

Preliminary communication

STUDY OF THE STEREOCHEMISTRY OF SILVER(I) BIS(PYRIDINE-2-CARBALDEHYDE-IMINE) TRIFLATE COMPLEXES IN SOLUTION: APPLICATION OF INEPT ^{109}Ag AND $^1\text{H}\{-^{109}\text{Ag}\}$ NMR

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Summary

$[\text{Ag}^{\text{I}}\text{L}_2](\text{O}_3\text{SCF}_3)$ complexes have been obtained from the 2/1 reaction of pyridine-2-carbaldehyde-imine (L) with AgO_3SCF_3 . INEPT ^{109}Ag and $^1\text{H}\{-^{109}\text{Ag}\}$ NMR studies of $[\text{Ag}\{(S)(6\text{-Me-2-C}_5\text{H}_3\text{N})\text{C(H)=NC(H)PhMe}\}_2](\text{O}_3\text{SCF}_3)$ reveal that the tetrahedral $\text{Ag}^{\text{I}}\text{L}_2$ cation of this complex exists below 235 K in two diastereoisomeric forms with a strong preference for one of the molecular configurations (probably the $\Lambda(S)(S)$).

Only a few papers concerning studies of silver(I) complexes by direct or indirect detection of $^{109(107)}\text{Ag}$ resonances have been published [1], a fact which is connected to the low γ values, very large T_1 values and hence very low detectability of both ^{107}Ag and ^{109}Ag isotopes. We have recently reported [2] that if the Ag nucleus in silver(I) complexes shows ^1H resolved scalar couplings, then ^{109}Ag NMR spectra can be easily recorded via the INEPT sequence [3].

We now report the application of $^1\text{H}\{-^{109}\text{Ag}\}$ NMR and INEPT ^{109}Ag NMR for the elucidation of electronic and structural characteristics of silver(I) bis-(pyridinecarbaldehyde-imine) triflate complexes $[\text{Ag}\{(6\text{-R-C}_5\text{H}_3\text{N})\text{C(H)=N-R}'\}_2](\text{O}_3\text{SCF}_3)$ (Ia: R = H, R' = cyclohexyl; Ib: R = Me, R' = cyclohexyl; II: R = Me, R' = (S)-1-phenylethyl). These new complexes** contain tetrahedral $\text{Ag}^{\text{I}}\text{L}_2$

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**The complexes were obtained from the 1/2 reactions of AgOTf with the pyridinecarbaldehyde-imine ligands in methanol. They have been fully characterised by F.D. mass spectrometry and correct analytical data.

cations which in the case of II can exist in two diastereomeric forms (cf.: Fig. 1).

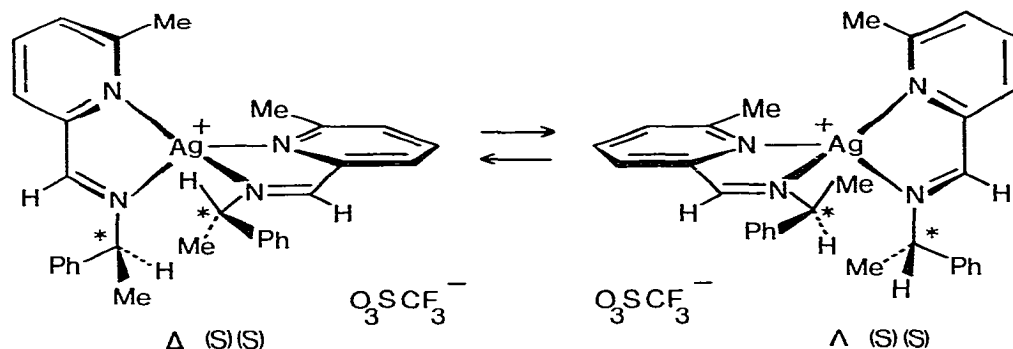


Fig. 1. The two diastereoisomers of complex II.

The ^1H NMR spectrum* of Ia shows at room temperature only one singlet for the imine protons; at low temperature ($T = 223\text{ K}$) we observe a splitting of this proton signal. In contrast, the ^1H spectrum of complex Ib already shows this splitting at room temperature. In similar cases, $^1\text{H}\{-^1\text{H}\}$ decoupling together with ^1H NMR experiments at 60, 100 and 250 MHz indicated that such a splitting could arise from a $^3J(^1\text{H}\text{---}^{107,109}\text{Ag})$ coupling [4]. Very clear evidence for this coupling was obtained by $^1\text{H}\{-^{109}\text{Ag}\}$ studies**. These experiments, which have not previously been described, were carried out by tuning the observing coil of a multinuclear 10 mm probehead to the ^{109}Ag frequency, injecting the ^{109}Ag decoupling frequency (1 W power) through the coil, and recording the ^1H spectrum via the proton decoupling coil of the multinuclear probe. Very good proton spectra were obtained with such an arrangement, and the results show the imine proton resonance as a characteristic 1/2/1 triplet-like pattern, due to ^{109}Ag decoupled protons (central singlet 48.2%), flanked by a doublet corresponding to ^{107}Ag non-decoupled protons (51.8%) (see Fig. 2).

That the compounds Ia, Ib and II are subject to inter-(intra-)molecular rearrangements is revealed by the temperature dependence of the observed $^3J(^1\text{H}\text{---}^{107,109}\text{Ag})$ coupling upon the R moiety (vide supra). Such exchange processes lead to an inversion of configuration at the tetrahedral silver site. This latter process is not detectable with Ia and Ib because the two stereoisomers (enantiomers) are indistinguishable by NMR in achiral solvents. To investigate this aspect we prepared silver(I) complex II with pyridinecarb-aldehyde-imine ligands having a chiral $^*\text{C}$ -atom with the stable (S) configuration. In this diastereomeric complex, the configuration at the silver centre (Λ or Δ , see Fig. 1) can in principle be detected by NMR.

* ^1H , $^1\text{H}\{-^{109}\text{Ag}\}$ and ^{109}Ag INEPT NMR experiments were recorded on a Bruker WM250 spectrometer (^1H : 250 MHz, ^{109}Ag : 11.64 MHz).

** $^3J(^{107,109}\text{Ag}\text{---}^1\text{H}(\text{imine}))$ for Ia is 8.9 Hz (δ 8.69 ppm) and for Ib 7.4 Hz (δ 8.65 ppm).

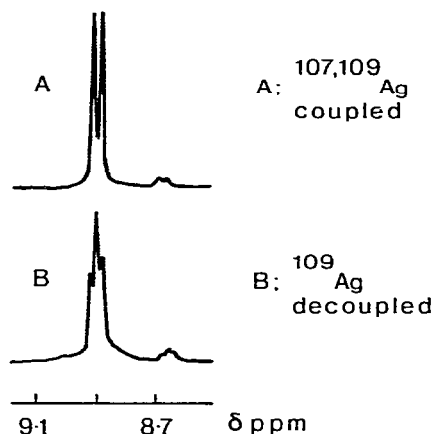


Fig. 2. Imine region of the ^1H NMR spectrum of complex II in CD_3OD at 223 K with Me_4Si as internal standard.

At room temperature, the imine protons of II appear as one singlet. On lowering the temperature, this signal broadens and we observe ($T < 235$ K) two doublets in a 20/1 ratio. A $^1\text{H}\{-^{109}\text{Ag}\}$ NMR experiment as described above proved unambiguously that the doublet patterns for these resonances are due to $^3J(^1\text{H}\text{--}^{107,109}\text{Ag})$ couplings (δ 8.92 ppm, 3J 7.2 Hz; δ 8.65 ppm, 3J 7.7 Hz) (Fig. 2). These signals represent the imine protons of the two separate diastereoisomers and indicate that below 235 K intermolecular exchange between the two silver sites is frozen on the ^1H NMR time scale.

It was attractive, then, to record the ^{109}Ag NMR spectrum using the INEPT sequence (3J) at low temperatures ($T < 235$ K) to study in particular the effect of a chiral centre near the silver atom on the $\delta(^{109}\text{Ag})^*$. The ^{109}Ag ^1H coupled INEPT spectrum of I (Fig. 3) shows, indeed, two resonances (δ +636.0 ppm, δ +612.1 ppm) likewise in a 20/1 ratio, representing the ^{109}Ag centres of the two diastereoisomers. The triplet fine structure on each signal (Fig. 3A) is due to a small $^3J(^{109}\text{Ag}\text{--}^1\text{H})$ with the $^*\text{C}\text{--}\text{H}$ protons of the chiral carbon centres. This was deduced from a selective $^*\text{C}\text{--}\text{H}$ heterodecoupling experiment which was made after the $^1\text{H}\text{--}^{109}\text{Ag}$ polarization transfer preparation sequence and during ^{109}Ag FID acquisition (Fig. 3B).

We assume that the high selectivity (95%) for one of the diastereoisomers is the result of different steric strains between the (*S*)-C(H)MePh groupings of the two ligands in each of the isomers (see Fig. 1). Since the phenyl groups are likely to determine the relative rotamer conformations in these isomers, it appears that in the $\Lambda(S)(S)$ isomer the two small H-atoms are in close contact whereas in the $\Delta(S)(S)$ isomer there is a less favourable interaction between two methyl groups.

* ^{109}Ag INEPT: $\alpha^{90}(^1\text{H})$ 35 μs ; $\alpha^{90}(^{109}\text{Ag})$ 50 μs ; number of scans, 4000 for the coupled spectrum (Fig. 3A), 1200 for the selectively decoupled spectrum (Fig. 3B) and 1400 for the BB decoupled spectrum (Fig. 3C); a positive δ indicates a higher resonance frequency ("deshielding") with respect to the reference frequency.

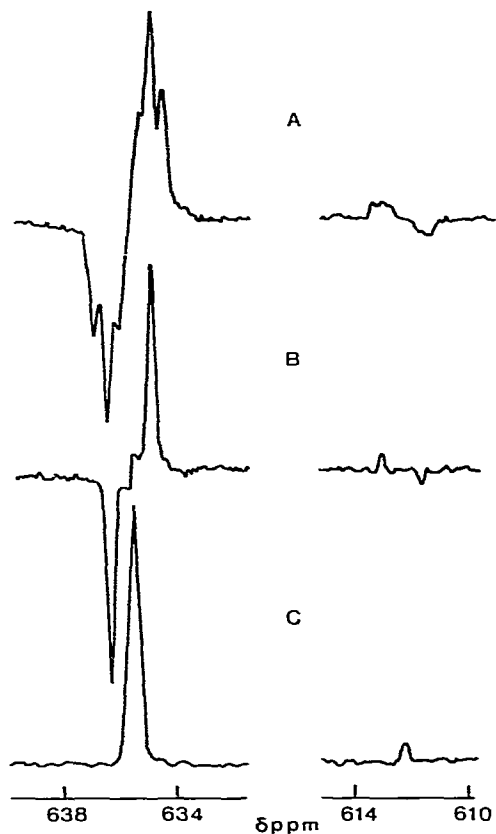


Fig. 3. INEPT ^{109}Ag NMR spectra of II in CD_3OD at 223 K (referenced from AgNO_3 , 2 M in $\text{D}_2\text{O}/\text{H}_2\text{O}$ 1/1). A, ^1H coupled; B, ^1H ($^*\text{C}-\text{H}$) selectively decoupled (see text) and C, ^1H decoupled (BB).

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