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Structures of the Silver Complexes with Lutidines According to the NMR Data. Crystal Structure of $[AgNO_3(3,5\text{-}Lut)_2]$

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Abstract—The silver(I) nitrate complexes with 2,3-, 2,4-, 2,6-, and 3,5-lutidine (Lut, dimethylpyridine C_7H_9N), $[AgNO_3(Lut)_2]$, are synthesized and studied by multinuclear NMR (^1H, ^{13}C, and ^{15}N) in various solvents (chloroform, dimethyl sulfoxide, and acetonitrile). The influence of steric and electronic factors of the organic ligand on the parameters of the NMR spectra is revealed. It is shown that the ^{15}N NMR spectra are the most informative. The structure of complex $[AgNO_3(3,5\text{-}Lut)_2]$ is determined. The crystals are monoclinic, space group $C2/c$, $a = 14.599(1)$ Å, $b = 8.422(1)$ Å, $c = 12.954(1)$ Å, $\beta = 99.60(1)°$, $V = 1570(2)$ Å^3, $\rho_{calcd} = 1.625$ g/cm^3, $Z = 4$. The structure is built of discrete neutral complexes $[AgNO_3(3,5\text{-}Lut)_2]$. The coordination mode of the Ag^+ ion includes two nitrogen atoms of two crystallographically equivalent lutidine ligands (Ag–N 2.194(5) Å, angle NAgN 147.6(3)°). The nitrate ion behaves as a weak chelating ligand with respect to the Ag^+ ion (Ag···O 2.674(6) Å).

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Owing to specific features of the molecular design of 1D–3D coordination silver polymers often having unexpected structural motifs, compounds of similar type are promising from the viewpoint of the construction of new materials for using in catalysis, ion exchange, and medicine; as containers for gases, luminescent materials, etc. In the most part of cases, ditopic organic ligands with N-containing heterocycles, such as bipyridines, pyrazines, pyrimidines, and others, are used for the formation of polymer chains. Almost all publications in this field of coordination chemistry concern the study of the compounds by X-ray diffraction analysis and IR spectroscopy and obtaining data on their thermal behavior and luminescence properties. Published works on studying the coordination state of the metal in a solution during the synthesis of polymers are lacking, although similar information makes it possible to control the course of the synthesis of the compounds. The latter is well illustrated by the fact that single crystals suitable for X-ray diffraction analysis are prepared only due to the slow ligand exchange between the intermediate complex $[Ag(NH_3)_2]^+$ with ditopic molecules of the N-containing ligand [1]. The $\{Ag[CH_2(C_6H_4NH_2)_2]_2(CH_3C_6H_4NH_2)_2\}NO_3$ complex was similarly synthesized by the reaction of the $[AgL_2]^+$ precursor (L = 3,5-lutidine) with 4,4'-diaminodiphenylmethane $CH_2(C_6H_4NH_2)_2$ and studied by X-ray diffraction analysis [2].

The purpose of this work is to elucidate an informative content of multinuclear NMR spectroscopy, including ^1H, ^{13}C, and ^{15}N, in a solution upon the complex formation of the N-containing heterocyclic ligands with silver nitrate. We chose 2,3-, 2,4-, 2,6-, and 3,5-lutidines (Lut, dimethyl derivatives of pyridine) as model compounds. They form complexes soluble not only in coordinating solvents, such as dimethyl sulfoxide, acetonitrile, and dimethylformamide, but also in chloroform, which allows one to vary the conditions of the medium for both synthesis and recording NMR spectra. It seems interesting to compare the data of NMR spectroscopy in solutions with the X-ray diffraction analysis results of the complexes. It is known that the structure of $[AgNO_3(2,6\text{-}Lut)_2]$ [3] includes a discrete neutral complexes (distances Ag–N 2.186(4) and 2.178(4) Å, angle NAgN 169.6(2)°). Continuing the studies of similar compounds, we obtained single crystals of silver nitrate with 3,5-lutidine of the composition $[AgNO_3(3,5\text{-}Lut)_2]$ (**I**) and determined the structure of the complex by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis. Silver nitrate $AgNO_3$ (reagent grade) and 2,3-, 2,4-, 2,6-, and 3,5-lutidines (Aldrich) were used. Deuterated solvents ($CDCl_3$, CD_3CN, and $(CD_3)_2SO$) were dehydrated above molecular sieves 4 Å. The complexes of $AgNO_3$ with 2,3-, 2,6-, and 3,5-Lut were synthesized similarly by mixing acetonitrile solutions of the reactants in the nitrate to ligand molar ratio 1 : 2 (the salt content in the mixture was ~1.5%). The reaction mixture was kept in the dark until the most part of the solvent evaporated. The crys-

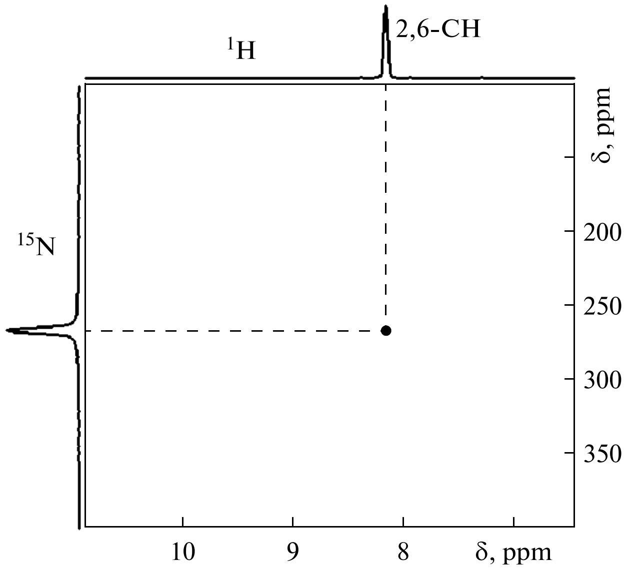


Fig. 1. 2D ^{1}H–^{15}N NMR spectrum (HMBC, long range) of a solution of the $[Ag(NO_3)(3,5\text{-}Lut)_2]$ complex in $CDCl_3$ at 298 K.

tals formed were washed with a small amount of acetonitrile and dried at ambient temperature in air. According to the elemental analysis data, all synthesized compounds correspond to the composition of the $AgNO_3$ complex with two lutidine molecules.

For $C_{14}H_{18}AgN_3O_3$ (**I**)

anal. calcd. (%):	N, 10.93;	C, 43.73;	H, 4.68.
Found (%):	N, 10.70;	C, 43.59;	H, 4.48.

For the compounds with the 2,3- and 2,6-Lut ligands, the analysis data nearly coincide with the above presented results. Single crystals of compound **I** suitable for X-ray diffraction analysis were obtained by recrystallization from a solution in a mixture of MeCN and $CHCl_3$ taken in equal amounts. In the case of a similar synthesis of the compound with 2,4-Lut, the solid phase was isolated only after the almost complete removal of the solvent. The same was observed for an attempt to recrystallize the product from chloroform. Therefore, the conclusion about the structure of the silver complex with 2,4-lutidine in a solution was made only on the basis of the NMR spectral data.

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker AV 400 spectrometer with working frequencies of 400.13, 100.61, and 40.54 MHz, respectively, and with internal stabilization with respect to deuterium at ambient temperature (298 K). Chemical shifts of the ^{1}H and ^{13}C nuclei are presented relatively to tetramethylsilane, and those of ^{15}N are given relatively to liquid NH_3.

For the assignment of ^{13}C NMR signals of CH_3, CH_2, and CH groups of the organic ligand, the spectra were recorded by the DEPT method using the 45°, 90°, and 135° sorting pulse [4].

The signals in the proton and carbon resonance spectra were corresponded using a 2D heterocorrelation experiment ^{13}C,^{1}H HMQC (heteronuclear multiple quantum correlation).

For the accumulation of ^{15}N signals and correspondence of signals in the proton and nitrogen resonance spectra, we used the procedure of 2D inverse heterocorrelation experiment ^{1}H–1/^{15}N HMBC (heteronuclear multiple bond correlation) through long-range spin-spin coupling constants $^nJ(^1H,^{15}N)$ = 10–15 Hz (Fig. 1).

The values of spin-spin coupling constants $^nJ(^1H, ^1H)$ were determined by the iteration simulation of NMR spectra using the NUTs program [5].

X-ray diffraction analysis. An experimental material for crystals **I** was obtained on an Enraf-Nonius CAD-4 automated diffractometer. The structure was solved by a direct method (SHELXS-97) [6] and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [7]. Positions of hydrogen atoms were calculated geometrically and included in the riding model with fixed isotropic temperature parameters.

Selected crystallographic data and experimental characteristics for structure **I** are given in Table 1. The full crystallographic data were deposited with the Cambridge Crystallographic Data Centre (no. 870555; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C{H}NMR spectra of free lutidines and their complexes show that the NMR spectral parameters change slightly upon the coordination of the organic ligand (Table 2). The least changes (from 0.35 to 0.82 ppm) are observed in the ^{1}H NMR spectra. For the coordination of 3,5-lutidine, the downfield signals from the protons of the methyl groups are shifted only by 0.35 ppm. At the same time, the maximum downfield shift is observed in the complex with 2,6-lutidine for the protons of the CH ring in positions 3 and 5.

Interestingly, the chemical shifts of the 4CH protons in the NMR spectrum of free 2,6-, 2,3-, and 3,5-lutidines almost coincide (about 6.85 ppm). However, upon coordination the downfield shift of these signals from the protons increases in the series: 3,5-Lut ($\Delta\delta$ = 0.49 ppm) < 2,3-Lut ($\Delta\delta$ = 0.65 ppm) < 2,6-Lut ($\Delta\delta$ = 0.79 ppm).

The downfield shift of the signals in the carbon spectrum upon complex formation is somewhat higher (from 0.5 to 3.8 ppm) depending on the arrangement of the carbon nuclei.

Contrary to the changes observed in the proton and carbon NMR spectra, the changes in the ^{15}N NMR spectra are more significant. The signal from the coordinated nitrogen atom in the lutidine ligand is arranged in a higher field compared to the signal of free lutidine. This is explained by the change in the value of the local paramagnetic contribution upon the coordination of lutidines to the silver atom due to the lone electron pair of the nitrogen atom [8]. The maximum changes in the ^{15}N chemical shifts are observed for the coordination of 3,5-lutidine ($\Delta\delta = -45.7$ ppm), and the least changes are observed for 2,6-lutidine ($\Delta\delta = -34.2$ ppm). The values of $\Delta\delta$ for 2,3- and 2,4-lutidines are intermediate. Thus, the order of changes in chemical shifts of the signals from the nitrogen atoms in the ^{15}N NMR spectra of the studied lutidines upon coordination is directly opposite to the order indicated above for the shift of the 4CH protons in the ^1H NMR spectrum. It is most likely that the steric factor also exerts an effect on screening of the nitrogen atoms upon the coordination of lutidines.

The absence of additional splittings in the proton and carbon resonance spectra and the presence of only one signal in the ^{15}N NMR spectrum of each isolated complex indicate that the positions of two coordinated lutidine molecules are equivalent.

Structure **I** is built of discrete neutral complexes $[AgNO_3(3,5\text{-Lut})_2]$ (Fig. 2). The silver atom localized in the plane of the *m* symmetry is bound to two nitrogen atoms of the crystallographically equivalent 3,5-lutidine ligands (Ag(1)–N(1) 2.194 Å, angle N(1)AgN(1A) 147.6(3)°). The planar nitrate group NO_3 is a weakly chelating ligand and has the contact Ag···O 2.674(6) Å; in this case, the linear geometry of the silver atom is strongly distorted. The C–H···O intermolecular contacts (C···O < 3.65 Å) observed in the structure can be attributed to hydrogen bonds, where the methyl groups of the ligands can be proton donors and the terminal oxygen atoms of the NO_3 groups can serve as proton acceptors: C(5)···O(2*B*) $(1/2 + x, 1\frac{1}{2} - y, 1/2 + z)$ 3.511(8) Å, C(7)···O(2*A*) $(1 - x, 1 - y, 1 - z)$ 3.581(9) Å. As a result of these interactions, the 3D supramolecular structure is formed.

A comparison of the results obtained for structure **I** with those known for $[AgNO_3(2,6\text{-Lut})_2]$ shows that the discrete complexes are formed in both cases in spite of differences in the structures. The Ag–N bond lengths in these compounds are nearly equal (2.19 Å). This means that the position of the methyl groups in the pyridine ring exerts no effect on the Ag–N bond length. However, there is a strong distortion of the linear geometry of the silver atom in structure **I** compared to the silver nitrate complex with 2,6-Lut [3]. The NMR data obtained for the structures of the silver complexes with lutidines in chloroform are consistent with the X-ray diffraction data.

Table 1. Crystallographic data and selected experimental characteristics for the structure of $[AgNO_3(3,5\text{-Lut})_2]$

Parameter	Value
FW	348.18
Crystal size, mm	0.13 × 0.10 × 0.10
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell parameters:	
a, Å	14.599(1)
b, Å	8.422(1)
c, Å	12.954(1)
β, deg	99.60(1)
V, Å^3	1570.5(2)
Z	4
ρ_{calcd}, g/cm^3	1.625
Absorption coefficient, mm^{-1}	10.418
F(000)	776
T, K	293
Radiation (λ, Å)	CuK_α (1.54178), graphite monochromator
Scan mode	ω
θ range, deg	6.09–67.86
Index ranges	$-17 \le h \le 17$, $-9 \le k \le 10$, $-1 \le l \le 15$
Total number of reflections (R_{int})	2907/1412 (0.0481)
Number of reflections with $I \ge 2\sigma(I)$	1082
Number of refined parameters	98
Goodness-of-fit for F^2	1.083
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0527$, $wR_2 = 0.1313$
R (all data)	$R_1 = 0.0712$, $wR_2 = 0.1424$
Extinction coefficient	0.023(3)
Residual electron density (max/min), *e*/Å^3	2.212/–0.611

To study the donor ability of lutidines with respect to the silver atom, we studied the NMR spectra of solutions of the lutidine complexes with different ligands and upon the addition of an equimolar amount of coordinating solvents. An attempt to displace lutidines from the coordination sphere of silver in the $[AgNO_3(3,5\text{-Lut})_2]$ and $[AgNO_3(2,3\text{-Lut})_2]$ complexes by adding such solvents as acetonitrile and dimethyl sulfoxide in the ratios lutidine : solvent = 1 : 2 and 1 : 3 to their solutions in $CDCl_3$ was unsuccessful. This is indicated by the absence of changes in the ^{13}C and ^{15}N NMR spectra of solutions of the complexes in d-chloroform. Nevertheless, lutidines are displaced from the

Table 2. Parameters of the NMR spectra of lutidines and their complexes with Ag(I) in $CDCl_3$ solutions

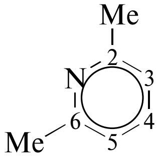
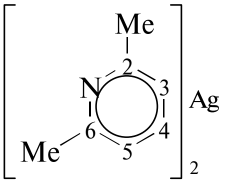
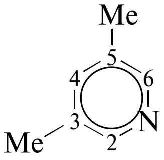
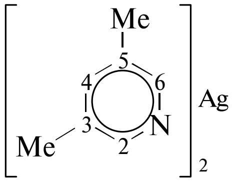
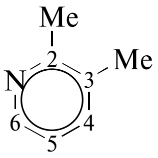
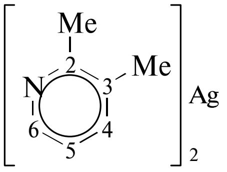
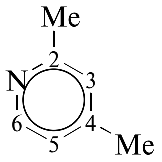
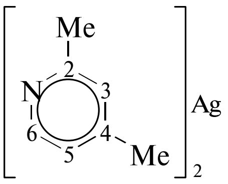
Compound	Atoms and groups	^{1}H NMR, ppm*		^{13}C NMR*		^{15}N NMR**	
	Me	1.94		23.1			
	N					311.2	
	2,6-C			156.3			
	3,5-CH	6.32		118.9			
	4-CH	6.83 ($^3J_{HH}$ = 7.5 Hz)		135.2			
			Δδ***		Δδ		Δδ
	Me	2.75	0.81	26.7	3.6		
	N					277.0	−34.2
	2,6-C			157.9	1.6		
	3,5-CH	7.14	0.82	121.5	2.6		
	4-CH	7.62	0.79	138.6	3.4		
	Me	1.81		17.0			
	N					312.2	
	2,6-CH	7.80		146.2			
	3,5-C			131.4			
	4-CH	6.80		136.0			
			Δδ		Δδ		Δδ
	Me	2.16	0.35	17.9	0.9		
	N					266.5	−45.7
	2,6-CH	8.17	0.37	148.8	2.6		
	3,5-C			133.9	2.5		
	4-CH	7.29	0.49	139.0	3.0		
	2-Me	2.03		22.4			
	3-Me	1.77		18.9			
	N					310.1	
	6-CH	7.87		145.3			
	2-C			155.9			
	4-CH	6.89		135.9			
	3-C			130.3			
	5-CH	6.54		120.5			
			Δδ		Δδ		Δδ
	2-Me	2.68	0.65	25.5	3.1		
	3-Me	2.31	0.54	19.6	0.7		
	N					272.9	−37.2
	6-CH	8.49	0.62	148.8	3.5		
	2-C			156.7	0.8		
	4-CH	7.54	0.65	139.0	3.1		
	3-C			133.0	2.7		
	5-CH	7.16	0.62	122.4	1.9		

Table 2. (Contd.)

Compound	Atoms and groups	^{1}H NMR, ppm*		^{13}C NMR*		^{15}N NMR**	
	2-Me	2.12		23.2			
	4-Me	1.88		19.9			
	N					301.0	
	6-CH	7.95		147.9			
	2-C			157.0			
	3-CH	6.55		123.2			
	5-CH	6.50		120.8			
	4-C			146.5			
			Δδ		Δδ		Δδ
	2-Me	2.70	0.58	26.8	3.6		
	4-Me	2.30	0.42	21.0	1.1		
	N					261.9	−39.1
	6-CH	8.50	0.55	151.0	3.1		
	2-C			157.5	0.5		
	3-CH	7.20	0.65	125.3	2.1		
	5-CH	7.00	0.50	123.0	2.2		
	4-C			150.3	3.8		

Notes: * Relative to TMS.

** Relative to NH_3.

*** $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$.

coordination sphere of silver upon the action of triphenylphosphine on the complexes in the ratio lutidine : $PPh_3 = 1 : 2$. This is indicated, for example, by a comparison of the $^{13}C\{H\}$ spectrum of the $[AgNO_3(2,3\text{-Lut})_2]$ complex in d-chloroform (Fig. 3a) with that recorded upon the addition of PPh_3 to this sample (Fig. 3b) and the spectrum of the free ligand in $CDCl_3$ (Fig. 3c). The addition of triphenylphosphine to the complex does not result in the appearance of signals from the initial complexes in the ^{13}C NMR spectrum (Fig. 3), but the signals of free 2,3-Lut are observed. This conclusion is confirmed by recording ^{15}N NMR spectra. The signal from the nitrogen atom of the complex with 2,3-Lut has a shift at 272.9 ppm and that of free lutidine exhibits a shift at 310.1 ppm (Table 2), whereas the signal at 309 ppm is observed in the ^{15}N NMR spectrum after a twofold amount of triphenylphosphine was added to a solution of the

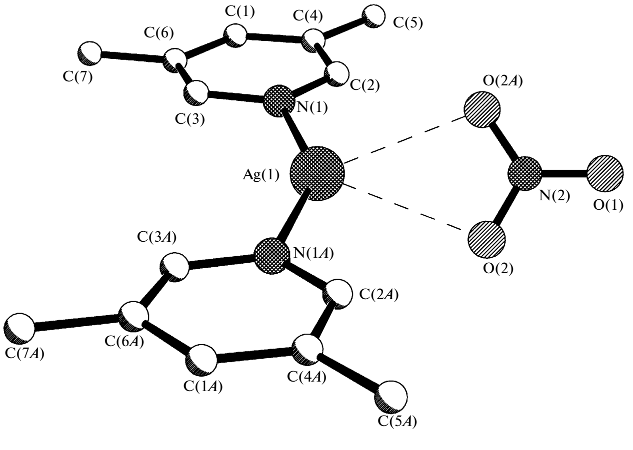


Fig. 2. Structure of the $[Ag(NO_3)(3,5\text{-Lut})_2]$ complex.

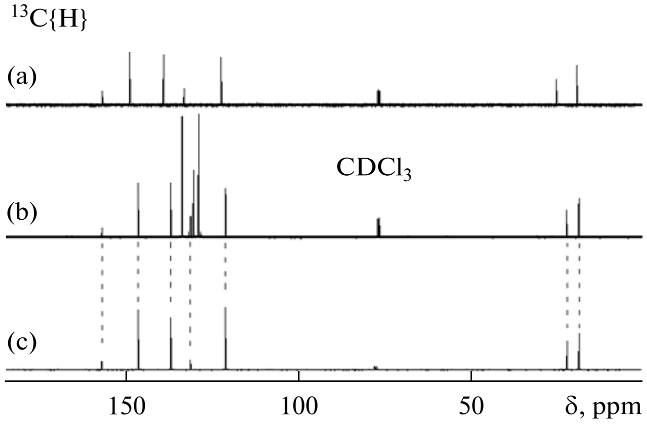


Fig. 3. $^{13}C\{H\}$ NMR spectra of the (a) $[Ag(NO_3)(2,3\text{-Lut})_2]$ complex in $CDCl_3$, (b) with the addition of an equimolar amount of PPh_3 to sample (a), and (c) free 2,3-Lut in $CDCl_3$.

Table 3. Dependence of the parameters of the ^{15}N NMR spectra of free and coordinated 2,3-Lut on the solvent

Solvent	ε (25°C)	δ^{15}N(Lut-2,3), ppm	δ^{15}N[Ag(Lut-2,3)$_2$NO$_3$], ppm	Δδ, ppm*
$CDCl_3$	4.7	311.2	272.9	38.3
CD_3CN	37.5	315.8	283.7	32.1
d$_6$-DMSO	48.9	317.3	289	28.3

* $\Delta\delta = \delta^{15}$N (Lut-2,3) – δ^{15}N [Ag(Lut-2,3)$_2$NO$_3$].

complex in chloroform. Taking into account considerable spectral changes characteristic of the nitrogen nucleus, we can surely ascribe this signal to free lutidine.

It is interesting that the chemical shift of the nitrogen atom of free and bound lutidine in the ^{15}N NMR spectra depends on the solvent. The signals from free and coordinated 2,3-lutidine exhibit downfield shifts with an increase in the dielectric constant (ε) of the solvent (Table 3). In this case, the value of Δδ, which characterizes binding of the lone electron pair of the nitrogen atom, decreases noticeably. The observed effect can be explained by the fact that in apolar aprotic solvents (chloroform is among them) the lone electron pair of the nitrogen atom of lutidine is bound only upon the coordination by the silver ion, since the solvent does not actively solvate a free lutidine molecule in this case. In strongly coordinating solvents (DMSO), the solvent itself along with the silver ion affects the process of electron pair binding upon the coordination of lutidine; i.e., the electron pair in free lutidine is already solvated in part by the solvent. This effect should especially be pronounced in the case of the strong ligand exchange. According to published data [9, 10], many silver complexes are prone to the fast (in the NMR time scale) intra- and intermolecular exchange, which substantially impedes the interpretation of the spectra.

The reaction of $AgNO_3$ with 2,6- and 3,5-lutidines in a ratio of 1 : 1 : 1 in deuterated chloroform controlled by NMR spectroscopy suggested that a mixed complex [$AgNO_3$(3,5-Lut)(2,6-Lut)] was formed in the solution. This asymmetric complex can also be obtained by the displacement of one of the ligands in the symmetric complex by another lutidine. This is indicated by the almost coincident ^{1}H, ^{13}C{H}, and ^{15}N NMR spectra of solutions of [$AgNO_3$(3,5-Lut)$_2$]–2,6-Lut (at the 1 : 2 molar ratio) and [$AgNO_3$(2,6-Lut)$_2$]–3,5-Lut (1 : 2 molar ratio) mixtures in $CDCl_3$ (Fig. 4). Interestingly, the ^{15}N NMR spectra exhibit two signals at 289 and two signals at 293 ppm (Fig. 5), whose positions are averaged, if a high rate of ligand exchange in the solution is accepted

$$[\mathrm{AgNO_3(2,6\text{-}Lut)_2}] \rightleftarrows \mathrm{2,6\text{-}Lut}\ (277 + 311.2)/2 = 294.1\ \mathrm{ppm}$$

$$[\mathrm{AgNO_3(3,5\text{-}Lut)_2}] \rightleftarrows \mathrm{3,5\text{-}Lut}\ (266.5 + 312.2)/2 = 289.35\ \mathrm{ppm}$$

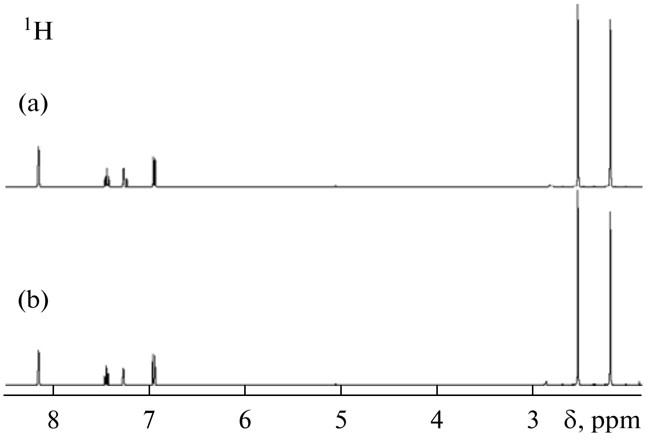


Fig. 4. ^{1}H NMR spectra of solutions of the mixtures in $CDCl_3$: (a) [Ag(NO$_3$)(2,6-Lut)$_2$] + 3,5-Lut in a ratio of 1 : 2 and (b) [Ag(NO$_3$)(3,5-Lut)$_2$] + 2,6-Lut in a ratio of 1 : 2.

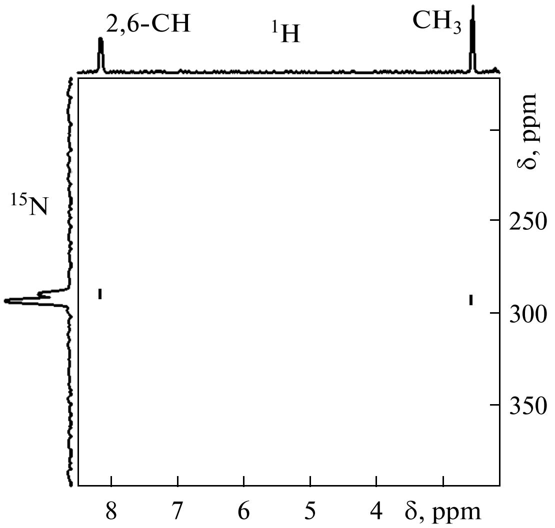


Fig. 5. 2D ^{1}H–^{15}N NMR spectrum (HMBC, long range) of a solution containing [Ag(NO$_3$)(2,6-Lut)$_2$] + 3,5-Lut in a ratio of 1 : 2 in $CDCl_3$.

Thus, now it is impossible to conclude unambiguously about the formation of mixed $AgNO_3$ complexes with lutidines, because the fast intermolecular exchange in the lutidine complexes in the studied solutions cannot be excluded.

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