

METHYL NICOTINATE-COPPER(I) COMPLEXES SYNTHESIS AND CHARACTERIZATION

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The preparation of nine copper(I) complexes of methyl nicotinate (MeN) has been described. The isolated complexes are characterized by their analytical data, conductivity, electronic and infrared spectra. Copper(I) ion was proposed to have trigonal planar geometry in $(\text{MeN})\text{CuX}$ ($\text{X} = \text{halide, cyanide, and thiocyanate}$) and $(\text{MeN})_3\text{CuClO}_4$ complexes, and tetrahedral geometry in $(\text{MeN})_2\text{CuX}$ ($\text{X} = \text{Cl, Br, ClO}_4$) complexes. In the case of $(\text{MeN})_2\text{CuClO}_4$ the perchlorate ion acts as a bidentate ligand.

Previously we have reported the copper(I) complexes of nicotinic acid and its ethyl ester¹ which have been prepared by the reduction of copper(II) salts in presence of the ligand by ascorbic acid followed by the addition of the desired anion. In the case of ethyl nicotinate, the steric hindrance of the carboethoxy group in the 3-position of pyridine prevents the formation of copper(I) halide complexes with ligand contents higher than 1 : 1. Examination of the complex formation of methyl nicotinate (MeN) showed that it is able to form a variety of copper(I) complexes. As these complexes have not yet been mentioned in the literature, we reported here their synthesis and characterization.

EXPERIMENTAL

Chemicals and Apparatus

Methyl nicotinate was very kindly provided by Dr M. Ferles, Department of Organic Chemistry, Institute of Chemical Technology, Prague. The other chemicals were Lachema (*p.a.*).

Magnetic, conductivity, X-ray powder patterns, electronic and reflectance spectral measurements were carried out as previously described². Infrared spectra in the region $400-4000\text{ cm}^{-1}$ were measured on a UR-20 (Zeiss-Jena) spectrophotometer, while spectra in the region 200 to 400 cm^{-1} have been measured on a Perkin Elmer 325 apparatus both as nujol mulls or KBr pellets.

Micro-analysis of C, H and N were carried out on the Perkin-Elmer 240 elemental analyzer. Halogens were determined gravimetrically as AgX. Copper was determined either by titration against disodium EDTA or gravimetrically as CuSCN after degradation and oxidation of the complexes with boiling mixtures of concentrated H_2SO_4 and 30% H_2O_2 .

Preparation of the Complexes

The complexes have been generally prepared and recrystallized according to the method described previously^{1,2}, except the cyanide and thiocyanate complexes. The latter ones have been prepared as follows. After precipitation of the 1 : 3 perchlorate compound, a solution of potassium cyanide or thiocyanate (1 : 1 molar ratio to copper) was added dropwisely at vigorous stirring until the yellow colour of solution disappeared and a faint yellow precipitate was obtained. The IR spectra of the obtained powders showed that they are completely free from the perchlorate anion.

All the isolated complexes were filtered off and dried in vacuum, except the 1 : 2 perchlorate which was dried under dry nitrogen.

RESULTS

Table I summarizes the elemental analysis of the isolated complexes. In Table II the reflectance spectral data and conductivities measurements are collected.

All the isolated complexes are diamagnetic at room temperature, coloured and stable with respect to air oxidation, except the perchlorate of 1 : 2 complex. However,

TABLE I
Analytical Data

Formula (m.wt.)	Analysis						Appearance
	%	Cu	X	C	H	N	
(C ₇ H ₇ NO ₂)CuCl (235·1)	found:	26·54	15·31	35·42	2·93	5·94	pale yellow
	calc.:	26·91	15·01	35·60	2·98	5·93	needles
(C ₇ H ₇ NO ₂)CuBr (280·6)	found:	22·42	28·06	29·85	2·63	5·13	pale yellow
	calc.:	22·64	28·48	29·96	2·51	4·99	needles
(C ₇ H ₇ NO ₂)CuI (327·6)	found:	19·62	38·84	26·13	2·18	4·21	pale yellow
	calc.:	19·39	38·67	25·66	2·15	4·27	powder
(C ₇ H ₇ NO ₂)CuCN (226·7)	found:	28·40		42·01	3·32	12·21	pale yellow
	calc.:	28·03		42·38	3·11	12·35	powder
(C ₇ H ₇ NO ₂)CuSCN (258·7)	found:	24·43		37·14	2·69	10·81	faint yellow
	calc.:	24·56		37·15	2·70	10·81	powder
(C ₇ H ₇ NO ₂) ₂ CuCl (373·2)	found:	16·92	9·29	44·38	3·73	7·38	red-orange
	calc.:	17·02	9·50	44·05	3·78	7·50	needles
(C ₇ H ₇ NO ₂) ₂ CuBr (417·7)	found:	15·52	19·47	40·01	3·33	6·49	orange
	calc.:	15·21	19·13	40·25	3·38	6·70	needles
(C ₇ H ₇ NO ₂) ₂ CuClO ₄ (437·2)	found:	14·32		38·17	3·09	6·22	white micro
	calc.:	14·53		38·45	3·23	6·40	cryst. powder
(C ₇ H ₇ NO ₂) ₃ CuClO ₄ (574·2)	found:	11·62		43·47	3·58	7·23	canarian yell.
	calc.:	11·85		43·90	3·68	7·31	crystals



the stability toward oxidation increases with the number of ligands per copper(I) ion and from the chloride to iodide. The X-ray powder patterns showed that the 1 : 1 and 1 : 2 halide complexes are isomorphous.

The perchlorates of 1 : 2 and 1 : 3 complexes behave as 1 : 1 electrolytes in nitrobenzene³ and acetone⁴ as seen from Table II. The other complexes, generally, dissociate to the ligand and simple 1 : 1 complex or cuprous salts in solvents like acetone, alcohols and chloroform, and gave non-conducting solutions in such solvents. The dissociation was also confirmed by the fact that the intense red-orange color of a concentrated solution of the 1 : 2 halide complex changes very rapidly to a very faint yellow upon dilution. The spectra of this dilute solution did not show the $M \rightarrow L$ charge transfer bands in the visible region which are observed in the spectra of the solid complexes (Table II).

Generally the electronic absorption spectra of the complexes in acetone or chloroform solutions are quite similar to that of the free ligand in the UV and visible regions. In the solid state both the free ligand and the complexes showed absorption bands around 275 nm, similar to that observed in the spectra of their solutions. This absorption is attributed to the $\pi - \pi^*$ transitions of the free ligand in comparison to that of the parent acid⁵.

TABLE II

Electronic Absorption Spectra and Conductivities

(w = weak, s = strong, br = broad)

Compound	λ , nm $M \rightarrow L^a$		Molar conductivities ^b $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	
			nitrobenzene	acetone
MeN	275			
(MeN)CuCl	275	420 w	insoluble	insoluble
(MeN)CuBr	275–280	410 w	insoluble	insoluble
(MeN)CuI	275–280	410 w	insoluble	insoluble
(MeN)CuCN	280	400 w	insoluble	insoluble
(MeN)CuSCN	280	400 w	insoluble	insoluble
(MeN) ₂ CuCl	270–280	450 s, br	2.4	14
(MeN) ₂ CuBr	270–280	440 s, br	1.0	faint yellow ppt.
(MeN) ₂ ClO ₄	275–280	—	28.0	126
(MeN) ₃ ClO ₄	275–280	430 s, br	32.0	142

^a Appeared only in the reflectance spectra of the solid samples; ^b the conductivities given are based on the formula weights.

The IR spectral data of the free ligand and some of its copper(I) complexes are given in Table III. The assignments of the vibrational frequencies is given in accordance with those observed earlier for MeN (ref. 6-8) or compared to other 3-substituted pyridines^{1,9}. In Table IV the vibrational frequencies of the perchlorate, cyanide and thiocyanate anions, in complexes are given.

DISCUSSION

The isolation of 1 : 2 copper(I) halide complexes with methyl nicotinate confirms our previous conclusion that the steric hindrance prevents the formation of complexes of higher ligand contents other than 1 : 1 in case of ethyl nicotinate¹.

TABLE III
Infrared Spectral Data (cm^{-1})

Abbreviations: v = very, w = weak, m = medium, s = strong, b = broad, st = stretching, X-sens. = substituent sensitive.

MeN	1 : 1 bromide	1 : 1 cyanide	1 : 2 chloride	1 : 3 perchlorate	Assignments
1 740 vs, b	1 745 vs	1 730 vs	1 740 vs	1 735 vs	$\nu\text{C}=\text{O}$ st.
1 595 s	1 605 wm	1 605 m	1 600 m	1 600 m	$\nu 8a, \nu(\text{C}-\text{C})$
	1 585 vw	1 590 w	1 580 wm	1 585 w	$\nu 8b, \nu(\text{C}-\text{C})$
1 430 vs	1 430 ms	1 425 ms	1 430 ms	1 425 s	$\nu 19b, \nu(\text{C}-\text{C}, \text{C}-\text{N})$
			1 420 s		
1 340 s	1 325 wm	1 330 ms	1 325 m	1 330 m	$\nu 14, \nu(\text{C}-\text{C}, \text{C}-\text{N})$
1 290 vs	1 290 vs	1 308 vs	1 300 vs	1 305 vs	νCOO
				1 295 vs	
1 250 m	1 250 w	1 250 vw	1 250 wm	1 250 w	νCCO
1 205 s	1 190 wm	1 190 w	1 195 wm	1 200 wm	$\nu 9a, \beta(\text{C}-\text{H})$
1 120 vs	1 120 vs	1 125 m	1 120 vs	1 125 ms	$\nu\text{CCO}, \beta(\text{C}-\text{H})$
1 030 vs	1 050 w	1 050 w	1 045 m	1 050 m	$\nu 1, \text{ring}, \beta(\text{C}-\text{M})$
1 005 w ^a	1 035 vw	1 035 w	1 035 w	1 035 m	$\nu 12, \text{ring}$
955 m	960 w	955 ms	960 m	960 m	$\nu 5, \gamma(\text{C}-\text{H})$
830 ms	840 w	835 wm	840 m	840 m	$\gamma(\text{C}-\text{H})$
750 vs	750 vs	750 s	750 vs	750 vs	$\delta\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$
	730 wm	735 m	725 wm	720 m	
710 vs	700 wm	690 ms	695 s	700 m	$\nu 4, \text{ring}$
625 m	645 w	645 w	640 w		$\nu 6b, \text{ring}$
480 m	495 w	490 w, b	495 w	500 w, b	$\nu 6a, \text{ring}, \text{X-sens.}$
430 m	445 wm	445 w, b	445 wm	440 w, b	$\nu 16a, \text{ring}$

Since the perchlorates of 1 : 3 and 1 : 2 complexes of MeN behave as 1 : 1 electrolytes in solutions, these may be formulated as $[(\text{MeN})_3\text{Cu}]^+\text{ClO}_4^-$ and $[(\text{MeN})_2\text{Cu}]^+\text{ClO}_4^-$, in which copper(I) ion is trigonally coordinated in the former and linearly coordinated in the latter complex.

As seen from Table II, all the isolated complexes, except the white 1 : 2 perchlorate, showed absorption bands in the visible region of their reflectance spectra. These bands are undoubtedly due to $M \rightarrow L$ charge transfer transitions^{10,11}. Similar intense absorption bands are observed¹² with analogical complexes. It is also observable that the λ_{max} of the $M \rightarrow L$ bands are shifted to longer wave length as the number of ligands increases per copper(I) ion in the complex molecule. This behaviour reflects the effect of the increasing reducing power arised from the electron attractive power of the carbomethoxy group with the number of ligands.

As the reflectance spectra of the cation $[(\text{MeN})_3\text{Cu}]^+$ is more or less similar to those of 1 : 1 complexes, it is, therefore, reasonable to propose trigonal structure for the 1 : 1 complexes through bridging halide, cyanide and thiocyanate anions.

Examination of Table III shows that the ring C—C, C—N stretching vibration frequencies (in particular the highest frequency, ν_{8a}), ring breathing ν_1 and ν_{12} modes, and ring CH out of plane deformation vibrations are blue shifted upon coordination of MeN. Similar blue shifts are observed for coordinated pyridine¹³. Clark and Williams¹⁴ and others¹⁵ have pointed out that the ring in-, and out-of plane deformation vibrations below 650 cm^{-1} are sensitive to the stereochemistry of the complexes and show a fairly blue shifts upon coordination of pyridine and substituted pyridines. In accordance with this, the vibration bands attributed to ν_{6b} , ν_{6a} and ν_{16a} (due to ring in-, and out- of plane) are blue shifted upon complex

TABLE IV

Vibrational Frequencies (cm^{-1}) of the Perchlorate, Cyanide and Thiocyanate Anions (For abbreviations see Table III)

Compound	ClO_4			ν_{CN}	ν_{CS}	δ_{SCN}
	ν_1	ν_3	ν_4			
$(\text{MeN})_3\text{CuClO}_4$	935 w	1 110—1 090 vs	625 s			
$(\text{MeN})_2\text{CuClO}_4$	930 w	1 120 vs	635 s			
		1 090 vs	625 s			
		1 060 s	618 m			
$(\text{MeN})\text{CuCN}$				2 140 vs		
$(\text{MeN})\text{CuSCN}$				2 135 vs	760 m	460 wm
				2 080 ms		410 w

formation of methyl nicotinate. It is also observable from Table III that the stretching C=O vibration frequency is constant in both free and coordinated MeN. These observations indicate the coordination of MeN through the nitrogen atom of the pyridine ring.

Examination of Table IV shows that the perchlorate of 1 : 3 complex is ionic, since the vibrations of the perchlorate group are consistent only with non-coordinated group¹⁶. Trigonal structure is, therefore, assigned for this complex in the solid state too. The perchlorate of 1 : 2 complex, on the other hand, showed splitting in the antisymmetrical stretching ν_3 and the antisymmetrical bending ν_4 modes into three components for each. Such splitting is consistent with bidentate perchlorate groups¹⁶. In the solid state, this complex is therefore, formulated as $[(\text{MeN})_2\text{CuClO}_4]$, in which copper(I) ion is tetrahedrally coordinated. Similar structures were assigned for other perchlorates of 1 : 2 complexes¹⁷.

Since the cyanide 1 : 1 complex of MeN showed only one band of very strong intensity at 2140 cm^{-1} due to the cyanide stretching vibration, a bridged cyanide group^{18,19} were assigned for this complex. For MeN.CuSCN complex, two cyanide stretching bands are observed; A very strong and sharp band at 2135 cm^{-1} attributed to S-bonded and a weak band at 2080 cm^{-1} due to N-bonded thiocyanate group²⁰. The appearance of two weak bands at 460 cm^{-1} and 410 cm^{-1} in the region of δSCN absorption²¹ suggests a bridged thiocyanate group for this complex.

Since there are no bands attributable to Cu(I)—Cl stretching vibrations above 200 cm^{-1} for both 1 : 1 and 1 : 2 chloride complexes, structures of type *I* and *II*;



(L = MeN and X = halide ion)

may be assigned for the 1 : 1 and 1 : 2 halide complexes, because the terminal Cu(I)—Cl frequencies are above 200 cm^{-1} (ref.²²⁻²⁴). In the structure *I* and *II* given above, copper(I) ion attains approximately trigonal and tetrahedral geometries, through bridging halide ions.

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