SURVEY OF UNSATURATED AMINES.

21. ¹³C AND ¹H NMR SPECTRA OF COMPLEXES OF CONJUGATED IMINES AND PYRIDINES WITH COMPOUNDS OF A1(III) AND Cr(III)

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It was noted in a previous communication [1] that according to ¹³C and ¹H NMR data conjugated imines $R^1R^2C=CRCH=NCMe_3$ (I) and PhCH=NCMe₃ (II) in MeOH form complex compounds (CC) with salts of A1(III) and Cr(III) of a 1:1 composition.

Data from the NMR investigations of these CC and also of complexes of these same metals with some pyridines (Py) is presented in the present work.

The investigated CC are complexes of the nv type with a donor-acceptor bond $N \rightarrow M$ (M = A1, Cr). Complexes of CrCl₃ and AlCl₃ with amines [2] are the closest analogs of these CC; the introduction of a ligand containing nitrogen into the system of unsaturated bonds did not influence the character of the CC: as also unsaturated amines, conjugated imines (I) and (II) reacted with Al and Cr salts according to the nv and not the πv type. First of all this gives rise to a significant increase in the ¹J_{C,H} constant for the sp² atom of C adjacent to the N atom (~15%, Table 1). The growth of the constant as a result of the shift of electron density from the heteroatom occurs, for example, during the conversion from aldehydes to

their cationic forms. Thus, in $CH_2=0$, ${}^{1}J_{CH} = 172$ Hz [3], and in $CH_2=0$ H thevalue of J increases to 198-210 Hz, i.e., by 15-22%. The alternated change of shielding of ${}^{13}C$ nuclei of a conjugated chain $C^1=C^2-C^3=N$ is also characteristic for the nv-imine complex: signals of C^1 and C^3 are shifted to the weak field and C^2 to the strong field. A similar alternation of $\delta^{13}C$ is also observed in complexes of derivatives of Al(III) halides with α -carbonyl derivatives of thiophene, in which the C=0 and C^3 signals are shifted to the weak field and C^2 signals to the strong field with reference to the original thiophene [4]. It is of inter-est to note that in the assumed conditions (CD_3OD , $30^{\circ}C$) formation of the complex (π v-type) of butadiene with [Al(OH_2)₆]Cl₃ is not observed and the $\delta^{13}C$ value is practically unchanged.

As is seen in Table 2, the $J_{1,2}$ constant $(R' = H^1, R = H^2)$ is equal to 15-16.5 Hz in both the free and in the complex-bonded imine; consequently, the trans position of the substituent R'' (Me, Et, Ph) and the CH=NCMe₃ fragment is preserved in the original (I) and also in the corresponding ligands.

The data in Table 1 shows that a significant change of $\delta^{13}C$ of C^1 , C^2 , and C^3 occurs as a result of the formation of CC. In the case of CC of imine (Ic) with $M = [Al(OH_2)_6]Cl_3$, $\delta^{13}C$ is changed to a value of 20.16 to 27.26 for C^1 , -5.77 to -9.25 for C^2 , and 12.63 to 14.89 ppm for C^3 ; 31.21, -7.16, and 12.27 ppm for AlCl_3; and 27.02, -7.16, and 12.27 for [Cr- $(OH_2)_4Cl_2]Cl_2H_2O$. Considering the relatively good correlation between $\delta^{13}C$ and the total $(\pi + \sigma)$ electron density both for the C=C bond in monosubstituted ethylenes [5], and for the conjugated system of double bonds of butadiene [6], one can assume that $\delta^{13}C$ is determined chiefly by the change of electron density $(\pi + \sigma)$ also in the azabutadiene chain $C^1=C^2-C^3=N$. Specifically it concerns the C^1 , of which other effects, as for example, anisotropy of the N \rightarrow M bond. influence the $\delta^{13}C$ to a lesser degree.

A significant change of δ^{13} C for C¹ in the azadiene chain C¹=C²-C³=N indicates a deficit of electron density on C¹. The high activity of azaolefins in reactions of the electrophilic substitution type, for example, heterocyclization [1] can be a consequence of this.

In the case of trans-l-substituted-l,3-butadienes [6] the δ^{13} C change with variation of the substituent is attributed to a large extent to the change of π -electron density, since alternation of both of these quantities is observed. At the same time, the best linear cor-

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¹³C NMR Spectra of Compound (I) in CD₃OD (δ^{13} C relative to TMS ±0.06 ppm, ¹J_C,H, Hz) TABLE 1.

relation of $\delta^{13}C$ occurs upon calculation of the change of the total $(\pi + \sigma)$ electron density. It follows from this correlation that for electron-acceptor substituents a decrease of electron density on C_{β} and C_{γ} leads to a shift of their signals in the ¹³C spectrum to the weak field. In constrat to $\delta^{13}C$ during complex formation of imines, $\delta^{14}H$ increases for all protons of the conjugated chain and alternation of $\delta^{14}H$ does not occur.

The data of Tables 1 and 2 show also that δ^{i} and δ^{i} H of complexes depends very little on the nature of the investigated cations. So, δC^1 in the complex of imine (Ic) with M = $[A1(OH_2)_6]Cl_3$ is equal to 27.26 ppm and with $M = [Cr(OH_2)_4Cl_3]Cl_2H_2O$ is equal to 27.02 ppm. Agreement of the change of δ^{13} C and δ^{1} H (both according to magnitude and to sign) upon formation of CC with diamagnetic Al(III) and paramagnetic Cr(III) indicates the relatively small contact shifts under the influence of chromium. Thus, one can assume that the change of chemical shifts in ligands (I), (II) CC with Al(III) and Cr(III) are produced by the same causes and are determined mainly by a transfer of electron density of $N \rightarrow M$. The results of the research of PMR spectra of complex compounds of 2,2-dipyridyl with Cr(III) and Cr(II) also confirm this conclusion; in CC with $CrCl_2$ the α -H signal is shifted to the strong field by 28 ppm compared to the free ligand and is broadened to 700 Hz [7], while in the complex with $[Cr(OH_2)_4Cl_2]Cl_2H_2O$ the δ^1H is not more than 0.18 ppm in the weak field, as also in CC of [A1(0H₂)₆]Cl₃ (0.27 ppm). The paramagnetism of Cr(III) appears only in the broadening of the lines of the spectra, especially noticeable in concentrated solutions. So, with the concentration of (Ic) with $M = [Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$ of 8.4 $\cdot 10^{-4}$ mole/liter (in MeOH) narrow proton signals are visible in the spectrum and lines of the ¹H triplet are well resolved. Upon an increase in the CC concentration to $5 \cdot 10^{-2}$ mole/liter a broadening of the signals occurs without a change of chemical shift ('H spectrum becomes unresolved). With further increase in CC concentration not only are the imine signals broadened but also those of methanol ('H and ¹³C). Evidently these changes are caused by an exchange between molecules of H₂O in the inner sphere and molecules of the solvent, as is described for example for M^{2+} (M = Co, Li) [8], or by solvation in the outer sphere, which was observed in systems Cr(III) -MeCN-H₂0 [9].

The significantly greater influence on δ^{13} C indicates the nature of the original ligand. In this case δC^1 in the complex of the tert-butylimine of cinnamaldehyde (Id) is changed least of all (20.16 ppm), where the azabutadiene chain is conjugated with a phenyl ring; the maximum δC^1 shift was observed in the complex derivative (Ic) (27.26 ppm; the cation is [Al-(OH₂)₆]Cl₃).

The maximum δC^1 change (31.21 ppm) was observed in the molecular CC (Ic) with AlCl₃ in the nonaqueous medium of CH₂Cl₂. However, additional unresolved signals, evidently corresponding to polymerization products of (Ic), appear in the strong field region in the PMR spectra in this case. The possibility of such a process confirms, for example, the easy polymerization of ethyleneimine in CH₂Cl₂.

The marked effect of the protons of the solvent on the ¹³C NMR spectra of the free imines (I) and (II) should be mentioned. So, in the case of (Ia) the difference in the δ^{13} C of the pure liquid and a solution in CD₃OD is 5.08 ppm for C¹, -1.83 ppm for C², 4.46 ppm for C³, and somewhat less for the C of the substituent (see Table 1). The character of the change of the signals here is the same as with complex formation: protonation (deuteration) of the N atom or the formation of a H bond with H₂O and MeOH causes a change of the same qualitative character in the conjugated chain C=C-C=N as the transfer of charge (N^{δ +} \rightarrow M^{δ -}) in complex systems.

An important property of CC was discovered during the investigation of solutions with a different molar ratio of the original imine to Al(III) or Cr(III). The maximum shift of all of the signals in the ¹³C spectrum is observed with an imine:M ratio = 1:1. Both ¹³C and ¹H spectra contain one collection of lines which remain practically unshifted during temperature changes from 30 to -20° C. An increase in the M(III) concentration does not effect the magnitude of the chemical shifts, but upon dilution of the 1:1 mixture by a new quantity of imine, the spectral pattern is changed because of the gradual shifting of all signals to positions which they occupy in the spectrum of the free imine. For example, with a ratio change from 1:1 to 4:1 δ^{1} H is changed from 7.13 to 6.68, δ H³ from 8.40 to 8.20, δ Me₃C from 1.53 to 1.40, δ MeC from 2.00 to 1.93, and δ Et from 1.15 to 1.10 and from 2.50 to 2.40 ppm in the ¹H spectrum of the (Ic) complex with M = [A1(OH₂)_6]Cl₃ (see Table 2). Thus during CC formation signals of all of the protons of the imine are shifted to the weak field, and an excess of the imine returns them to the original position. In the ¹³C spectrum, where also one collection of lines is observed for any imine:M value, dilution of an equimolar mixture by imine to the ratio of (Ic):M of 8:1 leads to a decrease in the δ C¹ from 168.23 to 146.55; δ C² is

pound R R' R' M H' H'' H''' H''' H''''''''''''''''''''''''''''''''''''	٩ıH			J _{H,H}	
(Ia) H ² H ¹ Me [Al(OH ₂)•]Cl ₃ $7,46$ $6,33$ $6,22$ $7,92$ $ 1,85$ $ 1,33$ (Ib) H ² Me Me [Al(OH ₂)•]Cl ₃ $7,46$ $6,77$ $8,68$ $ 2,13$ $ 1,93$ (Ib) H ² Me Me [Al(OH ₂)•]Cl ₃ $ 5,90$ $8,15$ $ 1,92$ $ 1,93$ (Ic) Me H ¹ Et [Al(OH ₂)•]Cl ₃ $ 5,75$ $ 7,73$ $ 1,00; 2,16$ $ 1,03; 2,22$ Me H ¹ Et [Al(OH ₂)•]Cl ₃ $ 5,93$ $ 7,73$ $ 1,00; 2,16$ $1,02; 2,22$ Me H ¹ Et [Al(OH ₂)•]Cl ₃ $ 5,90$ $ 7,73$ $ 1,00; 2,16$ $ 1,03; 2,22$ Me H ¹ Et [Al(OH ₂)•]Cl ₃ $ 7,13$ $ 8,40$ $2,00$ $1,13; 2,52$ Me H ¹ Et [Al(OH ₂)•]Cl ₃ $ 7,73$ $ 8,77$ $2,20$ $1,13; 2,52$ (Id) H ² H ¹ Ph [Al OH ₂)•[Cl ₃]Cl ₃ $ 7,73$ $ 8,77$ $2,20$ $1,13; 2,52$ (Id) H ² H ¹ Ph [Al OH ₂)•]Cl ₃ $ 7,73$ $ 8,77$ $2,20$ $1,13; 2,52$ (Id) H ² H ¹ Ph [Al OH ₂)•]Cl ₃ $ 7,79$ $7,90$ $7,27$ $ 8,65$ $2,00$ $1,13; 2,52$ (Id) H ² H ¹ Ph [Al OH ₂)•]Cl ₃ $ 7,00$ $7,27$ $ 8,65$ $2,00$ $1,13; 2,52$ (Id) H ² H ¹ Ph [Al OH ₂)•]Cl ₃ $ 8,00$ $ 7,00$ $7,00$ $ 7,00$ $ 7,00$ $ 7,00$ $ 7,00$ $ 7,00$ $ 7,00$ $ 8,00$ $ -$	R" R'	MeaC	J _{2.3}	J _{1,2}	other constant
(Ib) H ² Me Me [Al(OH ₂), a]Cl ₃ = $5,90$ 8,15 = $1,493$ H ² Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $5,75$ = $7,73$ = $7,73$ = $2,22$ Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $5,93$ = $7,73$ = $7,73$ = $1,001$ 2,16 Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $7,13$ = $8,40$ 2,00 1,155 2,222 Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $7,13$ = $8,17$ 2,20 1,165 2,257 Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $7,73$ = $8,17$ 2,20 1,155 2,257 Me H ¹ Et [Al(OH ₂), a]Cl ₃ = $7,73$ = $7,73$ = $7,700$ 1,155 2,257 H ² H ¹ Ph = $1,10$ = $7,73$ = $7,702$ 1,732 = $7,00-7,67$ (Id) H ² H ¹ Ph = $1,10$ = $7,73$ = $7,00-7,67$ = $7,00-7,67$ (Id) H ² H ¹ Ph = $1,10$ = $7,702$ 6,85 8,05 = $-7,00-7,67$ = $7,00-7,67$ = -1 = $8,008$ = $-7,00-7,67$ = $-1,100$ = $7,00-7,67$ = $-1,100$ = $7,0$	1,85 2,13	1,12	8,0 9,5	15,2 1, 15,0 1,	^{гн¹} , же=5,2 ^{гн¹,} же=6,5
(Ic) Me H! Et $-$ Me H! Et	1,93 1,87 2,22 2,12	1,18 1,45	9,2 10,0	 	'н², же — 1,2 'н², же — 1,0
(Id) H ² H ¹ Ph $-$ 6668 6.82 7.88 $-$ 7.00–7.67 H ² H ¹ Ph $-$ 6.68 6.82 7.88 $-$ 7.00–7.67 H ² H ¹ Ph $[\Lambda I(OH_2)_{\bullet}]CI_3$ 7.99 7.90 8.82 $-$ 6.88–7.88 (II) $ +$ $ -$ 8.08 $ -$ 6.88–7.88	1,00; 2,18 1,03; 2,22 1,15; 2,50 1,13; 2,43 1,15; 2,58 1,15; 2,58	1,17 1,18 1,53 1,53 1,53 1,53 1,17 1,17 1,17 1,17 1,17 1,17 1,17 1,1	11111		, н', сн ₁ =7,0 сн ₂ . же=7,5 л', сн ₂ =7,2
(II)	7,00–7,67 7,00–7,85 6,88–7,88	1,18 1,20 1,50	0'20 0'20	15,0 15,0 15,0 15,0	сн. же /, 3 11', н'=2,0 н', н'=2,0
$[Al(OH_2)_{\bullet}]Cl_{3}$	J I I J I I	1,18 1,20 1,63	111		Ph 7,00–7,18 Ph 7,15–7,88 Ph 7,57–8,30

¹H NMR Spectra of Compound (I) in CD₃OD (8¹H relative to TMS, ±0.01 ppm, J_{H,H}, Hz) R². R (I) TABLE 2.

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increased from 131.25 to 135.80, and δC^3 is decreased from 172.44 to 163.67 ppm. In other words, the shielding of the ¹³C nucleus is changed alternately, as with complex formation, but in the opposite order. Shifting of ¹³C signals to their original values also occurs for the C atoms of the substituent: δMe_3C is decreased from 61.56 to 57.91, $\delta \underline{Me_3C}$ is increased from 28.17 to 29.87, $\delta \underline{MeC}$ is increased from 10.74 to 11.22, δCH_2 is decreased from 24.46 to 22.64, and δMe is increased from 12.50 to 13.50 ppm. In the case of the complex with Cr(III) (M = [Cr(OH_2)_4Cl_2]Cl.2H_2O) the values of δH^1 (6.18 ppm) and δH^3 (7.90 ppm) at an imine: M ratio of 6:1 approach the values of the free (Ic) (5.75 and 7.73 ppm, respectively) and at a (Ic): M ratio of 11:1 the δH^3 difference in the free and the complex imine amounted to only 0.1 and a δH^1 difference of 0.3 ppm. Such a change in the chemical shifts of ¹³C and ¹H indicate an exchange process between a molecule of (Ic) in the inner complex sphere and the free imine in solution

$$[Al(OH_2)_{5} \cdot imine]Cl_3 + imine^* \gtrsim [Al(OH_2)_{5} \cdot imine^*]Cl_3 + imine$$
(1)

$$[Cr(OH_2)_3 \cdot \text{imine} \cdot Cl_2]Cl \cdot 2H_2O + \text{imine} * \gtrsim [Cr(OH_2)_3 \cdot \text{imine} \cdot Cl_2]Cl \cdot 2H_2O + \text{imine}$$
(2)

The exchange takes place with a rate at which the spectra of the free and the complex imine cannot be observed separately. According to the δC^1 change, which reacts more strongly at the CC formation, one can expect that the rate of exchange >4.10² sec⁻¹. A similar exchange between molecules in the inner sphere and in the solvent are also observed in a series of other systems, for example in aqueous solutions of A1(ClO₄)₃ and Me₂SO₄ [10], by the NMR method.

Pyridine bases also form complexes of a 1:1 ratio in salt solutions of A1(III) and Cr-(III), which, however, strongly differ from CC with conjugated imines in spectral characteristics. Chemical shifts of C_{α} , C_{β} , and C_{γ} atoms of the Py ring are changed upon complex formation less than is observed in CC of (I) and (II) for C¹, C², and C³, and the direction of the δ^{13} C changes takes on an ionic character. If in conjugated imines δ C³ (analog of C_{α} of the Py ring) is increased, and δ C² (analog of C_{β} in Py) is decreased, then the reverse occurs in the Py: δ C_{α} is decreased from -4.4 to -8.3 and δ C_{β} increases from 2.7 to 6.8 ppm (Py:M ratio = 1:1). Only the chemical shifts of C¹ in imines and C_{γ} in Py are changed in a similar manner; they are increased in the series of imines (from 20.16 to 27.26 ppm) and in Py (from 10.6 to 15.1 ppm).

Since during the complex formation of $Py \rightarrow M$ one should expect a decrease in electron density of the C_{α} [11], and since there is a linear dependency between the total $(\pi + \sigma)$ electron density and $\delta^{13}C$, then the shift of the C_{α} signal to the strong field must be caused by other reasons. Three basic factors are examined during the discussion of a similar effect in proton spectra: 1) decrease of the paramagnetic shielding of the ¹⁴N nucleus [13]; 2) anisotropy of the forming N \rightarrow M bond; and 3) change of ring current.

Evidently the unexpected δ^{13} C shift in the investigated complexes is caused mainly by the first factor because the signal of the N atom of Py in the ¹⁴N spectrum is significantly shifted to the strong field. So, δ^{14} N is shifted to 62.7, 64.4, and 59.2 ppm in pyridineborane, 2-methylpyridineborane, and 4-methylpyridineborane, respectively [14]. The influence of the anisotropic bond N \Rightarrow M on the shift of the C_{α} signal, on the other hand, evidently is small, since the analogous C_{α} shift to the strong field (-7.2 to -7.5 ppm) occurs also in protonated (ionic) forms of Py bases [15]. The change of ring current as a result of complex formation must reflect equally on the shifts of the signals of the Py cycle. In contrast to C_{α} the C_{γ} changes in CC are determined basically by a decrease in electron density on the C_{γ} atom, since the effects in this position of the ring mentioned above must be at a minimum [16].

Analysis of the data in Table 3 shows that in the Py series, as also in conjugated imines, the δ^{13} C changes for complexs with Cr(III) and Al(III) are caused primarily by the same effects, and the contribution of the paramagnetic effect of Cr(III) is small and appears only in a broadening of the signals in the ¹H and ¹³C spectra. This conclusion also pertains to δ^{1} H of compounds of Al(III) [18], B(III) [15], and Cr(III) (see Table 4).

One must note the existence of the dependence of δ^{13} C of aromatic hydrocarbons with a Py ring both on the nature of the base and also on the complexing cation. In the case of complexes $[(NH_3)_5C0\cdot C_5H_5N]^{3+}$ and $[(NH_3)_5Rh\cdot C_5H_5N]^{3+}$, the complex formation of Co(III) and Rh(III) leads to a change in δC_{γ} of 3-4 ppm [15], while with salts of Cr(III) and Al(III) the change is 12-14 ppm; the change in δC_{α} is 3-4 and -4 to -8 ppm, respectively, i.e., differences also

¹³C NMR Spectra of Compound (III) (δ^{13} C relative to TMS, ±0.06 ppm, ¹J_{C,H}, ±1 Hz) -È

(III) M⊷N

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Com- pound	æ	Ж	M	Solvent	Pyridine:M molar	ຮວ	св	сy	<u>۳</u>	ж	Literature citations
(IIIa)	H	H		1	1	150,6 1177 BY	124,5	136,4	·I	I	[3]
	ннн	ннн	[Al (0H2) 6]Cl3 [Al (0H2) 6]Cl3 [Al (0H2) 6]Cl3	CD ³ OD CD ³ OD CD ³ OD	415 1:2	142,67 142,67 142,85	125,555 128,95	148,50 148,50 148,48	111	111	
	нннн	ННН	[Al(OH2),]Cl3 [Al(OH2),6]Cl3 [Al(OH2),6]Cl3	CD30D D20* D20*	4 	(146,49 144,49 141,52 141,52	(1/4) (27,49 124,82 127,80 126,58	(170) 145,58 137,94 147,58 144,56			
(qIII)	Ме	Н	i	1	1	450,1	126,7	147,7	21.5	1	[3]
	Me Me	нн	[Al(OH ₂),e]Cl ₃	CD ₃ OD	1:1	149,77 141,76 (190)	126,34 129,37 (175)	150,02 162,76 -	21,00 22,64 (129)	11	
(IIIc)	Н	Me	ſ	1		159,9	123,4	137,2	. f	25,1	[3]
				<u>.</u>		(C ⁻) 149,8 (C ⁶) (172)	(164) (164)	(159)	t	(127)	[17]
. <u></u>	Н	Me	[Al(0H2),]Cl3	CD ₃ OD	1:1	155,18 (C ²)	129,37 (C ³)	147,77	_	19,85	
						441,88 (C ⁶) (191)	(176) 125,85 (C ⁵) (174)	(169)		(128)	
(IIIA)	Me	Ме	T	i I	l	158,52 - 148.92	125,25 (160) 122.8	149,23	20,76 (127)	23,68 (128)	
	Me	Me	[Al(OH2),]Cl3	CD ₃ OD	1:1	$\begin{pmatrix} (C^{6}) \\ 154,02 \\ 154,02 \\ (C^{2}) \\ (C^{2}) \\ (C^{2}) \\ (C^{2}) \\ (C^{2}) \end{pmatrix}$	$\begin{array}{c} (C^5) \\ (165) \\ (185) \\ (129,56 \\ (C^3) \\ (170) \\ (170) \\ (C^5) \\ (172) \end{array} \\ (172) \end{array}$	161,86	22,22 (129)	19,43 (130)	
(IIIe)	Н	Н	$[Cr(OH_2)_4Cl_2]Cl\cdot 2H_2O$	CD ₃ OD	1:1	146,25	131,31	150,86	1	I	
*6 ¹³ C ar	te meas	sured f	rom MeOH as an inn	er standa	ird and are	e revised	to TMS (ôMeOH 49.	.3 ppm).		_

TABLE 4. PMR Spectra of Compounds (III) and (IV) ($\delta^{1}H$ relative to TMS, ± 0.01 ppm) M (IV)

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Literature citations	[14] [14]					[2]		
Mey	ସ୍ଥ୍ୟ 8889 889 1 । । ।	1	1	1	1	1	. I	1
Mea	1111	I	i	ł	. I	1	I	1
Нγ		+8,44	+8,23	+8,30	+8,04	+16,86	+8,46	+8,37
$H_{\beta}(\beta')$	6,94 7,79 7,78 7,78 7,45 (3,37 (5,57) (5,57)	8,63 (3,3') 7,91 (5,5')	8,46 (3,3') (5,5')	8,54 (3,3') (5,5') (5,5')	8,38 (3,3') 7,55 (5,5')	4,73 (3,3') (5,5') (5,5')	8,69 (3,3') (5,5')	8,53 (3,3') (5,5')
Нα	8,88,88 8,44 8,42 8,53 7,31 8,42 8,53 7,31 8,42 8,53 7,31 8,44 8,53 7,31 8,44 8,53 7,31 8,44 8,53 8,54 8,54 8,54 8,54 8,54 8,54 8,54 8,54	8,89	8,77	8,83	8,70	19,26	8,92	8,83
Ligand: M. molar	्रास्त्रस्य संसर्ग्त	स्न • • स्न	1:1	3:1	, ເ. ເວ	3.1	1:2	1:2
Solvent	CD30D CD30D CCL CCL CCL CCL	CD ₃ OD	CD ³ OD	CD3OD	CD ₃ OD	CD30D	CD30D	CD30D
M	[Al (OH2) a]Cl3 [Cr (OH2), Cl2]Cl-2H2O AlCl3 BH3 -	[Al(OH2)e]Cl3	[Cr(OH2) (Cl2]Cl-2H2O	[Al(OH2),]Cl3	[Gr (0H2) (Gl2] Gl 2H20	GrG12	[Al (OH2) a]Cl3	[Cr(0H2), Cl2]Cl·2H20
R,	ннннн і	I	1	1	I	1	1	ł
щ	Mee Mee Mee Mee	· 1	I	I	ł	l	1	I
pound-		(IV)	(11)	(11)	(11)	(VI)	(VI)	(AI)

 $\begin{array}{c|c} R & & \\ &$

in sign for the two cation pairs. An analogous pattern is also observed for Py derivatives. While for the same cation (A1) δ^{13} C is increased in the order 2-methylpyridine (10 ppm) < pyridine (12 ppm) < 4-methylpyridine (15 ppm).

Not only δ^{13} C but also ¹J_{CH} are measured in CC of Py derivatives, especially for C_{α}. For example, in the complex of Al(III) with α -picoline [compound (IIIc), see Table 3] ¹J_{CH} increases for C⁶ from 172 Hz [16] in free α -picoline to 191 Hz in its CC.

As also in CC of conjugated imines, an excess of the Py ligand shifts the ¹³C signals to the side of the uncomplexed Py base, and an increase in the concentration of $[Al(OH_2)_6]Cl_3$ has practically no effect on the magnitude of $\delta^{13}C$, i.e., an equilibrium of the type (1) and (2) occurs in solution.

It is of interest to note that upon solution of the Py base in protic or deuterated solvents, as also upon complex formation, chemical shifts of the ring C atoms are changed to a lesser degree than in the case of conjugated imines, but in the same direction (see Tables 1 and 3), as also upon the formation of ions of pyridine [15].

EXPERIMENTAL

Imines are obtained according to [19] by the condensation of tert-butyl amine and the corresponding aldehydes. tert-Butylimine of crotonaldehyde (Ia), 74% yield, bp 54-56°C (25 mm). Found: C 76.85; H 12.23; N 11.11%. C₈H₁₅N. Calculated: C 76.74; H 12.06; N 11.18%. tert-Butylimine of dimethylacrylaldehyde (Ib), 65% yield, bp 85-87°C (30 mm). Found: C 77.93; N 12.28; N 10.22%. C₉H₁₇N. Calculated: C 77.63; H 12.36; N 10.06%. tert-Butylimine of 2-methyl-2-pentenal (Ic) (condensation product of tert-butylamine and propanol) [20], 82% yield, bp 93-100°C (35 mm). Found: C 78.48; H 12.55; N 9.25%. C₁₀H₁₉N. Calculated: C 78.36; H 12.49; N 9.13%.

tert-Butylimine of benzaldehyde (II), 88% yield, bp 93-95°C (8 mm). Found C 81.75; H 9.28; N 8.68%. C₁₁H₁₅N. Calculated: C 81.93; H 9.37; N 8.68%. tert-Butylimine of cinnamaldehyde (Id) is obtained in benzene, 80% yield, bp 148-150°C (10 mm). Found: C 83.13; H 9.28; N 7.56%. C₁₃H₁₇N. Calculated: C 83.37; H 9.15; N 7.48%.

Complexes of the imines, referred to above, and Py bases are obtained by the addition of a solution of the corresponding imine in MeOH (CD_3OD) to a solution of $[A1(OH_2)_6]Cl_3$ or $[Cr-(OH_2)_4Cl_2]Cl-2H_2O$ (also in MeOH) in a 1:1 ratio and by subsequent vacuum evaporation at 40-50°C.

The determination of Cl is conducted by argentimetric titration with a K_2CrO_4 indicator [21]. Al(III) is determined in the form of the oxide; the water, not bound in the complex, in the chromium compounds was calculated according to Werner [22]. The chemical shifts of ¹³C were determined from spectra of double resonance of ¹³C-{¹H}. J₁₃C,H constants were determined from high-resolution spectra; "gated decoupling" is removed in the system; the inner standard is TMS (or HMDS). Spectra are obtained on a "Bruker WP-60" instrument (15.08 MHz) pulsed with the utilization of a Fourier transform. PMR spectra are recorded on this same instrument (60 MHz). The reference of signals in ¹³C spectra is conducted by the method of selective double resonance of ¹³C-{¹H}, and also according to the $\delta^{13}C$ and J_{13C,1H} values.

CONCLUSIONS

1. Complexes of conjugated imines and some pyridine bases with Al(III) and Cr(III) compounds are studied by ¹³C and ¹H NMR methods. The investigated complexes belong to the nv type with a donor-acceptor bond of N \rightarrow metal and have a 1:1 composition.

2. The formation of complexes with imines $R'R''C^1=C^2R-C^3H=NCMe_3$ is accompanied by an alternating change of chemical shifts of ¹³C along the conjugated chain. A significant $\delta^{13}C$ change for the ring carbon in the azabutadiene chain (~30 ppm to the weak field) indicates the formation of an electrophilic center.

3. The nature of the studied ligands, containing nitrogen, and of the metallic cations influences the $\delta^{13}C$ changes upon formation of complexes.

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