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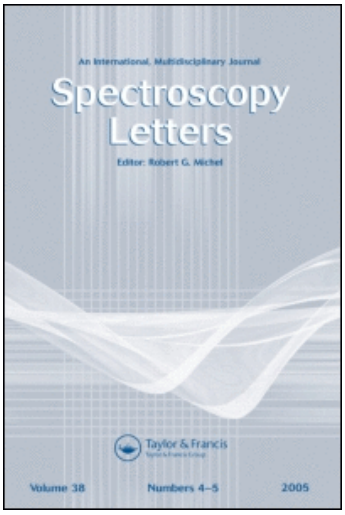

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IR Study of Complex Between Salicylalbenzoylhydrazone (SBH) and Iron III: Normal Mode Assignment Assisted by Quantum Mechanical Calculation

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IR STUDY OF COMPLEX BETWEEN SALICYLALBENZOYLHYDRAZONE (SBH) AND IRON III : NORMAL MODE ASSIGNMENT ASSISTED BY QUANTUM MECHANICAL CALCULATION.

Key Words :Salicylalbenzoylhydrazone, Iron III complex, Infrared, Normal mode analysis, *ab initio* calculations.

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ABSTRACT

A theoretical investigation of SBH and a bicomplex ion, $[(Fe\ III\ (SBH)_2)]^+$ is used as a basis to control and clarify previous vibrational assignments for complexes formed between iron and ligands related to SBH. Main conclusions are the following :

1. Complexation shifts the νC=O vibration by about 100 cm^{-1} towards low wavenumbers.
2. νC=N and δHC=N modes are enhanced by complexation.
3. In the complex, the enhanced νC=N mode hides the amide II vibration.

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4. The $\nu\phi$-O^- stretching mode is expected to be near 1400 cm^{-1} in the complex.
5. Point 1 provides a criterion for carbonyl involvement in complexation. Points 2 and 4 are possible probes for hydrazide nitrogen and phenate involvement.
6. Despite *ab initio* calculations, the vibration at 1360 cm^{-1} is, as previously, assigned to the amide III mode.

INTRODUCTION

Molecules related to salicylalbenzoylhydrazone (SBH) are able to mobilize iron in living media. They have been proposed to replace the drug desferrioxamine currently used in the therapy of iron overload (1,2). In contrast to desferrioxamine, no cytotoxicity is expected. SBH complexes are also good catalysts for chemical reactions such as Diels-Adler reactions (3,4).

A large number of physicochemical and spectroscopic studies have been performed on such compounds (5-17). Complexation of SBH with Fe II ions involves two kinetically distinguishable steps (17) followed by oxidation of the metal ions (16). Finally a Fe III bicomplex is formed.

In some cases X-ray studies of ligands (13,14) and complexes (7-10) provide full structural information about deprotonation and complexation sites but more often IR spectroscopy is the only tool available. In such a case, the study is restricted to the 2000-1200 cm^{-1} range, broad bands related to dimeric and polymeric associations preventing examination at higher frequencies.

Despite systematic deuteriation of ligands and complexes, assigning normal modes in the 2000-1200 cm^{-1} range remains a difficult exercise

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vibrational modes being numerous and often highly coupled. We will here use theoretical calculations to make assignments easier.

METHODS

Because of the size of the molecular systems, *ab initio* calculations (18) were performed on SBH and a bicomplex ion $[Fe\ III\ (SBH)_2]^+$ using a minimal basis set (STO-3G). Starting geometries were taken from X-ray structures of the ligand (14), a FeIII/SBH monocomplex (8) and a bicomplex formed between iron II and pyridoxalisonicotinoylhydrazone (10).

The minimized FeIII/SBH bicomplex has C_2 symmetry, the two ligand molecules lying in two perpendicular planes. Consequently two modes, A and B, correspond to each frequency. Their descriptions, if limited to one SBH molecule, are identical. Two such A and B modes are denoted below as "one" or "the" mode.

For thermodynamic calculations, STO-3G frequencies have to be multiplied by 0.85, and it is well known that high frequencies are then still overestimated while low frequencies are underestimated. Here, also, the overestimation of *ab initio* harmonic vibrational frequencies has been found to be non-uniform and in order to compare experimental and calculated spectra more easily, we have decided to use *two* different scale factors instead of one *mean* scale factor. We will apply scale factors of 0.8 and 0.9 to elongation modes and other modes, respectively.

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RESULTS AND DISCUSSION

GEOMETRY AND ELECTRON DELOCALIZATION

Our STO-3G geometric parameters (Table) compare rather well with those taken from available X-ray structures (8,14). In particular *ab initio* calculation finds that the C=O bond is lengthened by complexation but overestimates the ϕ-O bond shortening. We can, therefore, expect νC=O and νϕ-O normal modes to be shifted by complexation towards low frequencies for the former and to high frequencies for the latter.

However, a major discrepancy has to be noted. The STO-3G basis set does not reproduce the electron delocalization in the amide and hydrazone moieties. In contrast with experiment, calculated NN and CN bonds are typical single bonds. We can, therefore, anticipate that the frequencies of normal modes involving NN and CN bonds will be wrongly calculated.

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CORRESPONDANCE BETWEEN CALCULATED AND EXPERIMENTAL SPECTRA

Figure 2 compares theoretical spectra for SBH and [Fe III $(SBH)_2]^+$; Figure 1 shows experimental spectra. The latter are taken here as representative of many ligands and Fe III complexes related to SBH (12,13,16) (scheme). The overall similarity of the two figures suggests that the calculations are pertinent.

TABLE

(Selected bond lengths (Å))

	Experimental		Calculated	
	SBH (14)	monocomplex (8)	SBH	$[Fe\ III\ (SBH)_2]^+$
CC_{amide}	1.502	1.477	1.521	1.501
C=O	1.221	1.256	1.218	1.252
C-N	1.332	1.336	1.461	1.406
N-N	1.365	1.380	1.428	1.435
C=N	1.291	1.293	1.286	1.320
ϕ-O	1.356	1.326	1.378	1.296

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νC=O SHIFT

Our previous assignments (16) are confirmed. Complexation shifts the amide I mode, denoted by 1 and 1' in the figures, by about 100 cm^{-1} towards low wavenumbers. Obviously, this very large shift is due to the lengthening of the carbonyl bond. Nevertheless, it does not mean that the carbonyl should be a single bond in the complex ($r_{C=O\ calc}$ = 1.252 Å, $r_{C=O\ exp}$ = 1.256 Å (8)).

νC=N ENHANCEMENT AND DISAPPEARANCE OF THE AMIDE II VIBRATION

Ligand normal modes 2 and 4, νC=N and δHC=N (Figure 2), have very low calculated intensities and are not observed in the experimental spectrum

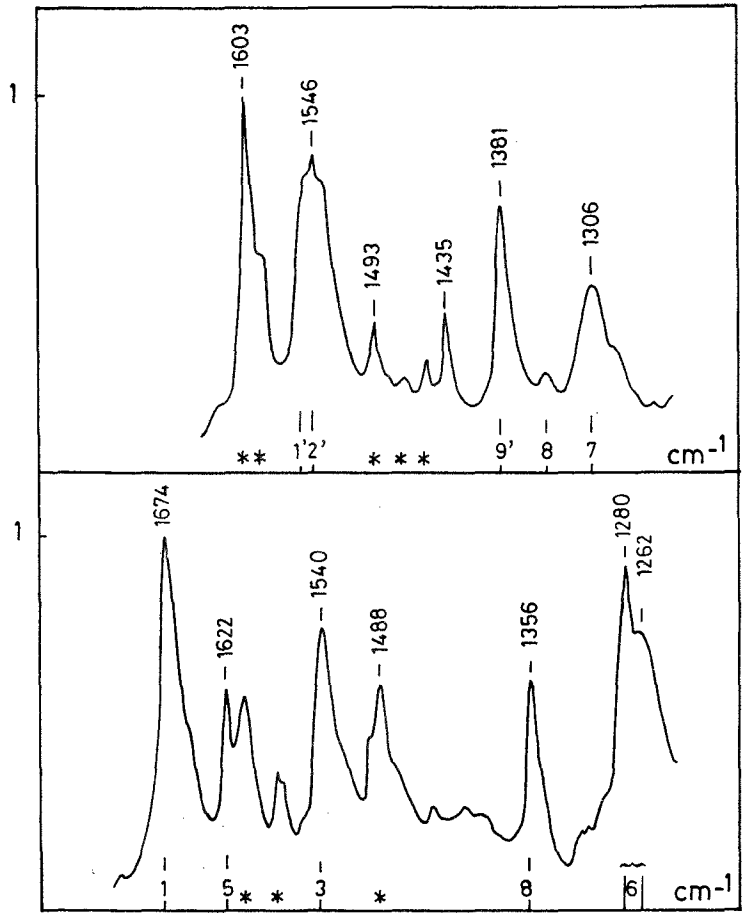

FIG. 1 : Experimental absorption spectra of Fe III/SBH complex (above) and SBH (below) in solid state (KBr pellets). Previous assignements (16): 1, $\nu C{=}O^a$; 1', $\nu C{=}O^d$; 2, $\nu C{=}N^d$; 3, amide II trans ; 5, $\delta OH^e + \nu C{=}C$; 6, $\delta OH^e + \nu\phi\text{-}O$ and $\delta OH^{c,b} + \nu\phi\text{-}O$; 7, orthophenol + $\nu C{=}N$; 8, amide III trans ; 9', $\nu\phi\text{-}0 + \delta OFe$; * ring modes ; a) free form ; b) associated form ; c) chelated form ; d) bonded with iron.

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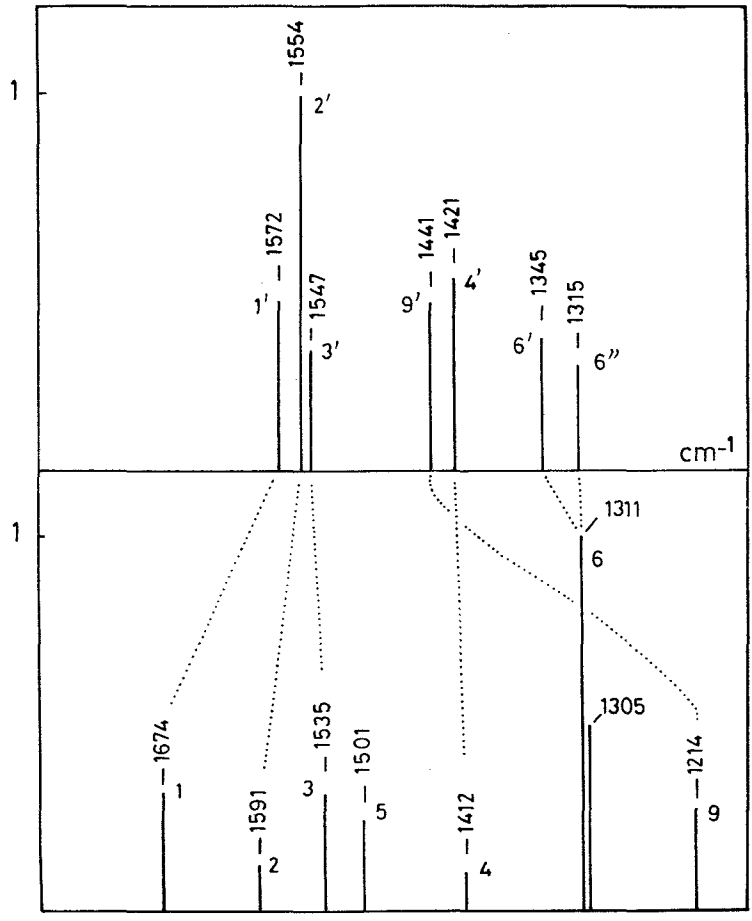

FIG.2 : Theoretical spectra of $[Fe\ III\ (SBH)_2]^+$ (above) and SBH (below) : 1, $\nu C{=}O^a$ (a: free mode) ; 1', $\nu C{=}O^d$ (d: involved in complexation) ; 2, $\nu C{=}N$; 2', $\nu C{=}N^d$; 3, δNH + benzoyl ring ; 4, $\delta HC{=}N^a$; 4', $\delta HC{=}N^d$; 5, δOH^a + ϕOring ; 6, ϕOring + $\delta HC{=}N \pm (\delta NH + \nu CC)$ amide + δOH ; 6", ϕOring ; 6', $(\delta NH + \nu CC)$ amide ; 9, $\nu\phi$-O + $(\delta CH + \delta OH)$ phenol ; 9', $\nu\phi$-O^- + δNH + δCH benzoyl.

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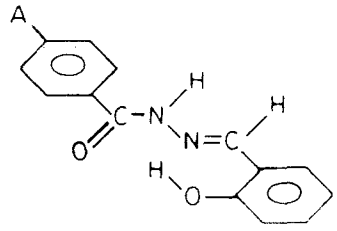

Scheme .Substituted salicylalbenzoylhydrazones (A = H for SBH, otherwise A = NH_2, OH, OMe, tBu,F, Cl, Br).

(Figure 1). Calculation shows that these two modes should be strongly enhanced by complexation because of better local charge separation in the complex HC=N moiety than in the ligand. Moreover, complexation shifts νC=N, mode 2, by about 40 cm^{-1} towards low wavenumbers while δHC=N, mode 4, has roughly the same frequency in the ligand and in the complex. In contrast to mode 2, the amide II trans mode, mode 3, is not shifted by complexation and its relative intensity is unchanged. Consequently, in the complex, modes 2 and 3, the νC=N and amide II trans modes are at nearly the same wavenumber and the former can hide the latter.

This scheme corresponds very well with the experimental observation (16). The normal mode located at ~ 1540 cm^{-1} is maintained in the spectra of the deuteriated complex (and logically assigned to νC=N (16)) whereas it disappears when the ligand is deuteriated (12) (δNH + νC-N). It follows that the absence of the amide II trans mode from the spectra of complexes does not necessarily signify the disappearance of the amide II trans moiety.

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POSSIBLE CRITERION FOR NITROGEN INVOLVEMENT IN COMPLEXATION

We previously assigned mode 9' (1380 cm^{-1}) in the experimental spectra of the complexes to a $\nu\phi$-O^- + δOFe vibration (16). The present *ab initio* calculation suggests two candidates :

i) a $\nu\phi$-O^- stretching coupled with amide and benzoyl deformations. This mode is probably calculated at too high a wavenumber, the calculated ϕ-O^- bond being too short in the complex.

ii) a δHC=N mode (mode 4) enhanced by complexation. One of the two possibilities could apply to mode 9' (1380 cm^{-1}) and the other to the neighboring mode at 1435 cm^{-1}.

Up to now, there has been no criterion for demonstrating that the hydrazide nitrogen is involved in complexation. The νC=N and δHC=N enhancements might be such a criterion. This point could be checked by studying complexes in which the ligand or the metal is different.

THE 1280 CM^{-1} DOUBLET : TWO HIGHLY DELOCALIZED MODES

In the experimental ligand spectrum (Figure 1) three normal modes (5 and doublet 6) at 1622, 1280 and 1262 cm^{-1} involve the δOH angular deformation. Complexation provokes OH deprotonation and suppresses these modes.

These three normal modes are calculated to be at 1500, 1311 and 1305 cm^{-1}, and for the first, the difference from the experimental value is large.

However, in this respect, we must recall the following points :

i) δOH modes are very sensitive to intermolecular and intramolecular association (19-21).

ii) Calculations correspond to a free OH group because the STO-3G calculation is performed on a single molecule and does not correctly reproduce the intramolecular bond.

The 1311-1306 cm^{-1} doublet 6 corresponds to two highly delocalized modes. Nevertheless, at this very low level, the theoretical investigation does not provide any notion of coupling between δOH and νϕ-O, modes 6 and 9 (Figure 2), as suggested by analysis of the experimental spectrum (16). Two reasons can be suggested for this absence of coupling at this calculation level : firstly, the force constants are overestimated for stretchings and underestimated for bendings and secondly, νϕ-O stretching is certainly calculated at too low a wavenumber, the calculated ϕ-O bond being too long in the ligand. We therefore estimate that coupling between modes 6 and 9 is very probable despite the calculations.

The three main contributions involved in the 1311-1305 cm^{-1} doublet come from phenol (δCH + δOH), HC=N (δCH) and amide (δNH + νCC) groups. The two modes are strongly coupled: for both, cartesian atom displacements are nearly identical but in the two modes, the amide group atoms vibrate in opposite directions.

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In the complex, modes 6' and 6", δNH + νCC and ϕ-O⁻ ring modes, respectively, appear as residues of doublet 6 after deprotonation of the OH group. Mode 6" could be mode 7 observed at 1306 cm^{-1} in the experimental spectra of complexes. Mode 6' (1345 cm^{-1}) is calculated to be at nearly the same wavenumber as mode 8 (see below) and the latter could hide the former. Figure 2 summarizes the relationships between ligand and complex normal modes suggested by the theoretical study.

AMIDE III NORMAL MODE

Mode 8 (Figure 1) near 1350 cm^{-1} was previously assigned to the amide III normal mode (νC-N as a main component). For obvious reasons, the amide III normal mode is calculated to be outside the spectral domain investigated (~ 1000 cm^{-1}). Indeed, it corresponds to the computed CN single bond, 1.46 Å, and not to the experimental one, 1.33 Å, which has high double bond character. On the naive basis of an isolated diatomic vibrator and assuming that small variations in C=O and C=N bond lengths change νC=O and νC=N wavenumbers similarly, we calculate a rough value near 1390 cm^{-1} for the amide III normal mode. We therefore maintain our previous assignments.

CONCLUSION

It is difficult to assign modes in the 2000-1200 cm^{-1} domain correctly. Thanks to theoretical calculation, and despite the minimal basis set, we have

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been able to throw some light on this question and also to suggest criteria for specifying complexation and deprotonation sites.

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