Raman and SERS Investigation of New Synthesized Nicotinic Acid Metallic Complexes

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Nicotinic acid and their complex combinations with copper and cobalt acetate were characterized using Raman and SERS spectroscopy.FT-Raman spectra emphasize significant differences in the wavenumber and intensity of aromatic system bands and in the ranges of the ring modes upon coordination. SERS results revealed chemisorptions of the ligand species through the hydroxyl groups with respect to the metal surface. The differences between the chemisorbed oriented geometry and the coordinated ligand are discussed.

Keywords: nicotinic acid, FT-Raman, SERS, complex combination, copper, cobalt

Nicotinic acid contains heterocyclic nitrogen-containing ring structures in addition to carboxylic acid groups, capable of forming complexes with trace metals.

Nicotinic acid is essentially pyridine-3-carboxylic acid and the metal complexes of nicotinic acid with various metals, e.g. manganese, cobalt, nickel, copper and zinc had been previously reported [1,2]. The chemical structure is presented in figure 1.

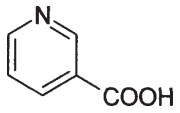

Fig. 1. The structure of nicotinic acid

Experimental part

The composition of the synthesized compounds was determined by elemental analyses and confirmed by the data of vibrational spectroscopy. The syntheses were performed using as starting materials acetate salts $Cu(CH_3COO)_2 \cdot H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ (all analytical grade) and nicotinic acid (high-purity grade). The nicotinic acid used is reagent from Trans Medical Pharma GmbH, Germania.

To a solution of 2.5 g of nicotinic acid in 100 mL of water was added drop wise a solution of 1.83 g of $Cu(CH_3COO)_2 \cdot H_2O$ in 25 mL water. The formed blue precipitate, was removed by filtration, then washed with H_2O and EtOH, and finally dried at room temperature. The resulting acetate complex has a composition corresponding to the formula $Cu(LH)_2(ac)_2$ and appears as a blue powder. A cobalt complex with the formula $Co(LH)_2(ac)_2$ was synthesized using an analogous procedure. The resulted pink precipitate was similarly treated. The coordination of the synthesized compounds were established based on the data of elemental analyses, physicochemical measurements, and FT-IR spectroscopy [3].

A small amount of complex of LH was dropped on 2 mL of Ag sol resulting a final concentration of 2.1×10^{-3} mol dm^{-3}. Model 2020 was employed for excitation of the SERS spectra. Back scattering configuration was performed with micro-Raman set-up. A Photometrics Model 9000 CCD camera detection system and analyzing software package MAPS V0 98.5 were employed for the acquisition of data. The spectral resolution was 1 cm^{-1}.

Results and discussion

The elemental analysis performed for C, H, N, with respect to the investigated complexes are given in table 1.

The Raman and SERS spectra of studied complexes and ligands are presented in the figures 2 and 3 respectively and the assignment of the characteristic FT-IR, Raman and SERS bands of the nicotinic acid and complexes are presented in table 2.

Table 1
ELEMENTAL ANALYSIS OF THE INVESTIGATED COMPLEXES

No.	Compound	Color	C% Found/Calc	H% Found/Calc	N% Found/Calc
1.	$[Cu(LH)_2(CH_3COO)_2]$ M = 427.5	Blue	44.868/ 44912	3.812/ 3.743	6.423/ 6.549
2.	$[Co(LH)_2(CH_3COO)_2]$ M = 422.9	Pink	45.214/ 45.400	3.824/ 3.783	6.534/ 6.621

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Table 2

ASSIGNMENT OF THE CHARACTERISTIC FT-IR, RAMAN AND SERS BANDS OF THE NICOTINIC ACID AND COMPLEXE COMBINATIONS V: VERY, S: STRONG, M: MEDIUM, W: WEAK, ν: STRETCHING, γ: OUT- OF- PLANE BENDING, δ: IN PLANE BENDING

Assignment	Nicotinic acid FT-IR	Nicotinic acid Raman	Nicotinic acid SERS	$Cu(LH)_2(CH_3COO)_2$ FT-IR	$Cu(LH)_2(CH_3COO)_2$ Raman	$Cu(LH)_2(CH_3COO)_2$ SERS	$Co(LH)_2(CH_3COO)_2$ FT-IR	$Co(LH)_2(CH_3COO)_2$ Raman	$Co(LH)_2(CH_3COO)_2$ SERS
ν(OH) acid	3400w	-	-	-	-	-	-	-	-
ν(CH)	3115s	-	-	3075s	-	-	3073s	-	-
νC=O	1684s	1690m		1691vw	-		1690vw	-	-
ν(ring) nic	1595s	1594m	1594m	1629s	1594m	-	1590m	1584m	-
ν(CN)	1412s	-	-	1426m	-	-	1468w	-	-
	1323m	-	1377m	1360s	1371m	1377wv	1385s	1389s	1377wv
ν(CC)	1300m	1298m	-	1310wv	-	-	1320wv	-	-
δ(CN)	1160s	1180m	-	1157w	-	-	1160m	1198m	-
ν(ring)nic	1040s	1037vs	1029s	1049m	1033vs	1060wv	1051s	1029vs	1061wv
δ(OH)acid	970					931m			931m
γ(CH) ring	746s	811m	838wv	759s	846m	760wv	759s	829m	755wv
δ(CH) ring	692s	638m	653wv	692s	642m	-	699s	638m	648wv
νMe-O	-				555wv	509wv			504wv

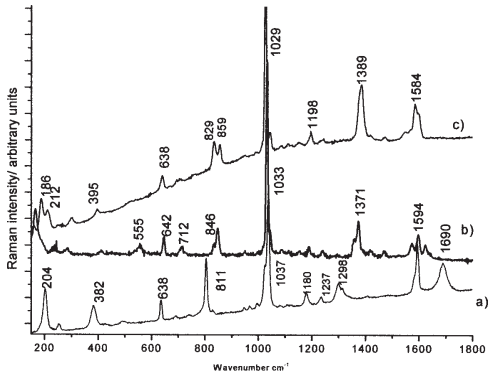

Fig. 2. Raman spectra of nicotinic acid (a) and complexes with Cu (II)- (b) and Co(II)- (c)

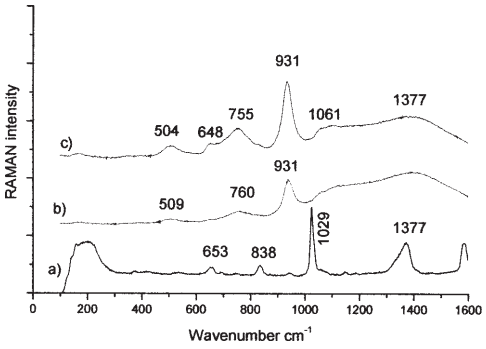

Fig. 3. SERS spectra of nicotinic acid (a) and complexes with Cu(II)-(b) and Co(II)- (c)

FT-Raman spectrum of nicotinic acid presented band 811, 1037, 1594 cm^{-1} assigned to the γ(CH) and ν(ring) ring mode. Additionally, the resident band νC=O is presented at 1690 cm^{-1} as a fingerprint of this ligand. The characteristic bands assigned to the pyridine ring are observed in the expected spectral regions.

Upon the coordination, significant differences appear in the following regions:

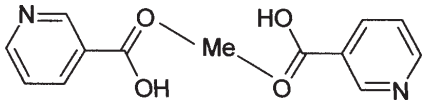

Fig. 4. The coordination of nicotinic acid

- 1500-1600 cm^{-1} from $\nu_{(C-C)\,ring}$ of pyridine are down shifted because of the coordination to the metallic centre;

- the characteristic band of γ(CH) ring (811 cm^{-1}) which appear as a narrow, strong band is up shifted; splitted upon coordination indicating the ring deformation.

- the specific modifications due to the Me- ligand bound are visible around 500 cm^{-1}.

The SERS spectrum is compared to the corresponding SERS spectra of the complexes containing monodentate coordinated ligands.

SERS spectrum of LH contains both γ(CH) and ν(ring) ring modes at 838, 1029 cm^{-1}, respectively, with reverse in relative intensities. The SERS feature is specific for the molecules containing N ring atom adsorbed on silver surface [4].

The shoulder at 1300-1500 cm^{-1} in the SERS spectrum a complex combination suggests the surface interaction of the carboxyl modes. The presence of enhanced ν_sCOOH mode in the SERS spectrum of LH as a very strong band at 1377 cm^{-1} confirms a chemisorption of the LH molecule on the surface through the carboxylate group [5]. The corresponding band for both complexes appear as a broad shoulder as an evidence of the coordination via -C=O group. The new strong band at 931 cm^{-1} present in the SERS spectra of complexes is attributed to δ(OH)acid, which remains uncoordinated.

The appearance of new weak bands around 509 cm^{-1} is attributed to the Me-O (ligand) bound. The spectral results in our study are in concordance with other reported papers in the same field [6].

The spectral data of the complexes suggested a monodentate coordination with the proposed coordination given in the figure 4.

Conclusion

Spectral data confirm monodentate coordination of nicotinic acid with Cu(II) and Co(II). We may conclude that the coordination through the –C=O in our complexes is evidenced by the FT-IR and FT-Raman spectra. A similar coordination mode of nicotinic acid was observed in magnesium complexes [7].

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Manuscript received: 4.10.2008

manifestări ştiinţifice 2009

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