

Silver(I) and Copper(I) Bis(pyridine-2-carbaldehyde-imine) Triflate Complexes Studied in Solution by ^1H , $^1\text{H}\{-^{109}\text{Ag}\}$, INEPT ^{15}N and INEPT ^{109}Ag NMR

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The reactions of the neutral pyridine-imine, 6-R-py-2-CH=N-R' (NN'), donor ligands with $[M(\text{O}_3\text{SCF}_3)]$ [$M = \text{Ag(I)}$ or Cu(I)] yield ionic complexes, consisting of a $[M(\text{NN}')_2]^+$ cation and a O_3SCF_3^- anion. ^1H NMR studies of the complexes which contain the prochiral substituent (R') *i*-Pr or the chiral (S)-CHMePh show that in the slow exchange limit the metal IB centres have tetrahedral geometries as a result of chelate bonding of the pyridine-imine ligands. The metal IB centres have either Δ or Λ configurations. The complexes with R' is (S)-CHMePh exist in solution in two diastereomeric forms, i.e. $\Delta(\text{S}/\text{S})$ and $\Lambda(\text{S}/\text{S})$, the most abundant of which (according to ^1H NMR spectra) is the $\Lambda(\text{S}/\text{S})$ diastereomer. The (diastereomeric) selectivity is higher for the silver(I) complexes ($\Lambda(\text{S}/\text{S})/\Delta(\text{S}/\text{S})$ for $R = \text{H} > 99/1$; $R = \text{Me}$, 95/5) than for the corresponding copper(I) complexes ($\Lambda(\text{S}/\text{S})/\Delta(\text{S}/\text{S})$ for $R = \text{H}$, 85/15; $R = \text{Me}$, 75/25). An INEPT ^{109}Ag NMR study, which was performed for the silver(I) complex with R is Me and R' is (S)-CHMePh shows a large chemical shift difference (24 ppm) between the signals arising from the Ag(I) centres in the two diastereoisomers. Temperature-dependent ^1H NMR experiments of the complexes with R' is *i*-Pr show that fluxional processes occur. In the case of the silver(I) complex with R is Me and R' is *i*-Pr it was established by ^1H and INEPT ^{15}N NMR that both an intramolecular process involving inversion of configuration ($\Delta \rightleftharpoons \Lambda$) at the metal centre and a slower intermolecular ligand exchange process are taking place. It appeared that the rates of these processes depend on the bulkiness of the 6-pyridine as well as the imine substituents, R and R'. Moreover, the copper(I) complexes are more stable than the corresponding silver(I) complexes. Possible mechanisms for the observed exchange processes are discussed.

Introduction

In previous papers [1] we have reported the synthesis and characterization of the silver(I) and copper(I) complexes with the neutral N_4 -donor ligands 1,2-(6-R-py-2-CH=N)-R' ($R = \text{H}$ or Me, $R' = (R)(S)\text{-cyclohexane}$ or ethane). These metal IB complexes consist of $[M_2(\text{N}_4)_2]^{2+}$ di-cations (see Fig. 1) and O_3SCF_3^- anions in the solid (X-ray). This structure is retained in solution as could be concluded from ^1H , ^{13}C and INEPT ^{15}N and ^{109}Ag NMR studies. The latter studies revealed that the metal IB centres in the di-cations have distorted tetrahedral geometries, both having the same configuration ($\Delta\Delta$ or $\Lambda\Lambda^*$), and that the structures in which the metal centres have opposite configurations ($\Delta\Lambda$) were not detected.

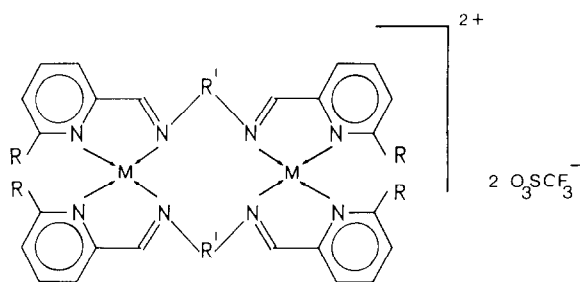


Fig. 1. Schematic representation of the $[M_2(\text{N}_4)_2](\text{O}_3\text{SCF}_3)_2$ complexes ($M = \text{Ag(I)}$ or Cu(I) , $R = \text{H}$ or Me and $R' = (R)(S)\text{-1,2-cyclohexane}$ or 1,2-ethane).

It was deduced from ^1H NMR results [1b] that the silver(I) complexes were subjected to metal-ion exchange reactions involving initial Ag–N bond dissociation. This exchange reaction which takes

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*For the abbreviations Δ and Λ denoting the stereochemical configuration of the metal centres see ref. 2.

place at one side of the di-cation, *i.e.* in one $\text{Ag}(\text{NN}')_2^+$ compartment, may induce an inversion of configuration ($\Delta\Delta \rightleftharpoons \Lambda\Lambda$) at both metal IB centres. To investigate the mechanism of this process in detail we have prepared the copper(I) and silver(I) complexes with two pyridine-imine ligands, 6-R-py-2-CH=N-R'. This NN' bidentate ligand system represents only one half of the N_4 ligand system and hence the formed $[\text{M}(\text{NN}')_2]^+$ cations (see eqn. 1) can be regarded as one half of the $[\text{M}_2(\text{NN}')_2]^{2+}$ dications. Since the dynamic behaviour of these dications is very sensitive to the nature of the 6-pyridine substituent the pyridine-imine-ligands with 6-R is H as well as those with 6-R is Me have been studied.

This paper reports the syntheses of the silver(I) complexes with the pyridine-imine ligands 6-R-py-2-CH=N-R' (R = H or Me, R' = Me, *c*-Hex, *i*-Pr or (*S*)-CHMePh) and some of the corresponding copper(I) complexes (R = H or Me, R' = *i*-Pr or (*S*)-CHMePh) and their characterization by field desorption mass spectrometry and temperature dependent ^1H NMR. INEPT ^{15}N NMR [3] of the silver(I) complex with R is Me and R' is *i*-Pr and an INEPT ^{109}Ag NMR [4] study of the silver(I) complex with R is Me and R' is (*S*)-CHMePh are included in this paper.* These latter studies support our earlier [1] view that replacement of Cu(I) by Ag(I), which has a suitable NMR handle,** is a good approach for a detailed study of the dynamics of metal IB ligand complexes.

*Part of this work has been reported as a preliminary communication [5].

**The γ values for ^{107}Ag [51.82%] and ^{109}Ag [48.18%] are -1.0828 and $-1.2449 \times 10^7 \text{ rad. T}^{-1} \text{ s}^{-1}$ respectively. Both nuclei have $I = 1/2$ [6].

TABLE I. Analytical Data of $[\text{M}(6\text{-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3)$ [M = Ag(I) or Cu(I)].

Compound		Found (Calc.)				
R	R'	C	H	F	N	S
<i>M</i> = Ag(I)						
(1a) H	Me	36.53(36.23)	3.25(3.24)	11.40(11.46)	11.26(11.27)	6.45(6.45)
(1b) Me	Me	38.42(38.87)	3.76(3.84)	10.75(10.85)	10.43(10.67)	6.01(6.10)
(2a) H	<i>c</i> -Hex	47.15(47.40)	5.08(5.09)	8.86(9.00)	8.77(8.84)	5.08(5.06)
(2b) Me	<i>c</i> -Hex	48.65(49.02)	5.55(5.49)	8.52(8.62)	8.45(8.47)	4.87(4.85)
(3a) H	<i>i</i> -Pr	41.27(41.24)	4.38(4.37)	10.08(10.12)	10.30(10.30)	5.64(5.79)
(3b) Me	<i>i</i> -Pr	43.84(43.38)	4.79(4.85)	9.85(9.80)	9.21(9.64)	5.46(5.51)
(5a) H	(<i>S</i>)-CHMePh	51.37(51.41)	4.42(4.17)	8.03(8.42)	8.00(8.27)	4.55(4.74)
(5b) Me	(<i>S</i>)-CHMePh	52.38(52.77)	4.57(4.57)	7.95(8.08)	7.82(7.94)	4.56(4.54)
<i>M</i> = Cu(I)						
(4a) H	<i>i</i> -Pr	44.47(44.83)	4.73(4.75)	11.40(11.20)	10.80(11.01)	6.30(6.30)
(4b) Me	<i>i</i> -Pr	46.47(46.96)	5.24(5.25)	10.65(10.61)	10.27(10.43)	5.94(5.97)
(6a) H	(<i>S</i>)-CHMePh	54.51(55.01)	4.44(4.46)	8.97(9.00)	8.60(8.85)	5.04(5.06)
(6b) Me	(<i>S</i>)-CHMePh ^a	54.66(54.82)	5.00(5.05)	8.72(8.39)	8.03(8.25)	4.51(4.72)

^aData calculated for $[\text{M}(6\text{-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3) \cdot \text{H}_2\text{O}$.

Experimental

All reactions were carried out under a nitrogen atmosphere in freshly distilled solvents. The 6-R-pyridine-2-carbaldehyde-imines (R = H or Me) were prepared *via* condensation reactions of 6-R-pyridine-2-carbaldehyde with the corresponding primary amines in a 1/1 molar ratio in diethyl ether. Commercially available silver(I) trifluoromethanesulfonate $\cdot 1/2\text{C}_6\text{H}_6$ was prepared as described in the literature [7]. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, T.N.O., Utrecht (The Netherlands). Data are given in Table I.

$[\text{Ag}(6\text{-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3)$ (R = H or Me)

6-R-py-2-CH=N-R' (2.1 mmol) (for R' see eqn. 1) dissolved in methanol (10 ml) was added to a solution of $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ (1.0 mmol) in methanol (10 ml). This reaction mixture was stirred for 15 min. and then filtered through celite to remove small amounts of solid impurities. The solvent was evaporated at low pressure affording a white powder, which was washed with diethyl ether to remove excess 6-R-py-2-CH=N-R' and dried *in vacuo*. Yields were 90–100%.

$[\text{Cu}(6\text{-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3)$ (R = H or Me, R' = *i*-Pr or (*S*)-CHMePh)

Addition of a solution of 6-R-py-2-CH=N-R' (2.1 mmol) in benzene (25 ml) to a solution of $[\text{Cu}(\text{O}_3\text{SCF}_3)] \cdot 1/2\text{C}_6\text{H}_6$ (1 mmol) in benzene (25 ml) resulted in immediate precipitation of the complex. The brown suspension was stirred for 15 min. and the mother liquor then decanted off. The precipitate was

TABLE II. F.D.-M.S. Data^a of $[M\{(6-R-py-2-CH=N-R')\}_2](O_3SCF_3)$ [$M = Ag(I)$ or $Cu(I)$].

	Compounds		M/Z (calc.) ^b		M/Z [%] (obs.) ^c
	R	R'	[M(NN') ₂]O ₃ SCF ₃ ^a	M(NN') ₂ ⁺	
<i>M</i> = Ag(<i>I</i>) ^d					
(1a)	H	Me	496	347	347[100], 349[72]
(1b)	Me	Me	524	375	375[100], 377[59]
(2a)	H	c-Hex	632	483	483[100], 485[80]
(2b)	Me	c-Hex	660	511	511[96], 513[100]
(3a)	H	i-Pr	552	403	403[70], 405[100]
(3b)	Me	i-Pr	580	431	431[100], 433[98]
(5a)	H	(<i>S</i>)-CHMePh	676	527	527[100], 529[88]
(5b)	Me	(<i>S</i>)-CHMePh	704	555	555[84], 557[100]
<i>M</i> = Cu(<i>I</i>) ^d					
(4a)	H	i-Pr	508	359	359[100], 361[43]
(4b)	Me	i-Pr	536	387	387[100], 389[41]
(6a)	H	(<i>S</i>)-CHMePh	632	483	483[100], 485[45]
(6b)	Me	(<i>S</i>)-CHMePh	660	511	511[100], 513[57]

^aEmitter current amounts to 5 mA except for the complexes with (S)-CHMePh (10 mA).
 $M(NN')_2^+$ calculated with Ag = 107, Cu = 63. ^cOnly the most intense peaks are listed.
^d⁶³Cu, 69.09%; ⁶⁵Cu, 30.91%.

^bM/Z for $[M(NN')_2]O_3SCF_3$ and
^d¹⁰⁷Ag, 51.82%; ¹⁰⁹Ag, 48.18%;

washed with benzene (3×10 ml) and diethyl ether (3×10 ml) and then dried *in vacuo*. Yields were 90–100%.

Physical Measurements

Field desorption (FD) mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer equipped with a combined EI/FI/FD ion source and coupled to a spectro-system MAT 100 data acquisition unit [8]. The samples were loaded onto the emitter with the dipping technique [9]. (See Table II).

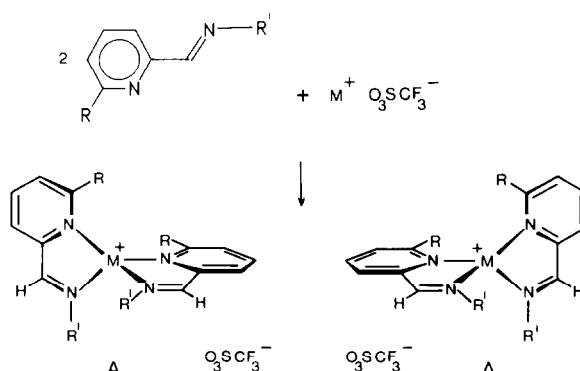
¹H NMR spectra were recorded on Varian A-60-D, Bruker WM 250 and AM 400 spectrometers with tetramethylsilane (TMS) as either internal standard or external reference. The ¹H NMR data are listed in Table III. ¹H-¹⁰⁹Ag NMR experiments (see Fig. 2) were carried out on a Bruker WM 250 spectrometer (¹H, 250 MHz; ¹⁰⁹Ag, 11.64 MHz) by tuning the observer coil of a multinuclear 10 mm probehead to the ¹⁰⁹Ag frequency, injecting this as a decoupling frequency (1 W power) through this coil and recording the ¹H NMR spectrum *via* the proton decoupling coil.

Natural abundance ¹⁵N and ¹⁰⁹Ag NMR spectra were recorded in methanol-d₄ on Bruker AM 300 and WM 250 spectrometers respectively applying the INEPT sequence. The procedure for obtaining these spectra is described in previous papers [1, 4].

The ¹⁵N and ¹⁰⁹Ag NMR data are relative to MeNO₂ (in C₆D₆, 80/20 v/v) and AgNO₃ (2 M in D₂O) respectively which were used as external references.

Results

The 1/2 molar reactions of $[M(O_3SCF_3)]$ [$M = Ag(I)$ or $Cu(I)$] with the NN' donor ligands 6-R-py-2-CH=N-R' (R = H or Me; R' = Me, c-Hex, i-Pr or (S)-CHMePh, see eqn. 1) in either methanol or benzene afforded stable light yellow silver(I) or reddish brown copper(I) complexes. The elemental analyses confirmed the 1/2 metal salt-to-ligand stoichiometries. Field desorption mass spectra showed the parent molecular ions, $[M(NN')_2]^+$ with no other fragmentation patterns. The complexes are air and water stable, are not light-sensitive and have good solubilities in chloroform, dichloromethane and methanol but are insoluble in apolar solvents.



Eqn. 1. R = H, a or Me, b.

M = Ag(I), R' = Me, 1; c-Hex, 2; i-Pr, 3 or (S)-CHMePh, 5.

M = Cu(I), R' = i-Pr, 4 or (S)-CHMePh, 6.

TABLE III. ^1H NMR Data^a of 6-R-py-2-CH=N-R' and their Silver(I) and Copper(I) Complexes.

Compounds			δ (ppm)					$^3\text{J}(\text{Hz})[\text{T}_\text{c}(\text{K})]$	
			H(im)	H-6	H(6-Me)	N-C-H	N-C-CH ₃	$^1\text{H}(\text{im}) - ^{107, 109}\text{Ag}$	
<i>Ligands</i>									
R	R'								
H	Me		8.30 q ^b	8.56 d		3.52 d ^b			
Me	Me		8.28 q ^b		2.57 s	3.51 d ^b			
H	c-Hex		8.33 s	8.55 d		3.27 m			
Me	c-Hex		8.32 s		2.53 s	3.27 m			
H	i-Pr		8.35 s	8.58 d		3.62 se	1.26 d		
Me	i-Pr		8.34 s		2.58 s	3.61 se	1.30 d		
H	(S)-CHMePh		8.48 s	8.60 d		4.60 q	1.60 d		
Me	(S)-CHMePh		8.48 s		2.61 s	4.58 q	1.59 d		
<i>Silver(I) complexes</i>									
(1a)	H	Me	8.55 s	8.47 d		3.72 s			
(1b)	Me	Me	8.62 d		2.39 s	3.68 s		8.0[200]	
(2a)	H	c-Hex	8.71 d	8.64 d		3.71 m		8.9[210]	
(2b)	Me	c-Hex	8.65 d		2.32 s	3.62 m		7.4[305]	
(3a)	H	i-Pr	8.74 s	8.72 d		4.09 se	1.30 d		
(3b)	Me	i-Pr	8.67 d		2.47 s	3.96 dse	1.25 d	9.0[306]	
							1.31 d		
(5a)	H	(S)-CHMePh	8.70 d	7.75 d		4.92 dq	1.61 d	7.9[200]	
(5b)	Me	(S)-CHMePh ^c	95% 8.91 d		1.54 s	5.04 dq	1.76 d	8.0[260]	
		5%	8.65 d		2.29 s	4.47 dq	1.49 d	7.7[260]	
<i>Copper(I) complexes</i>									
(4a)	H	i-Pr	8.64 s	8.42 d		4.02 se	1.11 d		
							1.21 d		
(4b)	Me	i-Pr	8.65 s		2.28 s	4.06 se	1.16 d		
							1.27 d		
(6a)	H	(S)-CHMePh	85% 8.79 s	— ^d		5.20 q	1.86 d		
		15%	8.73 s	— ^d		4.39 q	1.55 d		
(6b)	Me	(S)-CHMePh	75% 8.94 s		1.28 s	5.07 q	1.90 d		
		25%	8.69 s		2.06 s	4.00 q	1.58 d		

^aSpectra were taken in CD_2Cl_2 . ^b $^4\text{J}(^1\text{H}-^1\text{H})$ coupling is present between $\text{H}-\text{C}=\text{N}-\text{C}-\text{H}_3$, only observed in the 60 MHz spectrum. ^cSpectrum taken in methanol- d_4 . ^dThese resonances could not be assigned with certainty; s = singlet, d = doublet, q = quartet, dq = doublet of quartets, se = septet, dse = doublet of septets.

The Complexes in Solution

^1H NMR data of the $[\text{M}(\text{NN}')_2](\text{O}_3\text{SCF}_3)$ complexes have been obtained in CD_2Cl_2 or methanol- d_4 . The spectra of the silver(I) complexes **1b**, **2a** and **2b** show one pattern for the pyridine-imine H-atoms of the ligands with a doublet for the imine-H atoms, a singlet for the methyl groups in **1b** and a multiplet pattern for the cyclohexanyl-H atoms in **2a** and **2b**. Upon coordination the pyridine H-3, H-6 and 6-CH₃ resonances are shifted upfield while the pyridine H-4, H-5 as well as the imine-H resonances undergo a downfield shift (see Table III). The spectra are temperature-dependent and in Table III the data are given for the complexes in the slow exchange limit. For various complexes this situation could not be

reached [i.e. the silver(I) complexes **1a** (R = H, R' = Me) and **3a** (R = H, R' = i-Pr)].

The imine-H resonances of the silver(I) complexes appear as doublets due to $^3\text{J}(^1\text{H}-^{107, 109}\text{Ag})$. The appearances of these signals as doublets instead of doublet of doublets is because of the small difference in γ values of ^{107}Ag and ^{109}Ag .^{*} Thus, when recording the ^1H NMR spectra with selective ^{109}Ag decoupling a characteristic 1/2/1 triplet like pattern was observed for these imine-H atoms. This pattern consists of a doublet due to the ^{107}Ag coupled

^{*}See footnote**, p. 30.

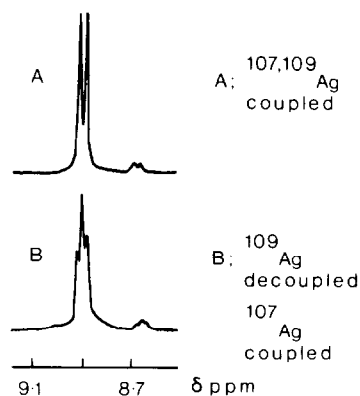


Fig. 2. Part of the ^1H NMR spectrum (250 MHz) of $[\text{Ag}(\text{6-Me-py-2-CH=N-(S)-CHMePh})_2](\text{O}_3\text{SCF}_3)$ (**5b**) in methanol- d_4 at 223 K.

(51.82%) and a central singlet due to the ^{109}Ag decoupled imine-H-atoms (48.18%) (see Fig. 2). The imine-H resonances of the copper(I) complexes appeared as singlets. Scalar couplings of these H-atoms with either ^{63}Cu (69.09%) or ^{65}Cu (30.91%) are not resolved because of the large quadrupole moments of both copper isotopes (both have $I = 3/2$) [10].

The above data however do not provide information about the coordination geometry around the metal IB centre in these complexes in solution. This can be either a tetrahedral geometry in which both pyridine-imine ligands are chelate bonded, a trigonal one as a result of monodentate coordination of one of the ligands or a linear coordination geometry as a result of monodentate coordination of both pyridine-imine ligands by the imine-N site. However, it must be noted that the monodentate coordination mode is less stable for pyridine-imines than the chelate bonding mode (*cf.* ref. 11).

If the metal IB centre has a tetrahedral coordination geometry, then the metal centre can have either a Δ or Λ configuration. This situation can be identified by ^1H NMR if prochiral or chiral groups are present in the ligand. For this reason we have prepared the 2/1 pyridine-imine/ $[\text{M}(\text{O}_3\text{SCF}_3)]$ [$\text{M} = \text{Ag(I)}$ or Cu(I)] complexes with the pyridine-imine ligands having either the prochiral *i*-Pr group or the (S)-CHMePh group containing a chiral $^*\text{C}$ -atom with a selected absolute configuration (S) as imino substituents. For a tetrahedral geometry in the slow exchange limit the methyl groups of the *i*-Pr substituent will be diastereotopic, giving rise to two anisochronous methyl doublets in the ^1H NMR spectra. When a chiral group, (S)-CHMePh, is introduced a tetrahedral metal IB complex can exist in two diastereomeric forms, *i.e.* $\Delta(\text{S})(\text{S})$ and $\Lambda(\text{S})(\text{S})$, and each will have its own ^1H resonance pattern in the slow exchange limit. Using the *i*-Pr or (S)-CHMePh containing complexes it is also possible to

probe processes involving inversion of configuration at the metal centre. When inversion of configuration becomes a fast process the two anisochronous methyl doublets in the ^1H NMR spectra of the complexes with R' (*i*-Pr) will coalesce to one doublet and the two ^1H patterns of the complexes containing the (S)-CHMePh groups will coalesce to one such pattern.

The ^1H NMR spectra (250 MHz) in CD_2Cl_2 at 180 K of the silver(I) complex **3a** ($\text{R} = \text{H}$, $\text{R}' = \text{i-Pr}$) shows one pyridine-imine pattern containing a singlet imine-H resonance and only one doublet resonance for the isopropyl-methyl groups. However, in the spectra of the silver(I) complex **3b** and the copper(I) complexes **4a** and **4b** at sufficiently low temperatures (see section dynamic behaviour of the complexes) one pyridine-imine but two doublet resonances for the isopropyl-methyl groups are observed. In the spectrum of the silver(I) complex **3b** in addition to a $^3\text{J}(\text{H}-^{107,109}\text{Ag})$ on the imine-H resonance a $^3\text{J}(\text{H}-^{107,109}\text{Ag})$ was also observed on the isopropyl-H resonance. The diastereotopic splitting between the two isopropyl-methyl doublets is small and for the silver(I) complex **3b** amounts to 0.06 ppm in CD_2Cl_2 (0.08 ppm in CD_3OD). For the copper(I) complexes **4a** and **4b** this splitting is 0.10(0.11) ppm and 0.11(0.13) ppm respectively.

These results indicate that i) in solution the metal IB centres of the $[\text{M}(\text{NN}')_2]^+$ cations have a tetrahedral geometry, which is stable on the NMR time scale at low temperatures, and ii) the slow exchange limit of the process involving inversion of configuration at the metal IB centre can be reached for the silver(I) complex **3b** and the copper(I) complexes **4a** and **4b**, but not for the silver(I) complex **3a**.

For the silver(I) complex **5a** ($\text{R} = \text{H}$, $\text{R}' = (\text{S})\text{-CHMePh}$) in CD_2Cl_2 at 180 K only one ligand pattern was observed in the 250 MHz as well as the 400 MHz ^1H NMR spectrum pointing to the presence of only one diastereoisomer in solution. The spectra of the silver(I) complex **5b** in methanol- d_4 and the copper(I) complexes **6a** and **6b** in CD_2Cl_2 , however, in the slow exchange region (223 K) showed two ligand patterns in a 95/5 (**5b**), 85/15 (**6a**) and 75/25 (**6b**) intensity ratio. These data are consistent with the existence of both diastereoisomers in solution and indicate that exchange between the two diastereoisomers in the silver(I) complex **5b** and the copper(I) complexes **6a** and **6b** is in the slow exchange limit at this temperature.

In the silver(I) complexes **5a** and **5b** $^3\text{J}(\text{H}-^{107,109}\text{Ag})$ was observed on the imine-H resonances as well as on the (S)-C-H resonances. Furthermore, a $^1\text{H}\{-^{109}\text{Ag}\}$ NMR experiment as described above proved unambiguously that the doublet patterns found for the two signals in the imine proton region of **5b** are due to $^3\text{J}(\text{H}-^{107,109}\text{Ag})$ (δ 8.92, ^3J 8.0 Hz, 95%; δ 8.65, ^3J 7.7 Hz, 5%; see Fig. 2).

Dynamic Behaviour of the Complexes

The temperature dependency of the ^1H NMR spectra of the silver(I) (**3b**) and copper(I) complexes (**4a** and **4b**) containing the *i*-Pr substituent was studied in detail. In the spectra of **3b** the two doublets observed for the *i*-Pr-methyl groups coalesced to one resonance at 253 K in methanol- d_4 and 273 K in CD_2Cl_2 , while for **4a** this coalescence was observed at 270 K and 276 K in methanol- d_4 and CD_2Cl_2 respectively (see Table IV).

Coalescence of the two doublets for the copper(I) complex **4b** could not be achieved either in CD_2Cl_2 (310 K) or in methanol- d_4 (330 K). Attempts to measure spectra of **4b** at higher temperatures in tetrachloroethane- d_2 were unsuccessful, due to decomposition of the complex in this solvent. Thus it can be concluded that the cation of **4b** has a rigid structure in CD_2Cl_2 (to 310 K) and methanol- d_4 (to 330 K).

Direct information about the character of the dynamic process which causes the coalescence of the *i*-Pr-methyl-H atoms emerged from the temperature dependency of the $^3\text{J}(\text{H}^{107,109}\text{Ag})$ in the silver(I) complex **3b**. Since at 253 K in methanol- d_4 (273 K in CD_2Cl_2) the *i*-Pr methyl groups have become enantiotopic, then rapid inversion of configuration at the Ag(I) centre is taking place. However, it is the observation of unchanged $^3\text{J}(\text{H}^{107,109}\text{Ag})$ on both the imine-H and *i*-Pr-H resonances that establishes the intramolecular nature of this process (see Fig. 3). At higher temperatures these couplings disappear, resulting in a singlet imine-H and a septet *i*-Pr-H resonance. Loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ on the imine-H resonance was observed not only for **3b** (at 306 K in CD_2Cl_2 and 280 K in methanol- d_4) but also for the other silver(I) complexes, *i.e.* **1b** (200 K), **2a** (210 K), **2b** (305 K), **5a** (200 K) in CD_2Cl_2 and **5b** (260 K) in methanol- d_4 .

It may be concluded that above these temperatures an intermolecular process involving complete

Ag-pyridine-imine-ligand dissociation is taking place. This process is dependent on the bulkiness of the substituents near the Ag–N(pyridine) bonds, as well as near the Ag–N(imine) bond. This is reflected by the fact that the loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ occurs at higher temperatures for R is Me than for R is H and for R' is *c*-Hex or *i*-Pr as compared with R' is Me. Furthermore, these temperatures are neither dependent on the concentration of the pure complex nor on the magnetic field used (60, 250 or 400 MHz). This indicates that the disappearance of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ can be used as a probe for the rate of the intermolecular exchange. In an attempt to prove quantitatively the existence of both an inter- and intra-molecular exchange process in samples of **3b**, we have calculated the rates of the processes as evidenced by the loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ and coalescence of the *i*-Pr-methyl doublets respectively. The rates at coalescence temperatures were calculated using the approximate equation of Pople [12]; $k_c = (\pi/\sqrt{2})\Delta\nu$, in which $\Delta\nu$ represents the splitting in Hz of the coalescing signals measured in the slow exchange limit. The loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ is regarded as if it were coalescence of two singlets, in a symmetrical two sites problem. If this presupposition is valid the rate k_j for the intermolecular exchange, calculated with $\Delta\nu = 9.0 \text{ Hz } [^3\text{J}(\text{H}(\text{imine})^{107,109}\text{Ag})]$, amounts to 20 s^{-1} , in methanol- d_4 at 280 K as well as in CD_2Cl_2 at 306 K. The rate k_i of the process causing the isopropyl-methyl doublets to coalesce is 44 s^{-1} in methanol- d_4 at 253 K and 33 s^{-1} in CD_2Cl_2 at 273 K. These data confirm the view that $[\text{Ag}(\text{NN}')_2]^+$ cations are involved in two dynamic processes and that the intramolecular process is already faster at lower temperatures than is the intermolecular one causing the loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$.

Finally ^1H NMR experiments of the silver(I) complex **3b** in the presence of added $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ or free ligand were carried out. The ^1H NMR spectrum of **3b** (0.051 M) in the presence of

TABLE IV. Variable Temperature ^1H NMR Data (250 MHz) of the Complexes $[\text{M}(6\text{-R-py-2-CH=N-}i\text{-Pr})_2](\text{O}_3\text{SCF}_3)$ (M = Ag(I) or Cu(I), R = H or Me).

Complexes	Solvent	δ (ppm) H-im	^3J (Hz) H-im	T_c (K)	δ (ppm) <i>i</i> -Pr-CH ₃	$\Delta\nu$ (Hz) <i>i</i> -Pr-CH ₃	T_c (K)
<i>M</i> = Ag(I)							
3a (R = H)	CD_2Cl_2	8.74 s		< 180	1.30 d		< 180
3b (R = Me)	CD_3OD	8.83 d	9.0	280	1.29 d; 1.37 d	20.0	253
	CD_2Cl_2	8.67 d	9.0	306	1.25 d; 1.31 d	15.0	273
<i>M</i> = Cu(I)							
4a (R = H)	CD_3OD	8.84 s			1.15 d; 1.26 d	27.5	270
	CD_2Cl_2	8.64 s			1.11 d; 1.21 d	25.0	276
4b (R = Me)	CD_3OD	8.80 s			1.16 d; 1.29 d	32.5	> 330
	CD_2Cl_2	8.65 s			1.16 d; 1.27 d	27.5	> 310

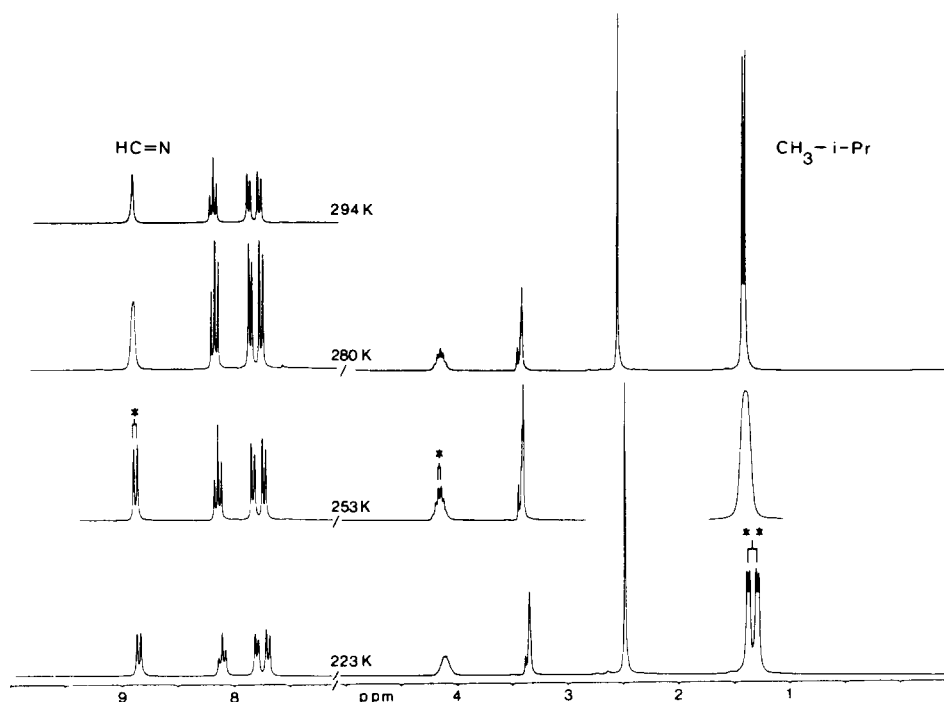


Fig. 3. ^1H NMR spectra (250 MHz) of $[\text{Ag}(6\text{-Me-py-2-CH=N-i-Pr})_2](\text{O}_3\text{SCF}_3)$ (**3b**) in methanol- d_4 .

$[\text{Ag}(\text{O}_3\text{SCF}_3)]$ (0.014 *M*) shows no $^3\text{J}(^1\text{H}-^{107,109}\text{Ag})$ on either the imine-H or the *i*-Pr-H resonances at 180 K in CD_2Cl_2 (lower temperature limit). The isopropyl-methyl groups then appear as a single doublet. These results show that already at 180 K intermolecular Ag^+ exchange is taking place, with a rate which is fast compared to the NMR time scale.

The ^1H NMR spectrum of **3b** (0.050 *M*) in the presence of an excess of free ligand (0.228 *M*) at 225 K in CD_2Cl_2 showed two well-separated ^1H patterns, one for the pure complex and one for the free ligand. At this temperature intermolecular ligand exchange is still in the slow exchange limit, as established by the observation of $^3\text{J}(^1\text{H}-^{107,109}\text{Ag})$ on the imine-H and *i*-Pr-H resonances of **3b**. However, when the temperature is increased all signals broadened and at room temperature only one ^1H pattern is present, in which the imine-H and *i*-Pr-H resonances have lost their $^3\text{J}(^1\text{H}-^{107,109}\text{Ag})$ and the isopropyl-methyl groups appear as one doublet. Accordingly, at this temperature the intermolecular ligand exchange in this 0.050 *M* **3b**/0.228 *M* ligand mixture is fast. These results show that intermolecular Ag^+ and ligand exchange processes are feasible. Moreover, from the qualitative measurements it can be seen that the intermolecular process in **3b** is proceeding faster when excess $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ is present than when excess free ligand is present.

Because of the absence of coupling information in the ^1H NMR spectra of the copper(I) complex **4a** ($\text{R} = \text{H}$, $\text{R}' = \text{i-Pr}$) it is not possible to determine

whether the observed coalescence of the *i*-Pr methyl-H doublets is caused in this complex by an intra- or an inter-molecular process. However, the higher coalescence temperatures found suggest that the copper(I) complexes are more stable than are the corresponding silver(I) complexes.

INEPT ^{15}N and ^{109}Ag NMR

For two selected silver(I) complexes, *i.e.* **3b** ($\text{R} = \text{Me}$, $\text{R}' = \text{i-Pr}$) and **5b** ($\text{R} = \text{Me}$, $\text{R}' = (S)\text{-CHMePh}$) either natural abundance ^{15}N NMR or ^{109}Ag NMR experiments were performed as part of a broader NMR study concerning the dynamic behaviour of the dinuclear silver(I) and copper(I) complexes $[\text{M}_2(\text{N}_4)_2](\text{O}_3\text{SCF}_3)_2$, mentioned in the Introduction of this paper.

^{109}Ag NMR spectra of **5b** were recorded using the INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) sequence. The $^{109}\text{Ag}-^1\text{H}$ coupled spectrum showed two resonances at $\delta + 636$ and $\delta + 612^*$ (Fig. 4) in a 95/5 intensity ratio respectively which corresponds to the intensity ratio of the two ^1H NMR resonance patterns (Fig. 2). Accordingly, the two ^{109}Ag resonances correspond to the respective ^{109}Ag centres in the two diastereoisomers $\Delta(S)(S)$ and $\Lambda(S)(S)$. The triplet fine structure on each signal was deduced to be due to a small $^3\text{J}(^{109}\text{Ag}-^1\text{H})$ with the $(S)\text{-C-H}$ protons from the results of a selective $(S)\text{-}$

*A positive δ corresponds with a higher resonance frequency ('deshielding') with respect to the reference frequency.

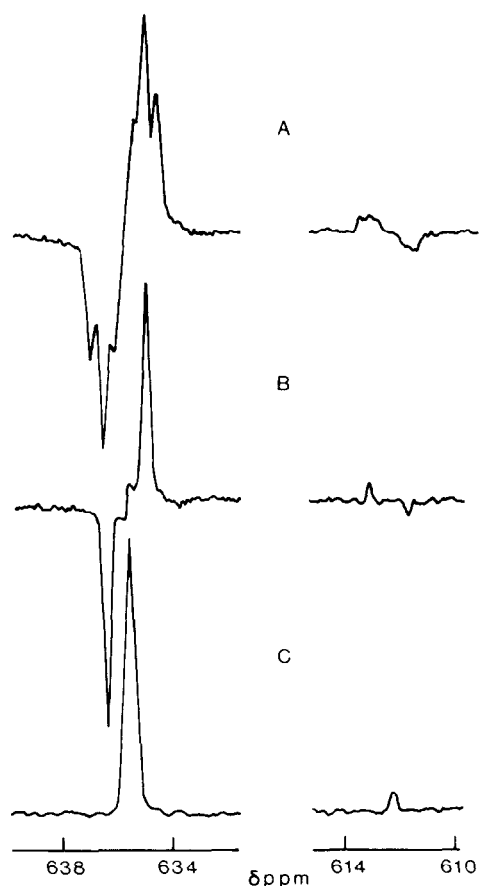


Fig. 4. INEPT ^{109}Ag NMR spectra of $[\text{Ag}(\text{6-Me-py-2-CH=N-(S)-CHMePh})_2](\text{O}_3\text{SCF}_3)$ (**5b**) in methanol- d_4 at 223 K. A, ^1H coupled; B, $^1\text{H}[(\text{S})\text{-C-H}]$ selectively decoupled and C, ^1H decoupled (BB).

C–H heterodecoupling INEPT ^{109}Ag NMR experiment.

Natural abundance ^{15}N NMR spectra were measured in methanol- d_4 at various temperatures using the INEPT method. The spectrum of **3b** ($\text{R} = \text{Me}$, $\text{R}' = i\text{-Pr}$), which is temperature-dependent, showed two resonances; $\delta = -62$ and $\delta = -101^*$ at 248 K. Based on a comparison of these data with those of $[\text{Ag}_2(\text{N}_4)_2]^{2+}$ (see Introduction) we have assigned the downfield resonance to the ^{15}N -imine atoms and the upfield to the ^{15}N -pyridine atoms. Both signals at this temperature appeared as a doublet of doublets. Broadband $^{15}\text{N}\{-^1\text{H}\}$ measurements proved that the small coupling on each resonance is due to $^n\text{J}(^{15}\text{N}-^1\text{H})$ [**1a**] and therefore the larger couplings, *i.e.* 42 Hz (imine- ^{15}N) and 25 Hz (pyridine- ^{15}N), are caused by $^1\text{J}(^{15}\text{N}-^{107,109}\text{Ag})$. When the temperature was increased the spectra first showed around 286 K a broadening of the pyridine- ^{15}N signal with disap-

pearance of the $^1\text{J}(^{15}\text{N}-^{107,109}\text{Ag})$ (25 Hz), while the imine- ^{15}N resonance remained unchanged. At 308 K the pyridine- ^{15}N resonance had become a sharp doublet [$^n\text{J}(^{15}\text{N}-^1\text{H})$] while the imine ^{15}N resonance was now a broad doublet on which $^1\text{J}(^{15}\text{N}-^{107,109}\text{Ag})$ (42 Hz) was lost. Finally, sharp doublets for both the pyridine- and imine- ^{15}N atoms were observed above 308 K. The disappearance of $^1\text{J}(^{15}\text{N}-^{107,109}\text{Ag})$ at higher temperatures is in line with the conclusions drawn from the ^1H NMR spectra of **3b**, namely that above 280 K (in methanol- d_4) an intermolecular process involving complete Ag–ligand dissociation (*vide supra*) is taking place.

Discussion

In the present study we have shown that both the copper(I) and silver(I) complexes $[\text{M}(\text{6-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3)$ can be easily prepared by a direct method which involves the reaction of the pure metal IB trifluoromethanesulfonate salts $[\text{M}(\text{O}_3\text{SCF}_3)]$ with two equivalents of the pyridine-imine ligands in either benzene or methanol.* For the preparation of the copper(I) complexes rigorous exclusion of oxygen from the reaction mixture was necessary because $[\text{Cu}(\text{O}_3\text{SCF}_3)]$ is easily oxidized.

The analytical and spectroscopic data establish that the compounds exist in the solid state as well as in solution as $[\text{M}(\text{NN}')_2]^+$ cations and trifluoromethanesulfonate anions. It is known that the nature of the counterion plays an important role in determining the stability of the copper(I) complexes, for example halides stabilize dinuclear complexes with a 1/1 copper/ α -diimine ratio by forming bridge bonds [15]. For this reason we selected the O_3SCF_3^- anion as a counterion in our complexes. In earlier studies this counterion was likewise used rather than BF_4^- or ClO_4^- [1].

The copper(I) complexes reported in this study belong to the larger group of cationic 1/2 copper(I) complexes with α -diimine ligands, which contain the $\text{N}=\text{C}-\text{C}=\text{N}$ moiety [16]. Knowledge that 1/2 copper(I)/ α -diimine complexes can be formed has been used for a long time for the colorimetric determination of copper(I) ions in solution [17]. Recently there has been a renewed interest in the study of these copper(I) complexes because they are prone to photo-induced redox reactions, a property which may be of importance for storage of solar energy. For this reason Leupin and Schläpfer [13] have studied the resonance Raman spectra of copper(I) complexes with various α -diimine ligand systems.

*A positive δ corresponds with a higher resonance frequency ('deshielding') with respect to the reference frequency.

*The complexes Leupin and Schläpfer [13] and others [14] have investigated have been prepared by the reaction of $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ with Cu powder in CH_3CN with two equivalents of the α -diimine ligands.

According to our knowledge silver(I) complexes of these ligand systems have not been reported before. It appeared that in the case of the pyridine-imine ligands used in our study, not only the Cu(I) but also the Ag(I) complexes are accessible. This is important because of the fact that both silver isotopes, ^{107}Ag and ^{109}Ag have $I = 1/2^*$ and this allows a detailed NMR study of intermolecular metal or ligand exchange processes. In view of the similarity of the coordination properties of the IB metals the silver(I) complexes may then serve as models in the study of the dynamic processes involving the corresponding copper(I) complexes.

Structures of the $[M(\text{NN}')_2](\text{O}_3\text{SCF}_3)$ Complexes in the Slow Exchange Limit

The ^1H NMR spectra of the cationic silver(I) and copper(I) complexes $[\text{M}(6\text{-R-py-2-CH=N-R}')_2](\text{O}_3\text{SCF}_3)$ in which R' is either the prochiral *i*-Pr or the chiral (*S*)-CHMePh grouping, establish unambiguously that in solution the metal IB centres in these cations have tetrahedral geometries, *i.e.* Δ or Λ configuration, in the slow exchange limit.

The cations in which R' is (*S*)-CHMePh can exist in two diastereomeric forms which have either $\Delta(\text{S})$ -(*S*) or $\Lambda(\text{S})$ -(*S*) configurations. It is interesting to see that ^{109}Ag NMR is a very powerful tool for the detection of these diastereoisomers in solution. Particularly important for further applications (*cf.* ref. 1b) is the observation that relatively large chemical shifts (*i.e.* 24 ppm for **5b**) correspond with only small stereochemical changes in the surrounding of the ^{109}Ag (I) centres in the two diastereoisomers.

The different intensities of the ^1H NMR patterns of the cations of **5b** (95/5), **6a** (85/15) and **6b** (75/25) as well as of the two signals observed in the ^{109}Ag NMR spectrum of **5b** (95/5) point to a distinct difference in stability of the $\Delta(\text{S})$ -(*S*) and $\Lambda(\text{S})$ -(*S*) diastereomers, which may be due to the difference in steric repulsions between the (*S*)-CHMePh groupings of the two chelate bonded pyridine-imine ligands in each of the diastereomers (see Fig. 5).

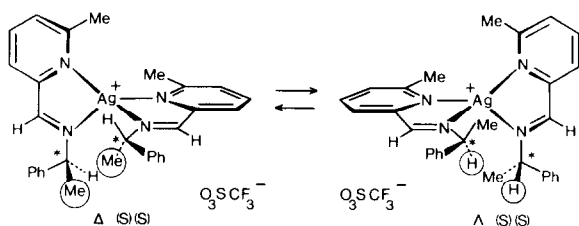


Fig. 5. The two diastereoisomers of $[\text{Ag}(6\text{-Me-py-2-CH=N-(S)-CHMePh})_2](\text{O}_3\text{SCF}_3)$ (**5b**).

This can be best illustrated by considering the possible rotamer conformers of the imine-N-C bond. The population of the rotamer states will be determined to a great extent by the mutual position of the phenyl groups in the cations. The most likely situation is the one in which the phenyl groups are pointing away from each other. Consequently in the $\Lambda(\text{S})$ -(*S*) isomer the two small H-atoms are in close contact whereas in the $\Delta(\text{S})$ -(*S*) isomer there is a less favourable interaction between two methyl groups; this suggests that the more abundant diastereomer has the $\Lambda(\text{S})$ -(*S*) configuration. However, it must be noted that according to the Boltzmann population distribution the energy difference between the ground states of the diastereoisomers is very small. This indicates that the difference in steric repulsions between the (*S*)-CHMePh groups in $\Delta(\text{S})$ -(*S*) and $\Lambda(\text{S})$ -(*S*) is also very small.

Comparison of the diastereomeric ratios of the silver(I) and copper(I) complexes suggests that the preference for the $\Lambda(\text{S})$ -(*S*) isomer is slightly larger in the case of the silver(I) cations. A possible explanation of this difference can be found in the slightly altered geometry of the Cu complexes. There is for example an indication of stronger Cu-N(pyridine) interactions in the large upfield shift (δ 1.28) of the 6-Me resonance of the 75% abundant isomer of **6b**. This upfield shift is caused by a ring current of a nearby situated pyridine ring of the second ligand in this isomer. As a result the imine-N substituents, R' , are placed at a slightly longer distance from each other in the Cu(I) cations than in the $[\text{Ag}(\text{NN}')_2]^+$ cations. Accordingly, the steric interactions of the two (*S*)-CHMePh groups, which are considered as the origin of the difference in stability of the diastereoisomers, is decreased.

Dynamic Behaviour of the $[M(\text{NN}')_2](\text{O}_3\text{SCF}_3)$ Complexes in Solution

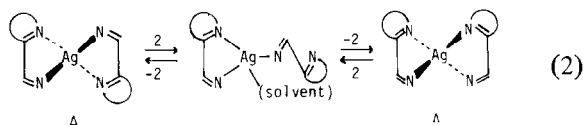
Various $[\text{M}(\text{NN}')_2](\text{O}_3\text{SCF}_3)$ complexes reported in this paper show temperature-dependent ^1H (and ^{15}N) NMR spectra which evidence the occurrence of exchange processes in the tetrahedral $[\text{M}(\text{NN}')_2]^+$ cations. In the case of the silver(I) complex **3b** it could be established that intramolecular as well as intermolecular processes are taking place. The intramolecular exchange process involves inversion of configuration of the silver(I) centre (see Results). This may proceed *via i*) a four coordinate transition state in which both the chelate bonded pyridine-imine ligands and the silver(I) centre are in one plane or *via ii*) a three-coordinate species in which one of the ligands is monodentate-coordinated as a result of Ag-N bond dissociation. These possible routes are similar to those proposed by Holm *et al.* [18] for the intramolecular exchange processes in which the neutral, tetrahedral bis(β -aminothionato)zinc(II) complexes take part.

*See footnote**, p. 30.

On the basis of steric arguments we can exclude the possibility that the intramolecular exchange in the $[\text{Ag}(\text{NN}')_2]^+$ cations proceeds without Ag–N bond breaking, *i.e.* via a planar transition state containing two chelate bonded pyridine-imine ligands (process *i*, see above). Such planar states become particularly unlikely when the cations contain the 6-Me substituent. We have shown earlier that otherwise kinetically-unstable five-coordinate pyridine-imine olefin dichloro platinum(II) complexes can be stabilized by destabilizing the four coordinate planar pyridine-imine dichloro platinum(II) product by using pyridine-imine ligands with the 6-Me substituent [19].

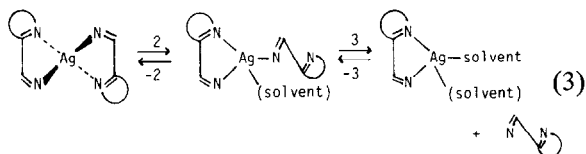
All the present evidence favours an intramolecular process for **3b** that involves initial Ag–N(pyridine) bond dissociation. This latter bond breaking results in formation of a silver(I) intermediate containing one chelate bonded and one monodentate bonded ligand (*cf.* process *ii*). Such Ag–N(pyridine) bond dissociation is considered more likely than breaking of the Ag–N(imine) bond from a comparison of the $^1\text{J}(\text{N}^{107,109}\text{Ag})$ values found for the silver(I) complex **3b**; *i.e.* $^1\text{J}(\text{N}^{107,109}\text{Ag}) > ^1\text{J}(\text{N}^{107,109}\text{Ag})$ (pyridine)– $^{107,109}\text{Ag}$. In this respect it is important to note that the metal IB centres in the complexes studied are in a formal oxidation state of one and have a closed, d^{10} , valence shell and therefore use mainly *s* and *p* type orbitals for binding the ligands. When this is taken into account a correlation between $^1\text{J}(\text{N}^{107,109}\text{Ag})$ values and N–Ag(I) bond strengths does not seem to be *a priori* excluded. Accordingly, a large ^1J value would indicate a more efficient participation of *s* orbital density in the N–Ag(I) bonding [20]. For the bonding of the similarly hybridized (sp^2) N(pyridine) and N(imine) donor atoms to silver(I) these ^1J values then suggest that the isochronous imine–N sites are more strongly bonded than are the pyridine–N sites.

The inversion of configuration at silver(I), caused by the intramolecular process, is thought to occur by rotation around the Ag(I)–N(imine) bond of the monodentate-bonded pyridine-imine ligand. Reformation of the Ag–N(pyridine) bond then may lead to either inversion or retention of configuration at the Ag(I) centre (see eqn. 2). The difference in temperature at which in **3b** the coalescence of the *i*-Pr-methyl doublets in methanol- d_4 (253 K) and CD_2Cl_2 (273 K) takes place is evidence that this exchange may be solvent (or counterion, O_3SCF_3^-) assisted.

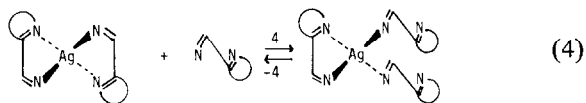


A possible route for the intermolecular exchange process which was found to be slower than the intra-

molecular process starts with an initial Ag–N(pyridine) bond dissociative step similar to the one proposed for the intramolecular process. This may be followed by complete dissociation of one ligand as shown in eqn. 3:



In the reverse reaction the $[\text{Ag}(\text{NN}')_2]^+$ cation is obtained. The involvement of a possible associative route (eqn. 4) must also be considered in this discussion. When the dissociated ligand in (3) (or free added ligand) attacks a $[\text{Ag}(\text{NN}')_2]^+$ cation it is possible to form a four coordinate intermediate, containing one bidentate and two monodentate pyridine-imine ligands.



Dissociation of one of the monodentate bonded ligands may result in ligand exchange. In this associative mechanism it can be seen that bulky substituents at the imine–N (R') and near the pyridine–N (R) sites will make it more difficult for a free ligand to approach the metal IB centre. This is consistent with the observation of an increase of the temperature at which the loss of $^3\text{J}(\text{H}^{107,109}\text{Ag})$ occurs on going from R is H to R is Me and from R' is Me to R' is *c*-Hex and *i*-Pr. Therefore, it may be assumed that for this intermolecular process an associative step is rate determining.

In the presence of $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ the rate of the intermolecular exchange is increased considerably. The external Ag^+ (or $[\text{Ag}(\text{O}_3\text{SCF}_3)]$) ion presumably attacks one free pyridine–N donor site and starts the exchange process.

The results show that the silver(I) complexes are less stable than the corresponding copper(I) complexes. Since the mechanisms discussed all involve M–N bond cleavage the reason for the stability of the copper(I) complexes may be explained by assuming that Cu(I)–N bonds and especially Cu(I)–N(pyridine) bonds are stronger than the corresponding Ag(I)–N bonds.

The smaller ionic radius of copper(I) gives rise to a contraction of the structure of the $[\text{M}(\text{NN}')_2]^+$ cation, which makes it difficult not only for rotation around one Cu–N bond in an intramolecular process, but also for dissociated ligands to approach the metal IB centre in the associative step of an intermolecular process. Such a contraction has been observed before

in the silver(I) and copper(I) structures $[M(N_2S_2)_2]-(O_3SCF_3)$ ($N_2S_2 = (R)(S)$ -1,2-(5-Me-thiophene-2-CH=N)₂-cyclohexane) [21]. When all these factors are taken together it is not surprising that the copper(I) complexes are less prone to fluxional processes as compared with the corresponding silver(I) complexes.

Conclusions

From the reactions of $[M(O_3SCF_3)]$ [$M = Ag(I)$ or $Cu(I)$] with two equivalents of the pyridine-imine ligands, 6-R-py-2-CH=N-R', complexes were obtained, consisting of a $[M(NN')_2]^+$ cation and a $O_3SCF_3^-$ anion.

¹H NMR spectra of the complexes which contain the prochiral i-Pr or chiral (S)-CHMePh substituents (R') show that the metal IB centres have tetrahedral geometries in the slow exchange limit. Accordingly these metal centres are coordinated by two chelate bonded pyridine-imine ligands and have either Δ or Λ configurations.

The ¹H NMR spectra of the complexes with R' is (S)-CHMePh revealed a large preference for one of the two, Δ(S)(S) and Λ(S)(S) diastereomeric forms. Based on steric arguments it was concluded that the most stable isomer is the Λ(S)(S). Because of the presence of resolved ³J(¹H-^{107,109}Ag) in the ¹H NMR spectra of the silver(I) complexes it was possible to record INEPT ¹⁰⁹Ag NMR spectra. The spectra of the silver(I) complex with R is Me and R' is (S)-CHMePh showed a large chemical shift difference (24 ppm) between the two resonances representing the silver(I) centres of the diastereoisomers. This demonstrates that ¹⁰⁹Ag NMR is a suitable technique for studying silver(I) centres in diastereomeric complexes because of the sensitivity of chemical shift values to the Ag(I) coordination sphere.

Variable temperature ¹H NMR spectra of the complexes with R' is i-Pr showed the occurrence of exchange processes. For the silver(I) complex with R is Me the occurrence of both an intramolecular and an intermolecular exchange process was established. The intramolecular process probably involved inversion of configuration of the silver(I) centre *via* an intermediate in which one ligand coordinates as a bidentate and one as a monodentate with the imine-N site. The intermolecular process, which is slower, could be detected by the loss of ³J(¹H-^{107,109}Ag) in the ¹H NMR and ¹J(¹⁵N-^{107,109}Ag) in the ¹⁵N NMR spectra of this silver(I) complex (R is Me, R' is i-Pr). The rates of these processes depend on the bulkiness of the substituents R and R'. The more bulky these substituents the slower are these processes. Moreover, the corresponding copper(I) complexes are more stable because of stronger Cu-N bonds and because of the smaller ionic radius of copper(I) which causes a contraction of the structure of the $[M(NN')_2]^+$

cation. However, because of the lack of coupling information in the spectra of the copper(I) complexes it was not possible to determine the nature of the observed process in the ¹H NMR spectra of the copper(I) complex with R is H and R' is i-Pr. The complex with R is Me and R' is i-Pr was rigid up to 310 K in CD₂Cl₂ and 330 K in methanol-d₄ (upper temperature limits in these solvents).

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