SYNTHESIS AND INFRARED EXAMINATION OF Cu(I) HALIDE COMPLEXES WITH NICOTINIC ACID AND ITS ETHYL ESTER

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Eight complexes of the general formula L_nCuX have been prepared, in which L is nicotinic acid or ethyl nicotinate, X is Cl, Br and I and $n = 1$ or 2. These complexes have been prepared by addition of ascorbic acid as a reducing agent to a solution containing Cu(II) salt and the ligand in question. The infrared spectra of the prepared complexes in the region $4000-400$ cm^{-1} have been examined. The complexes have been characterized by their magnetic properties and their X-ray powder patterns as well.

Many complexes of Cu(I) with pyridine and with substituted pyridines have been mentioned in the literature[1-5]. Such complexes have been prepared mainly either by a direct reaction between the cuprous halide and a solution of the ligand in question, or by the reduction of cupric salts by copper metal in presence of excess of the ligand. Despite of the existence of these complexes and of the fact that Cu(II) complexes with pyridine carboxylic acids[6-8] are well known, nothing have been mentioned yet concerning Cu(I) complexes of pyridine carboxylic acids and their derivatives. Study of such complexes could be interesting because of the possibility of pyridine carboxylic acids to behave either as bidentate or monodentate ligands with intermolecular hydrogen bonding. The present paper concerns the synthesis and properties of Cu(I) halide complexes with nicotinic acid and ethyl nicotinate.

EXPERIMENTAL

Nicotinic acid, BDH (99·5%) was recrystallized from double distilled water, ethyl nicotinate was GLC purified (b.p. 102·0°C). The other chemicals were Lachema (p.a.).

Copper was determined gravimetrically as CuSCN. Carbon, hydrogen, nitrogen and halogens were determined by elemental analysis on the Perkin Elmer 240 analyser. Infrared absorption spectra were measured in the region $400-4000$ cm^{-1} on a C. Zeiss UR 20 spectrophotometer. The solid samples were measured by nujol mull and KBr disc techniques. Liquid ethyl nicotinate was measured as a capillary film between KBr windows.

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Magnetic susceptibilities were determined by the Faraday method using torsion magnetic balance and the deviation of the sample was compensated by a known value of electrostatic potential put on a condenser system[9]. X-ray powder diagrams were recorded by Mikrometa 2 instrument (ϕ 57·3 mm, λ CuK$_\alpha$ = 1·5418 Å).

RESULTS

Synthesis and Properties

Aqueous or ethanolic solution of cupric salt (10^{-3}M) was mixed with a solution of the ligand in a suitable molar ratio. The formed blue precipitate of Cu(II) complex was then reduced by ascorbic acid added successively in small portions under vigorous stirring until the reduction was complete and a yellow, orange or red precipitate or solution arised. As a starting substance $CuCl_2 . 2 H_2O$ was used for synthesis of

TABLE I

Analytical Data for Complexes

Formula	%	Cu	X	N	C	H	Conditions	Color and appearance
$(C_6H_5NO_2)_2 .$. CuCl	found:	18·03	10·24	8·28	41·14	2·88	ethanol^a	bright red
	calc.:	18·40	10·26	8·11	41·74	2·92	1 : 2^b	sheets
$(C_6H_5NO_2)_2 .$. CuBr	found:	16·05	21·06	7·63	36·39	2·58	water^a	red orange
	calc.:	16·30	20·50	7·19	36·98	2·58	1 : 4^b	crystals
$(C_6H_5NO_2) .$. CuCl	found:	28·99	16·05	6·46	32·25	2·12	ethanol^a	yellowish
	calc.:	28·60	15·96	6·30	32·44	2·37	1 : 1^b	orange needles
$(C_6H_5NO_2) .$. CuBr	found:	23·62	29·69	5·75	27·28	1·93	water^a	yellow silky
	calc.:	23·83	29·97	5·25	27·01	1·87	1 : 1^b	powder
$(C_6H_5NO_2) .$. CuI	found:	20·10	40·04	4·55	22·85	1·59	water^a	yellow powder
	calc.:	20·26	40·47	4·46	22·98	1·60	1 : >2^b	
$(C_8H_9NO_2) .$. CuCl	found:	25·36	13·99	5·38	38·21	3·49	dil.aq.soln.^{a}	yellow needles
	calc.:	25·35	14·17	5·60	38·41	3·62	1 : >1^b	(from ethanol)
$(C_8H_9NO_2) .$. CuBr	found:	21·73	26·88	4·58	32·71	3·19	dil.aq.soln.^{a}	yellow powder
	calc.:	21·57	27·12	4·75	32·61	3·08	1 : >1^b	
$(C_8H_9NO_2) .$. CuI	found:	18·96	36·97	3·85	26·61	2·60	dil.aq.soln.^{a}	pale yellow
	calc.:	18·59	37·16	4·09	28·12	2·65	1 : >1^b	powder

^{a} Solvent, ^{b} Cu : L ratio.

chlorides. Bromides and iodides were prepared from $CuSO_4 . 5 H_2O$, and after reduction, KBr or KI was added to the reduced $Cu(I)$ complex solution. The obtained precipitates were filtered off, washed with cold water, ethanol and dried in air, dry nitrogen or in vacuum. The compounds obtained were recrystallized either by hydrothermal method in a sealed ampule at 130°C or from boiling ethanol in presence of ascorbic acid to prevent the oxidation. Table I summarizes the composition, analysis and some properties of the prepared complexes.

The prepared complexes are insoluble in the solvents like water, ethanol, acetone, *etc.* at room temperature, while at higher temperature they are soluble. In the solution they are oxidized in the air atmosphere in the absence of a reducing agent. The stability towards air oxidation increases for the complexes of the ratio L : Cu = 1 : 1 with the increasing halide ion radius. For example LCuCl is oxidized by air in the solid state as a powder, only in form of crystals it is relatively stable. The complexes of the composition $L_2 . CuX$ are much more stable than those of the formula L . CuX.

TABLE II

X-Ray Powders of the Complexes

$(nic)_2$ CuCl[a]		$(nic)_2$ CuBr		(nic) CuCl		(nic) CuBr		(nic) CuCl		$(enic)$ CuCl[b]		$(enic)$ CuBr		$(enic)$ CuI	
d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0	d, Å;	I/I_0
6·188	70	6·505	80	6·910	80	7·557	70	6·505	70	7·019	80	7·686	90	8·498	80
4·571	80	4·480	90	5·400	40	6·021	20	4·766	60	6·231	60	6·411	70	6·505	50
3·644	60	3·704	80	4·716	40	5·034	20	4·266	20	5·211	10	5·534	20	5·466	20
3·229	100	3·323	100	4·307	20	4·618	60	3·798	30	4·741	100	4·817	100	4·870	100
2·752	10	2·900	20	3·735	30	3·630	50	3·373	70	4·129	10	4·226	40	4·435	20
2·634	10	2·744	20	3·275	100	3·241	100	3·035	20	3·586	50	3·615	60	3·704	20
2·604	10	2·619	10	2·882	20	3·005	30	2·900	20	3·194	30	3·348	60	3·411	50
2·440	40	2·466	70	2·672	10	2·599	50	2·590	20	3·076	60	3·097	70	2·785	70
2·199	20	2·230	40	2·453	20	2·324	20	2·453	40	2·882	10	2·777	60	2·433	20
2·056	20	2·139	30	2·209	20	2·268	30	2·189	40	2·765	40	2·664	30	2·074	70
1·886	20	1·916	50	2·038	10	2·174	30	2·083	30	2·673	20	2·427	20	1·857	30
1·744	30	1·789	20	1·963	10	2·097	30	2·012	10	2·512	10	1·996	70	1·766	20
1·619	10	1·668	20	1·836	10	1·979	10	1·931	30	2·365	30	1·864	30	1·676	10
1·569	10	1·598	20	1·702	10	1·747	20	1·850	20	2·101	40	1·776	30		
		1·478	10			1·682	10	1·776	10	1·971	20	1·624	20		
										1·815	20	1·445	20		
										1·757	10	1·332	10		
										1·285	10				

[a] nic = nicotinic acid; [b] enic = ethyl nicotinate.

We did not manage to prepare complexes of higher ratio than L : Cu = 1 : 1 in the case of ethyl nicotinate.

All the mentioned complexes are diamagnetic, with the values of molar magnetic susceptibilities, χ_M, in the range from $-115.8 \cdot 10^{-6}$ to $-267.4 \cdot 10^{-6}$.

The chemical individuality of the prepared complexes was proved by comparison of their X-ray powder patterns with that of the free ligand and those of simple cuprous halides (Table II).

Infrared Spectra

The absorption bands and their assignments of the complexes studied and free ligands are presented in Tables III and IV. The spectral vibrational frequencies have been assigned according to the data published by other authors for nicotinic acid[10-13] and ethyl nicotinate[13-15]. Because, however, the assignment is not complete, we have completed it by comparison with those given for other 3-substituted pyridines[16,17].

For structural considerations the following groups of bands are important:

1) Bands at 3 450, 1 645, 1 625 (sh), 1 540 and 1 380 cm^{-1}, which were attributed to KBr—COOH group interaction[18]. *2)* Bands in the region of $1\,900 - 2\,690$ cm^{-1}, which were attributed[10,11] to hydrogen bonds of the N···H—O type between the heterocyclic nitrogen and carboxylic group, or of the O···H—O type between two carboxylic groups. In addition to the band at 935 cm^{-1} for nicotinic acid complexes that may be attributed to dimeric hydrogen bonding. *3)* Bands in the region 1 710 to 1 720 cm^{-1} for nicotinic acid and its complexes and $1\,730 - 1\,734$ cm^{-1} for ethyl nicotinate and its complexes, which were attributed to C=O stretching vibration in the carboxylic and carboxylate groups respectively. *4)* Bands in the region 1 410 to 1 600 cm^{-1} which may be attributed to C—C, C—N stretching vibrations. *5)* Bands in the region $1\,020 - 1\,052$ cm^{-1} which are either splitted or shifted upon complex formation may be attributed to ring breathing vibrations. *6)* Bands at $812 - 825$ cm^{-1} and $694 - 698$ cm^{-1} for nicotinic acid and at 790 cm^{-1} and $696 - 708$ cm^{-1} for ethyl nicotinate which may be attributed to the ring CH out of plane vibrations. *7)* Bands in the region $500 - 650$ cm^{-1} assigned as due to ring in plane vibrations[13], and those lying at lower frequencies belonging to ring out of plane vibrations.

DISCUSSION

Because the studied complexes are not sufficiently soluble in the common solvent, the best information concerning their properties can be gained by solid state investigations. The prepared monocrystals are not suitable for X-ray crystal structure examination and therefore the most valuable information about the mode of ligand coordination can be reached from the IR spectra of the solid complexes.

TABLE III

IR Spectral Data of Free and Coordinated Nicotinic Acid

Abbreviations: v very, b broad, w weak, medium, s strong, sp sharp, (nic) nicotinic acid, st stretching, pl plane, defn. deformation, (n) nujol absorption band.

Nicotinic acid			(nic)CuI		(nic)CuBr	
KBr	nujol	literature	KBr	nujol	KBr	nujol
3 450[a] b		3 400[18]	3 450 b		3 450 b	
3 080 – 2 900	3 080	3 100[10]	3 080 – 2 900	3 080	3 080 – 2 900	3 080
	b	2 900[10]		b		b
			2 690 b	2 690 b	2 690 b	2 690 b
			2 580	2 580	2 580	2 580
2 450 b	2 450 b	2 450[10,11]				
1 900 b	1 900 b	1 930[10], 1 880[11]				
1 720 s,b	1 718 s,b	1 720[20], 1 705[12]	1 710 vs	1 710 vs	1 710 vs	1 710 vs
1 645[a] s		1 640[18]	1 645 w		1 645 m	
1 625[a] sh		1 620[18]	1 625 sh		1 625 sh	
1 600 s	1 600 ms	1 591[24], 1 593[12]	1 600 s,b	1 600 s,sp	1 600 s,b	1 600 s,sp
1 585 sh	1 585 sh	1 580[12], 1 567[24]		1 585 sh		1 585 sh
1 540[a] w			1 550 sh		1 550 sh	
1 498 w	b	1 485	1 485 vw	b	1 485	b
1 450 sh			1 450 sh		1 450 sh	
1 423 s	1 423 s		1 428 s	1 428 s	1 430 s	1 428 s
1 380[a] s	1 380(n)	1 380[18]	1 380 m	1 380(n)	1 380 m	1 380(n)
1 330 s	1 330 s		1 330 m	1 330 m	1 330 m	1 330 m
1 308 s	1 305 s	1 300[10]	1 310 vs	1 310 vs	1 310 vs	1 310 vs
1 250 sh	1 250 sh		1 245 w	1 245 w	1 245 w	1 245 w
1 190 m	1 190 m		1 200 m	1 200 m	1 200 m	1 200 m
1 120 m	1 118 m		1 118 m	1 118 w	1 118 m	1 118 w
1 090 w	1 090 w		1 090 vw	1 090 vw	1 090 vw	1 090 vw
1 038 vs	1 038 s		1 048 w	1 048 w	1 048 w	1 048 w
			1 032 w	1 032 m	1 034 w	1 034 m
			935 m,b	935 m,b	935 m,b	935 m,b
835 m	835 sh		840 w	835 w	840 vw	840 vw
815 vs	812 ms		825 w	825 w	825 w	825 w
750 vs	750 vs		750 vs	750 vs	750 vs	750 vs
698 vs	698 vs		694 vs	694 vs	694 vs	694 vs
685 sh	685 sh	680[10]	678 sh		680 sh	
645 vs	645 vs					
500 m,b	500 m,b	496[13]	552 m,b	552 m,b	558 m,b	555 m,b
<400	<400	388[13]	433 w	433 vw	433 w	433 vw

TABLE III
(*Continued*)

(nic)CuCl	(nic)$_2$CuCl		(nic)$_2$CuBr	Assignments
KBr	KBr	nujol	KBr	
3 450 b	3 450 b		3 450 b	
3 080 — 2 900	3 080 — 2 850	3 080 *b*	3 080 — 2 900	ν CH st.
2 690 b	2 690 b	2 685 b	2 690 b	$\Big\}$ ν O···H—O
2 580	2 580	2 580	2 575	
				$\Big\}$ ν N—H—O
1 710 vs,b	1 710 vs,b	1 710 vs	1 710 s	ν C=O st.
1 645 m	1 645 w		1 645 w	
1 625 sh	1 625 sh		1 625 sh	
1 600 ms,b	1 600 ms,b	1 600 ms	1 600 s,b	ν C—C, C—N
	1 580 sh	1 580 sh		ν C—C, C—N
1 550 sh	1 550 sh		1 545	
1 484 vw	1 484 w	*b*	1 484 w	ν C—C, C—N
1 50 sh	1 445 sh		1 450 sh	
1 430 s	1 430 s	1 430 s	1 430	ν C—C, C—N
1 380 w	1 380 w	1 380(n)	1 380 m	
1 330 s	1 330 s	1 330 s	1 330 s	δ O—H in pl. defn.
1 310 vs	1 310 vs	1 310 vs	1 310 vs	ν C—O st.
1 245 vw	1 245 vw	1 245 vw	1 245 vw	
1 200 w	1 200 w	1 200 w	1 200 w	β C—H in pl.
1 118 w	1 118	1 118 w	1 120 w	β C—H in pl.
1 090 vw	1 090 vw	1 090 vw	1 090 vw	β C—H in pl.
1 050 w	1 050 vw	1 048	1 048 vw	ν_1 ring breathing
1 035 w	1 032 w	1 032 w	1 032 w	ν_{12} ring breathing
935 m,b	935 m,b	935 m,b	935 m,b	δ O—H out of pl. defn.
835 w	840 w	840 vw	840 vw	
	825 vw	825 vw	825 vw	γ C—H out of pl.
750 vs	750 vs	750 vs	750 vs	
694 vs	694 vs	694 vs	694 vs	γ C—H out of pl.
678 sh	675 sh		678 sh	δ C$\overset{\displaystyle O}{\underset{\displaystyle O}{<}}$
				ring in pl.
560 m,b	558 m,b	558 m,b	555 m,b	ring in pl.
434 w	433 w	433 w	431 w	ring out of pl.
♦				

[a] Bands appeared only in the dried acid spectrum (KBr); [b] masked by nujol absorption.

Nicotinic acid as well as ethyl nicotinate have two coordination sites and thus the comparison of their spectra with those of the coordinated ones can bring valuable information about which of these two sites is coordinated to the metal ion.

1) The bands marked *a* (Table III) appear only in the spectrum of dry acid and its complexes in KBr pellets and have not been observed in their spectra measured in nujol as well as in the spectrum of moisted nicotinic acid in KBr pellet (24 hours in normal air atmosphere after the first measurement). Such bands were observed also by Taylor[18], who attributed them to a KBr interaction with carboxylic group forming carboxylate ion COO^-. The fact that these bands appear in the same positions in both nicotinic acid and its complexes gives an evidence that the carboxylic group does not participate in the coordination bond.

2) The shift of the bands attributed to hydrogen bond upon complexation gives an evidence that hydrogen bonds of the type $N\cdots H—O$ originally present in the free nicotinic acid[10,11], changes to hydrogen bonds of the type $O\cdots H—O$ in its complexes. This fact can be explained by the displacement of the hydrogen bound to the nitrogen atom by copper with the formation of $N \rightarrow Cu$ coordination bond. The originally present hydrogen bonds are of the $N\cdots H—O$ type[10,11]. The interaction between KBr and the carboxylic group can affect the formation of hydrogen bond of the $N—H\cdots O$ type caused by the displacement of the hydrogen atom from the carboxylic group. The idea of the change of a $N—H—O$ type hydrogen bonding to the $O—H—O$ type upon complex formation is supported by the appearance of the $935\ cm^{-1}$ band ($O—H$ out of plane deformation) in the spectra of nicotinic acid complexes. The appearance of such a band was considered[19] as evidence of dimers formation. In accordance with the previous studies[10,11], we did not observe this broad, medium intensity band in the free nicotinic acid, and it also does not appear in the spectra of ethyl nicotinate and its complexes.

3) The small red shift of the $C=O$ stretching vibration frequency upon complexation of nicotinic acid cannot be considered as due to coordination through carbonyl oxygen. Such a consideration was supposed in the complex (nicotinic acid)$_2$ $CdCl_2$ (see[20]), because of a much larger red shift of the $C=O$ stretching band ($\Delta\tilde{v} = 20\ cm^{-1}$) than that we have observed. Our observation can be explained as an effect of the rearrangement of hydrogen bonds of the $C=O$ stretching vibration upon complex formation. This explanation is in good agreement with the constant position of the $C=O$ stretching band in the free and coordinated ethyl nicotinate.

4) For coordinated pyridine, the ring $C—C$, $C—N$ stretching, ring breathing and ring CH in plane deformation vibrations are blue shifted in comparison with the free ligand[21-23]. In the spectra of nicotinic acid only one ($1423\ cm^{-1}$) of the four $C—C$, $C—N$ bands. (The band at $1585\ cm^{-1}$ which appears as a shoulder is masked by the broad band appearing at $1600\ cm^{-1}$ in KBr pellet) is a little shifted to higher frequen-

cy, while in ethyl nicotinate a little blue shift is observed for the bands at 1595, 1 423 cm^{-1}. The constant position of the bands in free and coordinated nicotinic acid may be caused by the initial presence of the hydrogen atom bound to the heterocyclic nitrogen which was only substituted by Cu(I) ion. Mitchell[23] pointed out that the blue shifts of such bands caused by complex formation of pyridine are smaller for

TABLE IV

IR Spectral Data of Free and Coordinated Ethyl Nicotinate
Meaning of abbreviations see Table III.

Ethyl nicotinate		(enic)CuCl nujol	(enic)CuBr nujol	(enic)CuI nujol	Assignments
(see p. 26)	literature				
2 990^c s		b	b	b	ν C—H st.
1 730 vs,b	1 724[15]	1 734 vs,sp	1 734 vs,sp	1 734 vs,sp	ν C=O st.
1 595 vs,sp	1 598[14]	1 600 m,sp	1 600 m,sp	1 600 m,sp	ν C—C, C—N
		1 587 sh	1 587 sh	1 587 sh	ν C—C, C—N
1 480 m		b	b	b	
1 470 sh	1 470[15]	b	b	b	ethyl CH$_2$
1 450 w	1 447[15]	b	b	b	ethyl CH$_3$
1 423 s,sp,	1 422[14]	1 428 ms,sp	1 428 m,sp	1 430 m,sp	ν C—C, C—N
1 395 w	1 392	1 395 sh	1 395 sh	1 395 sh	ethyl CH$_3$
1 370 s	1 370[15]	1 370 ms	1 370 ms	1 370 ms	ethyl CH$_2$
1 328 wm	1 328[15]	1 328 w	1 328 w	1 328 w	⎫
1 290 vb,vs	1 284[15]	1 300 vs,sp	1 300 vs,sp	1 300 vs,sp	⎬ CCO
1 245 sh		1 245 w	1 245 w	1 245 w	⎭
1 196 w	1 193[14]	1 198 m	1 198 m	1 198 m	⎫
1 175 w	1 167[15]	1 170 sh	1 170 sh	1 170 sh	⎬ CCO
1 132 sh	1 128[15]	1 140 m	1 138 m	1 138 m	⎭
1 115 vs,b		1 118 m,sp	1 118 m,sp	1 118 m,sp	β CH
1 090 sh	1 086[15]	1 090 sh	1 090 w	1 090 w	ethyl, β CH
1 040 w	1 039^{c,14}	1 052 m	1 052 m	1 052 m	ν_1
1 029 s	1 027[14]	1 020 s	1 020 s	1 020 m	ν_{12} ring breathing
972 vw		970 vw	970 vw	970 vw	
875 sh		880 w	880 vw	880 vw	
855 wm	853[15]	862	862 w	862 w	
835 w		835 w	835 w	832 vw	
790 w					γ CH out of pl.
745 vs		745 vs	745 vs	745 vs	
708 vs	d	696 vs	696 vs	696 vs	γ CH out of pl.
624 ms	618^{d,13}	650 vw	650 vw	646 vw	ring in pl.
500 wm,b	490[13]	500 w,b	500 w,b	500 w,b	ring in pl.
400 w	388[13]	448 w,b	448 w,b	446 vw	ring out of pl.

^{c} This band was assigned to β-CH, ^{d} the values are abstracted directly from the spectra, enic ethyl nicotinate.

transition metal ions than for H^+-ions. For this reason they may be either not affected or red shifted upon substitution of hydrogen by $Cu(I)$ ion. The only shifted $1423 \, cm^{-1}$ bands does not represent a pure C—C, C—N vibration[24]. The complexation of ethyl nicotinate is not influenced by a N—H bond and therefore the C—C, C—N vibrations are blue shifted. The blue shift of v_1 breathing vibration frequency of both ligands. (The $1038 \, cm^{-1}$ band in the nicotinic acid spectrum can be considered as superimposed of v_1 and v_{12} ring breathing vibrations) is in accordance with that of coordinated pyridine[21-23]. The value of the shift of v_{12} vibration depends on the electron releasing and attracting power of the substituent as it was found for a series of 4-substituted pyridine complexes of $Cu(II)$ and $Zn(II)$ (see[25]). Since the 3-position substituent is different from the 4-position in the relative ease of electron donor and acceptor power of the ring[14], it is not surprising that the v_{12} band was shifted to lower frequency.

5) The ring C—H out of plane deformation frequency of both ligands exhibits systematic shifts upon complex formation like coordinated pyridines[21,22]. At the same time the intensity of the very strong $812 \, cm^{-1}$ band of nicotinic acid decreases greatly upon coordination. This may explain the disappearance of the corresponding weak band at $790 \, cm^{-1}$ in ethyl ester complexes. The great shifts $(\Delta v = 25 - 50 \, cm^{-1})$ of the ring vibrations caused by coordination are in full agreement with the results obtained for other pyridines[26]. The disappearance of the band at $645 \, cm^{-1}$ in the spectra of nicotinic acid complexes can be explained by its blue shifting (compared with that at $624 \, cm^{-1}$ of the ester) and superimposing upon that at $694 \, cm^{-1}$. It is surprising that the band at $500 \, cm^{-1}$ showed a very large blue shift of about $55 \, cm^{-1}$ in the coordinated nicotinic acid, while it did not shift at all in the coordinated ethyl nicotinate.

From the results obtained it follows that: 1) Both nicotinic acid and its ethyl ester act as monodentate ligands with the ring nitrogen as a coordination center. 2) The N···H—O hydrogen bond in the free nicotinic acid changes to a dimeric hydrogen bond of the type:
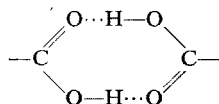
upon complex formation. This intermolecular hydrogen bond exists in both the 1 : 1 and 1 : 2 complexes forming an aggregation of complex molecules. 3) Ethyl nicotinate forms only simple isolated complex molecule. The existence of only 1 : 1 stable complexes leads to the conclusion that steric hindrance of the —$COOC_2H_5$ may prevent the formation of complexes with higher ligand content.

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