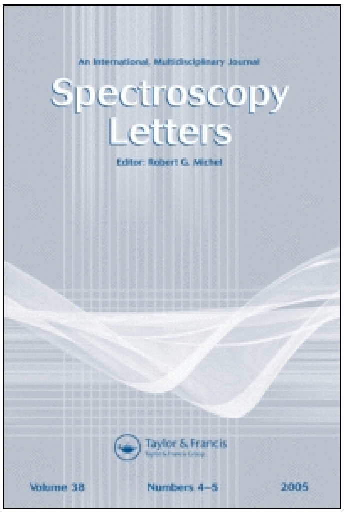

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VIBRATIONAL SPECTRA OF BENZALDAZINE AND SALICYLALDAZINE COMPLEXES WITH Zn(II) AND Fe(II) IONS

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ABSTRACT

The FT Infrared and FT Raman spectra of benzaldazine compound in the solid state in the wavenumber (1800–$200\,cm^{-1}$) are recorded. An assignment for nearly all fundamentals are proposed. For benzaldazine the complementarity of its IR and Raman spectra indicates that the molecular symmetry is most probably C_{2h}. The Zn(II) and Fe(II)-salicylaldazine complexes are synthesized and their structures are determined by elemental, thermogravimetric analysis, UV-Visible, IR and Raman spectral analysis. The two complexes are found to have the formula $FeL{\cdot}3H_2O$ and $Zn(HL)_2$. It is found that Fe(II) coordinate via a tridentate manner whereas Zn(II) coordinate via tetradentate manner.

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Key Words: Benzaldazine; Salicylaldazine complexes; Assignment; FT infrared; FT Raman

INTRODUCTION

Azine products which have an orthohydroxy group possess weak semiconducting properties which being enhanced by chelation with some 3d-block elements.[1] Despite of numerous previous spectroscopic studies dealing with the azine compounds,[2–6] less vibrational ones have been devoted toward the analysis and attribution of azine compounds in comparison with analogous conjugated polyene chains possessing (C=C) groups.[2,7,8] We have recently analyzed the FTIR and Raman spectra of some symmetric azines in the wavenumber range 1700–1500 and 1100–1000 cm^{-1}.[8] We present here, an almost complete vibrational assignment for the Benzaldazine compound (BAA) in the 1800–200 cm^{-1} range. We discuss, at first, the assignment of (BAA) IR and Raman spectra by comparison with monosubstituted benzene derivatives.[9] The Zn(II) and Fe(II)- salicylaldazine complexes abbreviated as ZnSAA and FeSAA respectively are synthesized and their structures are determined by elemental, thermogravimetric (TGA) analysis, UV-Visible, IR and FT and micro Raman spectral analysis.

EXPERIMENTAL

The compound (BAA) and was synthesized as previously given.[3] Its formula has been confirmed by elemental analysis and by obtaining the Vis. spectra as previously given[3] using a Cary 3 spectrophotometer. The BAA compound was sublimed under reduced pressure before recording the IR and Raman spectra.The two complexes ZnSAA and Fe-SAA are synthezied as previously given.[10] The synthesis of the two complexes can be represented as:

$$\text{Fe(II)} + \text{H}_2\text{SAA} = \text{Fe(II)-SAA} + 2\text{H}^+$$

$$\text{Zn(II)} + 2\text{H}_2\text{SAA} = \text{Zn(II)(HSAA)}_2 + 2\text{H}^+$$

Infrared spectra were recorded in the solid state as KBr pellets on Mattson 1000 FTIR spectrometer or dispersed in nujol mull between two CsI plates on a Perkin-Elmer 983 spectrometer. Elemental analysis was done using the Perkin-Elmer 2400 apparatus. UV and visible spectra were obtained using Cary 3 spectrophotometer. Raman spectra of BAA were recorded on a Perkin-Elmer FT Raman 2000R spectrometer equipped with a YAG Laser source of wavelength = 1064 nm. The samples were inserted in tubes of small diameter and excited using a laser power of about 100 mw. The spectra of SAA and the two complexes were recorded as micro samples using the xy Dilor spectrometer using laser lines of wavelengths equal to 632.816, 514.532 and 457.94 nm of an ionized Krypton and argon Lasers. The Laser power was about 0.240 mw.

The TGA curves are obtained on a Shimadzu thermogravimetric analyzer using a TGA—50 H detector in inert atmosphere (N_2 gas). The heating rate was 20°C/min in the temp. range 30—1000°C in a platinum cell.

RESULTS AND DISCUSSION

The IR and Raman spectra (1800—200 cm^{-1}) of (BAA) compound are displayed in Fig. 1 The IR and Raman wavenumbers are listed together with their proposed assignments in Table 1. (BAA) can be considered in comparison with (SAA) as centro symmetric molecule of C_{2h} symmetry.[8] The proposed molecular structures for the studied molecules are shown in Fig. 2.[3,10,11] For C_{2h} molecules, their modes are of (A_g, B_g) and (A_u, B_u) sorts, the former group of modes are Raman active while the latter ones are IR active. The assignment notations are those of Wilson[12] as adapted for substituted benzene derivatives.[9] Table 2 includes the IR and Raman wavenumbers for the FeSAA and ZnSAA complexes. Table 3 contains the analytical data of the studied complexes. Figs. 3 and 4 show the IR and Raman spectra of Fe-SAA and Zn-SAA.

Vibrational Analysis of (BAA)

According to C_{2h} symmetry, (BAA) has 78 modes represented as ($27A_g + 26B_u + 13A_u + 12B_g$). The spectra of this compound are assigned by analogy with trans stilbene[13] and similar monosubstituted benzene.[9,14] The ν_s C=N and ν_a C=N are observed at 1553 and 1624 cm^{-1} respectively (Table 1).[8] This assignment proves that (BAA) has nearly C_{2h} symmetry as previously proposed.[4,8] The νC-Ph mode can be assigned to the IR band at 1211 cm^{-1} and the Raman one at 1217 cm^{-1}. These wavenumbers are comparable with the νC-Ph of stilbene at 1218 cm^{-1}.[13]

The ν N-N stretch is expected with strong intensity between 1100 and 1000 cm^{-1} as for polyaza chains.[2,8] The ν N-N can be assigned to the strong Raman line at 998 cm^{-1}.[8] The two γCH imine are localized at 859(IR) and 873 cm^{-1} (Raman). The other vibrational modes lie in the expected region for a monosubstituted benzene.[9]

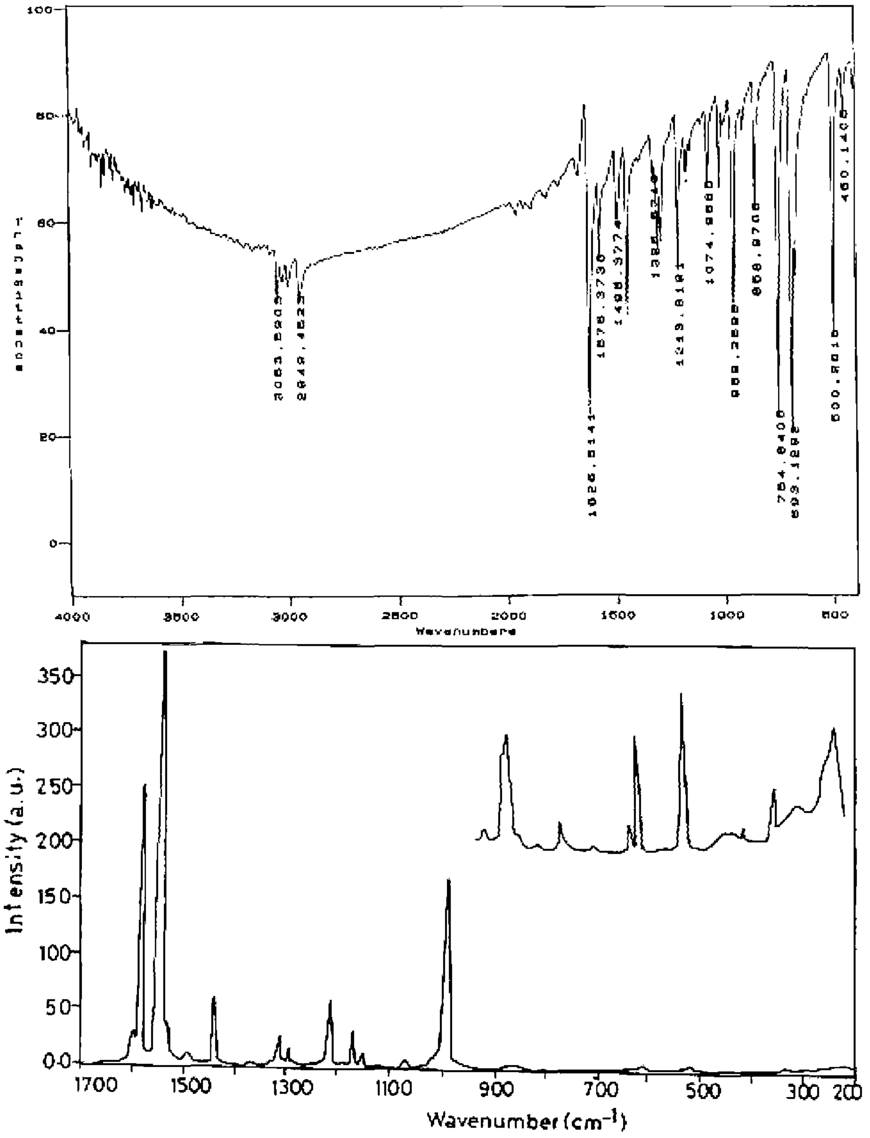

Figure 1. IR and Raman spectra of BAA.

Table 1. Raman and IR Spectra and Assignments of Benzaldazine (BAA)*

IR (Nujol)	IR (KBr)	Raman (Solid)	Raman (Soln)	Symmetry	Assignment
1632 s	1626 s			(B_u)	ν_a C=N**
1595 vw	1595 sh	1599 w		(A_g, B_u)	8a
1570 m	1576 m	1588 s	1592 (p)	(A_g, B_u)	8b
		1553 vs	1560 (p)	(A_g)	ν_s C=N**
1490 w	1496 m	1496 w	1496 (p)	(A_g, B_u)	19a
1446 s	1446 m	1445 m	1448 (p)	(A_g, B_u)	19b
1322 w	1226 w	1330 w		(A_g, B_u)	14
1305 m	1303 m	1314 m	1318 (p)	(A_g, B_u)	δ CH imine
1288 m	1288 m	1296 m	1296 (p)	(A_g, B_u)	3
1210 m	1211 m	1217 m	1220 (p)	(A_g, B_u)	ν C-Ph
1172 w	1172 w	1174 m	1174 (p)	(A_g, B_u)	9a
1157 w	1157 w	1154 w	1160 (p)	(A_g, B_u)	9b
	1075 m	1075 w	1078 (p)	(A_g)	18b
1019 m	1018 m	1025 vw		(A_g, B_u)	18a
999 vw	999 vw	998 s	998 (p)	(A_g, B_u)	νN-N,12
956 s	959 s		962 (dp)	(A_u, B_g)	17a
913 w	914 w	920 vw		(A_u, B_g)	17a
857 m	859 m	873 w	874 (dp)	(A_u, B_g)	γ CH imine
752 s	755 s	768 vw	766 (dp)	(A_u, B_g)	11
691 s	691 s	699 vw		(A_u, B_g)	4
675 m	675 m			(B_u)	δ CCN
			628 (p)	(A_g)	δ CCN
615 vw	615 vw	615 w	616 (dp)	(A_g, B_u)	6a
		521 w	522 (p)	(A_g, B_u)	6a
498 s	498 s			(A_u, B_g)	16a
448 m	450 m	438 vvw		(A_u, B_g)	16a
402 w	402 w	403 vw		(A_g, B_u)	15
		346 w		(A_u, B_g)	δ CCN
284 w		298 vw	291 (dp)	(A_u,B_g)	t C=N
240 w		222 w	203 (dp)	(A_u, B_g)	10a

*p: polarized, dp: depolarized and soln.: solution in CH_3CN.

**See Ref. (8).

Vibrational Spectra of $FeL{\cdot}3H_2O$ and $Zn(HL)_2$

The vibrational assignment will be done by comparison with the ligand modes and also with analogous complexes.[10] The observed spectra of the studied complexes will be divided into two regions.

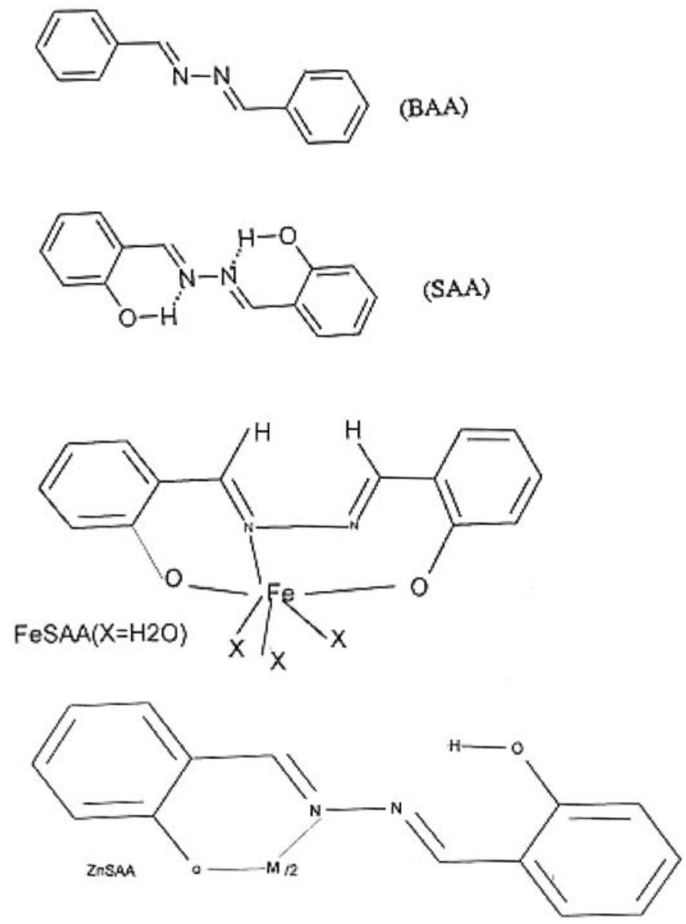

Figure 2. Proposed structure of BAA, SAA, FeSAA, and ZnSAA.

The 1700–1000 cm^{-1} Region

The ν_s C=N at 1551 cm^{-1} for the ligand[8,10] shifts to 1532 and 1534 cm^{-1} for the two complexes Zn SAA and Fe SAA respectively. It is of interest to note that this stretch becomes active for the two complexes and appears at 1532 and 1534 cm^{-1} for ZnSAA and FeSAA respectively. This was also found in the case of Cu(II), Ni(II) and Co(II) complexes of SAA.[10] For the modes ν_a C=N and the two aromatic modes 8a and 8b, no shift or very low one is observed. For ZnSAA complex two IR bands are observed

Table 2. IR and Raman Band Wavenumbers (cm^{-1}) and Assignment of (Zn SAA) and (FeSAA)

ZnSAA		FeSAA			SAA*		
IR	Raman	IR	Raman (Solid)	Raman (Soln.)	IR	Raman	Assignment
1626 s					1622 vs	1623 m	ν_a C=N
1618 sh	1618 w	1618 s		1607 m			ν_a C=N
	1608 w	1602 s	1602 m				8a
	1597 w						8a
	1584 m		1589 m	1593 w	1570 m		8b
	1575 w						
1545 sh	1547 m						ν_s C=N
1532 m	1532 s	1534 m	1534 w	1559 m		1551 vs	ν_s C=N
	1467 s		1468 w	1466 w	1484 m		19b
			1445 m	1448 m	1450 m	1453 s	19a
						1399 m	δOH
1365 m	1354 m	1365 msh			1365 msh	1383 m	14
1345 w	1348 m		1346 m	1345 m			νC-O complex
1308 w		1309 m	1309 w	1322 m	1316 m	1321 s	3, δ CH
1278 w		1271 m			1278 m	1279 vw	(7a)νCO,ligand
1190 s	1206 m	1195 m	1208 w	1212 w			13
1152 m	1155 m	1155 sh	1150 w	1153 m	1158 m	1154 m	9a
1145 m	1149 m	1151 m			1148 m		18a
1125 w		1124 w	1125 w	1125 w	1115 m	1119 m	
	1041 w			1052 m		1062 vs	νN-N
	1023 vs	1031 w	1035 w	1029 m	1032 m	1030 s	18b
985 w	986 w	984 w			984 m	997 vw	5
972 m	972 w	969 w			975 m	977 vw	17b
910 w	916 w	900 m	910 w				γ CH
		894 m			894 vs	906 vw	γ CH
802 w	812 m	783 m		808 w	785 s	794 m	12
756 m	758 vw	752 s		748 w	752 vs		11
740 m		738 m			731 s	738 w	1(ring (breathing)
681 w		682 m			683 s		4
	630 m	600 w	604 s	629 m	620 msh	631 m	νM-O
	614 m						16a
	585 m	565 w			565 m	570 w	δCCN
	518 vw		533 vw	535 w	548 w	527 m	δCCN
470 w	466 vw	459 w	467 vw	464 w	459 s	445 w	6b
468 m		472 m					νM-N
420 w		420 w	424 vw	426 w	422 m	437 vw	9b
345 vw	360 w	341 w			348 m		10a

From Ref. 10.

Table 3. Analytical Data for FeSAA and ZnSAA*

The Compound	%Calc. (Found) C	 H	 N	M. P.	Color
ZnSAA	61.83 (61.67)	4.08 (4.20)	10.30 (9.98)	Dec. > 250	Yellow
FeSAA	48.30 (48.50)	4.63 (4.11)	8.05 (7.95)	Dec. > 250	Dark brown

*The two complexes are not soluble in polar and nonpolar solvents.

at 1626 and 1618 cm^{-1} which may arise from a two types of C=N bonds. It is also observed that the ν N-N of SAA at 1062 cm^{-1}(8) shifts to lower wave numbers at 1041 and 1052 cm^{-1} for the ZnSAA and FeSAA respectively. Similar behavior was observed for the complexes (Cu SAA), (Co SAA) and

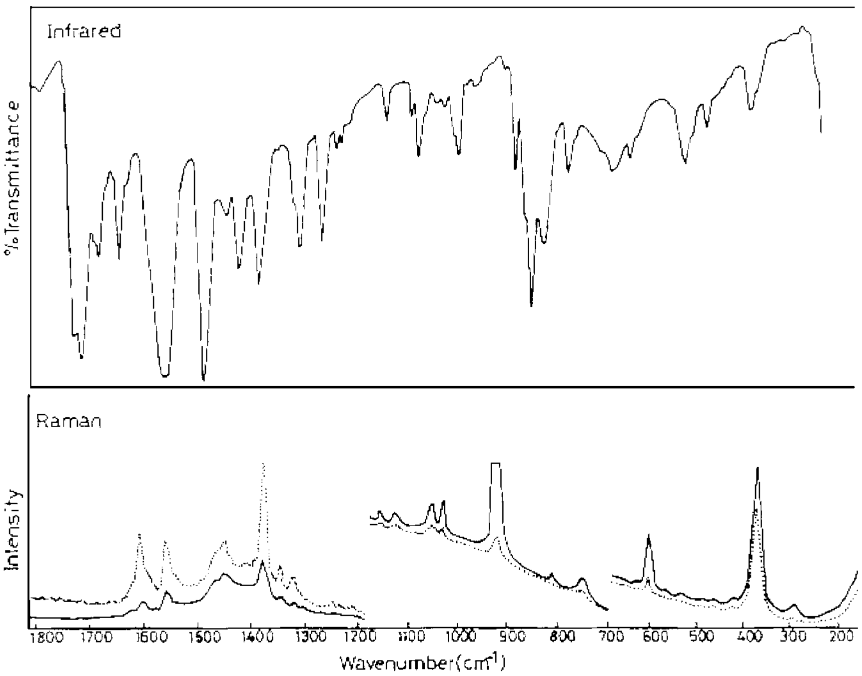

Figure 3. IR and Raman spectra of FeSAA.

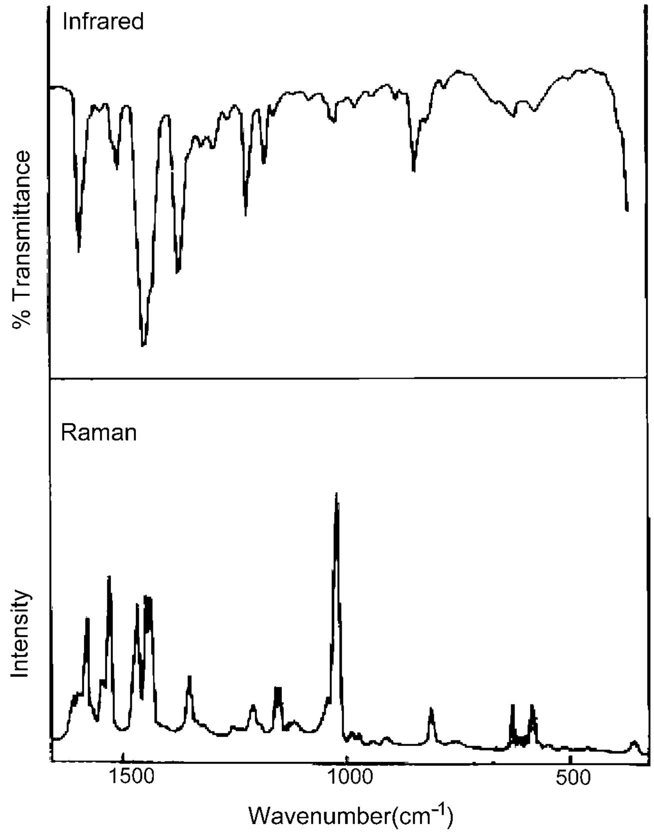

Figure 4. IR and Raman spectra of ZnSAA.

(Ni SAA).[10] These observations indicate that coordination occurs via the nitrogen atom of the imine group.[10,11] The splitting of ν_s C=N and ν_a C=N indicates that two types of C=N are present. The νO-Ph(7a) mode for SAA was assigned at 1278 cm^{-1} in the IR spectra.[10] This band moves to higher wave numbers upon complexation to Cu (II), Ni(II) and Co(II) ions.[8] For Salicylaldimine the ν O-Ph(7a) was attributed to the two bands at 1280 and 1310 cm^{-1} since these bands increases in frequency due to complexation.[11] For SAA complexes with Cu (II), Ni (II) and Co (II) ions,[8] the IR band at 1278 cm^{-1} is the only band that shifts to higher wavenumber (about 1345 cm^{-1}). For FeSAA, two bands are correlated to ν O-Ph(7a) 1271 cm^{-1} (IR) and 1346 (Raman). The first one is attributed to the weakly coordinated νO-Ph. The second one is assigned to the coordinated νO-Ph.[10,11]

For ZnSAA the two IR bands at 1278 and 1345 cm^{-1} represent the uncoordinated and coordinated νO-Ph respectively. The splitting of the νO-Ph(7a) stretch for the two complexes suggest the presence of dissimilar chelate rings. This behavior may also indicate that Fe(II) ion coordinate with the ligand SAA via a tridentate manner. However, For ZnSAA complex, the presence of νO-Ph at 1278 cm^{-1} exactly and knowing that the formula is $Zn(HL)_2$ indicates that the Zn(II) ion is coordinated only to one O-Ph group from each ligand.

The 1000–200 cm^{-1} Region

In this region, slight shift of the ligand bands is observed due to complexation.[10] The ν M-O and ν M-N stretches are expected about 500 and 400 cm^{-1} respectively.[10,11] Comparing the Raman and IR spectra of FeSAA and SAA in the solid phase and in solution indicate that the new band at 604 cm^{-1} (Raman) can be assigned to the M-O stretch as observed for similar compounds.[11] The Zn SAA complex exhibits a Raman of medium intensity at 614 cm^{-1} which may be assigned by analogy to the νM-O stretch. Likewise, the two new medium bands observed in the IR spectra at 468 and 472 cm^{-1} may be attributed to the νM-N stretch of Zn SAA and FeSAA respectively.

The UV and Visible Spectra

The UV and visible spectra of free ligand salicylaldazine exhibits three intense bands at 218,293 and 354 nm in acetonitrile. The two bands at 218 and 293 nm were assigned to π-π* transitions.[1] The third band at 354 nm. was assigned as n-π* type (1). The third band was not observed for benzaldazine and was attributed to the presence of the -OH group in position ortho to the imine group (3). For the complex (FeSAA), we observe three bands at 219, 392 and 355 nm in methanol. The first two bands represent the π-π* transitions whereas the 355 nm. band may corresponds to the LMCT transition. However, for the complex (ZnSAA) which have a yellow color, we also observe three bands at 205 (strong), 297 (medium) and 404 (medium) nm. The two bands at 205 and 297 nm. represent the two ligand transitions of π-π* type.[1,3] A weak shoulder is also obtained at about 335 nm which may represent the n-π* transition. The n-π* transition of the ligand at 360 nm in methanol (3) is bathochromic shifted for the complex ZnSAA to 404 nm due to chelation with Zn(II) ion. This may proves that coordination occurs via the oxygen atom of the -OH group. The 404 nm. band can be assigned to MLCT transition.

Thermal Analysis of FeL·3H_2O and Zn$(HL)_2$

The TGA curve of Zn$(HL)_2$ (Table 4) shows that it decomposes in two decomposition steps:

1. The first one includes the loss of two nitrogen molecules in the temp. range 132–271°C and 274–424°C.
2. The second step leads to the removal of of the two fragments 2(C_7H_6O) in the temp. range 424–547°C.

The remaining fragment corresponds to the formula Zn$(C_7H_5O)_2$.

For the FeL·3H_2O complex, the first decomposition step leads to nitrogen elimination (exp. Weight loss = 4.35, calc. 4.02), the intermediate steps are rather complex, however the final step corresponds to the formation of H2FeO2 (exp. weight loss = 26.01 mg, calc. 25.81 mg).

CONCLUSION

The FTIR and FT Raman spectra are measured for the three molecules BAA, ZnSAA and FeSAA. We were able to assign the spectral bands in the wavenumber range 1800–200 cm^{-1} on the basis of C_{2h} symmetry and polarization measurements in the Raman in solution for BAA. The vibration ν C-O of the ligand SAA was observed at 1278 cm^{-1} and shifted to higher wavenuumber due to complexation with Zn(II) and Fe(II) transition metal ions as previously found for Schiff base compounds. The Fe(II) and Zn(II) give complexes with SAA having the formula FeL·3H_2O and

Table 4. TGA Data of the Complex Zn(HL)2

	The Decomposition Steps			
		Weight Loss		
Complex	Temp. Range (°C)	Exp.	Calc.	The Corresponding Fragment
Zn(HL)2	1) 132–271,			$2N_2$
	274–424	10.7	10.5	
	2) 424–547	39.9	39.0	2(C_7 H_6 O)

$Zn(HL)_2$ where L represent the ligand. The Fe(II) and Zn(II) coordinate to SAA in tridentate and bidentate manner respectively.

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