# Syntheses and crystal structures of Cu$^{II}$ and Ag$^{I}$ coordination complexes based on the hydrolysis of N-salicylidene-2-aminopyridine

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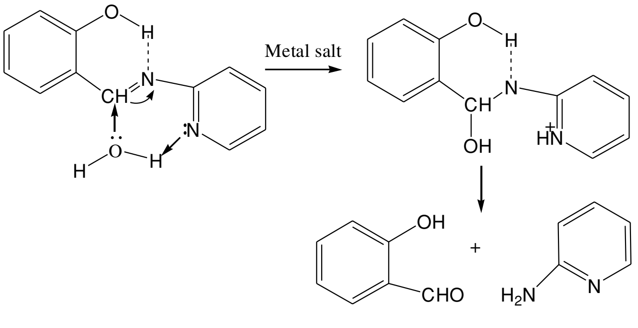
A mononuclear salicylaldehydato copper(II) complex and an infinite 2-aminopyridyl silver(I) coordination polymer have been synthesised by the self-assembly reaction based on the metal-induced hydrolysis of N-salicylidene-2-aminopyridine. The latter chain-like polymer is novel and unavailable under usual reaction conditions. Additionally, an interesting 2D polymeric network is formed from the weak intermolecular interactions.

**Keyword:** Schiff base, hydrolysis, coordination complex, crystal structure, hydrogen bonds

In recent years, a great effort has been devoted to the self-assembly of organic and inorganic molecules, as it provides more opportunities of designing new supramolecular materials with desirable physical and chemical properties.[1] Among the various types of interactions used for self-assembly, coordination and hydrogen bonds are the most widely used tools to construct organic-inorganic supramolecular arrays.[2] In some cases, hydrogen bonding is a key intermolecular force resulting in the great structural diversity of supramolecular systems, and the versatile hydrogen bonding interactions (such as O–H···O, N–H···O, C–H···O, and metal–hydride bonds) incorporated in organometallic chemistry have been widely illustrated.[3,4]

N-Salicylidene-2-aminopyridine, a potential multidentate Schiff base ligand, has been studied earlier with regard to the photochromophore process[5] and hydrolysis kinetics and mechanism.[6] Although metal complexes of Schiff bases are usually resistant towards hydrolytic cleavage even in water media,[7] N-salicylidene-2-aminopyridine tends to readily hydrolyse in the presence of metal ions.[6] This is probably due to both the pyridyl nitrogen and phenolic group being involved in the intramolecular catalysis mechanism on the neutral hydrolysis of the imine (see Scheme 1). Therefore, only a few dialkylgallium (dialkylindium) complexes of this ligand have been reported to date.[8]

As part of our current research on dealing with transition metal Schiff base complexes,[9] we are continuing the study of the reaction of two transition metal ions ($Cu^{2+}$ and $Ag^{+}$) with N-salicylidene-2-aminopyridine ligand in organic solvents. Accordingly, the metal-induced hydrolytic cleavage of the imine occurs during slow crystal growth, with the crystal formation of two unexpected metal complexes. We now report the syntheses and crystal structures of a mononuclear bis(salicylaldehydato)-Cu$^{II}$ complex (**1**), and a chain-like coordination polymer, 2-aminopyridyl-Ag$^{I}$ (**2**).



**Scheme 1** The proposed hydrolysis mechanism of N-salicylidene-2-aminopyridine induced by metal salts.

Interestingly, two reactions of N-salicylidene-2-aminopyridine with Cu$^{II}$ or Ag$^{I}$ salts in $CH_2Cl_2$–MeOH resulted in the hydrolysis of the imine of the ligand, and then complexation with metal ions. While in the case of $Cu(OAc)_2{\cdot}H_2O$, the

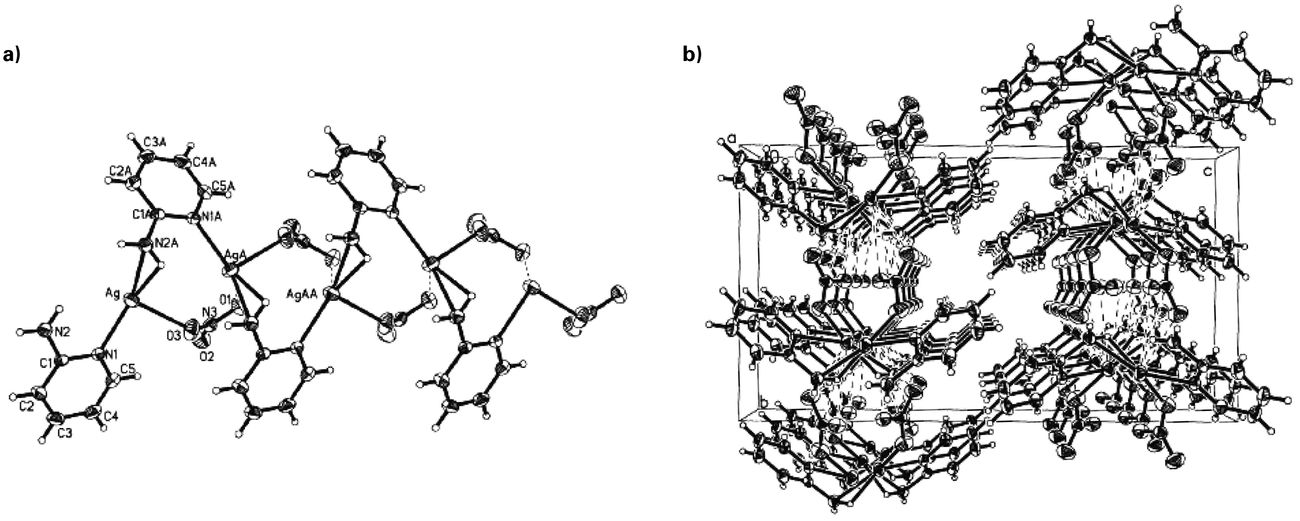


**Fig. 1** (a) The ORTEP structure of partial polymeric chain in complex 2 (30% thermal ellipsoid probability). (b) The crystal packing along crystallographic *a* axis showing the 2D network structure in **2** by interchain N–H···O hydrogen bonds and weak Ag···O bonds. Selected bond lengths and angles: Ag–N(1) 2.238(2); Ag–N(2) 2.318(2); Ag–O(3) 2.538(3); O(1)–N(3) 1.242(3); O(2)–N(3) 1.232(3); O(3)–N(3) 1.239(4); N(1)–C(1) 1.336(4); N(1)–C(5) 1.339(4); N(2)–C(1) 1.399(4); N(1)–Ag–N(2) 152.25(9); N(1)–Ag–O(3) 89.81(9); N(2)–Ag–O(3) 112.30(10).

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hydrolytic product, 2-aminopyridine was ruled out in the crystals, and a bis(salicylaldehydato)-Cu$^{II}$ complex (**1**) was isolated; in the case of AgNO$_3$, only 2-aminopyridine was involved in the crystals and an infinite polymer (**2**) was obtained. Although the mononuclear complex **1** was readily prepared from the direct reaction of salicylaldehyde and Cu$^{II}$ salts,[10] the linear polymer **2** is a unique product only formed under the condition of slow hydrolysis of N-salicylidene-2-aminopyridine.[11]

The crystallographic analysis reveals that complex **1** is a mononuclear copper(II) salicylaldehydato complex. The metal ion is four-coordinate with two salicyladehyde units in centrosymmetry mode to form a plane structure. This structure is very similar to the reported results,[10] with just slight differences in the cell dimensions.

Unlike complex **1**, complex **2** features a metal-organic polymeric structure, (Fig. 1a) in which each Ag$^I$ centre coordinates to one pyridine-N of aminopyridine and one amino-N of an adjacent aminopyridine, and one oxygen atom from the bridging nitrate counterion, with a tri-coordinated mode. On the other hand, each ligand is linked with two Ag$^I$ atoms to form the infinite chain-like polymer. The bond distance of Ag$^I$–N$_{py}$ is slightly shorter than that of Ag$^I$–N$_{amino}$, [2.238(2) *vs* 2.318(2)Å], indicating the stronger electron-donating ability of pyridine-N. The Ag$^I$–O bond distance is 2.538(3)Å and the weak Ag$^I$···O contact distance is 2.654(3)Å. The adjacent Ag···Ag nonbonding distance is 3.569Å. Interestingly, with exception of the Ag$^I$–N$_{amino}$ covalent interaction, the Ag$^I$ atom also weakly interacts with one hydrogen atom of amino group by a well-defined N–H···Ag agostic bonding,[12] the H···Ag separation is short at 2.115Å, and the N–H···Ag angle is 92.5°. This polymeric structure is remarkably distinct from the reported trinuclear Ag$^I$ complex,[11] in which three Ag$^I$ ions are coordinated with four 2-aminopyridine ligands with two different modes, the centric Ag$^I$ ion is four-coordinate with four amino groups from four distinct ligands by a slightly distorted tetrahedral geometry, while the other two Ag$^I$ ions act as bridges to interact with two pyridine-N atoms of two ligands in a two-coordinate manner, respectively. Three uncoordinated nitrate ions exist as counteranions in each asymmetric unit. Additionally, in the crystal lattice of **2**, both intermolecular N–H···O hydrogen bonds and weak Ag···O interactions play a crucial role in extending the 1D polymeric chain into a 2D network structure (Fig. 1b).

In summary, we have investigated the self-assembly of a mononuclear salicylaldehydato copper(II) complex and an infinite 2-aminopyridyl silver(I) coordination complex on the basis of the hydrolysis reaction of N-salicylidene-2-aminopyridine in the presence of transition metal ions. X-ray structure analysis confirmed that complex **2** is a novel chain-like polymer that is unavailable under other reaction conditions. Various hydrogen bonds present in the crystals play an essential role in constructing the multidimensional polymeric network.

## Experimental

FT-IR spectra were recorded on a BIO-RAD FT-165 IR spectrometer using KBr pellets. Elemental analysis was carried out with a Carlo Erba-1106 Instrument. The melting points were determined on a Yanaco MP-500 micro-melting point apparatus. All reagents were used as received. The ligand N-salicylidene-2-aminopyridine (**L**) was prepared by condensation of salicylaldehyde with 2-aminopyridine.

*Synthesis of bis(salicylaldehydato)-Cu$^{II}$ complex* (**1**): A solution of **L** (0.198g, 1mmol) in CH$_2$Cl$_2$ (10ml) was slowly added to a solution of Cu(OAc)$_2$·H$_2$O (0.199g, 1mmol) in MeOH (5 ml) under stirring. The resulting solution was stirred for 30 min at room temperature, then filtered. The filtrate was allowed to evaporate slowly in a refrigerator (5°C). After about one month, platelet brown crystalline products appeared, which were collected, washed with absolute methanol and dried under vacuum. Yield: 0.081g, 53% based on L, m.p. > 200°C (decomp.); FT-IR (KBr pellets): ν = 3434, 3054, 3013, 2365, 1608, 1523, 1431, 1335, 1198, 1149, 1022, 903, 768, 665, 615, 548, 429cm$^{-1}$; Anal. Calc. for: C$_{14}$H$_{10}$CuO$_5$, C, 55.0; H, 3.3. Found: C, 54.7; H, 3.2%. *Cell parameters for* **1**: C$_{14}$H$_{10}$CuO$_4$, M$_r$=305.76, monoclinic, space group P2$_1$/c, $a$=11.708(2), $b$=4.0123(8), $c$ = 12.471(3) Å, $\alpha = \gamma = 90.00°$, $\beta = 90.48(3)$ °, $V$ = 585.8(2) Å$^3$.

*Synthesis of 2-aminopyridyl-Ag$^I$ complex* (**2**): Complex **2** was prepared by a procedure similar to that of **1** except that one equivalent AgNO$_3$ (0.170g, 1mmol) was added during the reaction. Block-like light yellow crystals of **2** were obtained by slow evaporation of the reactant solution in a refrigerator (5°C) for one month. The products were collected, washed with absolute methanol and dried under vacuum. Yield: 0.110g, 42% based on **L**, m.p. 142–144°C; FT-IR (KBr pellets): ν = 3452, 3351, 2395, 1762, 1620, 1567, 1487, 1386, 1268, 1156, 1045, 1000, 824, 770, 734, 525, 417cm$^{-1}$; Anal. Calc. for: (C$_5$H$_6$AgN$_3$O$_3$)$_n$, C, 22.8; H, 2.3; N, 15.9. Found: C, 23.0; H, 2.4; N, 16.1.

*Crystal data of* **2** (CCDC No. 266373): C$_5$H$_6$AgN$_3$O$_3$, M$_r$ = 264.00, orthorhombic, space group Pbca, $\rho_{calcd}$ = 2.302 g cm$^{-3}$, $Z$ = 8, $\mu$(Mo$_{K\alpha}$) = 2.614mm$^{-1}$ $a$ = 6.8997(3), $b$ = 11.0241(4), $c$ = 20.0304(11)Å, $\alpha = \beta = \gamma = 90.00°$, $V$ = 1523.57(12) Å$^3$, $T$ = 293(2) K. The final R indices: R(F) = 0.0280 based on 1318 reflections ($I > 2(\sigma)$), wR($F^2$) = 0.0807 based on 1650 observed reflections (all data) and 110 parameters, GOF = 1.086. The data were collected on a Rigarku Raxis Rapid IP diffractometer with Mo Kα radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. The structure was solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on $F^2$. The hydrogen atoms were added theoretically and riding on the concerned atoms. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data centre (CCDC 266373). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk /conts/retri eving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk ).

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