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Structural Investigations of Silver(I) and Copper(I) Complexes with Neutral N_4 Donor Ligands: X-ray Crystal and Molecular Structure of the Dimer $[Ag_2\{\mu\text{-}(R,S)\text{-}1,2\text{-}(py\text{-}2\text{-}CH{=}N)_2Cy\}_2](O_3SCF_3)_2$ and ^1H, ^{13}C, and INEPT ^{109}Ag and ^{15}N NMR Solution Studies

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Abstract: The reactions of the neutral N_4 donor system (R,S)-1,2-(6-R-py-2-CH=N)$_2$Cy (R = H or Me, Cy = cyclohexane) with $[M(O_3SCF_3)]$ (M = Ag(I) or Cu(I)) yielded ionic complexes, consisting of a dinuclear $[M_2(N_4)_2]^{2+}$ dication and $O_3SCF_3^-$ monoanions. An X-ray crystallographic study defined the molecular structure of $[Ag_2\{\mu\text{-}(R,S)\text{-}1,2\text{-}(py\text{-}2\text{-}CH{=}N)_2Cy\}_2](O_3SCF_3)_2$ as monoclinic, space group $P2_1/c$, a = 10.412 (2) Å, b, = 33.310 (8) Å, c = 13.197 (2) Å, β = 105.38 (2)°, and Z = 4, for 3092 independent reflections. The structure was refined to R = 6.7. The two N_4 ligands coordinate to the silver(I) centers as dibidentates with alternating short Ag–N(imine) [Ag(1)–N(2), 2.251 (11) Å; Ag(2)–N(6), 2.240 (12) Å] and Ag–N(pyridine) [Ag(1)–N(8), 2.242 (11) Å; Ag(2)–N(4), 2.252 (13) Å] and two longer Ag–N(imine) [Ag(1)–N(7), 2.440 (11) Å; Ag(2)–N(3), 2.430 (11) Å] and Ag–N(pyridine) distances [Ag(1)–N(1), 2.455 (12) Å; Ag(2)–N(5), 2.429 (11) Å]. The silver(I) centers have distorted tetrahedral geometries and lie in a distance of 3.254 (2) Å of each other. The structures of these metal 1B complexes in solution have been studied by multinuclear ^1H, ^{13}C, ^{15}N, and ^{109}Ag NMR spectroscopy. The ^1H and ^{13}C NMR (room temperature) results revealed by the presence of two nonequivalent pyridine imine moieties that (i) the structural features found for the $[Ag_2(N_4)_2]^{2+}$ dication in the solid are retained in solution and (ii) the silver(I) and copper(I) complexes have similar structures in solution. The imine proton resonances in the ^1H NMR spectra of the silver(I) complexes have been split due to $^3J(^1H\text{-}^{107,109}Ag)$ couplings which enabled the application of INEPT ^{109}Ag NMR. The δ ^{109}Ag appeared to be very sensitive with regard to the ligand environment (e.g., $\Delta\delta$ ^{109}Ag for $[Ag_2(N_4)_2]^{2+}$ with R = H and R = Me is 32 ppm). Natural abundance INEPT ^{15}N NMR spectra of the silver(I) complexes unambiguously established through the ^{15}N chemical shift and the $^1J(^{15}N\text{-}^{107,109}Ag)$ values that the characteristic sequence of Ag–N distances found in the solid is also present in the solution structures of these dications.

Coordination chemistry of copper(I) salts with polydentate ligands has become an important research area with respect to the search for model compounds that can either mimic or even ideally duplicate one or more of the important specific physical and chemical properties of copper proteins, in which the metal center exists in the reduced Cu(I) state. The structural features of certain of these copper(I) coordination complexes have been studied in the solid state by X-ray methods, and species having either 2-, 3-, or 4-coordinate Cu(I) centers have been determined.[1] It has been found that special polydentate ligands with rigid stereochemistry can even stabilize a square-pyramidal 5-coordinate geometry of copper(I) (20-electron complexes).[2]

Surprisingly it has not been determined whether the structural features of these copper(I) complexes are retained in solution. In our opinion such information is crucial when a rationale for the reactivity of a certain copper(I) center or a set of copper(I) centers is based on particular conformational and configurational features of the copper(I)–polydentate complex. We have now set out to study this aspect in particular by synthesizing copper(I) complexes with the neutral N_4 and N_2S_2 donor ligand systems schematically represented in Figure 1 and investigating the structural features and reactivities of these complexes both in the solid and in solution. These systems were selected because they allow a study of the influence of both the conformation of the hydrocarbon chain (R′) connecting the two ligating (-N=C—C=N- or -S=C—C=N-) moieties and the nature of the heteroatoms, N and S, on the mode of coordination. In general it can be anticipated that such ligands coordinate in either a quadridentate or a dibidentate manner. (This subject has been discussed already in a preliminary communication.[3])

Furthermore, throughout this comparative study we have chosen to use the trifluoromethanesulfonate anion ($O_3SCF_3^-$) in order to minimize anion coordination and thereby to achieve exclusively coordination of the polydentate ligand to the metal 1B monocation center. Moreover, the $O_3SCF_3^-$ anion itself is very stable and as a result of its cylindrical structure and low dipole moment is very suitable when anion–cation complexes are desired.[4]

In contrast to copper(II) complexes, for which the metal properties can be studied exclusively by EPR and UV spectroscopic techniques, copper(I) complexes can be studied by NMR spectroscopy to provide information concerning the polydentate ligand

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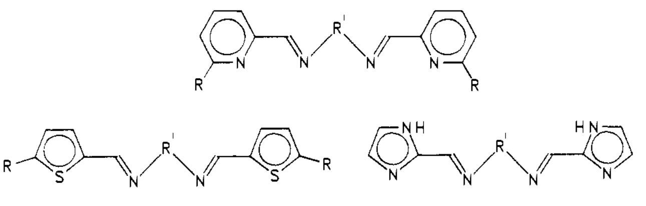

Figure 1. Schematic representation of (6-R-py-2-CH=N)$_2$R' (top), (5-R-thiophene-2-CH=N)$_2$R' (bottom left), and (imidazole-2-CH=N)$_2$R' (right).

skeleton. However, the d^{10} copper(I) center itself has no easy spectroscopic "handle". As a result of the large quadrupole moment of both ^{63}Cu and ^{65}Cu (both $I = {}^3/_2$, natural abundances 69.09% and 30.91%, respectively) Cu NMR is not applicable for obtaining detailed information about the direct coordination sphere around the metal center.[5] For this reason we also included in our studies the corresponding silver(I) complexes. Silver exists with two isotopes, ^{107}Ag and ^{109}Ag (natural abundances 51.82% and 48.18%, respectively), both having $I = {}^1/_2$ and therefore seems to be excellent for studying metal 1B properties. A drawback is the low γ values which, however, as we have demonstrated,[6] can be overcome by making novel use of the INEPT pulse sequence for observing these metal nuclei.

Morris and Freeman[7] have shown that by using the INEPT sequence one can expect a large gain in sensitivity and experimental time saving by using the polarization transfer scheme when measuring $I = {}^1/_2$ nuclei with low γ values. In fact for a X–H system, this sensitivity gain amounts to γ_H/γ_X and the repetition time of the accumulated spectra is only dependent upon the T_1^H relaxation time, which is in general much shorter than the T_1^X relaxation time. Of course, this sequence can be used only if a scalar ^nJ(X–H) coupling is present and it is the value of this coupling which defines the refocalizing time τ as $\tau = (4J)^{-1}$. Up to now the INEPT sequence has been utilized mainly with ^1J(X–H) couplings (X = ^{13}C,[7,8] ^{15}N[9]) and ^2J(X–H) (X = ^{29}Si and ^{119}Sn[10]).

Our recent results have demonstrated the power of the sequence to obtain ^{109}Ag spectra via {^{1}H}–^{109}Ag INEPT NMR using ^3J(^{1}H–^{107,109}Ag).[6,11] Finally it must be noted that an important prerequisite for the use of these silver(I) complexes as models for the corresponding copper(I) complexes is that the structural features of the Cu^I and Ag^I complexes are comparable.

In this paper we report the synthesis and structural characterization in the solid and in solution of copper(I) and silver(I) complexes of the N$_4$ donor ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (R = H, **1a**; R = Me, **1b**). The X-ray crystal and molecular structure of [Ag$_2${μ-(*R*,*S*)-1,2-(py-2-CH=N)$_2$Cy}$_2$](O$_3$SCF$_3$)$_2$ containing dibidentate bonded N$_4$ ligands will be discussed. Furthermore it will be shown that in addition to ^{1}H and ^{13}C NMR, application of INEPT ^{109}Ag NMR, which we recently developed,[6] as well as (natural abundance) INEPT ^{15}N NMR provides important information concerning the structure in solution.

Strong evidence is obtained that these copper(I) and silver(I) compounds have similar structures in the solid and in solution.

Experimental Section

Preparation of the Compounds. All reactions were carried out under a nitrogen atmosphere in freshly distilled solvents. Pyridine-2-carbaldehyde, 6-methylpyridine-2-carbaldehyde, and silver(I) trifluoromethanesulfonate are commercially available. Copper(I) trifluoromethanesulfonate–$^1/_2$-benzene was prepared as described in the literature.[12] Pure (*R*,*S*)-1,2-diaminocyclohexane was separated from the commercially available mixture of cis [(*R*,*S*)] and trans [(*R*,*R*),(*S*,*S*)] isomers via the method described in ref 13. Elemental analyses were carried out by the Analytical section of the Institute for Organic Chemistry, T.N.O., Utrecht (The Netherlands).

(*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (R = H, 1a, or Me, 1b). A solution of 10 mmol of (*R*,*S*)-1,2-diaminocyclohexane in diethyl ether was slowly added to a solution of 20 mmol of 6-R-pyridine-2-carbaldehyde (R = H or Me) in diethyl ether at room temperature. The solution was stirred for 19 h, dried with Na$_2$SO$_4$, and filtered. The filtrate was evaporated at low pressure, affording a light yellow powder for **1a** (R = H) and an oily product for **1b** (R = Me). The latter was purified by distillation in vacuo, and **1a** could be crystallized from diethyl ether at 233 K. Yields of **1a** and **1b** were 70–80%.

[Ag$_2${μ-(*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy}$_2$](O$_3$SCF$_3$)$_2$ (R = H, 2a, or Me, 2b). To a solution of [Ag(O$_3$SCF$_3$)] (2 mmol) in methanol (10 mL) a solution of **1a** or **1b** (2 mmol) in methanol was added. The reaction mixture was stirred for 15 min. Pale yellow solids **2a** and **2b** were obtained by evaporation of the solvent. When a small excess of free ligands was used, the solids were washed with diethyl ether (3 × 10 mL) and crystallized from methanol. Anal. Calcd for C$_{19}$H$_{20}$AgF$_3$N$_4$O$_3$S (**2a**): C, 41.54; H, 3.67; F, 10.38; N, 10.20. Found: C, 41.17; H, 3.72; F, 10.11; N, 10.12. Calcd for C$_{21}$H$_{24}$AgF$_3$N$_4$O$_3$S (**2b**): C, 43.69; H, 4.19; F, 9.87; N, 9.70. Found: C, 43.69; H, 4.27; F, 9.22; N, 9.68.

[Cu$_2${μ-(*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy}$_2$](O$_3$SCF$_3$)$_2$ (R = H, 3a, or R = Me, 3b). A solution of 2 mmol of **1a** or **1b** in benzene (10 mL) was added to a solution of 2 mmol of [Cu(O$_3$SCF$_3$)]·$^1/_2$C$_6$H$_6$ in benzene (10 mL), resulting in immediate precipitation of the complexes. The brown suspensions were stirred for 15 min, and the solution was then decanted off. The precipitates were washed with benzene and dried in vacuo at 330 K. The complexes (**3a**, **3b**) were crystallized from a methanol–diethyl ether mixture (2:1 v/v). Yields of **3a** and **3b** were 80–90%. Anal. Calcd for C$_{19}$H$_{20}$CuF$_3$N$_4$O$_3$S·H$_2$O (**4a**): C, 43.64; H, 3.86; F, 10.90; N, 10.71. Found: C, 43.63; H, 3.94; F, 10.65; N, 10.70. Calcd for C$_{21}$H$_{24}$CuF$_3$N$_4$O$_3$S·H$_2$O (**4b**): C, 45.82; H, 4.72; F, 10.35; N, 10.18. Found: C, 45.80; H, 4.39; F, 10.45; N, 10.15.

Physical Measurements. Infrared (IR) spectra were measured on a Perkin-Elmer 283 spectrophotometer as KBr pellets. IR spectra were also measured on a Nicolet Model 7199B FT-IR spectrometer with a liquid N$_2$ cooled MCT detector and a resolution of 1 cm^{-1} as liquid films in methanol between AgCl windows with subtraction of the methanol spectrum (IR data in Table SI deposited as supplementary material).

The ^{1}H NMR spectra were recorded on Varian T-60, XL-100, and Bruker WM 250 spectrometers with tetramethylsilane (Me$_4$Si) as reference (Table III). ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer (Table IV). ^{19}F NMR data were obtained with a Varian XL-100 (CW) apparatus with CFCl$_3$ as external reference.

Natural abundance ^{15}N NMR spectra were recorded on Bruker WM 250 and WM 400 spectrometers (25.35 and 40.56 MHz, respectively) applying the INEPT sequence (insensitive nuclei enhanced by polarization transfer[7]) [$90°_{H,x}–\tau–180°_{H,x}$, $180°_{M,x}–\tau–90°_{H,y}$, $90°_{M,x,x,-x,-x}$ acquire] or with ^{1}H (BB) decoupling [$90°_{H,x}–\tau–180°_{H,x}$, $180°_{M,x}–\tau–90°_{H,y}$, $90°_{M,x,x,-x,-x}–\Delta–$(BB) acquire] with $\tau = (4J)^{-1}$, $\Delta = (4J)^{-1}$, $90°_H = 35$ μs (48 μs), $90°_N = 50$ μs (35 μs) on 250 MHz (400 MHz). The ^{15}N NMR spectra were recorded in the FT mode with quadriture detection from solutions of **1a**, **1b** and **2a**, **2b** in methanol-d_4 (50 mg/mL) at 294 K using 10-mm tubes with MeNO$_2$ in C$_6$D$_6$ 80:20 v/v as external reference (for data see Table V). The number of scans was in the order of 4000 for the spectra of the free ligands **1a** and **1b** and 40 000 for the spectra of the silver(I) complexes. As J(^{15}N–^{1}H) is the driving coupling in the INEPT experiment, the sum of the expected values for the ^nJ(^{15}N–^{1}H) couplings ($n > 1$) in the molecules was taken. Hence the refocalizing time τ was chosen as 7 ms. Selective proton decoupling experiments were preformed, i.e., after the ^{1}H–^{15}N polarization transfer during ^{15}N FID acquisition.

INEPT ^{109}Ag NMR spectra were recorded on a Bruker WM 250 spectrometer (using the same solutions of **2a** and **2b** as for the ^{15}N NMR measurements) at 295 K with AgNO$_3$, 2 M in D$_2$O, as external reference. The acquisition time was 1.364 s and the delay time 0.7 s. The number of scans was in the order of 10 000.

Crystal data. (C$_{19}$H$_{20}$AgF$_3$N$_4$O$_3$S)$_2$ (**2a**), M_r = 1098.7, monoclinic, space group $P2_1/c$, $Z = 4$, a = 10.412 (2) Å, b = 33.310 (8) Å, c = 13.197 (2) Å, β = 105.38 (2)°; V = 4413.0 Å^3, D_{obsd} = 1.65 g/cm^3 (by flotation in 1,2-dibromoethane and CCl$_4$), D_{calcd} = 1.654 g/cm^3. The structure determination was carried out with 3092 independent reflections

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Table I. Positional Parameters and Their ESD (in Parentheses) for $(AgC_{19}H_{20}N_4F_3SO_3)_2$[a]

atom	*x/a*	*y/b*	*z/c*
F(1)	0.085 (1)	0.4695 (4)	0.079 (1)
F(2)	−0.034 (1)	0.4230 (4)	0.0242 (9)
F(3)	−0.103 (1)	0.4688 (3)	0.1081 (8)
F(4)	0.718 (1)	0.3502 (3)	0.1716 (9)
F(5)	0.793 (1)	0.2950 (4)	0.2296 (9)
F(6)	0.701 (1)	0.3309 (4)	0.3216 (8)
Ag(1)	0.2721 (1)	0.41845 (4)	−0.3563 (1)
Ag(2)	0.1097 (1)	0.34774 (4)	−0.2732 (1)
S(1)	0.0764 (4)	0.4197 (1)	0.2210 (3)
S(2)	0.5370 (4)	0.2955 (1)	0.1604 (3)
O(1)	0.121 (1)	0.4504 (4)	0.2913 (9)
O(2)	0.172 (1)	0.3957 (4)	0.197 (1)
O(3)	−0.031 (1)	0.3995 (5)	0.240 (1)
O(4)	0.552 (1)	0.2846 (4)	0.0617 (9)
O(5)	0.445 (1)	0.3280 (4)	0.155 (1)
O(6)	0.524 (1)	0.2646 (3)	0.2290 (9)
N(1)	0.362 (1)	0.4867 (4)	−0.352 (1)
N(2)	0.110 (1)	0.4626 (3)	−0.3524 (8)
N(3)	−0.009 (1)	0.3847 (3)	−0.4285 (8)
N(4)	0.120 (1)	0.3104 (4)	−0.413 (1)
N(5)	−0.027 (1)	0.3194 (3)	−0.1675 (8)
N(6)	0.213 (1)	0.3620 (3)	−0.1056 (9)
N(7)	0.405 (1)	0.3709 (3)	−0.2307 (9)
N(8)	0.365 (1)	0.3754 (3)	−0.4469 (8)
C(1)	0.496 (1)	0.4994 (5)	−0.340 (1)
C(2)	0.533 (2)	0.5356 (5)	−0.303 (1)
C(3)	0.453 (2)	0.5620 (6)	−0.271 (1)
C(4)	0.324 (1)	0.5495 (5)	−0.282 (1)
C(5)	0.283 (1)	0.5120 (4)	−0.321 (1)
C(6)	0.142 (1)	0.4991 (4)	−0.335 (1)
C(7)	−0.031 (1)	0.4528 (4)	−0.3577 (9)
C(8)	−0.041 (1)	0.4393 (4)	−0.250 (1)
C(9)	−0.186 (1)	0.4304 (5)	−0.255 (1)
C(10)	−0.249 (1)	0.4008 (5)	−0.340 (1)
C(11)	−0.233 (1)	0.4135 (5)	−0.446 (1)
C(12)	−0.084 (1)	0.4224 (4)	−0.442 (1)
C(13)	−0.002 (1)	0.3655 (4)	−0.512 (1)
C(14)	0.067 (1)	0.3272 (4)	−0.508 (1)
C(15)	0.077 (1)	0.3102 (5)	−0.601 (1)
C(16)	0.139 (2)	0.2742 (5)	−0.598 (1)
C(17)	0.196 (2)	0.2577 (5)	−0.502 (1)
C(18)	0.183 (1)	0.2764 (5)	−0.412 (1)
C(19)	−0.139 (1)	0.2994 (3)	−0.1941 (9)
C(20)	−0.205 (2)	0.2874 (5)	−0.122 (1)
C(21)	−0.160 (2)	0.2990 (5)	−0.020 (1)
C(22)	−0.041 (2)	0.3201 (5)	0.010 (1)
C(23)	0.022 (1)	0.3300 (4)	−0.066 (1)
C(24)	0.152 (1)	0.3516 (4)	−0.038 (1)
C(25)	0.336 (1)	0.3847 (4)	−0.0651 (9)
C(26)	0.310 (1)	0.4291 (4)	−0.087 (1)
C(27)	0.436 (1)	0.4541 (5)	−0.052 (1)
C(28)	0.546 (1)	0.4375 (4)	−0.094 (1)
C(29)	0.574 (1)	0.3926 (4)	−0.074 (1)
C(30)	0.443 (1)	0.3682 (4)	−0.115 (1)
C(31)	0.454 (1)	0.3446 (4)	−0.279 (1)
C(32)	0.434 (1)	0.3462 (4)	−0.394 (1)
C(33)	0.492 (1)	0.3163 (4)	−0.443 (1)
C(34)	0.476 (1)	0.3186 (5)	−0.548 (1)
C(35)	0.411 (2)	0.3480 (5)	−0.601 (1)
C(36)	0.353 (1)	0.3773 (5)	−0.548 (1)
C(37)	−0.005 (2)	0.4444 (6)	0.102 (1)
C(38)	0.691 (2)	0.3203 (5)	0.224 (1)

[a] A table containing all refined parameters has been deposited.

Table II. Relevant Bond Lengths (Å) and Bond Angles (deg) of $(AgC_{19}H_{20}N_4F_3SO_3)_2$[a]

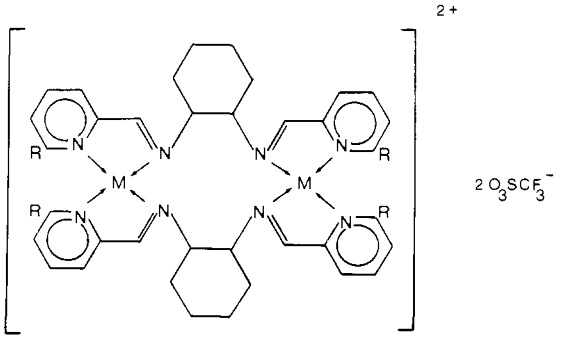
Bond Lengths					
Ag1···Ag2	3.254 (2)	C13–C14	1.455 (19)	N4–C14	1.352 (19)
Ag1–N1	2.455 (12)	C23–C24	1.487 (19)	N4–C18	1.306 (19)
Ag1–N2	2.251 (11)	C25–C30	1.544 (18)	N5–C19	1.308 (15)
Ag1–N7	2.440 (11)	C31–C32	1.473 (20)	N5–C23	1.346 (18)
Ag1–N8	2.242 (11)	N1–C1	1.426 (18)	N6–C24	1.281 (21)
Ag2–N3	2.430 (11)	N1–C5	1.314 (19)	N6–C25	1.453 (16)
Ag2–N4	2.252 (13)	N2–C6	1.267 (18)	N7–C30	1.472 (18)
Ag2–N5	2.429 (11)	N2–C7	1.483 (16)	N7–C31	1.264 (18)
Ag2–N6	2.240 (12)	N3–C12	1.466 (17)	N8–C32	1.301 (16)
C5–C6	1.491 (19)	N3–C13	1.291 (18)	N8–C36	1.313 (18)
C7–C12	1.499 (19)				
Bond Angles					
Ag2···Ag1–N1	153.1 (3)	C12–N3–C13	118.1 (11)		
Ag2···Ag1–N2	90.3 (3)	Ag2–N4–C14	115.8 (9)		
Ag2···Ag1–N7	63.5 (3)	Ag2–N4–C18	127.0 (10)		
Ag2···Ag1–N8	93.1 (3)	C14–N4–C18	116.8 (13)		
N1–Ag1–N2	71.1 (4)	Ag2–N5–C19	131.2 (8)		
N1–Ag1–N7	116.1 (4)	Ag2–N5–C23	110.0 (8)		
N1–Ag1–N8	112.9 (4)	C19–N5–C23	118.5 (11)		
N2–Ag1–N7	134.7 (4)	Ag2–N6–C24	115.7 (10)		
N2–Ag1–N8	149.5 (4)	Ag2–N6–C25	128.3 (8)		
N7–Ag1–N8	72.6 (4)	C24–N6–C25	115.7 (12)		
Ag1···Ag2–N3	62.8 (3)	Ag1–N7–C30	133.6 (8)		
Ag1···Ag2–N4	88.9 (3)	Ag1–N7–C31	109.7 (9)		
Ag1···Ag2–N5	155.4 (3)	C30–N7–C31	116.6 (11)		
Ag1···Ag2–N6	91.2 (3)	Ag1–N8–C32	116.5 (8)		
N3–Ag2–N4	73.3 (4)	Ag1–N8–C36	125.1 (9)		
N3–Ag2–N5	115.9 (4)	C32–N8–C36	118.4 (12)		
N3–Ag2–N6	136.8 (4)	N1–C5–C6	116.9 (13)		
N4–Ag2–N5	114.8 (4)	N2–C6–C5	120.2 (12)		
N4–Ag2–N6	144.3 (4)	N2–C7–C12	110.6 (10)		
N5–Ag2–N6	73.6 (4)	N3–C12–C7	113.9 (11)		
Ag1–N1–C1	129.3 (9)	N3–C13–C14	123.1 (12)		
Ag1–N1–C5	109.7 (9)	N4–C14–C13	118.0 (12)		
C1–N1–C5	116.8 (12)	N5–C23–C24	117.3 (12)		
Ag1–N2–C6	117.9 (9)	N6–C24–C23	122.8 (14)		
Ag1–N2–C7	126.3 (8)	N6–C25–C30	108.4 (10)		
C6–N2–C7	115.5 (11)	N7–C30–C25	113.4 (10)		
Ag2–N3–C12	132.3 (8)	N7–C31–C32	122.0 (12)		
Ag2–N3–C13	109.6 (9)	N8–C32–C31	119.1 (12)		

[a] A complete list of bond lengths and bond angles of $(AgC_{19}H_{20}N_4F_3SO_3)_2$ has been deposited as supplementary material (Table SII).

$I > 2.0\sigma(I)$. Data were collected on an Enraf-Nonius CAD 4 diffractometer using Zr-filtered Mo Kα radiation in the $\omega/2\theta$ scan mode. The quality of the data was rather poor but sufficient for the present purpose. Absorption correction was found not necessary on the basis of some Ψ scans. Data reduction was carried out by procedures as described previously.[14] The structure was solved by standard Patterson and Fourier techniques and refined by anisotropic blocked full-matrix least-squares techniques with the program ILIAS[15] to a final $R_F = 0.067$ ($R_{wF} = 0.07$), $w^{-1} = [\sigma^2(F) + 0.0027\,F^2]/1.97$. Hydrogen atoms were refined in the riding mode on their neighboring carbon atom. A final difference Fourier map did not show significant residual features (Tables I and II).

Results

The 1/1 complexes **2a**, **2b** and **3a**, **3b** were obtained from equimolar mixtures of the neutral quadridentate N-donor ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (R = H, **1a**, or R = Me, **1b**) with [Ag(O$_3$SCF$_3$)] and [Cu(O$_3$SCF$_3$)]·$^1/_2$C$_6$H$_6$, respectively, in methanol or benzene. The red-brown copper(I) and light yellow silver(I) complexes are air and water stable and not light sensitive.



M = Ag(I); R = H (2a); R = Me (2b)
M = Cu(I); R = H (3a); R = Me (3b)

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[14] van der Ploeg, A. F. M. J.; van Koten, G.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1052–1060.

[15] ILIAS-A DG-Eclipse/S230-minicomputer crystallographic program package derived from G. Sheldrick: SHELX-76.

Table III. ^1H NMR (250 MHz) Data (δ) of the N_4 Donor Ligands **1a** and **1b** and the Silver(I) and Copper(I) Complexes[a]

compd	site	H(im)	H-3	H-4	H-5	H-6	H(6-Me)	α-H
ligands								
1a		8.27 s	8.00 d	7.83 dd	7.40 dd	8.53 d		3.72 m
1b		8.27 s	7.80 d	7.65 dd	7.21 d		2.48 s	3.68 m
complexes								
2a	A	8.87 d[b]	7.91 d	8.10 dd	7.61 dd	8.38 d		4.21 m
	B	8.69 d[c]	7.47 d	7.79 dd	7.32 dd	8.13 d		
2b	A	8.89 d[d]	7.74 d	8.01 dd	7.52 d		2.16 s	4.21 m
	B	8.79 d[e]	7.48 d	7.69 dd	7.24 d		2.08 s	
3a	A	8.90 s	7.92 d	8.04 dd	7.52 dd	8.11 d		4.31 m
	B	8.40 s	7.10 d	7.72 dd	7.46 dd	8.11 d		
3b	A	8.90 s	7.81 d	8.00 dd	7.50 d		2.16 s	4.34 m
	B	8.44 s	6.97 d	7.68 dd	7.48 d		1.82 s	

[a] Spectra were taken in methanol-d_4. H(im) resonances of **2a** and **2b** appear as doublets due to $^3J(^{107,109}Ag–^1H)$ couplings. [b] 9.3. [c] 6.3. [d] 10.5. [e] 7.5 Hz. s = singlet, d = doublet, dd = doublet of doublets, m = multiplet.

They have good solubilities in methanol and acetone but are insoluble in apolar solvents such as benzene and pentane.

The elemental analytical data are in agreement with a 1:1 N_4 donor ligand-to-metal salt ratio in the complexes.

X-ray Crystal and Molecular Structure of $[Ag_2\{\mu\text{-}(R,S)\text{-}1,2\text{-}(py\text{-}2\text{-}CH{=}N)_2Cy\}_2](O_3SCF_3)_2$ (2a). The crystal structure of **2a** consists of four discrete $[Ag_2(N_4)_2]^{2+}$ dications, with twofold noncrystallographic axial symmetry, in the unit cell with eight $O_3SCF_3^-$ monoanions. The molecular geometry of the $[Ag_2\{\mu\text{-}(R,S)\text{-}1,2\text{-}(py\text{-}2\text{-}CH{=}N)_2Cy\}_2]^{2+}$ dication and the adopted numbering scheme are shown in a PLUTO drawing (Figure 2). The dication of **2a** consists of two Ag(I) centers which are at a distance of 3.254 (2) Å. The Ag(I) centers each have a distorted tetrahedral four-coordinate geometry being each coordinated by the N-atoms of two (py-2-CH=N) units from separate ligands. Accordingly, the ligands (**1a**) act as bridging dibidentates. Each Ag(I) cation takes part in two short Ag–N [Ag(1)–N(2), 2.251 (11); Ag(1)–N(8), 2.242 (11); Ag(2)–N(4), 2.252 (13); and Ag(2)–N(6), 2.240 (12) Å] and two longer Ag–N interactions [Ag(1)–N(1), 2.455 (12); Ag(1)–N(7), 2.440 (11); Ag(2)–N(3), 2.430 (11); and Ag(2)–N(5), 2.429 (11) Å]. The N–Ag–N angle between the two strongest bonded N-sites, comprising one imino-N and one pyridyl-N site, amounts to 147° [N(2)–Ag(1)–N(8), 149.5 (4)°; N(4)–Ag(2)–N(6), 144.3 (4)°]. The N–Ag–N angle between the weakest bonded N-sites, likewise a coordination of one imino-N and one pyridyl-N site, is ca. 116° [N(1)–Ag(1)–N(7), 116.1(4)°; N(3)–Ag(2)–N(5), 115.9 (4)°]. The small bite angles of the bidentate (py-2-CH=N) systems are in the range generally found for related bidentates participating in five-membered metal–chelate rings.[16] The PLUTO drawing only shows one of the two possible enantiomers present in the unit cell, i.e., the one in which both Ag(I) centers have the Δ configuration.

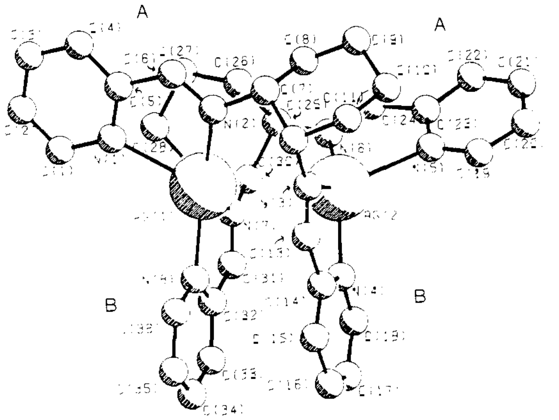

Figure 2. PLUTO drawing of $[Ag_2(N_4)_2]^{2+}$ unit of **2a**. Hydrogen atoms are omitted for clarity. Ag···Ag distance is 3.254 (2) Å.

Structures of 2 and 3 in Solution. Vapor pressure osmometric molecular weight measurements of the complexes in methanol did not provide data which were accurate enough to draw conclusions concerning their aggregation state in solution (i.e., the presence of 1/2 dication/anion electrolytes).

Infrared (IR) spectra of **2** and **3** in the solid and in methanol showed for all complexes the characteristic pattern for $O_3SCF_3^-$ anions with C_{3v} symmetry[17] (see Table SI, deposited as supplementary material). Accordingly, in solution **2** and **3** are likewise present as dication–anion species. Moreover, the ^{19}F NMR spectra of these complexes in methanol-d_4 showed one singlet ^{19}F resonance having chemical shift values (relative to $CFCl_3$) within the range expected for noncoordinating $O_3SCF_3^-$: δ[18] −78.4, **2a**; −78.5, **2b**; −78.3, **3a**; −78.4, **3b**. Cf. −78.3 $[Ag(O_3SCF_3)]$ (measured by the authors) and −78.5 for HO_3SCF_3 in D_2O.[19]

The ^1H and ^{13}C NMR data of the metal 1B complexes and especially the INEPT ^{109}Ag and ^{15}N data of the silver(I) complexes **2a** and **2b** point to the presence of dinuclear $[M_2(N_4)_2]^{2+}$ dicationic species as has been found for **2a** in the solid.

Hydrogen-1 NMR. The ^1H NMR spectra of the silver(I) and copper(I) complexes **2** and **3** in methanol-d_4 show two distinct resonance patterns for the pyridyl ring and the imine protons. The assignment of these resonance patterns to two distinct py-2-CH=N halves, A and B, present in each N_4 ligand was based on ^1H-homonuclear decoupling experiments (see Table III and Figure 3).

The assignment of the imine proton resonance at low field to the py-2-CH=N moiety containing ring A emerged from the results of a NOE difference experiment. Irradiation of this imine proton resonance in the spectra of **2b**, **3a** and **3b** shows enhanced intensity of the H-3 proton resonance of the A ring. When a NOE-difference experiment of a sample of **2a** is performed, the spectrum shows two imine proton signals, of the A and B sites, both projected downward, and two H-3 signals enhanced (see Discussion).

The two imine proton resonances of the Cu(I) complexes appear as singlets whereas in the case of the Ag(I) compounds doublets are observed which are not affected by the ^1H-homonuclear decoupling experiments. Furthermore, the values (in Hz) of these splittings (see Table III) in the 60-, 100-, and 250-MHz NMR spectra are constant. These observations make clear that these doublets arise from $^3J(^1H–^{107,109}Ag)$. Because of the small values of the couplings in combination with the small difference in γ values of ^{107}Ag and ^{109}Ag, the respective doublets arising from $^3J(^1H–^{107}Ag)$ and $^3J(^1H–^{109}Ag)$ are not resolved.[20]

The ^1H NMR data show that on complexation of the ligands (**1a** and **1b**) with Cu(I) and Ag(I) the imine proton and cyclo-

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[16] van der Poel, H.; van Koten, G.; Vrieze, K.; Kokkes, M.; Stam, C. H. *Inorg. Chim. Acta* **1980**, *39*, 197–205.

[17] Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969–977 and references cited therein.

[18] A positive δ corresponds with a higher resonance frequency ("deshielding") with respect to the reference frequency.

[19] Noftle, R. E.; Cady, G. H. *Inorg. Chem.* **1965**, *4*, 1010–1012.

[20] The γ values for ^{107}Ag ($I = {}^1/_2$, 51.82%), ^{109}Ag ($I = {}^1/_2$, 48.18%), ^{15}N ($I = {}^1/_2$, 0.37%), and ^1H are −1.0828, −1.2449, −2.7107, and 26.7510 × 10^7 rad T^{-1} s^{-1}, respectively. Because of the 15% larger γ value, the less abundant ^{109}Ag is the more receptive silver isotope to NMR observation but only by a factor of 1.4: Kidd, G. R.; Goodfellow, R. J. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; 258–260.

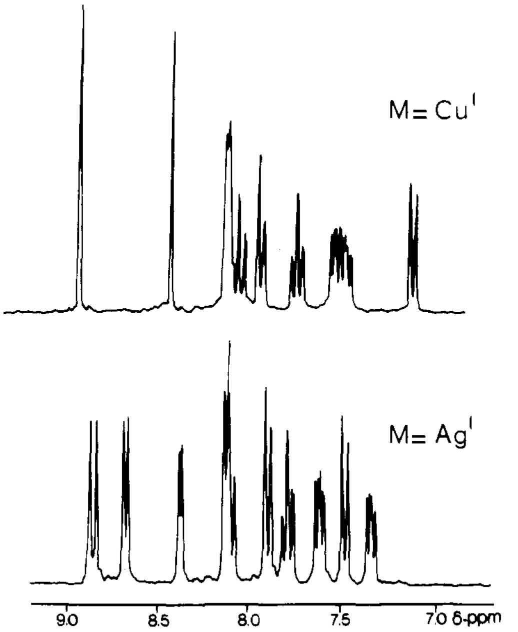

Figure 3. The aromatic region of the ^1H NMR (250 MHz) spectra of **2a** (M = Ag(I), 6-R = H) and **3a** (M = Cu(I), 6-R = H).

Table IV. ^{13}C NMR Data (δ) of the N_4 Donor Ligands **1a** and **1b** and the Silver(I) and Copper(I) Complexes[a]

compd	site	C(im)	C-2	C-6	C(6-Me)	α-C
ligands						
1a		160.9	155.4	149.4		71.5[b]
1b		161.8	155.1	158.9	24.0	72.3
complexes						
2a	A	166.2	150.5	152.2		72.6
	B	164.7	149.9	151.8		67.4
2b	A	166.5	149.4	160.5	25.8	73.0
	B	165.1	148.7	159.8	24.5	68.6
3a	A	166.4	151.7	149.8		74.1
	B	165.2	150.9	149.1		68.0
3b	A	167.0	151.1	160.0	24.4	74.4
	B	166.2	150.2	159.0	23.1	69.4

[a] Spectra were measured in methanol-d_4, which was also used as internal reference. [b] At $T < 218$ K two resonances are observed at δ 72.4 and 69.8.

hexanediyl-α-proton resonances as well as the pyridyl H-4 and H-5 shift downfield while the H-6 (6-R = H), 6-Me (6-R = Me), and H-3 resonances undergo an upfield shift. This behavior causes a characteristic change of the sequence of chemical shift positions of the pyridyl proton resonances compared to that in the free ligands: i.e., in $[Ag_2(N_4)_2]^{2+}$ (**2a**, **2b**) H-4, H-3, H-5, in $[Cu_2(N_4)_2]^{2+}$ (**3a**, **3b**) for A site H-4, H-3, H-5 and for B site H-4, H-5, H-3, and in the free ligands (**1a**, **1b**) H-3, H-4, H-5 from low to high field.

Carbon-13 NMR. The ^{13}C NMR spectra of the free ligands (**1a**, **1b**) only show one single resonance pattern for the 6-R-py-2-CH=N groupings and three resonances for the 1,2-(*R*,*S*)-cyclohexanediyl atoms as a result of fast chair–chair conformational changes of the cyclohexanediyl ring. This latter process is in the slow exchange limit below 218 K as shown by the observation of six resonances for the (*R*,*S*)-1,2-cyclohexanediyl groups and with still one pattern for the pyridine imine ^{13}C nuclei. In the spectra of the complexes the conformational chair–chair movement is blocked over the whole temperature range studied and six ^{13}C resonances are found for the cyclohexanediyl rings (Table IV).

The observation of two 6-R-py-2-CH=N resonance patterns is in accordance with the conclusions drawn from the ^1H NMR results. The absence of observable $^2J(^{13}C\text{-}^{107,109}Ag)$ in the ^{13}C NMR spectra of **2a** and **2b** is notable.

Table V. INEPT ^{15}N (Natural Abundance) NMR Data of the N_4 Donor Ligands **1a** and **1b** and the Silver(I) Complexes **2a** and **2b**[a]

		imine-^{15}N			pyridine-^{15}N		
compd	site	δ[b]	Δ[d]	^1J[c]	δ[b]	Δ[d]	^1J[c]
ligands							
1a		−32.8			−77.5		
1b		−33.5			−76.7		
complexes							
2a	A	−79.4	(−46.6)	48.8	−101.7	(−24.2)	23.9
	B	−76.3	(−43.5)	30.3	−110.5	(−33.0)	34.2
2b	A	−81.2	(−48.2)	49.5	−103.4	(−26.7)	15.6
	B	−78.2	(−44.7)	31.5	−110.2	(−33.5)	31.7

[a] Obtained in methanol-d_4 at 294 K with $MeNO_2$ in C_6D_6 80:20 v/v as external reference. [b] δ in ppm.[18] [c] $^1J(^{15}N\text{-}^{107,109}Ag)$ in Hz. [d] $\Delta = \delta_{complex} - \delta_{ligand}$.

INEPT Nitrogen-15 and Silver-109 NMR. Because nitrogen atoms play a key role in organometallic coordination and bioinorganic chemistry it is of prime importance to study the coordination and dynamic behavior of these ligating sites. Therefore, we would like to emphasize at this point the usefulness of the INEPT experiment to provide easily natural abundance ^{15}N spectra of sp^2-hybridized nitrogens (pyridine, imine, etc.). The NMR observation of such nitrogens is generally hampered by their long T_1 relaxation times (T_1(pyridine-^{15}N) = 80 s) and their NOE η factor very close to −1 due to remote proton environments and the negative gyromagnetic ratio of $^{15}N^{20}$ (the null signal problem!). However, because one can often find a $^2J(^{15}N\text{-}^1H)$ or $^3J(^{15}N\text{-}^1H)$ it is very easy to set up an INEPT experiment. A precise value of the $^{2(3)}J(^{15}N\text{-}^1H)$ coupling is not required and the τ value can be set with a realistic guess of the expected $^nJ(^{15}N\text{-}^1H)$ value(s). A misadjustment of this τ value will only result in a drop of the theoretical sensitivity gain of the experiment ($\gamma\ ^1H/\gamma\ ^{15}N = -9.87$) but will fully retain the main advantages of the method, namely a most reduced accumulation time due to a fast pulsing rate ($T_1{}^{^1H}$) and sizeable signal enhancement compared to normal accumulation. We generally found it easier to use the proton-coupled INEPT experiment especially when two or more types of $^{15}N\text{-}^1H$ couplings were present. This is because a suitable τ value comes readily from the average of the different estimated coupling constant values, but the calculation of the extra delay necessary to allow the different $^{15}N\text{-}^1H$ multiplets to rephase before switching the broad-band proton decoupler on can be a real problem.

The natural abundance INEPT ^{15}N (proton coupled) spectra of the free ligands (**1a**, **1b**) both show two resonances, each of which appears, as a result of the pulse sequence, as an "up–down" doublet whose splitting is dependent on $^nJ(^{15}N\text{-}^1H)$. The assignment of the resonances is based on the results of a selective ^1H(imine) heteronuclear decoupling experiment, which established that the signals at low field belong to the imine nitrogen and those at high field to the pyridine nitrogen atoms.

When the ^{15}N NMR spectra of the silver(I) complexes **2a** and **2b** is run at two different field values, 250- and 400-MHz spectrometers, it could be concluded that the spectra show four resonances (two imine and two pyridine), all of which appear as *doublet of doublets* patterns. The ^1H heteronuclear decoupling experiments proved that the smaller splitting of each doublet of doublets is caused by $^nJ(^{15}N\text{-}^1H)$ and, accordingly, the larger splitting can only arise from $^1J(^{15}N\text{-}^{107,109}Ag)$ (see Table V and Figure 4).

Because of the presence of resolved $^3J(^1H\text{-}^{107,109}Ag)$ in the ^1H NMR spectra of **2a** and **2b**, it was also possible to measure ^{109}Ag NMR spectra via the INEPT sequence (see Experimental Section). Delay times $\tau = (4J)^{-1}$ were taken as the sums of the $^3J(^1H(\text{imine})\text{-}^{107,109}Ag)$. The chemical shift value[18] relative to 2 M aqueous $AgNO_3$ for **2a** is $\delta = 580$ and for **2b** $\delta = 612$.

Discussion

Structures of the Complexes in the Solid. Busch and Bailar[21] were the first to study the coordination properties of the N_4 ligand

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(21) Busch, D. H.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1137–1142.

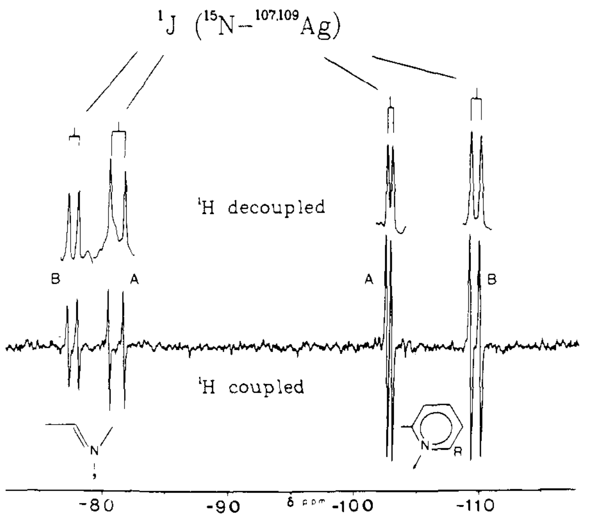

Figure 4. INEPT ^{15}N (natural abundance) NMR (40.56 MHz) spectrum of the silver(I) complex **2b** (6-R = Me).

system 1,2-(6-R-py-2-CH=N)$_2$C$_2$H$_4$ (R = H or Me), having a 1,2-ethanediyl group bridging two pyridine imine moieties with various metal salts, using visible, ultraviolet, and infrared spectroscopy. These authors and Goodwin and Lions,[22] at a later date, have reported various complexes of these ligands with copper(II). Harris and McKenzie[23] isolated complexes of 1,2-(py-2-CH=N)$_2$ethane with Cu(ClO$_4$)$_2$ with 1/1 and 2/3 metal salt-to-ligand ratios. It was postulated that in the 1/1 complex the ligand coordinates to the metal center in a quadridentate manner while in the 2/3 complex the ligands act as dibidentates bridging two Cu(II) centers. An X-ray structure of these complexes was not obtained. Instead the structure is reported[24] of the 1/1 complex [Cu(N$_4$)Br]ClO$_4$. Here the N$_4$ ligand, as a result of addition of 1 equiv of methanol over one of the H—C=N bonds, is converted into a system in which the ethanediyl group bridges one pyridine imine and one pyridine amine moiety.[25]

The novel copper(I) and silver(I) complexes with the neutral N$_4$ donor ligand system (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy (R = H or Me) and the noncoordinating O$_3$SCF$_3^-$ anions, which are reported in this paper, could only be obtained in 1/1 metal salt-to-ligand ratios. Any attempt to prepare complexes with other metal–ligand ratio failed, a result anticipated by ^{1}H NMR spectra of solutions containing excess ligand or metal salt taken at different temperatures.

The X-ray crystal and molecular structure of the silver(I) complex **2a** clearly reveals that in the [Ag$_2$(N$_4$)$_2$]$^{2+}$ unit each of the two N$_4$ ligands coordinate to the metal 1B center in a dibidentate manner. The cyclohexanediyl rings bridging the flat pyridine moieties are directed toward the metal centers and have equivalent chain conformations, i.e., either $\delta\delta$ or $\lambda\lambda$ (enantiomeric pair) in combination with $\Delta\Delta$ or $\Lambda\Lambda$ configurations, respectively, at the silver(I) centers.[26] As a result the dication has a helix (Δ or Λ) structure in which the metal centers are placed at a distinct distance of each other (Ag···Ag = 3.254 (2) Å) by the strain in the ligands' skeleton.

Structures of the Complexes in Solution. Infrared (methanol liquid film) and ^{19}F NMR data clearly reveal that the O$_3$SCF$_3^-$ anions do not coordinate to the metal 1B centers in solution, and therefore here also we are dealing with cationic metal–ligand species.

The presence of only one resonance in the INEPT ^{109}Ag NMR spectra of **2a** and **2b** indicates that there is only one complex (or enantiomeric pair) in solution. The INEPT ^{15}N NMR spectra of **2a** and **2b**, showing ^1J(^{15}N–^{107,109}Ag) couplings (see Results) unambiguously prove that in solution all four N atoms of each ligand coordinate to a metal 1B center. On the basis of these data and the presence of two pyridine imine patterns in the ^{1}H NMR spectra with ^3J(^{1}H(imine)–^{107,109}Ag) couplings and the ^{13}C NMR spectra of the silver(I) complexes, we conclude that these complexes have a dinuclear structure in solution similar to that established for **2a** in the solid. In the ^{1}H and ^{13}C NMR spectra of the copper(I) complexes **3a** and **3b** two pyridine imine patterns are also observed. Thus we conclude that the silver(I) and copper(I) complexes have similar [M$_2$(N$_4$)]$^{2+}$(O$_3$SCF$_3$)$_2^-$ structures in solution. Subtle differences in the molecular geometry of the copper(I) and silver(I) dications are reflected by the differences in the ^{1}H chemical shifts, e.g., the different sequences of the pyridine proton resonances (see Results). These can be accounted for by the fact that the ionic radius of copper(I) is smaller than that of the silver(I).[27] A smaller ionic radius results in a contraction of the molecular structure of the [M$_2$(N$_4$)$_2$]$^{2+}$ dication and small differences in the natural arrangement of the various molecular moieties. This effect has been demonstrated in a recent study of the copper(I) and silver(I) complexes with the N$_2$S$_2$ ligand (*R*,*S*)-1,2-(5-Me-thiophene-2-CH=N)$_2$Cy.[28]

On the basis of the molecular geometry found for **2a** in the solid, a rationale can be given for the observation that the pyridine protons of the B site are shifted upfield with respect to those of the A site in the ^{1}H NMR spectra of both the silver(I) and copper(I) complexes (see Results). The A-site pyridine rings are well separated but the structure shows mutually parallel positioned B-site pyridine rings whose protons therefore experience a shielding ring current. Also the smaller downfield shift of the imine protons in the B sites with respect to the ones of the A sites correlate well with the larger M–N(imine) interactions of the pyridine imine moieties N(7)–C(31)–C(32)–N(8) and N(3)–C(13)–C(14)–N(4), represented as the magnetically equivalent B sites. Accordingly, through these detailed NMR investigations an unambiguous assignment of the A- and B-site protons has been achieved. These criteria have proven to be useful for the assignment of the structure in solution of related [M$_2$(N$_2$S$_2$)$_2$]$^{2+}$ species.[29]

An interesting aspect of the possibility to study in detail the silver(I) complexes with ^{15}N NMR is the information that can be obtained concerning the Ag–N donor atom attachments. The pyridine and imine N atoms shift upfield when coordinated to the metal 1B center as commonly observed for sp^2-bonded nitrogens. The large differences in ^1J(^{15}N–^{107,109}Ag) couplings suggest that the "s" character of the individual imine and pyridine N–metal bonds differ considerably.[30] This is reflected by the fact that the ^1J(^{15}N–^{107,109}Ag) values correlate with the Ag–N bond lengths. For example, for **2a** the ^1J(^{15}N(imine) (A site)–^{107,109}Ag) has the largest value (48.8 Hz) while the Ag–N(imine) of the pyridine imine A moieties in the PLUTO drawing (Figure 2) have the shortest Ag–N bond lengths [Ag(1)–N(2), 2.251 (11) Å. Ag(2)–N(6), 2.240 (12) Å].

These helix type structured silver(I) complexes, **2a** and **2b**, are the first examples of discrete complexes in solution for which ^{109}Ag NMR spectra have been obtained and at present comparative ^{109}Ag chemical shift data are restricted. However, the δ ^{109}Ag values are seen to be very sensitive to differences in the metal–ligand interactions. When one goes from **2a** (6-R = H) to **2b** (6-R = Me), the introduction of a methyl group in the 6-position of the pyridine rings has a marked deshielding effect on the metal nucleus and a downfield chemical shift of 32 ppm results.

These NMR studies indicate that the pure metal 1B complexes have on the NMR time scale (to 300 K) rigid structures in so-

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lution. The spectra of the silver(I) complexes also show that exchange reactions are slow [e.g., observation of $^1J(^{15}N-^{107,109}Ag)$ and $^3J(^1H-^{107,109}Ag)$], and this is surprising because, as mentioned before, silver(I) complexes are prone to intermolecular exchange reactions.[11b] However, during the detailed $^1H-^1H$ decoupling and NOE difference experiments of complex **2a** at room temperature for establishing the assignment of the A and B site pyridine imine protons, an A $\rightleftarrows$ B site exchange was observed. A study on the mechanism of this process which is apparently dependent on the metal centers [Ag(I) or Cu(I)] and on the 6-R (R = H or Me) substituents is in progress.[31]

Conclusions

The silver(I) and copper(I) complexes of the N_4 ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy have similar $[M_2(N_4)_2]^{2+}(O_3SCF_3)_2^-$ structures in the solid and in solution, showing that the study of Ag(I) complexes as models of the corresponding Cu(I) complexes is feasible.

This paper shows for the first time that by using multinuclear NMR techniques (natural abundance ^{15}N and ^{109}Ag NMR) subtle differences in metal-ligand bond lengths, as found in the solid, can be detected in the solution structures of rather complex metal-polydentate ligand complexes. This result is of significance for future studies of structural and bonding features, not only in the coordination chemistry of metal 1B complexes but also in the field of biological copper-containing macromolecules when the Cu(I) ions can be replaced by Ag(I).[32]

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Registry No. 1a, 90605-88-2; **1b**, 90605-89-3; **2a**, 76317-71-0; **2b**, 76317-73-2; **3a**, 76317-75-4; **3b**, 90605-91-7; ^{13}C, 14762-74-4; ^{15}N, 14390-96-6; ^{107}Ag, 14378-37-1; ^{109}Ag, 14378-38-2; (*R*,*S*)-1,2-diaminocyclohexane, 1436-59-5; pyridine-2-carbaldehyde, 1121-60-4; 6-methylpyridine-2-carbaldehyde, 1122-72-1.

Supplementary Material Available: Listing of positional and thermal parameters for all atoms of **2a** (Table I), IR data of **2** and **3** (Table SI), bond lengths and bond angles of **2a** (Table SII), and listings of observed and calculated structure factors of **2a** (27 pages). Ordering information is given an any current masthead page.

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Preparation and ^{13}C NMR Spectroscopic Study of Fluoroadamantanes and Fluorodiamantanes: Study of $^{13}C-^{19}F$ NMR Coupling Constants

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Abstract: In mono-, di-, tri-, and tetrafluoroadamantanes the effect of progressive addition of fluorine on the ^{13}C chemical shifts and $^nJ_{CF}$ values were studied. Specific trends in both these values were shown. A series of monofluorodiamantanes and difluorodiamantanes were also prepared. SCS (substituent effect on ^{13}C chemical shifts) and $^nJ_{CF}$ values were analyzed on the basis of the type and the number of gauche interactions in the system. Fluorine-fluorine coupling constants and ^{13}C isotope induced fluorine chemical shift differences in the polyfluoro compounds were calculated by spin simulation technique and analyzed.

Structural ^{13}C NMR spectroscopic studies generally focus on ^{13}C NMR chemical shifts (δ_C) or $^{13}C-^1H$ coupling constants (J_{CH}). Applications are, for the most part, based on empirical correlations of ^{13}C shieldings or J_{CH} values and molecular geometry.[1-3] Empirical correlations of substituent effects on ^{13}C chemical shifts (SCS) have also been studied in recent years.[4]

There is continuing interest in spin-spin coupling between different nuclei and the factors that influence this phenomenon. Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory[5] that coupling via electrons originates from three types of interaction between the magnetic moments due to the nuclear spin and the electrons. The three types are (a) orbital interaction with the magnetic field due to the orbital motion of electrons, (b) dipolar interaction with the electron spin, and (c) Fermi contact interaction with the electron spin. While these three contributions may vary in sign as well as in magnitude, calculations indicate that coupling between the majority of first-row elements is dominated by the Fermi contact[6-12] and,

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