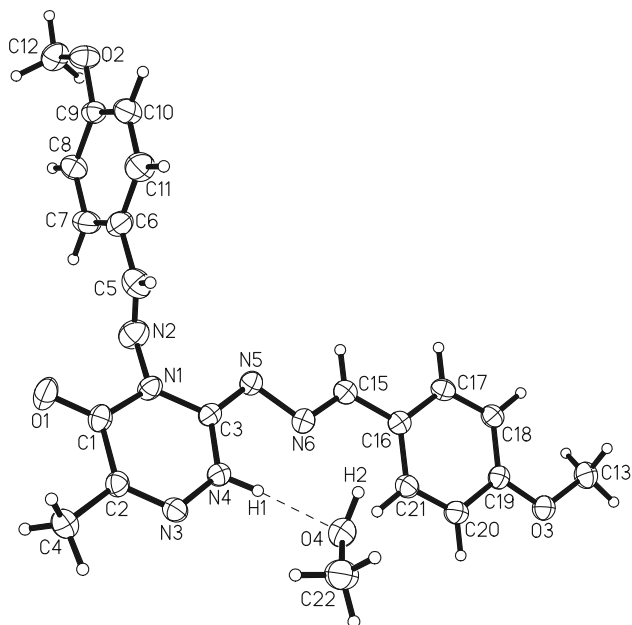


Fig. 4 Molecular structure and numbering scheme of **L44-CH₃OH**; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: N1–C3 138.9(3), N1–N2 142.7(3), N2–C5 123.5(3), N3–C2 129.2(3), C5–C6 1.476(4), N5–C3 130.4(3), N5–N6 141.1(2), N6–C15 128.5(3), C15–C16 1.462(3), N2–C5–C6 121.7(3), C5–N2–N1 112.4(2), N6–C15–C16 122.1(2), C15–N6–N5 113.2(2), C(3)–N(5)–N(6) 109.7(2)

Fig. 5 The packing of **L2** in the unit cell showing hydrogen bonding association as broken lines

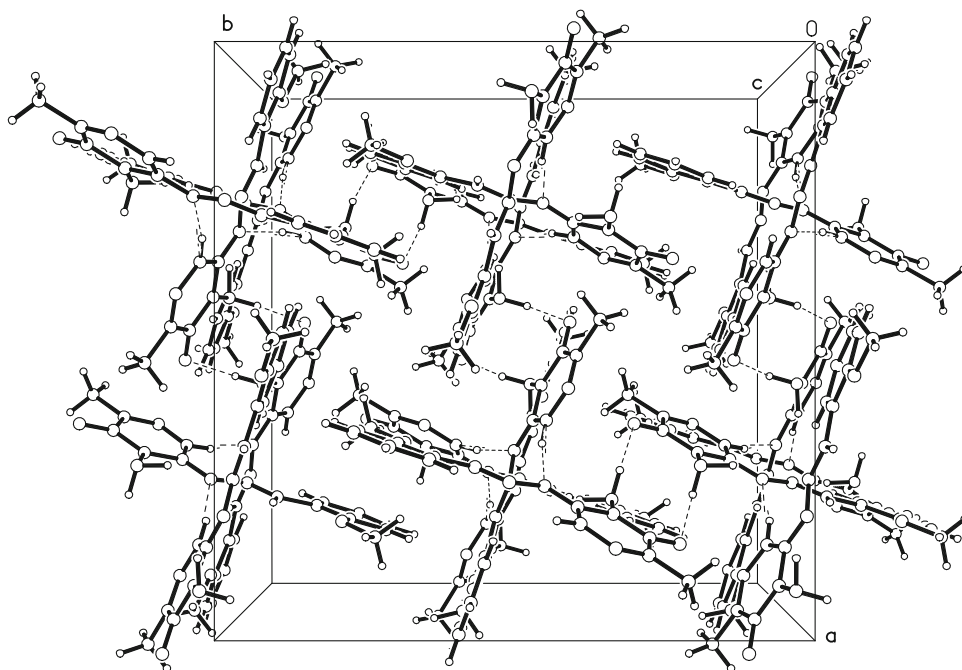


Fig. 6 View of the packing in the unit cell of **L4-CH₃CN** showing H bonds as dashed lines

In $\mathbf{L4}\cdot\text{CH}_3\text{CN}$, the nitrogen atom of solvate molecule acts as bridging agent and links the NH_2 group of each ligand to the endocyclic NH group of the adjacent one via hydrogen bondings ($\text{N1-H1}\cdots\text{N7}$: 308.0(2) pm and $\text{N4-H3}\cdots\text{N7a}$: 325.9(2) pm). The latter coordinates additionally to the iminic N6 atom via intramolecular H bonding ($\text{N1-H1}\cdots\text{N6}$: 259.0(2) pm). The H2 atom of the NH_2 moiety of each ligand coordinates simultaneously with its own exocyclic iminic nitrogen atom as well as with the endocyclic nitrogen atom of the adjacent molecule ($\text{N4-H2}\cdots\text{N5}$:

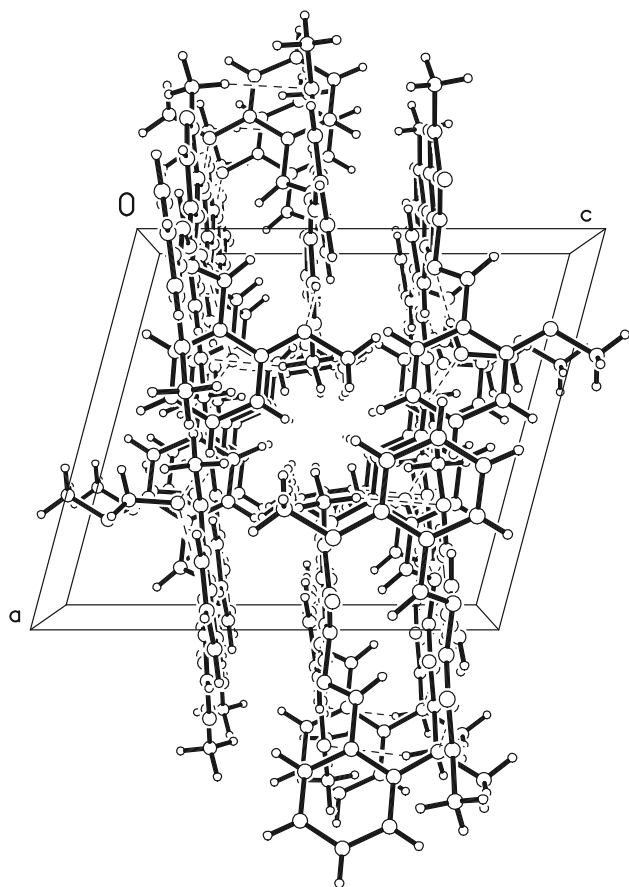
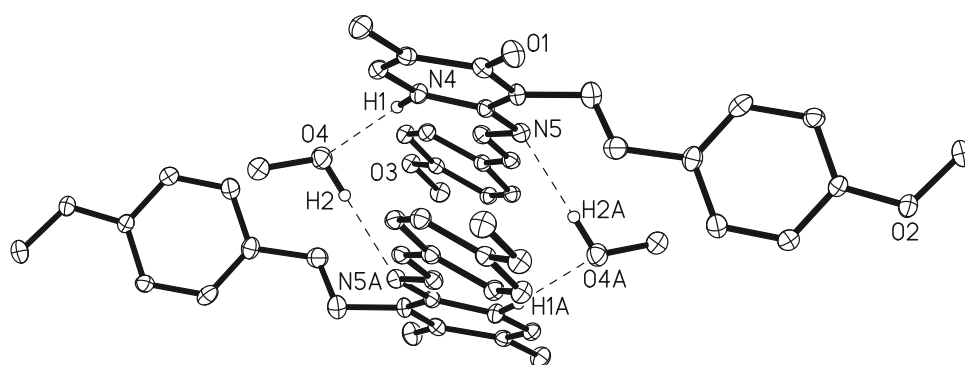


Fig. 7 View of the packing in the unit cell of $\mathbf{L22}\cdot\text{CH}_3\text{OH}$

Fig. 8 ORTEP representation of dimers of $\mathbf{L44}\cdot\text{CH}_3\text{OH}$. The H atoms of the phenyl rings are omitted for clarity



265.8(2) pm and $\text{N4-H2}\cdots\text{N2a}$: 333.8(2) pm). These coordination modes are responsible for the formation of layers parallel to (10-1), which are also networked among each other (Fig. 6).

The endocyclic NH group in $\mathbf{L22}\cdot\text{CH}_3\text{OH}$ acts as bridging agent between two adjacent diimine compounds and links the hydrazine nitrogen group of the own molecule to the oxygen atom of the methoxy moiety of the adjacent one via hydrogen bondings ($\text{N4-H1}\cdots\text{N6}$: 257.0(2) pm and $\text{N4-H1}\cdots\text{O3a}$: 304.8(2) pm). This coordination mode is responsible for the formation of chains of $\mathbf{L22}\cdot\text{CH}_3\text{OH}$ along [010]. In addition, the solvate molecule links the nitrogen atoms of the exocyclic imine group to nitrogen atom of the side chain imine group via hydrogen bondings ($\text{O4-H2}\cdots\text{N2}$: 320.0(2) pm and $\text{O4-H2}\cdots\text{N5}$: 287.7(2) pm) (Fig. 7).

The OH group of the methanol molecule in $\mathbf{L44}\cdot\text{CH}_3\text{OH}$ acts as bridging agent between two unsymmetrically bis-imine compounds and links the endocyclic NH group of one compound to the nitrogen atom of one of the exocyclic C=N group of the adjacent one via hydrogen bonding ($\text{N4-H1}\cdots\text{O4}$: 289.8(3) pm and $\text{O4-H2}\cdots\text{N5a}$: 292.7(3) pm, Fig. 8). The latter is responsible for the formation of centro-symmetric dimers of $\mathbf{L44}\cdot\text{CH}_3\text{OH}$ as depicted in Fig. 9.

Crystal structures of complexes 2 and 4

Complexes **2** and **4** are ionic compounds and consist of $[\text{Ag}(\text{Lx})_2]^+$ -cations ($\text{Lx} = \mathbf{L2}$ or $\mathbf{L4}$) and nitrate anions. In these complexes, the metal atom sits on an inversion center and each ligand acts as a monodentate one and coordinates with the metal center through its on ring bonded exocyclic imine nitrogen atom (Ag-N : 227.3(3) pm for **2** (Fig. 10) and 226.1(2) pm for **4** (Fig. 11)). These Ag-N bond lengths are relatively long compared with those found in complexes containing two coordinated silver ions [58–60], but they are shorter than the average values of 231–244 pm found for four-coordinated silver complexes [61–64]. The Ag-NH₂ distances of 265.5(2) pm for **2** and the Ag-O bond lengths of 270.0(2) pm for **4** are longer than the maximum atom distance generally accepted for Ag(I)-N bonds of

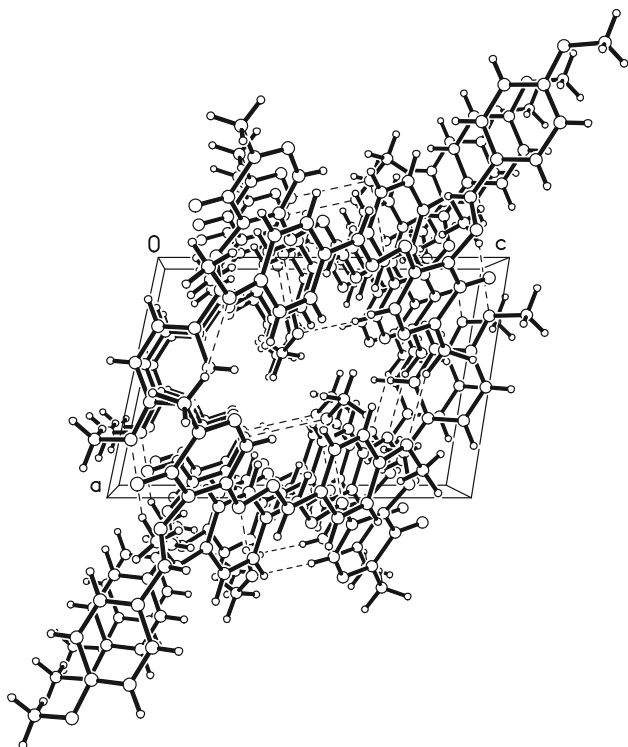


Fig. 9 View of the packing in the unit cell of **L44-CH₃OH**

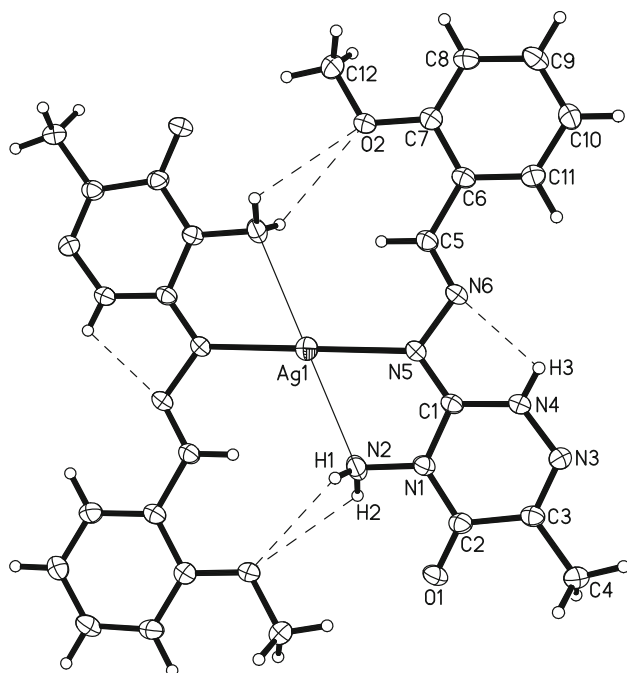


Fig. 10 Molecular structure and numbering scheme of complex **2**; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: Ag1–N5 227.3(3), Ag1–N2 265.5(2), N1–N2 140.8(4), N1–C1 138.3(5), N5–C1 129.7(5), N5–N6 141.5(4), N6–C5 125.8(5), C5–C6 1.476(5), N7–O5#2 1.04(1), N7–O5 1.04(1), N7–O3#2 1.24(1), N7–O3 1.24(1), N7–O4#2 1.414(9), N7–O4 1.414(9), N5–Ag1–N5#1 180.0, N6–N5–Ag1 124.5(2), N6–C5–C6 120.6(3), O5–N7–O3 137(2), O5#2–N7–O4#2 119(2), O5#2–O3–O4#2 112(2)

234 pm and Ag(I)–O bonds of 232 pm [65], but they are clearly shorter than the sum of the van der Waals radii of silver, nitrogen and oxygen atoms (Ag: 170 pm, N: 155 pm and O: 150 pm [66]). The steric hindrance induced by the position of the methoxy substituents in each ligand is responsible for the direct coordination of nitrate anion to the metal center, which was only observed in complex **4**. In spite of observed Ag–NH₂ contacts of 265.5(2) pm in **2**, no distortion in the linear geometry of the metal center is measured (N–Ag–N-axis: 180°). The N–Ag–N bond angle of 169.5(1)° in **4** is characteristic for a distorted linear coordination sphere caused by two additional two Ag–O contacts of 270.0(2) pm in **4**. Therefore, the coordination sphere for the metal centers in all complexes can be described as 2 + 2.

In **2**, the nitrate anions are disordered around an inversion center and their positions could not be fixed exactly (Fig. 12). In this complex, the molecules are stacked along the crystallographic axis [100] and are linked through nitrate anions via hydrogen bondings (N2–H1…O2a: 312.2(4) pm, N2–H2…O2a: 312.2(4) pm, N4–H3…N6: 254.9(4) pm, N2–H1…O3b: 313.5(1) pm, N2–H1…O4b: 316.2(1) pm, N2–H1…O5c: 279.3(1) pm, N4–H3…O3d: 279.6(1) pm, N4–H3…O4e: 287.7(1) pm).

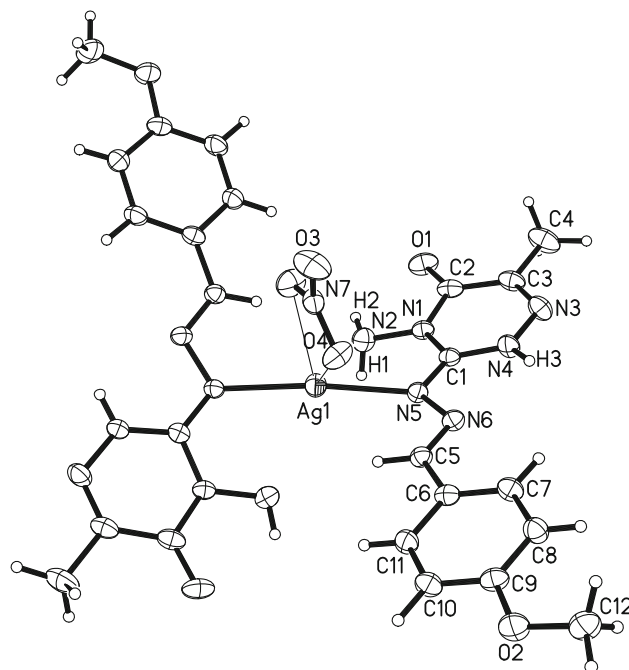


Fig. 11 Molecular structure and numbering scheme of complex **4**; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [pm] and angles [°]: Ag(1)–N(5) 2.261(2), Ag(1)–N(5)#1 2.261(2), Ag(1)–O(4) 2.700(2), Ag(1)–O(4)#1 2.700(2), N(1)–C(1) 1.373(3), N(5)–C(1) 1.306(3), N(5)–N(6) 1.401(3), N(6)–C(5) 1.277(3), N(7)–O(4) 1.233(3), N(7)–O(4)#1 1.233(3), N(7)–O(3) 1.246(4), N(5)–Ag(1)–N(5)#1 169.5(1), N(6)–N(5)–Ag(1) 120.7(1), C(5)–N(6)–N(5) 112.1(2), N(6)–C(5)–C(6) 124.0(2), O(4)–N(7)–O(4)#1 120.7(4), O(4)–N(7)–O(3) 120(2), O(4)#1–N(7)–O(3) 120(2)

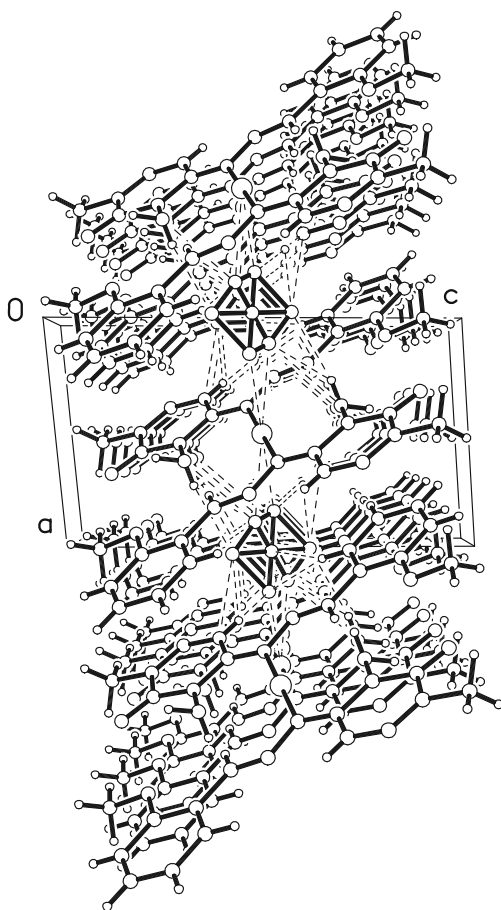
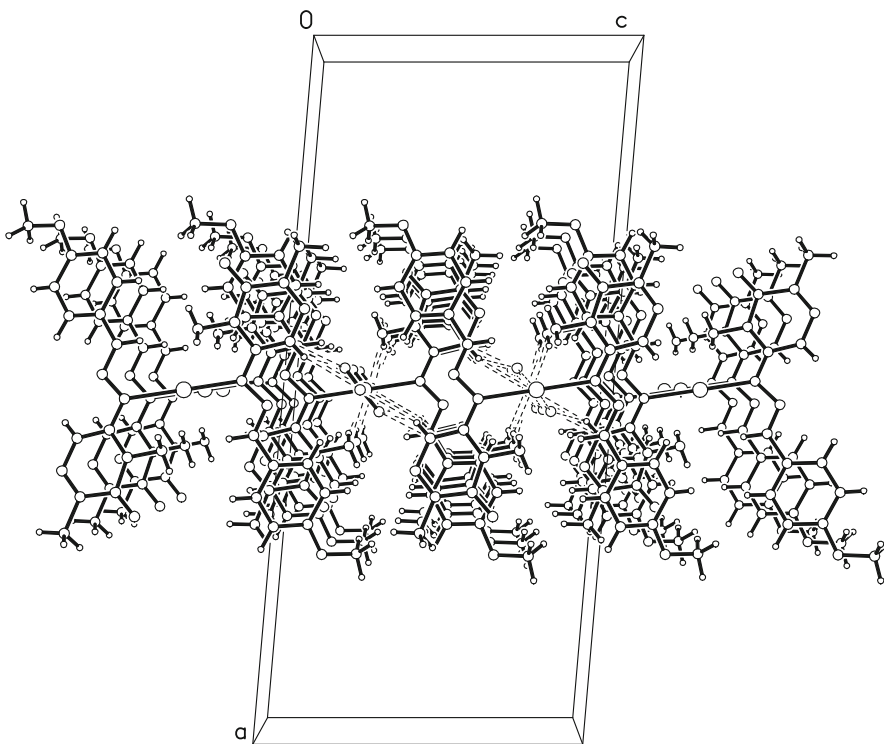


Fig. 12 View of the packing in the unit cell of complex **2**

Fig. 13 View of the packing in the unit cell of complex **4**



In **4**, the molecules are stacked along [010] and they are linked along (010) via H bonds (N2–H1...O3a: 294.5(3) pm, N2–H2...O1: 266.0(3) pm, N4–H3...O4a: 290.6(3) pm, Fig. 13).

The dihedral angle between the “best” planes in **2** (A: N1 N3 N4 N5 C1 C2 C3 and B: N6 C5 C6 C7 C8 C9 C10 C11) is 4°, while **4** is practically planar.

Conclusion

In conclusion, we have synthesized and characterized some mono- and bis-Schiff base compounds based on 1,2,4-triazine by the condensation reaction of 4-amino-3-hydrazinyl-6-methyl-1,2,4-triazin-5(4*H*)-one with *o*-, *m*- and *p*-methoxybenzaldehyde in good to high yields. According to the determined molecular structure, we have found that all synthesized mono- and bis-Schiff bases exist in the tautomeric form I (Scheme 1) in their solid states. We have also studied the behavior of the synthesized Schiff bases toward silver(I) ion and found that the mono-Schiff bases was allowed to react in a 2:1 molar ratio with silver(I) ion giving complexes with the general formula [Ag(Lx)₂]NO₃ (**2**, **3**, **4**). We have also found that under the same conditions, the bis-Schiff bases (**L22** and **L44**) undergo solvolysis reactions to form the corresponding mono-Schiff bases **L2** and **L4**, before the complexation reactions take place. According to the molecular structures of the complexes **2** and **4**, the corresponding ligands coordinate with the metal

ion as unidentate ones via their on the ring bonded exocyclic nitrogen atoms. This linear geometry around the metal center is distorted by the η^2 -coordination of oxygen atoms of nitrate anion to the metal center in **4**. Therefore, the coordination sphere for the metal centers in all complexes can be described as 2 + 2.

Supplementary data

CCDC 800143, 800144, 800145, 800146, 800147 and 800149 contain the supplementary crystallographic data for compounds **L2**, **L4**·CH₃CN, **L22**·CH₃OH and **L44**·CH₃OH and complexes **2** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax.: 44 (0)1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk.

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