

Accessory Material for

{Ag(isonicotinamide)₂NO₃}₂ – a stable form of silver nitrateThomas Dorn,^a Katharina M. Fromm^b and Christoph Janiak^{*a}^a Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de; Fax: +49 761 2036147; Tel: +49 761 2036127^b Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

This material contains

1) in Fig. 1-3 the species distribution plots calculated with the program SPEX – the species distribution program, Version 28.5.91 by R. J. Motekaitis, modified by R. Kissner.

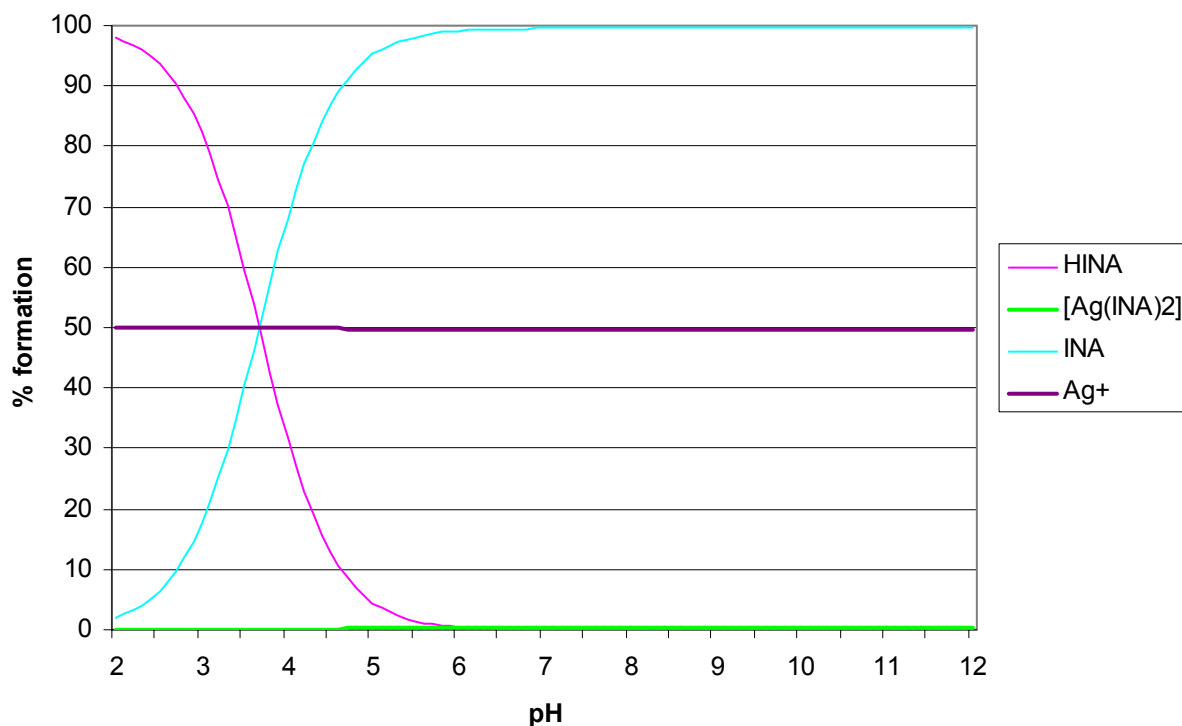
2) in Table 1 and 2 a comparative listing of NMR data for INA, {Ag(INA)₂(μ-O₃SCF₃)₂} and {Ag(INA)₂(μ-NO₃)₂} (**1**) with two ¹H NMR spectra of higher order for **1** shown in Fig. 4 and 5.

Fig. 1 Species distribution plot as a function of pH for a solution which is **1 mmol·l⁻¹ in Ag⁺** and **2 mmol·l⁻¹ in INA** based on the complex formation constant $pK_B = [Ag(INA)_2^+]/[Ag^+][INA]^2 = 3.01$ for and the pK_a value of 3.67 for the acid constant K_a of HINA (INA = isonicotinamide).

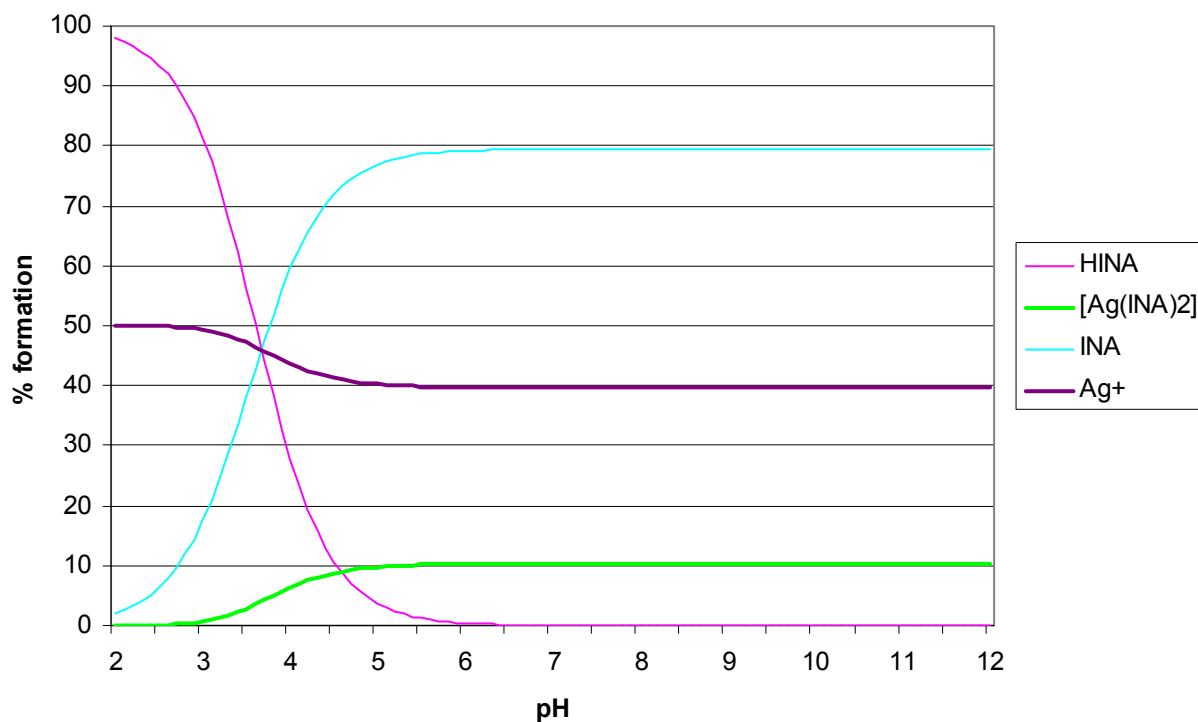


Fig. 2 Species distribution plot as a function of pH for a solution which is $10 \text{ mmol}\cdot\text{l}^{-1}$ in Ag^+ and $20 \text{ mmol}\cdot\text{l}^{-1}$ in INA based on the complex formation constant $\text{p}K_{\beta} = \frac{[\text{Ag}(\text{INA})_2^+]}{[\text{Ag}^+][\text{INA}]^2} = 3.01$ for and the $\text{p}K_a$ value of 3.67 for the acid constant K_a of HINA (INA = isonicotinamide).

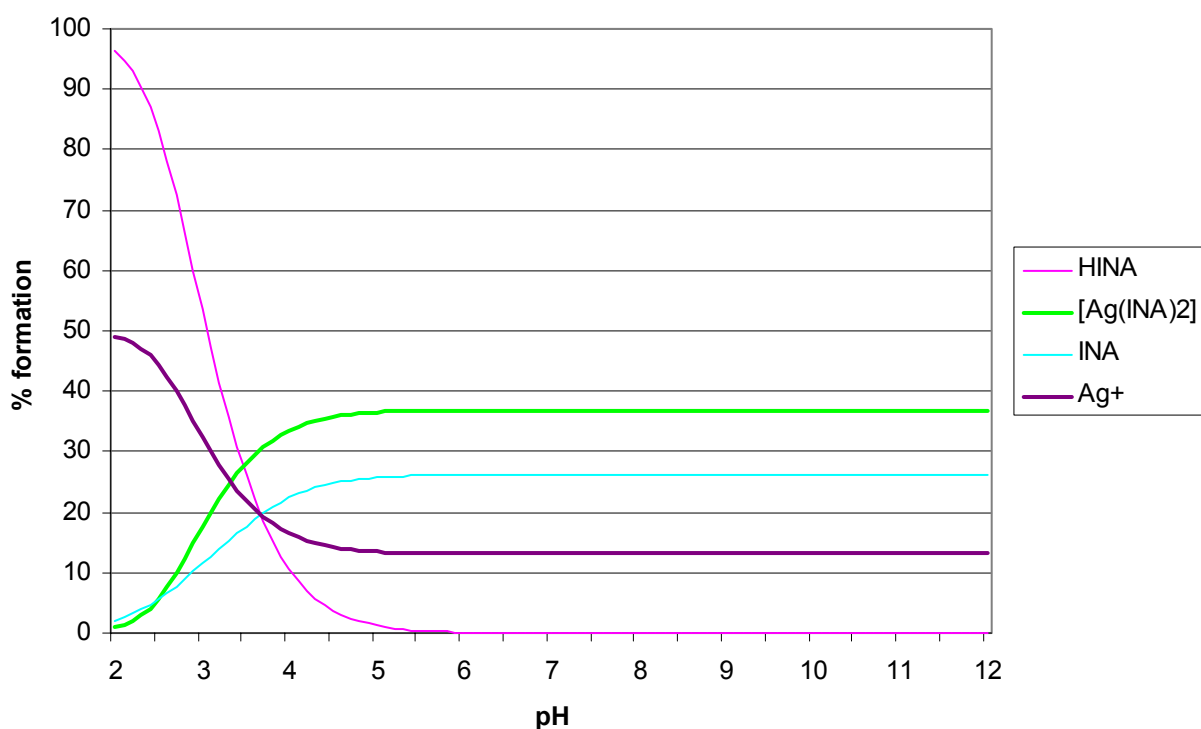


Fig. 3 Species distribution plot as a function of pH for a solution which is $100 \text{ mmol}\cdot\text{l}^{-1}$ in Ag^+ and $200 \text{ mmol}\cdot\text{l}^{-1}$ in INA based on the complex formation constant $\text{p}K_{\beta} = \frac{[\text{Ag}(\text{INA})_2^+]}{[\text{Ag}^+][\text{INA}]^2} = 3.01$ for and the $\text{p}K_a$ value of 3.67 for the acid constant K_a of HINA (INA = isonicotinamide).

Table 1: ^1H - and ^{13}C -NMR-data for INA, $\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$ and $\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (**1**) in DMSO-d_6 at $T = 303$ K with calibration against the residual protonated solvent signal ($\text{d}_6\text{-DMSO}$ ^1H NMR 2.52 ppm, ^{13}C NMR 39.5 ppm)

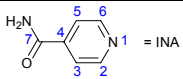
 H_2N 5 6 4 N1 = INA 3 2				
^1H -NMR ($\delta(\text{DMSO-d}_6)$ in ppm)				
	H2, H6	H3, H5	amide H	
INA	8.75 (s, 2H)	7.84 (d, 2H, $J = 5.5$)	8.28 (s, 1H), 7.76 (s, 1H)	
$\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$	8.75 (s, 2H)	7.84 (d, 2H, $J = 5.5$)	8.28 (s, 1H), 7.76 (s, 1H)	
$\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (1)	8.75* (s, 2H)	7.84* (d, 2H, $J = 5.5$)	8.28 (s, 1H), 7.76 (s, 1H)	
* see spectrum in Fig. 4				
^{13}C -NMR ($\delta(\text{DMSO-d}_6)$ in ppm)				
	C2, C6	C3, C5	C4	C7
INA	121.34	150.12	141.22	166.26
$\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$	122.22	150.54	141.68	166.04
$\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (1)	121.88	150.76	141.91	166.01

Table 2: ^1H - and ^{13}C -NMR-data for INA, $\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$ and $\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (**1**) in D_2O at $T = 303$ K with calibration against the residual protonated solvent signal (D_2O ^1H NMR 4.80 ppm, ^{13}C NMR external calibration)

^1H -NMR ($\delta(\text{D}_2\text{O})$ in ppm)				
	H2, H6	H3, H5	amide H	
INA	8.64-8.63 (m, 2H)	7.70-7.68 (m, 2H)	not seen, H-D exchange	
$\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$	8.69-8.68 (m, 2H)	7.80-7.78 (m, 2H)	not seen, H-D exchange	
$\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (1)	8.69- 8.68** (m, 2H)	7.80-7.79** (m, 2H)	not seen, H-D exchange	
** see spectrum in Fig. 5				
^{13}C -NMR ($\delta(\text{D}_2\text{O})$ in ppm)				
	C2, C6	C3, C5	C4	C7
INA	121.79	149.57	141.33	170.68
$\{\text{Ag}(\text{INA})_2(\mu\text{-O}_3\text{SCF}_3)\}_2$	122.28	150.78	141.99	170.39
$\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (1)	122.32	150.91	142.04	170.32

Experimental part

^1H and ^{13}C NMR spectra were collected on a Bruker Advance DRX 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C with ^1H broad band decoupling) 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).

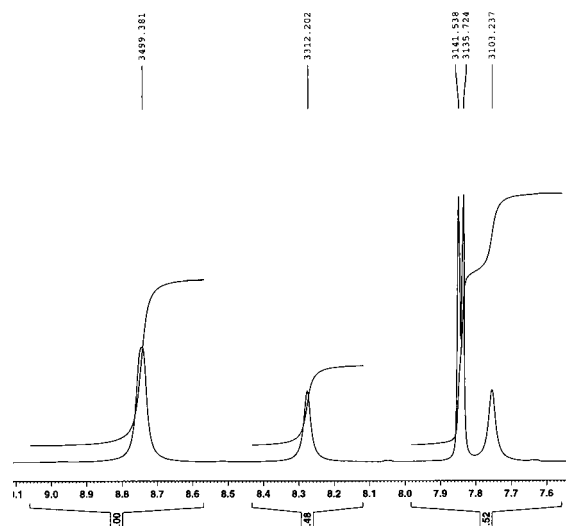


Fig. 4 ^1H NMR spectrum of $\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (**1**) in $\text{d}_6\text{-DMSO}$.

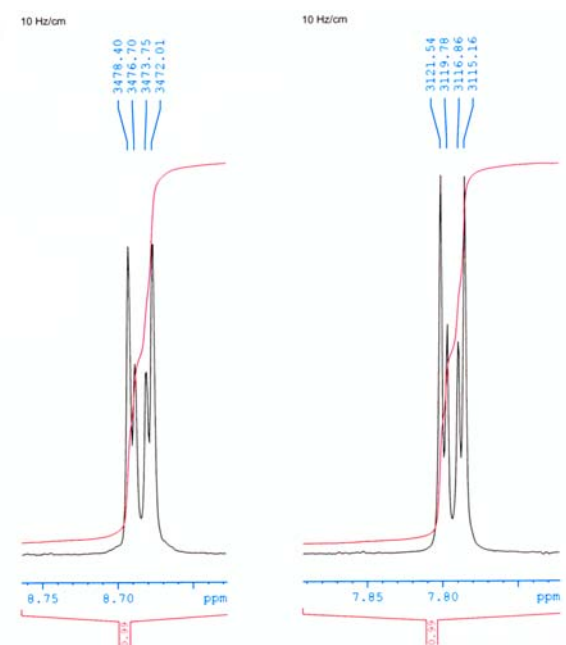
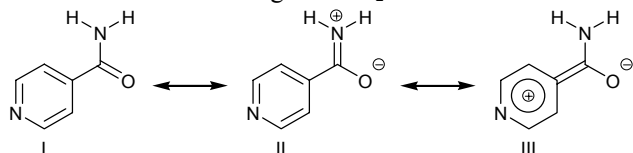


Fig. 5 ^1H NMR spectrum of $\{\text{Ag}(\text{INA})_2(\mu\text{-NO}_3)\}_2$ (**1**) in D_2O .

The following mesomeric resonance structures I \leftrightarrow II lead to an amide rotational barrier of $+14.1 \pm 0.2$ kcal $\cdot\text{mol}^{-1}$ around the C-N bond which renders the two NH_2 protons inequivalent. In addition, the resonance structure III renders the four C-H protons inequivalent, giving a spectrum of higher order.^[1] In D_2O the NH_2 protons are not visible due to exchange with D_2O .



[1] G. M. Leskowitz, N. Ghaderi, R. A. Olsen, K. Pederson, M. E. Hatcher, L. J. Mueller, *J. Phys. Chem. A* **2005**, *109*, 1152.