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Structures of Silver Nitrate Complexes with Quinolines according to NMR Data

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Abstract—Silver(I) nitrate complexes $[AgNO_3(L)_2]$, where L is quinoline or 2-, 4-, and 8-methylquinoline, are synthesized and studied by the multinuclear NMR (^1H, ^{13}C, ^{15}N) method in acetonitrile. The influence of steric and electronic factors of the organic ligand on the NMR spectral parameters is revealed. The fast chemical exchange of the free and coordinated ligands is observed at room temperature. The ^{15}N NMR spectra are most informative. The formation of a complex with 8-methylquinoline is impeded because of steric hindrances.

Keywords: ^1H, ^{13}C, ^{15}N NMR spectra, Ag(I) complexes, quinolines, chemical exchang

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INTRODUCTION

Coordination silver polymers evoke increased interest, since they are promising materials for use in various areas of science and technology, in particular, as luminescent materials [1, 2]. As a rule, organic ligands with N-containing heterocycles are used for the formation of polymer chains. Therefore, it seemed important to study the coordination state of the metal during the reactions with these ligands in solutions using the NMR method and to reveal the informative content of multinuclear NMR spectroscopy, including ^1H, ^{13}C, and ^{15}N NMR, for the complex formation of the N-containing heterocyclic ligands with silver nitrate.

Lutidines (2,3-, 2,4-, 2,6-, and 3,5-dimethylpyridines) have been chosen earlier [3] as model compounds. The complexes formed by them are soluble in such coordinating solvents as dimethyl sulfoxide, acetonitrile, and dimethylformamide and also in chloroform, which made it possible to vary the environmental conditions for synthesis and spectra recording. According to the X-ray diffraction analysis data, the structure of the isolated Ag(I) compound with 3,5-lutidine consists of discrete neutral complexes $[Ag(3,5\text{-}Lut)_2NO_3]$. Two nitrogen atoms of two crystallographically equivalent lutidine ligands are involved in the coordination of the Ag^+ ion. The nitrate ion behaves as a weak chelating ligand with respect to the Ag^+ ion. The NMR spectral data of the studied complexes with lutidines in solutions show their similar structures and agree with the X-ray diffraction analysis results.

In this work, we continued to study the compounds of silver(I) nitrate with the pyridine derivatives by multinuclear NMR spectroscopy. The results of the syntheses, peculiarities of the structures, and the NMR spectra in deuterated acetonitrile are presented for the following compounds: $[AgNO_3(Quin)_2]$ (**I**), $[AgNO_3(2\text{-}MeQuin)_2]$ (**II**), $[AgNO_3(4\text{-}MeQuin)_2]$ (**III**), and $[AgNO_3(8\text{-}MeQuin)_2]$ (**IV**), where L is quinoline (Quin) or 2-, 4-, and 8-methylquinoline (2-, 4-, and 8-Me-Quin).

EXPERIMENTAL

Quinoline-[^{15}N] was synthesized using described procedures with some changes in the scheme: $^{15}NH_4NO_3$–benzamide-[^{15}N] [4]–aniline-[^{15}N] [5]–quinoline-[^{15}N] [6]. The following reagents were used without additional puridication: $^{15}NH_4NO_3$ (25% ^{15}N), boric acid, $FeSO_4 \cdot 5H_2O$, and *o*-nitrophenol (all reagent grade) and benzoyl chloride (Acros). Glycerol (analytical grade) was distilled in vacuo. The preliminary synthesis was carried out with unlabeled NH_4NO_3. The reaction course and purity of the prod-

ucts were monitored by chromatography on the Silufol UV-254 plates. The wittingly known unlabeled compounds were used as reference samples. Chromatograms were developed in the UV light or with iodine vapors.

Synthesis of benzamide-[^{15}N] was carried out according to the published method [4] using $^{15}NH_4NO_3$ instead of $^{15}NH_4Cl$. A one-neck 200-mL flask equipped with a magnetic stirrer was loaded with $^{15}NH_4NO_3$ (1.22 g, 15.06 mmol), which was dissolved in distilled water (10 mL). The obtained solution was covered with a benzene layer (15 mL) and cooled to 7–10°C, and a cooled solution of NaOH (1.30 g, 32.50 mmol) in distilled water (8 mL) was added. Then a solution of benzoyl chloride (1.80 mL, 2.18 g, 15.50 mmol) in benzene (65 mL) was poured immediately by one portion, and the reaction mixture was magnetically stirred at room temperature for 2 h. A formed precipitate of benzamide was filtered off, washed with cold benzene and ice-cold water, and dried in air. The weight of the precipitate was 1.52 g. Additional amounts of benzamide were isolated from the filtrate. The benzene portion of the filtrate was dried over K_2CO_3 and evaporated, and the residue was washed with hexane to remove a benzoyl chloride excess (the yield was 0.08 g). The aqueous portion of the filtrate was extracted with chloroform, and the extract was dried over K_2CO_3 and evaporated to obtain benzamide (0.15 g). The overall yield of benzamide-[^{15}N] was 1.75 g (95%). The obtained product was chromatographically rather pure (R_f = 0.38 in a benzene–acetone (6 : 1) mixture) and used further without additional purification.

Synthesis of aniline-[^{15}N] was carried out by the Hofmann reaction using a described method [5]. Dibromine (0.89 mL, 2.76 g, 17.24 mmol) was added dropwise to a magnetically stirred and cooled to –3°C (bath with ice and salt) solution of KOH (4.00 g, 71.4 mmol) in water (24 mL) with such a rate that the temperature would not increase higher than 0°C. After dibromine was dissolved, stirring was continued at 0°C for 30 min. Then benzamide-[^{15}N] (1.75 g, 14.34 mmol) was added by several portions to the obtained solution of potassium hypobromite, and the mixture was stirred at 0°C to the complete dissolution of benzamide (~1.5 h). Then the reaction flask was equipped with a reverse condenser, placed in an oil bath preheated to 80–90°C, and kept at this temperature for 30 min. The formed aniline was isolated from the reaction mixture by vapor distillation. The distillation completeness was monitored chromatographically. The distillate was extracted with ether, the ethereal extract was dried with K_2CO_3, and the ether was evaporated on a rotary evaporator at 20°C to obtain aniline-[^{15}N] (1.20 g, 89%) as a light yellow oil. The chromatographically pure product (R_f = 0.54 in an ether–hexane (2 : 1) mixture) was used further without additional purification.

Synthesis of quinoline-[^{15}N] was carried out by the Skraup reaction using a described method [6]. Aniline-[^{15}N] (1.20 g, 12.77 mmol), *o*-nitrophenol (1.08 g, 7.77 mmol), boric acid (0.85 g, 13.71 mmol), $FeSO_4 \cdot 5H_2O$ triturated in a mortar (0.48 g), and freshly distilled glycerol (4.90 g, 53.26 mmol) were consequently placed in a round-bottom 150-mL flask. The mixture was heated, stirred to the dissolution of the solid components, and cooled, after which concentrated H_2SO_4 (2.4 mL) was added dropwise. The obtained mixture was stirred and heated on a small open fire (before the beginning of the vigorous exothermal reaction, the burner was not placed at the center of the flask). Then the flask was transferred to an oil bath preheated to 170°C, and the mixture was kept at this temperature for 3.5 h. The reaction mixture was cooled, diluted with water (25 mL), and filtered. An insoluble precipitate was extracted with hot 10% H_2SO_4 (by two portions 20 mL each) and filtered off. To remove an *o*-nitrophenol excess, the combined acidic filtrates were subjected to vapor distillation to the cessation of yellow coloring of the distillate upon alkalization. The cooled reaction mixture was added by NaOH (8–9 g) to an alkaline pH and again distilled with vapor. To remove a possible aniline impurity, the distillate was acidified with HCl to a highly acidic pH and $NaNO_2$ (0.9 g, 13.04 mmol) was added. The mixture was refluxed for 1 h and cooled, and NaOH was added to an alkaline pH. Quinoline was isolated from an alkaline solution by vapor distillation. The distillate (~100 mL) was extracted with ether, the ethereal extract was dried with KOH and filtered, and the ether was filtered on a rotary evaporator at 40°C. The yield of chromatographically pure (R_f = 0.39 in an ether–hexane (2 : 1) mixture) quinoline with the 25% enrichment in ^{15}N as a light yellow oil was 1.25 g (75%).

Syntheses of compounds I–III were carried out using $AgNO_3$ (reagent grade) and Quin, 2-Me-Quin, 4-Me-Quin, and 8-Me-Quin (high-purity grade). Quinoline was dried with anhydrous Na_2SO_4 and distilled over zinc dust.

The compounds with the Me derivatives of Quin were synthesized similarly by the reaction of the nitrate with the ligand (1 : 2) in acetonitrile similarly to the previous synthesis [3] (synthesis and NMR spectroscopy of the $AgNO_3$ complexes with lutidines). Prismatic crystals with the composition $[AgNO_3(2\text{-MeQuin})_2]$ were isolated from the reaction of the nitrate with 2-Me-Quin.

For $C_{20}H_{18}N_3O_3Ag$			
anal. calcd., %:	C, 52.60;	H, 3.94;	N, 9.20.
Found, %:	C, 53.44;	H, 3.93;	N, 9.46.

In the case of 4-Me-Quin, the results of an analysis of the isolated crystals were almost the same as those for the isolated crystals of $[AgNO_3(2\text{-MeQuin})_2]$. The synthesis procedure for complex **I** was changed at the stage of recrystallization because of the high solubility of the latter in both acetonitrile and ethanol. Therefore, a solution of the nitrate with a twofold excess of Quin in MeCN was evaporated at 40–45°C to a minimum amount of the liquid phase, which allowed one to separate the formed solid crystalline phase by decantation. This phase was dissolved in chloroform and filtered, and toluene was added dropwise with stirring to the solution until a blurring of the solution appeared (the blurring did not disappear with time). Then the obtained solution was filtered and kept for several hours in the dark at room temperature. Isolated plate-like crystals were separated from the solution, washed with toluene, and dried in air.

For $C_{18}H_{14}N_3O_3Ag$			
anal. calcd., %:	C, 50.44;	H, 3.27;	N, 9.81.
Found, %:	C, 51.04;	H, 3.24;	N, 9.46.

Attempts to isolate the complex with 8-Me-Quin were unsuccessful. No isolation of the solid phase occurs upon the reaction of $AgNO_3$ with 8-Me-Quin in acetonitrile until almost all the solvent was removed. A syrupy residue was formed and then crystallized over the whole volume. Recrystallization using ethanol and methanol did not give the desired result. Therefore, the conclusion about the structure of the silver complex with 8-Me-Quin in a solution is based on the NMR spectral data only.

^{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 by deuterium at room temperature (298 K). The ^{1}H and ^{13}C chemical shifts are presented relative to tetramethylsilane (TMS), and the ^{15}N are given relative to liquid NH_3.

To assign the signals of the CH_3, CH_2, and CH groups of the organic ligand in the ^{13}C NMR spectra, the spectra were recorded by the DEPT method using the 45°, 90°, and 135° grading pulses [7].

Signal assignment in the ^{1}H and ^{13}C NMR spectra was performed using the heteronuclear multiple quantum correlation experiment (^{13}C,^{1}H–HMQC).

The procedure of heteronuclear multiple bond correlation (^{1}H–1/^{15}N HMBC) through far-range spin–spin coupling constants ($^nJ(^1H,^{15}N)$ = 10–15 Hz) was used for ^{15}N signal scanning and for signal assignment in the ^{1}H and ^{15}N NMR spectra.

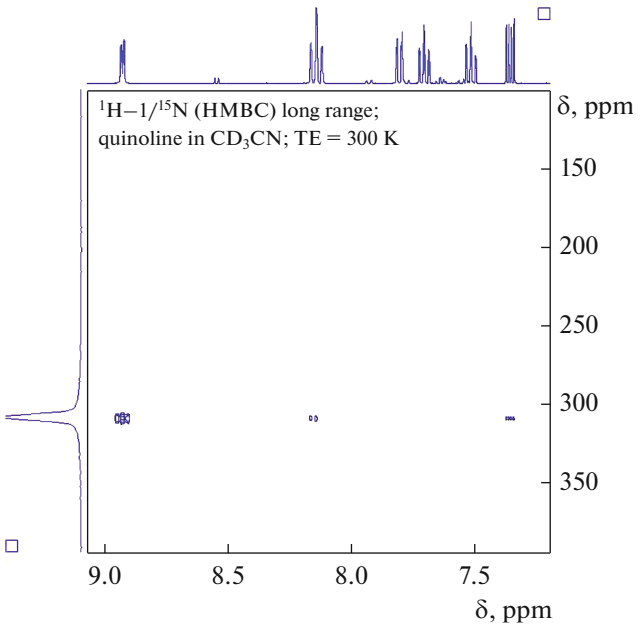


Fig. 1. 2D ^{1}H–^{15}N NMR spectrum (HMBC, long range) of a quinoline solution in CD_3CN at 300 K.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C{H} NMR spectra of free quinolines and their complexes show that their parameters change slightly upon the coordination of the organic ligand (table). The lowest changes (from –0.02 to 0.37 ppm) are observed in the ^{1}H NMR spectra. For the coordination of 4-MeQuin, the signals of the ring protons in position 8 undergo an upfield shift by 0.02 ppm. At the same time, the maximum downfield shift is observed in the spectra of the same complex for the CH protons of the ring in position 3.

The shift of the signals in the ^{13}C NMR spectrum upon complex formation is somewhat higher (from –1.2 to 2.9 ppm depending on the arrangement of the carbon nucleus).

It was found when recording the 2D ^{1}H–1/^{15}N HMBC spectra that, instead of one signal, several signals appeared in the ^{15}N projection (Fig. 2) in the case of the silver complexes with quinolines (unlike solutions of free quinolines (Fig. 1) and the complexes with lutidines [3]). The number and intensity of these signals depend on the value of the far-range spin–spin coupling constant $^nJ(^1H–^{15}N)$ specified in the pulse sequence used. To reveal reasons for this effect and the possibility of applying this procedure for the silver complexes with quinolines, as well as to establish the true number of signals in the ^{15}N NMR spectra of the studied compounds, we synthesized the silver complex with quinoline having the 25% enrichment in ^{15}N. The ^{15}N{H} NMR spectrum of the synthesized complex $[Ag(NO_3)(^{15}N\text{-Quin})_2]$ in CD_3CN was recorded in the "normal" scan mode (zg). According to the obtained

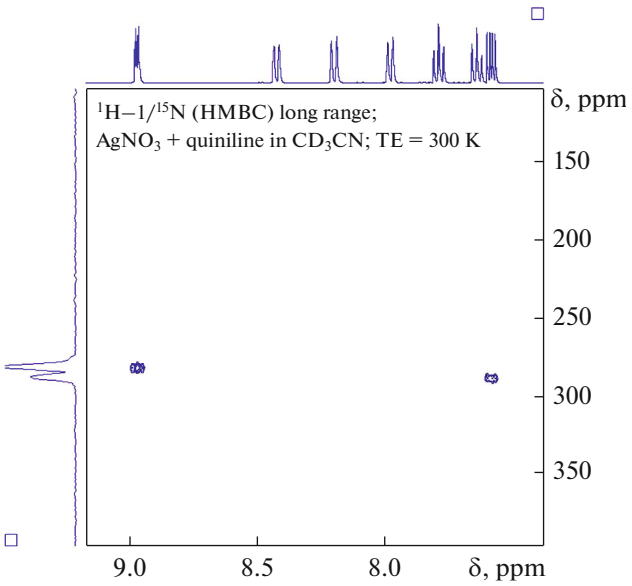


Fig. 2. 2D ^{1}H–^{15}N NMR spectrum (HMBC, long range) of a solution of $[AgNO_3(Quin)_2]$ in CD_3CN at 300 K.

spectrum, only one signal with a chemical shift of 283.1 ppm relative to liquid NH_3 corresponds to the complex with quinoline (Fig. 3).

The appearance of artifacts in the 2D NMR experiments is often observed when durations of 90° pulses are not fulfilled or for insufficiently prolong relaxation delays. In our case, the "mistuning" or deterioration of the quality factor of the resonance contour of the NMR detector occurs because of a solution of the ionic compound in the sample. This results in a significant elongation of the duration of the 90° pulse. The use of the 90° pulses obtained by the calibration of usual "non-salt" samples results in the appearance of artifacts. To fight against the appeared artifacts, it is necessary to calibrate the 90° pulse over the observation channel (1H) in 2D and multidimensional experiments after each exchange of the sample. This was described in more detail [8]. In our experiments, after the 90° proton pulse was calibrated and increased from 10 to 15 ms, the false signals in the ^{15}N projection disappeared.

The absence of additional splittings in the ^{1}H and ^{13}C NMR spectra (Fig. 4) and the presence of only one signal in the ^{15}N NMR of each isolated complex, as in the case of the complexes with lutidines [3], indicate that the positions of two coordinated molecules of quinoline (or its derivatives) are equivalent. It can be assumed that the structures of the silver complexes with quinolines and lutidines in solutions are similar.

Contrary to the changes observed in the ^{1}H and ^{13}C NMR spectra upon coordination, the changes in the ^{15}N NMR spectra are much more significant. The signal of the coordinated nitrogen atom in the quinoline ligand lies in a higher field compared to the signal of free quinoline. This is explained by the fact that the local paramagnetic contribution to the shielding of the nucleus (σ^p_{loc}) having a negative value is inversely proportional to the excitation energy between the low-lying electron transitions [9]: $\sigma^p_{loc} \propto 1/\Delta E$. The replacement of the $n \rightarrow \pi^*$ electron transitions by $\sigma \rightarrow \pi^*$ occurs upon the removal of the unpaired pair of the nitrogen atom due to its coordination. As a result, ΔE increases and the shielding of the nucleus increases. Therefore, the upfield shift of the nitrogen signal in the ^{15}N NMR spectrum of the complex com-

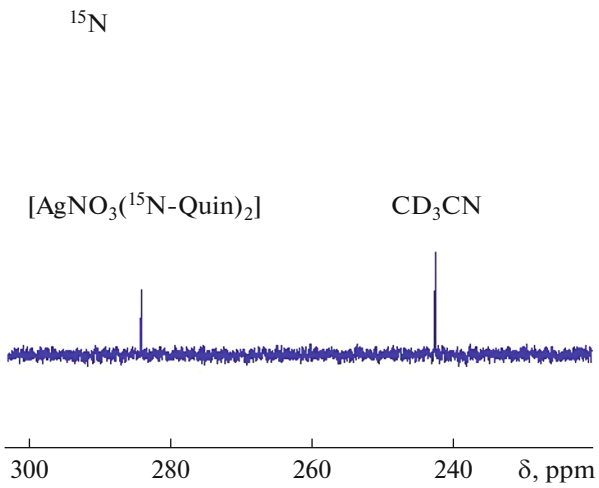


Fig. 3. ^{15}N{H} NMR spectrum of the complex $[Ag(NO_3)(^{15}N\text{-}Quin)_2]$ in CD_3CN.

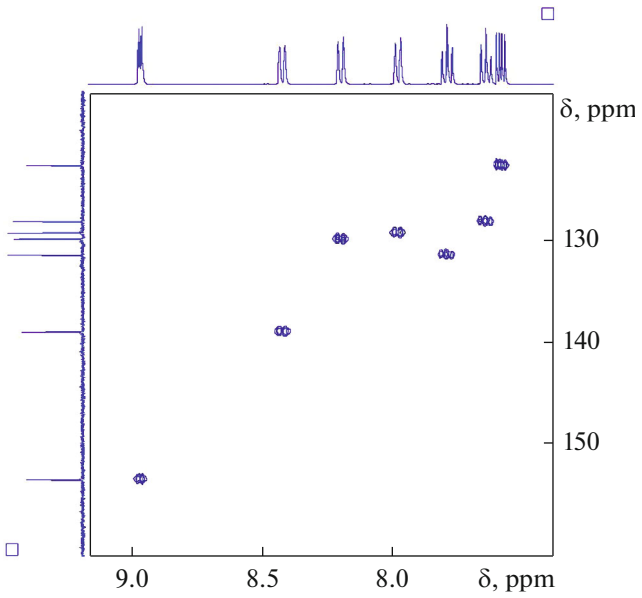


Fig. 4. 2D ^{1}H–^{15}C NMR spectrum (HMQC, long range) of a solution containing $[Ag(NO_3)(Quin)_2]$ in CD_3CN.

Parameters of the NMR spectra of solutions of quinolines and their complexes with Ag(I) in CD_3CN

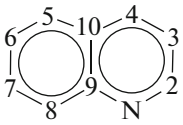
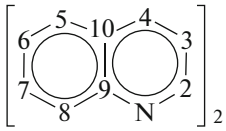
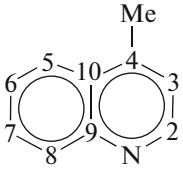
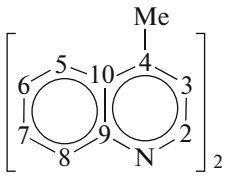
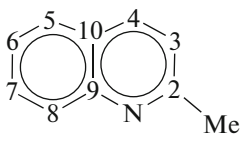
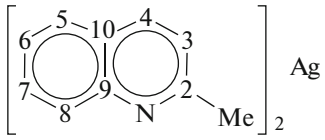
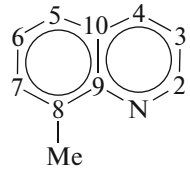
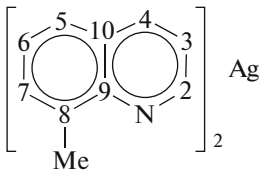
Compound	Atoms and groups	^{1}H NMR, ppm (relative to TMS)		^{13}C NMR, ppm (relative to TMS)		^{15}N NMR, ppm (relative to NH_3)	
	N					310.5	
	9-C			149.1			
	10-C			129.1			
	2-CH	8.92		151.3 ($^1J_{CN}$ = 1.3 Hz)		$^2J_{HN}$ = 11.5 Hz	
	3-CH	7.36		122.0			
	4-CH	8.13 ($^3J_{HH}$ = 7.5 Hz)		136.7 ($^3J_{CN}$ = 3.2 Hz)			
	5-CH	7.8 ($^3J_{HH}$ = 7.5 Hz)		128.8 ($^3J_{CN}$ = 2 Hz)			
	6-CH	7.52		127.3			
	7-CH	7.71		130.2 ($^3J_{CN}$ = 9.2 Hz)			
	8-CH	8.15		130.0 ($^2J_{CN}$ = 3.7 Hz)			
			(*) Δδ		Δδ		Δδ
	N					283.1	−27.4
	9-C			147.9	−1.2		
	10-C			129.8	0.7		
	2-CH	8.97	0.05	153.7	2.4	$^2J_{HN}$ = 9.5 Hz	
	3-CH	7.58	0.22	122.8	0.8		
	4-CH	8.43	0.28	139.1	2.4		
	5-CH	7.98	0.18	129.4	0.6		
	6-CH	7.64	0.12	128.3	1.0		
	7-CH	7.79	0.08	131.5	1.5		
	8-CH	8.20	0.07	130.0	0		
	N					305.8	
	Me	2.47		18.6			
	9-C			148.9			
	10-C			128.9			
	2-CH	8.78		150.9			
	3-CH	7.06		122.6			
	4-C			144.7			
	5-CH	7.83		124.8			
	6-CH	7.70		129.7			
	7-CH	7.48		126.9			
	8-CH	8.20		130.7			
			Δδ		Δδ		Δδ
	N					275.9	−29.9
	Me	2.76	0.29	19.0	0.4		
	9-C			148.3	−0.6		
	10-C			129.6	0.7		
	2-CH	8.81	0.03	153.0	2.1		
	3-CH	7.43	0.37	123.4	0.8		
	4-C			147.6	2.9		
	5-CH	8.15	0.32	125.6	0.8		
	6-CH	7.79	0.09	131.2	1.5		
	7-CH	7.67	0.19	128.0	1.1		
	8-CH	8.18	−0.02	130.6	−0.1		

Table. (Contd.)

Compound	Atoms and groups	^{1}H NMR, ppm (relative to TMS)		^{13}C NMR, ppm (relative to TMS)		^{15}N NMR, ppm (relative to NH_3)	
	N					304.3	
	Me	2.65		25.5			
	2-C			160.0			
	9-C			148.7			
	10-C			127.4			
	3-CH	7.24		122.9			
	4-CH	8.02		136.9			
	5-CH	7.78		128.6			
	6-CH	7.47		126.5			
	7-CH	7.67		130.2			
	8-CH	7.98		129.4			
			Δδ		Δδ		Δδ
	N					281.0	−23.3
	Me	2.81	0.16	27.1	1.6		
	2-C			161.4	1.4		
	9-C			147.8	−0.9		
	10-C			127.9	0.5		
	3-CH	7.48	0.24	123.6	0.7		
	4-CH	8.29	0.27	138.9	2.0		
	5-CH	7.94	0.16	129.1	0.5		
	6-CH	7.59	0.12	127.4	0.9		
	7-CH	7.77	0.10	131.3	1.1		
	8-CH	8.11	0.13	129.3	−0.1		
	N					307.0	
	Me	2.76		18.1			
	8-C			137.7			
	9-C			147.9			
	10-C			129.0			
	2-CH	8.87		150.1			
	3-CH	7.36		121.8			
	4-CH	8.10		136.9			
	5-CH	7.64		126.7			
	6-CH	7.39		127.0			
	7-CH	7.51		130.2			
			Δδ		Δδ		Δδ
	N					304.7	−2.3
	Me	2.77	0.01	18.1	0.0		
	8-C			137.6	−0.1		
	9-C			147.9	0.0		
	10-C			129.1	0.1		
	2-CH	8.91	0.04	150.4	0.3		
	3-CH	7.47	0.11	122.0	0.2		
	4-CH	8.25	0.15	137.2	0.3		
	5-CH	7.75	0.11	126.9	0.2		
	6-CH	7.48	0.09	127.2	0.2		
	7-CH	7.61	0.1	130.4	0.2		

* $\Delta\delta = \delta_{complex} - \delta_{ligand}$.

pared to a similar signal in the spectrum of free quinoline indicates the participation of this atom in the coordination of the ligand.

Among the silver complexes with quinoline, 2-methylquinoline, and 4-methylquinoline, the highest changes in the ^{15}N chemical shifts in CD_3CN are observed for the coordination of 4-methylquinoline ($\Delta\delta = -29.9$ ppm), whereas the lowest changes are observed for 2-methylquinoline ($\Delta\delta = -23.3$ ppm). The values $\Delta\delta = -27.4$ ppm for quinoline are intermediate. The changes found in the chemical shifts are by ~10 ppm lower than those for the coordination of lutidines in deuterated chloroform [3]. For the latter case, we showed [3] that the value of $\Delta\delta$ characterizing the binding of the unpaired electron pair of the nitrogen atom decreased noticeably with an increase in the dielectric constant of the solvent (ε).

In fact, in chloroform ($\varepsilon = 4.7$ at 25°C) the unpaired electron pair of the nitrogen atom of the organic ligand is bound only upon the coordination by the silver atom, because the solvent is inactive in this case. In a more polar solvent, which is CD_3CN ($\varepsilon = 37.5$ at 25°C), the electron pair of the nitrogen atom in the free ligand is already solvated partially by the solvent, which is manifested as a decrease in $\Delta\delta$. This effect should especially be pronounced in the case of a strong ligand exchange. Many silver complexes undergo a fast (in the NMR time scale) intra- and intermolecular exchanges [3, 10, 11]. This fact can be used to explain an anomalously minor change in the ^{1}H, ^{13}C, and especially ^{15}N NMR chemical shifts ($\Delta\delta = -2.3$ ppm) for the coordination of 8-methylquinoline (table). Since attempts to isolate this complex in the pure form failed, it can be assumed that the reaction of 8-methylquinoline with $AgNO_3$ in an ratio of 2 : 1 in acetonitrile affords an insignificant amount of complex $[Ag(NO_3)(8\text{-MeQuin})_2]$ because of the steric hindrances caused by the methyl group in position 8. Owing to a strong exchange of the free and bound ligands in a solution, the positions of signals in the NMR spectrum at a specified temperature will be averaged and determined by the ligand ratio. For example, if accepting for the pure complex $[Ag(NO_3)(8\text{-MeQuin})_2]$ in acetonitrile that the change in the chemical shift of the ^{15}N signal upon the coordination of 8-methylquinoline is −30 ppm, then the observed value $\Delta\delta = -2.3$ ppm means that only 7.7% of the complex were formed.

Thus, the complex formation of the Ag^+ ion with quinoline and its substituted analogs in an acetonitrile solution was studied by the multinuclear NMR method. The coordination of the Ag^+ ion with the N-containing aromatic ligands was shown to involve the fast chemical exchange between the free and coordinated N-containing ligand. It is mentioned that ^{15}N NMR spectroscopy is the most informative method for studying the complex formation of the N-containing heterocycles with the silver ion in solutions.

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