

[Ag(isonicotinamide)₂NO₃]₂ – a Stable Form of Silver Nitrate

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[Ag(isonicotinamide)₂NO₃]₂, 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.

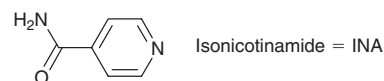
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Silver(I) nitrate is an active ingredient in medical and disinfectant formulations.^[1] Eye drops with 1% AgNO₃ are given to newborns in some countries to prevent eye inflammation.^[2] Bacterial adhesion on PVC endotracheal tubes can be inhibited by radio frequency oxygen glow discharge, followed by a two step wet treatment in NaOH and AgNO₃.^[3] Activated carbon fibers supported with Ag from immersion in AgNO₃ solutions possessed strong antibacterial activity and an inhibitory effect for growth of *Escherichia coli* and *Staphylococcus aureus*.^[4] AgNO₃ (0.1 mg L⁻¹) inhibits the growth of the microalgae *Chlorella vulgaris* and *Chlorella VT-1*.^[5] A solution of AgNO₃ had a significant stimulatory effect on chlorophyll, solution protein contents, and antioxidant enzyme activities.^[6] AgNO₃ together with 8-hydroxyquinoline sulfate and glucose is beneficial for the vase life of cut flowers, by controlling microbial growth.^[7] This short compilation shows a potential for stabilizing formulations of light-sensitive AgNO₃ without significant alterations to its solution behaviour. A silver(I)-sulfadiazine coordination polymer is the active ingredient, from which Ag⁺ are slowly liberated, in Brandiazin and Flammazin ointment for skin treatment after burns or acid etching.^[1,2] 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.^[8–10] Crystalline **1** can be prepared in very good yield with well-shaped crystals from an aqueous solution of isonicotinamide and AgNO₃, 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)₂⁺ units are joined by two bridging nitrate ligands and N–H··O hydrogen bonds



Scheme 1. Isonicotinamide.

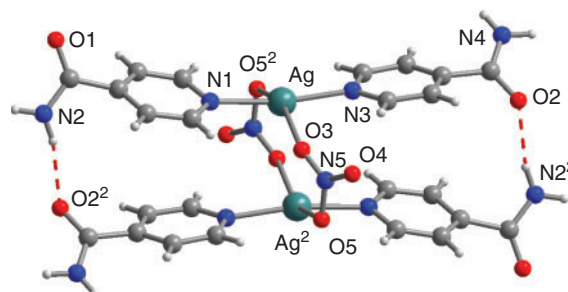


Fig. 1. Dinuclear units of [Ag(isonicotinamide)₂(μ-NO₃)₂] in **1**. Selected distances [Å] and angles [°] are Ag–N1 2.176(2), Ag–N3 2.167(2), Ag–O3 2.851(2), Ag–O5² 2.747(2), Ag–Ag² 3.1429(5); N1–Ag–N3 171.09(6), N1–Ag–O3 89.92(6), N1–Ag–O5² 88.40(6), N3–Ag–O3 94.36(6), N3–Ag–O5² 90.52(6). Symmetry transformation ² = 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 NO₃⁻ bridges pulls the two Ag ions together,^[11] 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)₂]BF₄ has a linear (180°) INA–Ag–INA moiety and no Ag··Ag contacts;^[12] in [Ag(INA)₂(μ-O₃SCF₃)₂] the INA–Ag–INA moieties in the dimeric units are bent outward so that the Ag··Ag length becomes 3.70 Å.^[13] 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.^[14] The centrosymmetric dinuclear dimeric units are assembled to a 3D supramolecular

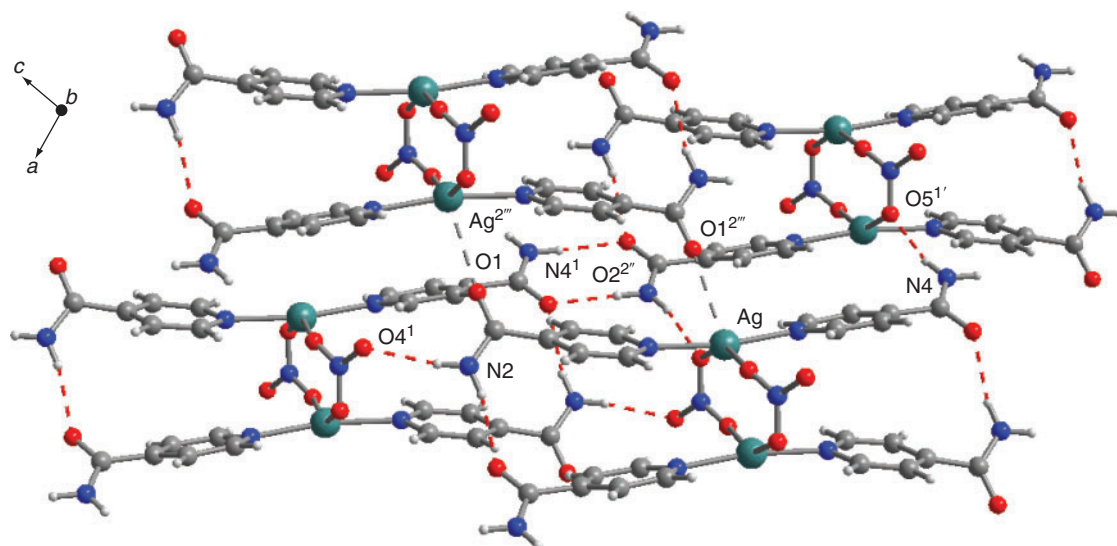


Fig. 2. Section of the packing diagram in **1** showing hydrogen bonds (red dashes) and the long bond Ag–O1^{2''} 3.081(2) (grey dashes). See Table 1 for details on hydrogen bonds. Additional symmetry transformations $2'' = 1 - x, -y, -z$; $2''' = 2 - x, 1 - y, 1 - z$. *a*, *b*, *c* are unit cell vectors.

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 ¹	0.86(3)	2.09(3)	2.941(3)	171(2)
N2–H···O2 ²	0.86(2)	2.07(2)	2.904(3)	166(2)
N4–H···O2 ^{2'}	0.90(3)	2.06(3)	2.955(2)	178(2)
N4–H···O5 ^{1'}	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.^[15]

Comparative solid-state fluorescence spectra of INA, and the d¹⁰ complexes **1** and [Ag(INA)₂(μ-O₃SCF₃)₂·4H₂O 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.^[16,17]

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⁻¹ solutions of AgNO₃, [Ag(INA)₂(μ-O₃SCF₃)₂·4H₂O, 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 AgNO₃ and [Ag(INA)₂(μ-O₃SCF₃)₂·4H₂O (Fig. 4).

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

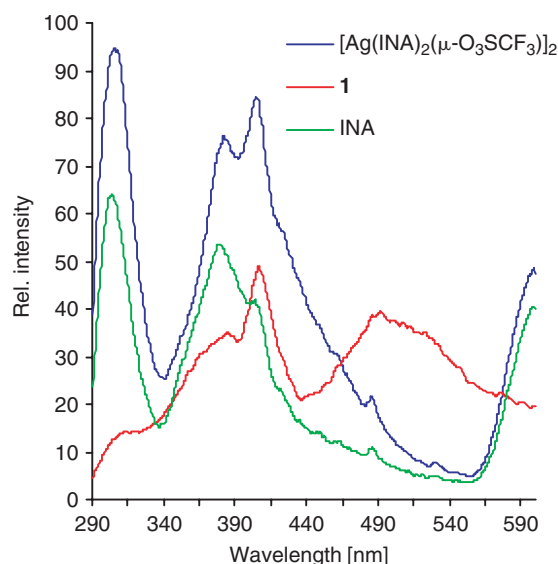


Fig. 3. Emission spectra of INA (λ_{ex} 235 nm), **1** (λ_{ex} 233 nm), and [Ag(INA)₂(μ-O₃SCF₃)₂] (λ_{ex} 233 nm) in the solid state at 77 K.

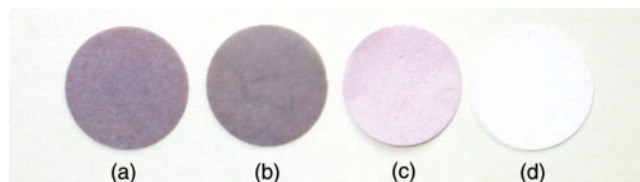


Fig. 4. Impregnated filter papers after 30 min irradiation with a 15 W energy saving lamp at a distance of 5 cm. (a) AgNO₃; (b) [Ag(INA)₂(μ-O₃SCF₃)₂·4H₂O; (c) compound **1**; (d) untreated filter paper.

AgNO₃, an intense black colour occurred on the skin after a short time.

In aqueous solution, compound **1** forms free Ag⁺, as does AgNO₃. 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

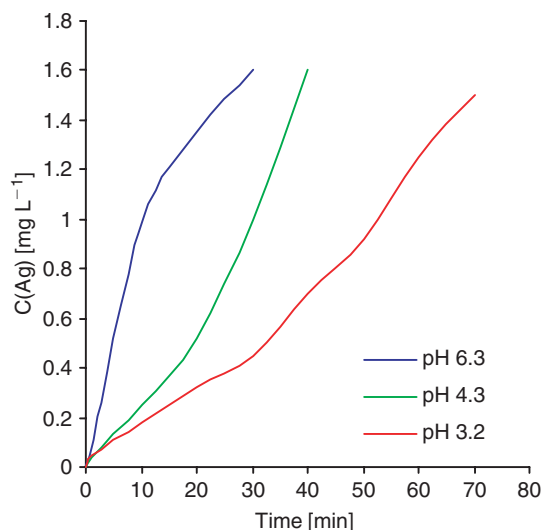


Fig. 5. Time-dependent silver concentrations from dissolution of **1** at pH 3.2, 4.3 and 6.3. An Ag^+ concentration of 1.6 mg L^{-1} was the upper limit for the electrode potential.

low.^[18] 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_{a} of H-INA, show only 10% complex formation for $\text{pH} > 5$, and a solution that is 10 mmol L^{-1} in Ag^+ and 20 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 D_2O indicate no significant chemical shift differences in either ^1H or ^{13}C NMR, which suggests a 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 ($\Delta\delta \approx 0.1\text{--}0.2 \text{ ppm}$),^[15,19] 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°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 AgNO_3 standard solutions. Fig. 5 shows the measured increase in 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. OH^- concentration, is reasoned by the OH^- becoming involved in hydrogen bonding with the amide groups of INA, to break apart the strong hydrogen-bonding network and form Ag^+ and 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 Ag^+ in solution. It should, therefore, offer potential as a stabilizing formulation of solid AgNO_3 .

Experimental

Infra-red spectra ($2\text{--}4 \text{ mg}$ compound/ 300 mg KBr pellet) were measured on a Bruker Optik IFS25 from 4000 to 400 cm^{-1} . ^1H and ^{13}C NMR spectra were collected on a Bruker Avance DRX 400 spectrometer (400 MHz for ^1H , 100 MHz for $^{13}\text{C}\{^1\text{H}\}$) with calibration against the residual protonated solvent signal ($[\text{D}_6]\text{DMSO}$ ^1H NMR 2.52 ppm , ^{13}C NMR 39.5 ppm ; D_2O 4.80 ppm). Luminescence spectra were measured on a Perkin–Elmer LS-50B (λ_{ex} 233 or 235 nm), split widths (em, ex) 5.0 nm , scan speed 2 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.^[13]

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 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 AgNO_3 , 0.73 g (6.0 mmol) of isonicotinamide and 15 mL of H_2O were placed in a 20-mL Teflon liner of a steel autoclave. An immediate voluminous precipitate formed. The mixture was heated to 120°C within 2 h and maintained for another 10 h, then cooled from 120°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%). ν_{max} (KBr)/ 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). δ_{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). δ_{H} (D_2O) $8.69\text{--}8.68$ (m, 2H, H2,6), $7.80\text{--}7.79$ (m, 2H, H3,5). δ_{C} ($\text{D}_6\text{-DMSO}$) 166.01 (C7), 150.76 (C3,5), 141.91 (C4), 121.88 (C2,6). δ_{C} (D_2O) 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 $11.127(2) \text{ \AA}$, α $95.912(3)^\circ$, β $99.698(3)^\circ$, γ $100.809(3)^\circ$, V $707.3(2) \text{ \AA}^3$, Z 2 , D_{calc} 1.945 g cm^{-3} , triclinic, $P\bar{1}$.

Data Collection

Bruker Smart AXS CCD, $\text{MoK}\alpha$ radiation (λ 0.71073 \AA), graphite monochromator, crystal size $0.21 \text{ mm} \times 0.15 \text{ mm} \times 0.13 \text{ mm}$, $298(2) \text{ K}$, ω -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 mm^{-1} , experimental absorption correction with *SADABS*.^[20]

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*.^[21] All non-hydrogen positions were found and refined with anisotropic temperature factors, and the amide hydrogen atoms (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 $R1 = 0.0240$, $wR2 = 0.0509$ for 2660 reflections with $I > 2\sigma I$, final $R1 = 0.0312$, $wR2 = 0.0525$ 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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