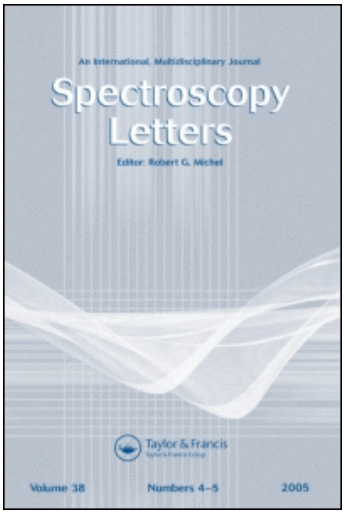

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SYNTHESIS AND SPECTROSCOPIC STUDY OF Cu(II), Ni(II), AND Co(II) COMPLEXES OF THE LIGAND SALICYLIDENE-2-AMINO THIOPHENOL

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ABSTRACT

The FTIR and Raman spectra of the ligand salicylidene-2-amino thiophenol (SATP) in the wave number range 4000–200 cm^{-1} are measured and assigned in terms of a C_s symmetry. The results indicate that SATP exhibits a zwitter ion structure of trans configuration in the ground solid state formed via proton transfer from the thiol group (-SH) to the imine group (–CH=N–). SATP complexes with Cu(II), Ni(II) and Co(II) ions are also synthesized and their structure are determined by elemental analysis, conductometric measurements, thermogravimetric analysis (TGA), UV-Visible and FTIR spectra. The complexes are found to have the formula

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($ML{\cdot}H_2O$) for Cu(II) and Ni(II) ions and $(NH_4)_2$ $[(Co)_2L(OH)_4]$ for Co(II) ion.

Key Words: FTIR; Raman; Salicylidene-2-amino thiophenol; Cu(II), Ni(II) and Co(II) complexes

INTRODUCTION

Due to its photochromic and thermochromic properties, the ligand salicylidene aniline (SA) was extensively studied[1–3]. The protonated form of this compound was created in a strong hydrogen bonding environment. The resulting protonated form was found to exhibit the zwitter ion structure[2–4] using IR, Raman and Nuclear Magnetic Resonance spectroscopy[2–4]. It was also stated that irradiation of (SA) induce a proton transfer forming a zwitter ion structure[2] or a transquinoid structure[3].

Recently, the ligand SATP complexes with Ce(IV) ion were synthesized and characterized[5]. It was found that SATP acts as a bidentate anion with tridentate ONS donors derived from the phenolic oxygen, azomethine nitrogen and the thiophenolic sulfur[5].

We have previously analyzed the vibrational spectra of o-hydroxy benzylidene aniline (OHBZA), and its Cu(II) and Ni(II) complexes[6]. The results indicated that coordination occurs via the nitrogen atom of the imine group (–CH=N–) and the two (O–Ph) groups[6a].

In this report, the ligand (SATP), a Schiff base which is analogous to (OHBZA) but exhibiting a thiol group (–SH) has been analyzed using UV-Visible, FTIR and Raman spectroscopic methods. Its complexes with Cu (II), Ni(II) and Co(II) ions are also synthesized and characterized using UV/Visible, elemental analysis, FTIR spectra, TGA, and conductometric measurements in order to gain more information about the sites of coordination and the possibility fof proton transfer for these types of compounds[1–3].

EXPERIMENTAL

The ligand SATP has been purchased from TCI-ACE Japan and used without further purification. The complexes Cu(II)SATP, Ni(II)SATP and Co(II)SATP are synthesized as previously given for OHBZA complexes but NH_4OH is used instead of NaOH[6]. The electronic spectra are measured in CH_3OH solvent using the unicam UV/2 spectrophotometer. The FTIR spectra are measured as KBr pellets on the Mattson 1000 FT

spectrophotometer. The Raman spectra of SATP are measured in the solid phase and in CH_3CN solvent on a dilor-Spex spectrophotometer using the laser line $\lambda = 647.12\,nm$ of a Kr^+ ion Laser (LASIR, Lille, France).

The elemental analysis was performed using the Perkin-Elmer 2400 apparatus. The conductometric measurements in CH_3OH at ca. $10^{-3}\,M$ were carried at 25 °C out using the HI9032 microprocessor conductivity meter with the HI76830w probe and the HI766912w temperature probe. The conductometer was calibrated against different calibration solutions before measurements. Magnetic measurements were done using the Guoy method. Diamagnetic corrections were carried out using Pascal' constants. The Guoy tube was calibrated using $Hg[Co(SCN)_4]$ compound.

The thermal analysis of NiSATP was done on a Shimadzu analyzer with A TGA-50H detector in nitrogen atmosphere in the temperature range 50–1000 °C (heating rate 10 °C/min.).

RESULTS

The analytical data of the ligand and its Cu(II), Ni(II) and Co(II) complexes are given in Table 1. The Raman spectra of SATP is shown in Fig. 1. The IR spectra is shown in Fig. 2. The attribution of SATP and its Cu(II), Ni(II) and Co(II) complexes abbreviated as CuSATP, NiSATP and CoSATP is collected in Table 2.

The ligand vibrations are represented as Γ vib. $= 49A' + 23A''$ in terms of a C_s symmetry[6]. The elemental analysis indicate that the three complexes have the formula ($ML{\cdot}H_2O$) for Cu(II) and Ni(II) ions, and $(NH_4)_2\,[(Co)_2L(OH)_4^-]$ for the Co(II) ion (Table 1). The conductivity data

Table 1. Analytical Data of SATP, CuSATP, NiSATP, and CoSATP

			%Calc. (found)			
The Compound	The Color	M.P.	C	H	N	μscm^{-1}
SATP	Yellow	128.2 °C	67.3 (66.91)	04.80 (4.75)	6.30 (6.21)	–
CuSATP	Dark	Decomposes > 350 °C	50.55 (50.63)	3.59 (3.35)	4.54 (4.89)	6.2
NiSATP	Brown	252 °C	53.68 (52.87)	3.12 (3.45)	4.80 (4.89)	4.3
CoSATP	Dark	Decomposes > 350 °C	34.75 (35.89)	4.71 (4.40)	9.35 (9.74)	36

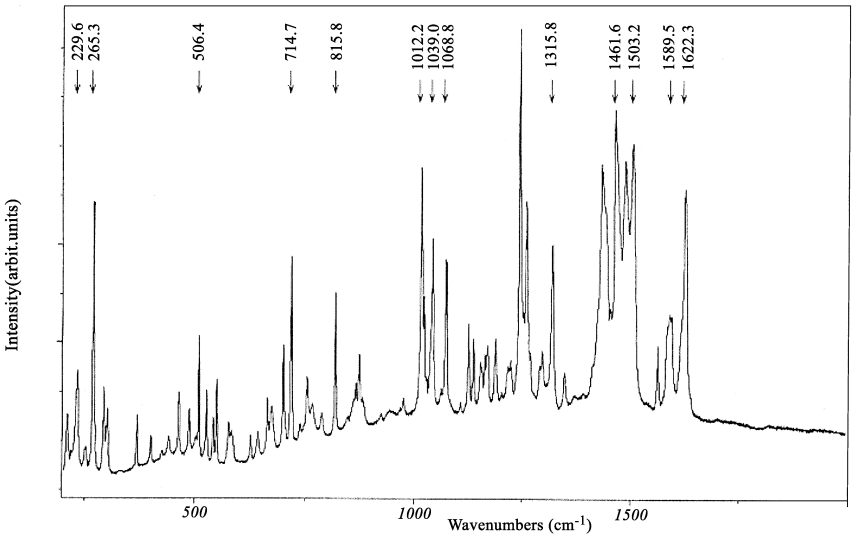


Figure 1. Raman spectra of SATP.

indicates that the two complexes of Cu(II) and Ni(II) ions are neutral and the Co(II) complex is a weak electrolyte (Table 1). The TGA analysis indicates that the NiSATP contains one water molecule and was correlated as a water of coordination. The decomposition steps are comparable to

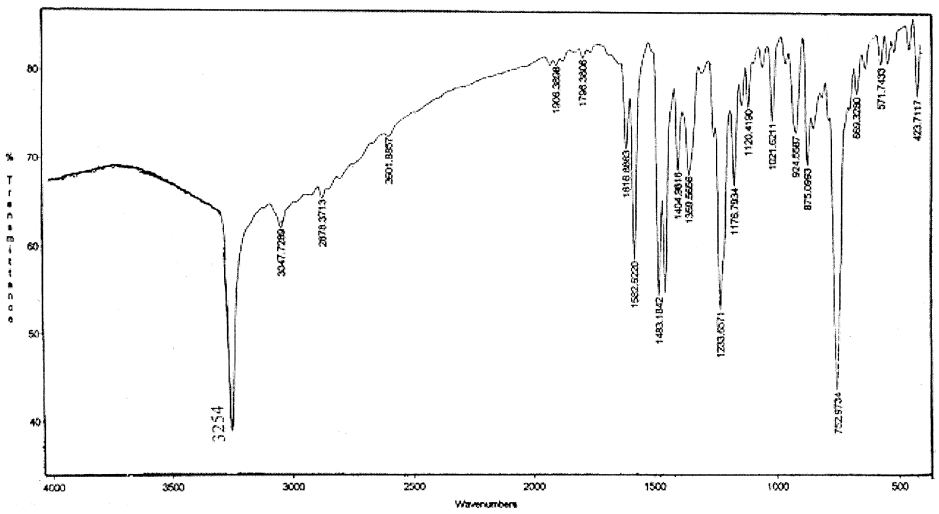


Figure 2. IR spectra of SATP.

Table 2. FTIR and Raman Spectra of SATP and FTIR Spectra of CuSATP, NiSATP, and CoSATP Assignment*

SATP(IR)	(SATP)Raman	CuSATP(IR)	NiSATP(IR)	CoSATP	Assignment
		3435 m,br	3435 m,br		νOH
3258 s	3258 w				$\nu N^{+}H$
				3130 s,br	$\nu(NH_4)^{+}$
1619 m	1625 s	1611 vs	1611 vs	1607 vs	νC=N
1587 s	1588 m,br			1581 m	$\delta N^{+}H$
	1562 s		1583 w		8a
		1530 s	1534 s	1526 s	
1487 s	1462 s	1458 s	1464 s		19b(ringA)
1445 s	1432 s	1437 s	1443 m	1445 m	19a(ringB)
				1406 vs	$\delta\ (NH_4)^{+}$
1408 m		1387 m	1379 m		νN-Ph
1364 m	1345 w				δOH
1330 w	1317 m	1336 m	1334 w	1326 m,br	14
1240 s	1257 s	1256 m	1290 w	1252 vw	7a(ν C-O)
1223 s	1242 vs	1234 m	1233 m	1234 vw	13 (νC-Ph)
1182 m	1185 w	1178 m	1177 m	1180 m	9a(ringB)
1143 w	1167 w	1152 m	1152 s	1148 m	18a(ringB)
1118 w	1134 w	1123 w	1128 m		18a(ringA)
1093 vw	1114 w				
1078 vw	1069 m	1072 w	1080 vw		
1028 m	1020 m	1034 w	1044 w		18b(ringB)
	1012 s				
974 m		928 w	932 w	928 w	17b
929 m,br					$\gamma N^{+}H$
882 m	871 vw	857 w	850 w	848 vw	γCH
860 m	864 vw	806 w	812 w		
832 m	816 m	806 w	812 w	815 vw	17a,12
758 s	751 w	755 s	747 s	750 s	11
705 m	715 s	706 w	710 m	734 w	1
678 w	698				
624 w	623 w				
578 w	573 w	554 w	561 m	554 m	6b, νM-O
537 w	537 w	529 vw	541 vw	546 vw	δCCN
525 w	522 w				γOH
		472 m	469 m		νM-N
452 w	448 w	460 w	454 w	464 vw	6b
427 m	437 w	425 vw	426 w	410	9b

*V: very, s: strong, w: weak, m: medium.

those previously given for Ce(IV)SATP complex[5] and can be described in the following steps.

$$\text{NiSATP} \cdot \text{H}_2\text{O} \xrightarrow[150-190^\circ\text{C}]{\text{H}_2\text{O Dehydration}} \text{NiSATP}$$

$$\text{NiSATP} \xrightarrow[\substack{209-325^\circ\text{C}\\359-419^\circ\text{C}}]{\text{1st Decomposition}} \text{Intermediates}$$

$$\text{Intermediates} \xrightarrow[528-644^\circ\text{C}]{\text{2nd Decomposition}} \text{NiO}$$

The synthesis of the complexes can be explained according to the following Scheme:

a) $2\text{CoCl}_2 + 4\ \text{NH}_4\text{OH} + \text{H}_2\text{L} = (\text{NH}_4)_2\ [(\text{Co})_2\text{L}(\text{OH})_4] + 2\text{NH}_4\text{Cl} + 2\text{HCl}$

b) $\text{MCl}_2 + \text{H}_2\text{L} + 2\ \text{NH}_4\text{OH} = \text{ML}\cdot\text{H}_2\text{O} + 2\ \text{NH}_4\text{Cl} + \text{H}_2\text{O}$

DISCUSSION

The Vibrational Spectra of SATP, CuSATP, NiSATP, and CoSATP Complexes

The infrared spectra (IR) of the ligand SATP shows a strong sharp band at 3258 cm^{-1}. The thiol group stretch SH expected at ca. 2500 cm^{-1} is absent. The 3258 cm^{-1} should represent the stretching mode (νN^+H, which is expected in this region[7–9]. The corresponding Raman line was observed at 3255 cm^{-1} with weak intensity, this band was not observed for OHBZA[6]. This assignment is analogous to that given for diphenyl ketimine $(C_6H_5)_2$ C=NH where νN^+H was localized at 3265 cm^{-1}[19]. The νN^+H mode was also found at 3265 cm^{-1} for semisalt of trans-α-di pyridyl ethylene at 3250 cm^{-1}[17]. The νN^+H was also found for the protonated salicylidene aniline at 3320 cm^{-1}[12]. The ν C=N of SATP can be assigned to the IR band at 1619 cm^{-1} and the Raman line at 1625 cm^{-1}[16a,6b]. Based on the assignment of νN^+H and νC=N, it is reasonable to conclude that SATP is present in the protonated form created by proton transfer from the (–SH) group to the imine group.

The NMR spectra indicate that SATP is present in non-protonated form, the chemical shift for the imine group expected at about $\delta = 8$ ppm[3] is absent whereas a strong peak at 9.9 ppm assigned to the OH group is observed[5], the -SH group is also observed at 3.4 ppm[5] which means that the ligand structure in the solution and in the solid phase is not the same.

The $\delta N^{+}H$ deformation (amide II band) is expected in the range 1650–1550 cm^{-1}[12,8]. The sharp IR band at 1588 cm^{-1} which disappears upon complexation can be attributed to this mode. It is observed at 1590 cm^{-1} in the Raman spectrum (solid phase) and shifts to 1583 cm^{-1} in solution in acetontrile.

The νC=N appears at 1611 cm^{-1} for both the complexes Cu SATP and Ni SATP and at 1607 cm^{-1} for CoSATP as a very strong sharp band. A similar shift was observed for Ce(IV) SATP complex. This indicate that complexation occurs via the nitrogen atom of the (–C=N-) group as for Cu(II) and Ni(II) of OHBZA[6]. The νC=N for Cu(II) OHBZA and Ni(II) OHBZA were observed as strong IR bands at 1610 and 1613 cm^{-1} respectively[6].

The three complexes are also characterized by the appearance of a new strong IR band at 1530 and 1534 and 1525 cm^{-1} for CuSATP, NiSATP, and CoSATP, respectively. For SATP, the IR band at 1408 cm^{-1} which shifts to 1387 and 1379 cm^{-1} for Cu SATP and Ni SATP, respectively can be assigned to the mode νN-Ph since it is expected in the 1400-1300 cm^{-1} range[6a]. This band is situated under the strong IR band at 1406 cm^{-1} assigned for the ammonium ion. The two ligand bands at 1364 and 525 cm^{-1} are assigned to δOH and γOH vibration since they disappear upon coordination[6a]. The $\gamma N^{+}H$ mode is observed at 929 cm^{-1} as a medium broad band which is absent for the three complexes. The two IR bands at 1240 and 1225 cm^{-1} assignable to the two coupled modes 7a and 13[6] shift to higher wavenumber upon coordination (Table 2). These two modes are observed as strong Raman lines at 1275 and 1242 cm^{-1} for the 7a and 13 modes respectively. It is interesting to note that the upward shift of 7a mode for Schiff bases is smaller than observed for azines[10]. For CoSATP, the bands characterizing the ammonium ion appears at 3130 (s) and 1406 cm^{-1} (vs) which can be safely assigned to the ammonium ion modes numbers ν_3 and ν_4 expected to be IR active[14] for tetrahedral structure. The $\nu_2 + \nu_4$ combination band appears at 3040 cm^{-1} indicating that ν_2 mode, active only in the Raman should be localized at ca. 1637 cm^{-1}. The νOH of the hydroxide ion is observed as a sharp band at 3595 cm^{-1}[14]. This band is absent for Cu SATP and Ni SATP. The low frequency region is assigned in comparison with analogous Schiff bases and azines[6,10,11]. The most characteristic mode of SATP in this region is the strong Raman line at 265 cm^{-1} as expected for o-substituted benzene[11]. It should be noted that the IR band at 758 cm^{-1} is better explained as γ CH[10,11] and not as νC-S vibration as previously given[5]. However the νC–S may contribute to the band at 678 cm^{-1} (IR) which disappears upon coordination.

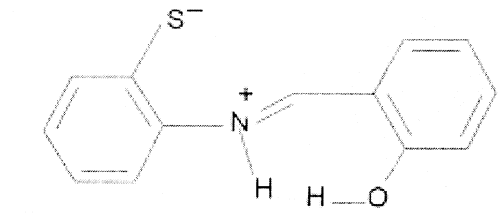
Finally, the metal ligand stretch $\nu M–O$ for Cu SATP, Ni SATP and CoSATP are assigned to the new medium IR bands at 554, 561 and 554 cm^{-1}, respectively. The $\nu M–N$ stretch for Cu SATP and Ni SATP are observed at 472 and 469 cm^{-1}, respectively. For Ce (IV)

SATP complexes $\nu M\text{-}O$ and $\nu M\text{-}N$ are found at ca. 650 and 440 cm^{-1}, respectively[5].

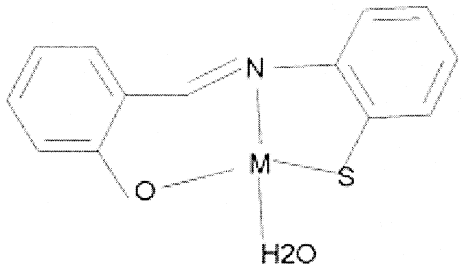
Hence, based on our data and by comparison with Ce(IV) SATP complexes[5], Cu(II) and Ni(II) of OHBZA[6]; the following structure for CuSATP and NiSATP are proposed in (Figure 3). For Zn(II) ions previous results indicated that it forms 1:1 and 1:2 molar ratio using NMR spectra[5].

The Electronic Spectra and Magnetic Moments

The electronic spectra of SATP in methanol shows three bands at 231 (vs) and 287 (s) and 334 (s) nm. These bands can be safely assigned to $\pi - \pi^*$ transitions[6]. A medium shoulder at ca. 350 nm may represent the $\pi - \pi^*$ transition upon coordination to Cu(II) and Ni(II) ions, the first two bands of the ligand slightly shift to lower wavelengths whereas the higher wavelength



SATP



MSATP.H2O(M=Cu(II),Ni(II))

Figure 3. Molecular structures of SATP, Cu SATP, NiSATP.

band shifts to 360 and 411 nm for Cu SATP an Ni SATP, respectively. These two bands are strong enough to be likely assignable to charge transfer transition[6,12], although contribution from d-d transitions are probable for these two bands. For CoSATP, a pattern of three new bands is observed in the UV/Visble spectra at 24690, 22222, and 16129 cm^{-1} which can be assigned in order of decreasing energy to $^1A_{1g} \rightarrow E_g$, $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions assuming square planar structure of the complex[13].

The two complexes Cu SATP and Co SATP are paramagnetic (magnetic moments = 1.62 and 1.87 BM, respectively. The 1.87 BM value of the CoSATP complex is consistent with a square planar structure. The 1.62 BM value of the CuSATP may indicate a tetrahedral configuration. The NiSATP has a magnetic moment value equals to 0.25 BM, this value as well as the elemental analysis and the TGA curve indicate that this complex has a square planar structure.

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