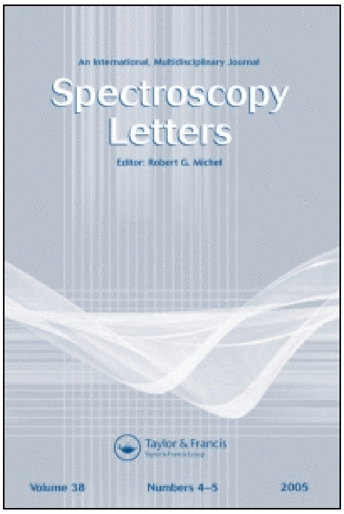

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IR Studies of Iron Complexes with Pyridoxal Isonicotinoyl Hydrazone and Three Other Similar Chelating Agents

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IR STUDIES OF IRON COMPLEXES WITH PYRIDOXAL ISONICOTINOYL HYDRAZONE AND THREE OTHER SIMILAR CHELATING AGENTS

Key words : Pyridoxal Isonicotinoyl Hydrazone, Pyridoxal Benzoyl Hydrazone. Salicylaldehyde Benzoyl Hydrazone, Salicylaldehyde Isonicotinoyl Hydrazone, Iron Complexes, Infrared. Solid state.

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ABSTRACT

Infrared studies of pyridoxal isonicotinoyl hydrazone and of three similar chelating agents in solid state brings out, after complexation with iron (III), the deprotonation of phenol for all the compounds ; for those which possess the pyridoxal group, a deprotonation of hydrazine leads to a transformation of the linkage between the rings and for the others, the drastic shift of the carbonyl band proves its engagement in the association with iron.

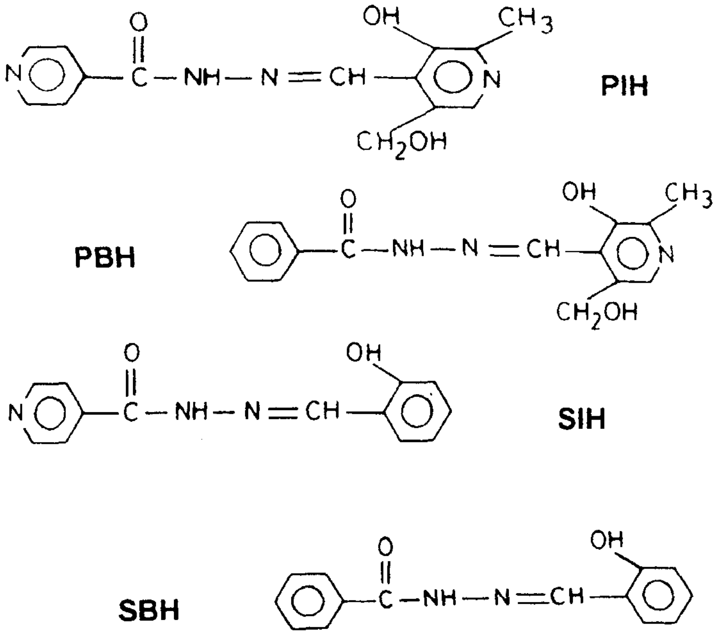

Figure 1

INTRODUCTION

Pyridoxal isonicotinoyl hydrazone (PIH), pyridoxal benzoyl hydrazone (PBH), salicylaldehyde isonicotinoyl hydrazone (SIH) and salicylaldehyde benzoyl hydrazone (SBH) (figure 1) were synthesized in order to replace the desferrioxamine presently used as a drug to eliminate excess iron in the organism /1-5/.

A large number of physicochemical and spectroscopic studies was done on PIH and analogs complexed with iron (II) and iron (III) ions /6-12/.

The crystallographic studies bearing on PIH, PBH and SBH complexed with iron(III) /7-8/ show a stucture in which iron

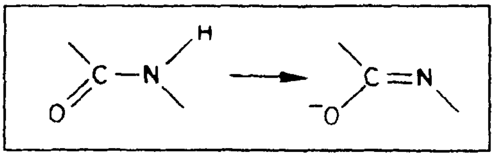

Figure 2

is linked to the phenol oxygen, to the amide oxygen and to the nitrogen imine . In addition these results seem to indicate a deprotonation of phenol for the ligands and a deprotonation of hydrazine in the case of PIH and PBH . These deprotonations can be accompanied by transfers of protons on the nitrogen of the rings (PIH and PBH). The rupture of the NH link of hydrazine for these two ligands causes a loss of identity of the amide group and the appearance of a new imine link (figure 2).

These points should be specified for the SIH - iron complex and confirmed for the other complexes with iron (III).

Vibrational spectroscopy is a tool particularly well adapted to the study of the permanence of identity of the OH phenolic link on one hand, and of the amide group on the other hand. We will here use this technique to study the structural modifications in a solid phase during the complexation by iron (III) .

EXPERIMENTAL SECTION.

PIH, PBH, SIH and SBH were kindly provided by Professor Ponka, from Montreal, Canada. They were recrystallised in an ethanol-ether mixture. The complexes were formed from a solution of products in tetrahydrofuranne (THF), to which were added the iron ions. The IR spectra of the complexes in a solid phase (KBr) were done after the elimination of the solvent. $FeCl_3$ (Prolabo) was dried before use. THF (Janssen Chimica) was stored under argon.

Spectroscopic measurements were performed with a Nicolet 60SX FTIR. The resolution was 2 cm^{-1}.The zone towards 3000 cm^{-1} is difficult to study, because the presence of included water disturbs the general appearance of the spectra, so the results discussed here were between 1800 cm^{-1} and 1100 cm^{-1}.

RESULTS AND DISCUSSION

Tables 1 & 2 present the wave numbers collected between 1800 cm^{-1} and 1100 cm^{-1} for the various normal modes, as well as the relative intensities. These were referenced with respect to the value of the most intense band of the spectrum. For the attributions presented otherwise /13, 14/, we based ourselves on the spectra of ligands and of the corresponding deuterated compounds, in solution and solid state.

AMIDE GROUP IDENTITY.

The amide group is distinctly identifiable by the amide I band ($\nu C=O$ for the main contribution) and, to a lesser degree, by the amide II and III bands. In fact, the amide I band is intense whereas the amide II and III bands are of medium intensity and can be shifted according to the cis or trans conformation /15/. Moreover, the amide III band is next to the δ CH_3 band, which complicates interpretations.

For the ligands, the O=C-NH link is distinctly identified : the amide I band is still the most intense of the spectrum for the four compounds. However, the

TABLE 1.

Selected Infrared Bands (Wave Number in cm^{-1} and Relative Intensity I) of Ligands.

ASSIGNMENT	LIGANDS				LIGANDS				ASSIGNMENT
	SBH		SIH		PBH		PIH		
	ν	I	ν	I	ν	I	ν	I	
amide I	**1674**	**100**	**1684**	**100**	**1648**	**100**	**1675**	**100**	amide I
	1622	20	1624	30			1605	6	
cycle	1607	35	1613	40	1603	30	1595	10	cycle
cycle	1579	20	1569	55	1578	20			cycle
amide II trans	1540	65	1554	20	1560	70	1556	60	amide II trans
					1541	10	1520	10	
	1488	40	1490	35	1483	10	1490	10	
cycle			1457	20	1441	15	1442	15	cycle
cycle			1408	30			1414	20	cycle
			1392	20	1400	35	1399	40	
					1377	25	1379	25	δ CH3
amide III trans	1356	45	1355	30	1364	55	1360	50	amide III trans
					1319	7			
					1298	15	1295	35	cycle -CH3
ν CO + δ OH*	**1272**	**80**	**1291**	**85**	**1280**	**95**	**1279**	**100**	ν CO + δ OH*
ν CO + δ OH	1263	15	1274	35	1249	15	1255	30	ν CO + δ OH

* Chelated form band.

TABLE 2.

Selected Infrared Bands (Wave Number in cm^{-1} and Relative Intensity I) of Complexes.

ASSIGNMENT	COMPLEXES				COMPLEXES				ASSIGNMENT
	SBH - IRON		SIH - IRON		PBH - IRON		PIH - IRON		
	ν	I	ν	I	ν	I	ν	I	
			1635	55			1635	40	
amide I	**1602**	**100**	**1600**	**100**	1610	30	1609	10	
							1601	20	
**	**1588**	**75**	1589	25	1591	50	**1588**	**100**	**
	1555	60	1544	40	1573	45			
amide II trans	**1541**	**75**	1529	70			1520	60	
			1507	55			1506	30	
	1490	35	1489	10	**1482**	**90**	1490	10	
							1473	20	
	1467	30	1468	30	1460	40	1462	30	
							1449	10	
**	1437	60	**1435**	**80**	1432	35	1410	20	
	1381	**75**			**1381**	**80**	**1379**	**90**	**
amide III trans	1351	30	1348	40	**1358**	**100**	1353	40	
	1330	15					1341	25	
	1313	25	1321	10	1324	35	1314	35	
	1301	10	1291	30	1304	20	1301	20	
	1292	60					1280	25	

** bands disturbed for both complexes - new or stronger intensity.

spectra of the iron complexes reveal the permanence of the amide group identity for SBH and SIH, but not for PBH nor PIH. For the complexes formed with SBH and SIH, the amide I band is very strongly shifted by the complexation (a drastic shift of 70 cm^{-1} proves the engagement of the carbonyl group in the association with iron), but remains the most intense in the spectrum. On the contrary, for the PBH and PIH complexes, the most intense band of the spectrum is not the amide I band, but other bands : 1358 cm^{-1} for PBH and 1588 cm^{-1} for PIH. The intensity decrease of amide I and amide II bands, and even the disappearance of the amide II band in the spectrum of the PIH complex is to be noted (which leads us to think that the bands in the 1360 cm^{-1} area are new bands, since there is no more amide III band) **The SBH and SIH complexes with iron do present the same O=C-NH linkage as the ligands whereas a strong modification affects this link for PBH and PIH during complexation**.

PHENOLIC HYDROXYL GROUP IDENTITY.

The normal mode situated towards 1280 cm^{-1} corresponds to the deformation of the OH group (δOH) coupled to the elongation of the simple bond C-O (νC-O). The νC-O + δOH band is, with the amide I band, one of the most intense of the spectrum of the ligands. It appears under the form of a multiplet, the component with the lowest frequency corresponds to the free OH group, and the component situated in a superior frequency corresponds to the deformation of the OH group engaged in an intramolecular association with the imine nitrogen resulting from a chelation /14/.

For all the complexes, the normal mode corresponding to νC-O + δOH is absent, and no band with a comparable intensity can be found in the area of study. This fact proves **the deprotonation of phenolic hydroxyl through complexation**.

CONCLUSION.

The most significant result of our study is the difference existing between the spectra of SBH and SIH complexes on one hand, and PBH and PIH complexes on the other hand. For the latter, the disappearance of the most intense bands with respect to the spectra of the ligands only leaves three or four main bands essentially due to ring vibration bands and the δCH3 bands disturbed by the presence of iron and by the formation of an ionic compound - but no attribution appears totally convincing regarding the formation of pyridinium ions.

Vibrational spectroscopy thus presents a good correlation with structures known through crystallography This therefore facilitates SIH analysis for which the permanence of the amide function shows that the difference between the complexes is only due to the nitrogen of the pyridoxal.

In the solid phase. it is therefore possible to state :

1)- the absence of transfer of the phenolic hydrogen and of the imine hydrogen for the four ligands .

2)- the deprotonation of phenolic hydroxyle common to the complexes formed with iron (III) .

3)- the permanence of the amide group for SBH and SIH, but the disappearance of the O=CNH link of PBH and PIH, which gives rise in the corresponding complexes to a O-C=N link (figure 2).

4)- the engagement of the νC=O vibration band in the association with iron.

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