

# [Ag(isonicotinamide)<sub>2</sub>NO<sub>3</sub>]<sub>2</sub> – a Stable Form of Silver Nitrate

Thomas Dorn,<sup>A</sup> Katharina M. Fromm,<sup>B</sup> and Christoph Janiak<sup>A,C</sup>

<sup>A</sup> Institut für Anorganische und Analytische Chemie, Universität Freiburg, 79104 Freiburg, Germany.

<sup>B</sup> Department of Chemistry, University of Basel, 4056 Basel, Switzerland.

<sup>C</sup> Corresponding author. Email: janiak@uni-freiburg.de

[Ag(isonicotinamide)<sub>2</sub>NO<sub>3</sub>]<sub>2</sub>, featuring a short Ag···Ag contact and a strong hydrogen-bonding network in the solid state, is a light-stable and still readily soluble form of silver nitrate, showing little complex formation in solution but a counter-intuitive decrease in dissolution rate with decrease of pH.

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Silver(I) nitrate is an active ingredient in medical and disinfectant formulations.<sup>[1]</sup> Eye drops with 1% AgNO<sub>3</sub> are given to newborns in some countries to prevent eye inflammation.<sup>[2]</sup> Bacterial adhesion on PVC endotracheal tubes can be inhibited by radio frequency oxygen glow discharge, followed by a two step wet treatment in NaOH and AgNO<sub>3</sub>.<sup>[3]</sup> Activated carbon fibers supported with Ag from immersion in AgNO<sub>3</sub> solutions possessed strong antibacterial activity and an inhibitory effect for growth of *Escherichia coli* and *Staphylococcus aureus*.<sup>[4]</sup> AgNO<sub>3</sub> (0.1 mg L<sup>-1</sup>) inhibits the growth of the microalgae *Chlorella vulgaris* and *Chlorella VT-1*.<sup>[5]</sup> A solution of AgNO<sub>3</sub> had a significant stimulatory effect on chlorophyll, solution protein contents, and antioxidant enzyme activities.<sup>[6]</sup> AgNO<sub>3</sub> together with 8-hydroxyquinoline sulfate and glucose is beneficial for the vase life of cut flowers, by controlling microbial growth.<sup>[7]</sup> This short compilation shows a potential for stabilizing formulations of light-sensitive AgNO<sub>3</sub> without significant alterations to its solution behaviour. A silver(I)-sulfadiazine coordination polymer is the active ingredient, from which Ag<sup>+</sup> are slowly liberated, in Brandiazin and Flammazin ointment for skin treatment after burns or acid etching.<sup>[1,2]</sup> Hence, also sought are formulations for the controllable release of silver ions.

The formation of bis(isonicotinamide) silver(I) nitrate (**1**), and its structure, fluorescence, light stability, and dissolution behaviour are described here. Isonicotinamide (INA, Scheme 1) and related compounds are versatile reagents in crystal engineering.<sup>[8–10]</sup> Crystalline **1** can be prepared in very good yield with well-shaped crystals from an aqueous solution of isonicotinamide and AgNO<sub>3</sub>, by evaporation under ambient conditions in the dark and by a hydrothermal method.

Single-crystal structure determination shows the expected close-to-linear coordination of the silver ion by two isonicotinamide ligands. Two of these Ag(INA)<sub>2</sub><sup>+</sup> units are joined by two bridging nitrate ligands and N–H···O hydrogen bonds



Scheme 1. Isonicotinamide.

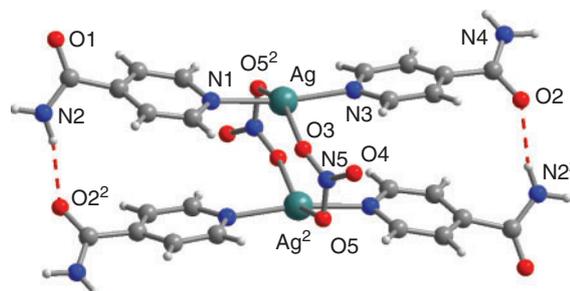
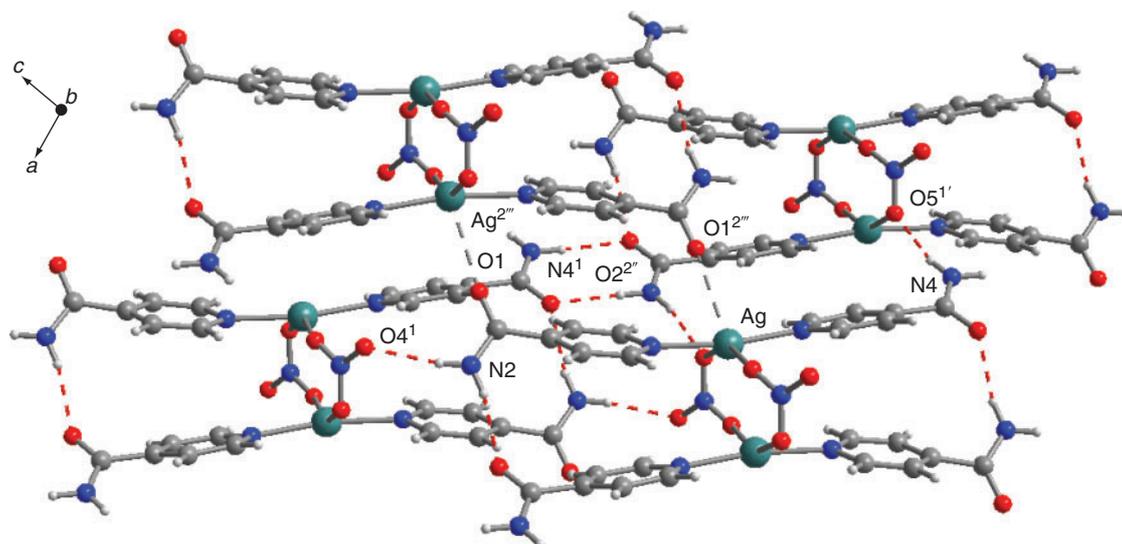


Fig. 1. Dinuclear units of [Ag(isonicotinamide)<sub>2</sub>(μ-NO<sub>3</sub>)<sub>2</sub>] in **1**. Selected distances [Å] and angles [°] are Ag–N1 2.176(2), Ag–N3 2.167(2), Ag–O3 2.851(2), Ag–O5<sup>2</sup> 2.747(2), Ag–Ag<sup>2</sup> 3.1429(5); N1–Ag–N3 171.09(6), N1–Ag–O3 89.92(6), N1–Ag–O5<sup>2</sup> 88.40(6), N3–Ag–O3 94.36(6), N3–Ag–O5<sup>2</sup> 90.52(6). Symmetry transformation <sup>2</sup> = 2 – x, 1 – y, –z.

(Fig. 1). The short Ag–Ag distance of 3.1429(5) Å in the dimeric units is noteworthy. It is evident that the clamping action of the NO<sub>3</sub><sup>-</sup> bridges pulls the two Ag ions together,<sup>[11]</sup> whereas hydrogen bonding between the neighbouring amide groups and also the π-stacking keeps the ligands further apart so that the INA–Ag–INA moiety bends inward. For comparison [Ag(INA)<sub>2</sub>]BF<sub>4</sub> has a linear (180°) INA–Ag–INA moiety and no Ag···Ag contacts;<sup>[12]</sup> in [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] the INA–Ag–INA moieties in the dimeric units are bent outward so that the Ag···Ag length becomes 3.70 Å.<sup>[13]</sup> The centroid–centroid π-stacking contact of the opposite pyridine rings in the dimeric unit of **1** is 3.870(1) Å with a large tilt angle of 16.3° between the planes, and perpendicular centroid-to-plane distances of 3.61 and 3.21 Å.<sup>[14]</sup> The centrosymmetric dinuclear dimeric units are assembled to a 3D supramolecular



**Fig. 2.** Section of the packing diagram in **1** showing hydrogen bonds (red dashes) and the long bond Ag–O1<sup>2''</sup> 3.081(2) (grey dashes). See Table 1 for details on hydrogen bonds. Additional symmetry transformations  $2'' = 1 - x, -y, -z$ ;  $2''' = 2 - x, 1 - y, 1 - z$ . *a*, *b*, *c* are unit cell vectors.

**Table 1.** Hydrogen bonding interactions in **1**

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
N2–H···O4 <sup>1</sup>	0.86(3)	2.09(3)	2.941(3)	171(2)
N2–H···O2 <sup>2</sup>	0.86(2)	2.07(2)	2.904(3)	166(2)
N4–H···O2 <sup>2'</sup>	0.90(3)	2.06(3)	2.955(2)	178(2)
N4–H···O5 <sup>1'</sup>	0.82(2)	2.11(2)	2.895(3)	162(2)

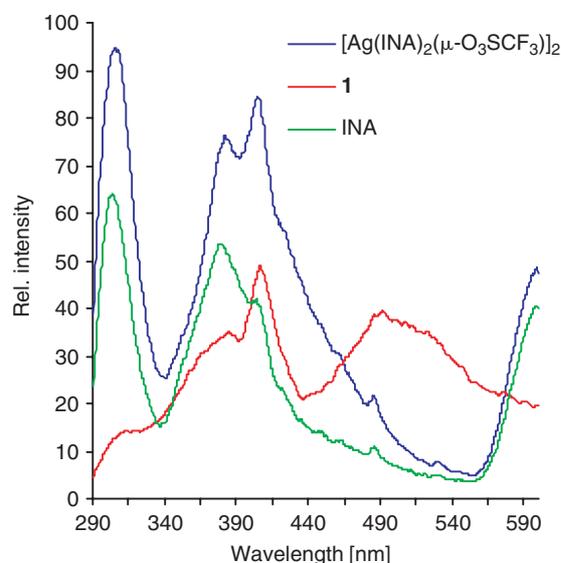
D = donor, A = acceptor. For found and refined atoms the standard deviations are given in parentheses. Symmetry transformations:  $1 = 1 + x, y, 1 + z$ ;  $1' = -1 + x, -1 + y, z$ ;  $2 = 2 - x, 1 - y, -z$ ;  $2' = -x, -y, -1 - z$ .

network through N–H···O hydrogen bonds and a third long Ag···O bond to each silver atom (Fig. 2). The surrounding of the pseudo trigonal-bipyramidal silver centre by three bridging nitrate ions in the equatorial plane and two axial pyridyl groups has been seen before.<sup>[15]</sup>

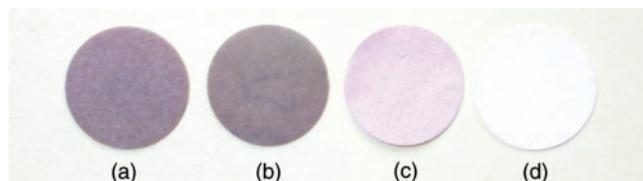
Comparative solid-state fluorescence spectra of INA, and the d<sup>10</sup> complexes **1** and [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O at low temperature (77 K) give evidence for an Ag···Ag *interaction* in **1** with the appearance of a new emission peak at 495 nm (Fig. 3). This region is typical for short Ag–Ag contacts.<sup>[16,17]</sup>

Compound **1** exhibits high light stability. Crystals of **1** could be stored open in daylight for weeks without visible darkening that otherwise is typical for many silver(I) compounds. For a more quantitative comparison of the light stability, filter papers (Ø 10 mm) were impregnated with aqueous 0.1 mol L<sup>-1</sup> solutions of AgNO<sub>3</sub>, [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and **1**. The filter papers were allowed to dry in the dark at room temperature. Then they were irradiated with a 15 W energy-saving lamp at a distance of 5 cm for 30 min. Compound **1** decomposes/blackens much more slowly than both AgNO<sub>3</sub> and [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Fig. 4).

Crystals of **1**, when rubbed with the fingers onto the skin, gave a light skin colorization only after a few hours. With



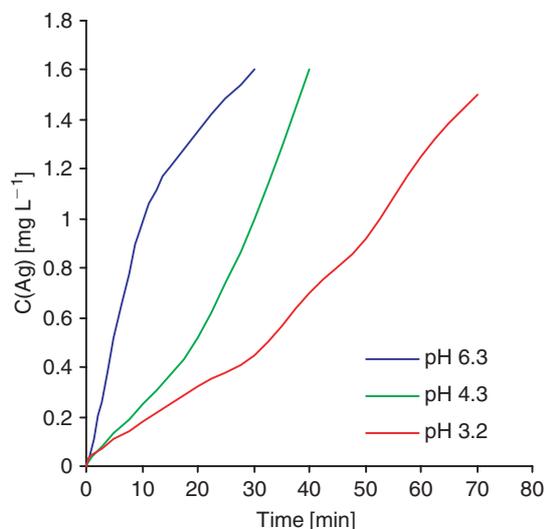
**Fig. 3.** Emission spectra of INA ( $\lambda_{\text{ex}}$  235 nm), **1** ( $\lambda_{\text{ex}}$  233 nm), and [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> ( $\lambda_{\text{ex}}$  233 nm) in the solid state at 77 K.



**Fig. 4.** Impregnated filter papers after 30 min irradiation with a 15 W energy saving lamp at a distance of 5 cm. (a) AgNO<sub>3</sub>; (b) [Ag(INA)<sub>2</sub>(μ-O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O; (c) compound **1**; (d) untreated filter paper.

AgNO<sub>3</sub>, an intense black colour occurred on the skin after a short time.

In aqueous solution, compound **1** forms free Ag<sup>+</sup>, as does AgNO<sub>3</sub>. The complex stability of **1** with  $\text{p}K_{\beta} = 3.01$  for the equilibrium constant  $K_{\beta} = [\text{Ag}(\text{INA})_2^+]/[\text{Ag}^+][\text{INA}]^2$ , is



**Fig. 5.** Time-dependent silver concentrations from dissolution of **1** at pH 3.2, 4.3 and 6.3. An  $\text{Ag}^+$  concentration of  $1.6 \text{ mg L}^{-1}$  was the upper limit for the electrode potential.

low.<sup>[18]</sup> Species distribution curves based on  $\text{p}K_{\beta}$  of **1** and  $\text{p}K_{\text{a}}$  of 3.67 for the acid constant  $K_{\text{a}}$  of H-INA, show only 10% complex formation for  $\text{pH} > 5$ , and a solution that is  $10 \text{ mmol L}^{-1}$  in  $\text{Ag}^+$  and  $20 \text{ mmol L}^{-1}$  in INA (see Accessory Materials).

Comparative NMR spectroscopic investigations of INA,  $[\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)]_2$  and **1** in  $[\text{D}_6]\text{DMSO}$  or  $\text{D}_2\text{O}$  indicate no significant chemical shift differences in either  $^1\text{H}$  or  $^{13}\text{C}$  NMR, which suggests a  $\text{Ag}$ –INA contact in solution in **1**. Hence, a high dissociation of the complex can be assumed. In DMSO, silver coordination to a pyridyl group should cause a small but obvious down-field shift of the proton signals with respect to those of the free ligand ( $\Delta\delta \approx 0.1\text{--}0.2 \text{ ppm}$ ),<sup>[15,19]</sup> which is not seen for **1**.

The dissolution rate of **1** in water is pH-dependent and controllable. The dissolution rate of **1** was followed by means of a silver ion-selective electrode (Ag-metal Titrode 6.0430.100, Metrohm, with built-in pH glass membrane reference electrode). The dissolution rate was measured under identical conditions by placing 0.100 g of crystalline **1** in 50 mL aqueous solutions of equal ionic strength ( $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ\text{C}$ ) at pH 6.3, 4.3, and 3.2, which was set with dilute nitric acid. The electrode was calibrated at each pH value with  $\text{AgNO}_3$  standard solutions. Fig. 5 shows the measured increase in  $\text{Ag}^+$  concentration with time at different pH values. Compound **1** dissolves more slowly at lower pH. This increase in dissolution rate with pH is somewhat counter-intuitive. We explain it with the low base strength of isonicotinamide ( $\text{p}K_{\text{a}}$  3.67), which is protonated only at  $\text{pH} < 4$ , so that the silver–ligand complex framework is not broken up rapidly by the usual competitive ligand protonation. The increase in dissolution rate of **1** with pH, i.e.  $\text{OH}^-$  concentration, is reasoned by the  $\text{OH}^-$  becoming involved in hydrogen bonding with the amide groups of INA, to break apart the strong hydrogen-bonding network and form  $\text{Ag}^+$  and  $\text{NO}_3^-$  separate from INA. Thus, supramolecular

hydrogen-bonding networks offer pH control of substrate dissolution behaviour.

Compound **1** combines light stability in the solid state with ready solubility and with the effective formation of free, unligated  $\text{Ag}^+$  in solution. It should, therefore, offer potential as a stabilizing formulation of solid  $\text{AgNO}_3$ .

## Experimental

Infra-red spectra (2–4 mg compound/300 mg KBr pellet) were measured on a Bruker Optik IFS25 from 4000 to  $400 \text{ cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on a Bruker Avance DRX 400 spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}\{^1\text{H}\}$ ) with calibration against the residual protonated solvent signal ( $[\text{D}_6]\text{DMSO}$   $^1\text{H}$  NMR 2.52 ppm,  $^{13}\text{C}$  NMR 39.5 ppm;  $\text{D}_2\text{O}$  4.80 ppm). Luminescence spectra were measured on a Perkin–Elmer LS-50B ( $\lambda_{\text{ex}}$  233 or 235 nm), split widths (em, ex) 5.0 nm, scan speed  $2 \text{ nm s}^{-1}$ , solid samples in quartz capillaries at 77 K.  $[\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)]_2 \cdot 4\text{H}_2\text{O}$  was prepared according to the literature.<sup>[13]</sup>

### Syntheses of Bis[bis(isonicotinamide)silver(*l*)]( $\mu\text{-NO}_3$ )

**Method 1:** 2.44 g (20.0 mmol) of isonicotinamide in 200 mL of water was added to a solution of 1.69 g (10.0 mmol) of  $\text{AgNO}_3$  in 200 mL of water (the order of addition is important). Crystallization proceeded in the open vessel in the dark, and after 3 days the first crystals formed. After another 5 days the colourless, well-shaped crystals were separated by filtration and washed with water (yield 2.89 g, 70%).

**Method 2:** 0.50 g (3.0 mmol) of  $\text{AgNO}_3$ , 0.73 g (6.0 mmol) of isonicotinamide and 15 mL of  $\text{H}_2\text{O}$  were placed in a 20-mL Teflon liner of a steel autoclave. An immediate voluminous precipitate formed. The mixture was heated to  $120^\circ\text{C}$  within 2 h and maintained for another 10 h, then cooled from  $120^\circ\text{C}$  to room temperature over 12 h to give colourless crystals (yield 1.06 g, 85%).

Both crystals gave identical analyses,  $\text{mp} > 180^\circ\text{C}$ . (Found: C 34.63, H 3.02, N 17.63%. Calc. for  $\text{C}_{24}\text{H}_{24}\text{Ag}_2\text{N}_{10}\text{O}_{10}$ : C 34.80, H 2.92, N 16.91%).  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3373 (br), 1661 (sh), 1552 (s), 1498 (m), 1366 (br), 1218 (s), 1149 (m), 1122 (m), 1064 (m), 1022 (w), 993 (w), 854 (s), 797 (s), 629 (s), 412 (s).  $\delta_{\text{H}}$  ( $[\text{D}_6]\text{DMSO}$ ) 8.8 (m, 2H, H2,6), 8.25 (s, 1H, amide-H), 7.8 (m, 2H, H3,5), 7.7 (s, 1H, amide-H).  $\delta_{\text{H}}$  ( $\text{D}_2\text{O}$ ) 8.69–8.68 (m, 2H, H2,6), 7.80–7.79 (m, 2H, H3,5).  $\delta_{\text{C}}$  ( $\text{D}_6\text{-DMSO}$ ) 166.01 (C7), 150.76 (C3,5), 141.91 (C4), 121.88 (C2,6).  $\delta_{\text{C}}$  ( $\text{D}_2\text{O}$ ) 170.32 (C7), 150.91 (C3,5), 142.04 (C4), 122.32 (C2,6).

### Crystal Structure Determination of **1**

#### Crystal Data

Molecular formula  $\text{C}_{12}\text{H}_{12}\text{AgN}_5\text{O}_5$ , formula weight 414.14  $\text{g mol}^{-1}$ ,  $a$  7.4192(14),  $b$  8.9359(17),  $c$  11.127(2) Å,  $\alpha$  95.912(3)°,  $\beta$  99.698(3)°,  $\gamma$  100.809(3)°,  $V$  707.3(2) Å<sup>3</sup>,  $Z$  2,  $D_{\text{calc}}$  1.945  $\text{g cm}^{-3}$ , triclinic,  $P\bar{1}$ .

#### Data Collection

Bruker Smart AXS CCD,  $\text{MoK}\alpha$  radiation ( $\lambda$  0.71073 Å), graphite monochromator, crystal size 0.21 mm  $\times$  0.15 mm  $\times$  0.13 mm, 298(2) K,  $\omega$ -scan,  $3.7^\circ \leq 2\theta \leq 57.7^\circ$ ,  $-9 \leq h \leq 9$ ,  $-11 \leq k \leq 11$ ,  $-14 \leq l \leq 14$ , 6395 reflections measured, 3292 independent,  $\mu(\text{MoK}\alpha)$  1.461  $\text{mm}^{-1}$ , experimental absorption correction with *SADABS*.<sup>[20]</sup>

#### Structural Analysis and Refinement

The structure was solved by direct methods (*SHELXS-97*), and full-matrix least-squares refinement on  $F^2$  was performed using *SHELXL-97*.<sup>[21]</sup> All non-hydrogen positions were found and refined with anisotropic temperature factors, and the amide hydrogen atoms ( $\text{NH}_2$ ) were found and refined with isotropic temperature factors  $U_{\text{eq}}(\text{H}) = 1.5 U_{\text{eq}}(\text{N/O})$ . Hydrogen atoms on aromatic carbon atoms were calculated using appropriate riding models (AFIX 43) and  $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . Final  $R$  = 0.0240,  $wR$  = 0.0509 for 2660 reflections with  $I > 2\sigma I$ , final  $R$  = 0.0312,  $wR$  = 0.0525 for all data, 232 refined parameters, goodness-of-fit on  $F^2$  = 0.917, largest difference peak and

hole  $0.501/-0.489 \text{ e } \text{\AA}^{-3}$  in the vicinity of the Ag atom. CCDC reference number 280861.

### Accessory Materials

Species distribution plots and listing of comparative NMR data are available from the author or, until January 2011, the *Australian Journal of Chemistry*.

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