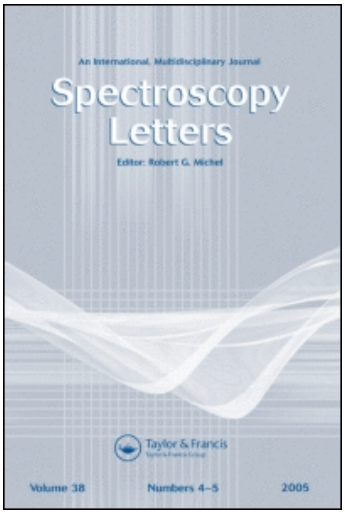

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Coordination Iron-Cysteine and Methylcysteine Complexes

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COORDINATION IRON-CYSTEINE AND METHYLCYSTEINE COMPLEXES

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ABSTRACT

Complexes of iron (II) with cysteine-HCl and methylcysteine-HCl are of interest as models for iron (II) coordination in proteine - Infrared and Raman spectra of these complexes and their free ligands are reported. These results show that cysteine is bounded to iron through sulfur, nitrogen and oxygen in $Fe(Cyst)(H_2O)_{1,5}$ (A) and through sulfur and nitrogen in $Na_2Fe(Cyst)_2\ H_2O$ (B), $Fe(metCyst)_2\ (H_2O)_{1,5}$ (C).

INTRODUCTION

The catalytic action of complexed iron cations in the oxidation of cysteine in aqueous solution has long been demonstrated.[1] Though numerous observations have been reported, no com-

plete explanation of the reaction mechanism is not yet available. Ferrous complexes of cysteine are postulated as essential intermediates [2-10] though very little is known about their structure in solution. On the other hand, studies on the solid state Fe-cysteine compounds give structural data but no crystallographic structure is available [11,12,13].

The present paper reports new infrared and Raman spectroscopic data on well defined phases prepared by a procedure described in the litterature [5], with certain modifications.

EXPERIMENTAL

- REAGENTS AND APPARATUS :

L-cysteine hydrochroride (FLUKA Puris grade) and methylcysteine hydrochloride (FLUKA Puris grade) have been used without further purification.

$(NH_4)_2Fe(SO_4)_2 . 6H_2O$ (PROLABO RP) was tested for the absence of iron (III) impurity by the addition of thiocyanate.

All stages of preparation were carried under an atmosphere of nitrogen purified through OXYSORB. L. Catalyst. (O_2<0,02 ppm).

Infrared spectra were recorded between 4000 and 200 cm^{-1} on PERKIN-ELMER 225 using nujol and fluorolub mulls with C_sI windows. Raman spectra were recorded on a CODERG PHO spectrometer with Argon ion laser source (5145 Å).

Solid state samples were cooled at -120°C in a sealed capillary and aqueous solution were recorded in glass cells at room temperature.

- PREPARATION OF IRON (II) COMPLEXES :

The preparative reactions and purification experiments have all been done under purified nitrogen or argon and monitored

by a potentiometric device till complete reaction with a microcombined electrode. Crystalline compounds had to be stored under argon.

1) Iron (II) - Cysteine

Dropwise and very slow addition of a degased 6,5 M sodium hydroxide solution into a 1:2 mole ratio aqueous solution containing iron salt and cysteine HCl yields a light yellow precipitate (A) when the pH stabilizes at 5,5. Further addition of alkali caused the dissolution of 1:1 solide complexe and the formation of 1:2 derivative isolated as their sodium salts at pH 8,5 (B). These compounds are then further precipitated by keeping the mixture at 50°C a few hours in controlled atmosphere. The solid phases are then isolated, thoroughly washed with water and alcool and dried over P_2O_5 under vacuum.

2) Iron (II) - Methylcysteine

This compound was prepared by essentially the same procedure which involved careful addition of hydroxide to aqueous anaerobic mixture of iron salt and methyl-cysteine. L.cysteine methylester gave directly 1:2 derivative. Attempts to prepare 1:1 and 1:3 complexes were unsuccessful.

3) Analysis

Microanalysis of these solid compounds was done by "Centre de microanalyse, CNRS (Lyon-France)".

The analytical figures are given in table 1.

RESULTS AND DISCUSSION

The position and attributions of the main vibration bands of different ligands and their ferrous complexes are given in Table 2.

TABLE 1

IRON (II) COMPLEXES	MOLECULAR FORMULA	COLOUR	FOUND (%)					CALCULATED (%)				
			C	H	N	S	Fe	C	H	N	S	Fe
$Fe(Cyst)(H_2O)_{1,5}$ (A)	$C_3H_8FeNO_{3,5}S$	light yellow	17,83	3,93	6,84	14,46	26,23	17,82	3,96	6,93	15,84	27,72
$Na_2[Fe(Cyst)_2]H_2O$ (B)	$C_6H_{12}FeN_2Na_2O_5S_2$	beige	17,75	3,84	7,03	14,84	17,65	20,11	3,35	7,82	17,88	15,64
$Fe(metcyst)_2(H_2O)_{1,5}$ (C)	$C_8H_{19}FeN_2O_{5,5}S_2$	red brown	28,39	5,15	8,08	17,98	17,05	27,35	5,41	7,97	18,23	15,95

TABLE 2

CYSTEINE,HCl	METHYL-CYSTEINE,HCl	A (FeL)	B (FeL_2)	C (FeL'_2)	ATTRIBUTION
3370 s					νH_2O
		3350			
		3322			
		3278 s	3310 w	3300 m	νNH_2
		3235	3225 w	3220 m	
		3150		3130 w	
∿ 3020 sh	∿ 3000 sh				νNH_3^+
				2950 w	
		2930 m	2900 w	2900 w	νCH_3, νCH_2
				2850 sh	
2950-2700 br	2900-2700 br				νNH_3^+, νCH_2, νCH_3 ...
2700-2200	2700-2200				νNH_3^+
2577 vs	2577 vs				νSH
	2010 m				
1740 s	1740 s			1730 s	$\nu C{=}O$
1642 w	1610 w	1640 sh	∿ 1640 sh		
1620 m	1598 w				$\delta_{as} NH_3^+$
1570 s	1578 s				
		1592 sh	1590 s	1572 m	δNH_2
		1563 s	∿ 1550 sh		$\nu_{as} COO^-$
		1518 sh			
1515 s	1512 s				$\delta_s NH_3^+$
	1440 s	1430 sh		1432 s	$\delta_{as} CH_3$, δCH_2
1427 s	1418 m	1424 m	1420 m		
		1400 m	1390 m		$\nu_s COO^-$
		1387 m			
	1388 m			1380 m	$\delta_s CH_3$
1395 s					$\nu CO + \delta OH(COOH)$
	1330 s				
	1245 s			1250 s	$\nu C{-}O$ (ester)
1220 s					$\nu CO + \delta OH(COOH)$
1205 s					

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; br = broad.

The alterations observed between the ligand spectra and their complexes at the level of the characteristic absorptions of the amino, thiol and carboxylic groups, allowed us to specify the coordination modes.

1) AMINO GROUP COORDINATION

The infrared spectra of cysteine-HCl and methylcysteine-HCl present a band at 3020-3000 cm^{-1} as well as broad absorption between 2950 and 2700 cm^{-1} and a serie of bands included between 2700 and 2200 cm^{-1}, characteristic of valence vibration $\nu(NH_3^+)$[14,15,16]. The different bands $\nu(NH_3^+)$ disappear in the IR spectra of these three complexes. On the other hand, several thin bands appear between 3350 and 3100 cm^{-1}, characteristic of the coordinated vibration mode $\nu(NH_2)$, according to some authors[17,18,19].

The bands due to deformation movements $\delta_{as}(NH_3^+)$(1620-1570cm^{-1}) and $\delta_s(NH_3^+)$(1515 cm^{-1}) are not seen in the spectra of the complexes.

A band observed at about 1570 cm^{-1} in the case of the compound (C) and about 1590 cm^{-1} in the complexes (A) and (B) of the cysteine must be attributed to the coordinated movement $\delta(NH_2)$.

2) THIOL FUNCTION COORDINATION

The valence vibration $\nu(SH)$ is characterized by a band situated between 2600 and 2500 cm^{-1} [14].

Kay and Mitchell[16] have attributed a band at 2500 cm^{-1} for the chlorhydrate of cysteine to this vibration. According to Garfinkel[20], it leads to a very intense band in Raman spectrometry at 2577 cm^{-1}.

We find again this intense band in the Raman spectrum of the ligands. In infrared, the presence of several thin bands in this region makes the attribution more difficult. These infrared and Raman bands do not appear in the spectra of the solid complexes, thus indicating a coordination mode through the thiol function.

3) CARBOXYLIC FUNCTION COORDINATION

In the infrared spectrum of methylcysteine at 1740 cm^{-1} [ν(C=O)] and at 1245 cm^{-1} [ν(C-O)], we observe characteristic absorptions of the ester group[14].

These absorptions are found unaltered in the complexe (C) spectrum. The acid carboxylic function of chlorhydrate of cysteine is characterized by the very intense ν(C=O) absorption at 1740 cm^{-1} and by the absorption about 1220-1205 cm^{-1} due to the ν(CO) and δ(OH) coupled vibrations.

The ν(C=O) vibration disappears in compound (A) spectrum, which implies a coordination mode in the complexe by the carboxylic group. The $\nu_{as}(COO^-)$ and $\nu_{s}(COO^-)$ bands are respectively situated at 1563 and 1400-1387 cm^{-1} [13,14]. These attributions are in agreement with previous work[13].

CONCLUSION

Cysteine has a chelation mode susceptible of appearing in a proteinic sequence. This property has already been shown in numerous studies. Within the whole of a study, this work specifies :

- on one hand, that the type of chelation do not always lead to a tridendate compound (complexe A);
- on the other hand, that the reactivity of functional groups of the cysteine molecule towards the ferrous ion in not always respected.

Considering the dissociation constants, in the first approach, this study shows that the groups corresponding to the weakest pka are not always the ones which are implicated in the bond with iron. These phenomena are explained by the influence of some factors in the formation of different bonds in these compounds and more particularly by the pH of the medium.

Thus at pH5, when the cysteine molecule is under zwitterion method, the negatively charged carboxylic group constitutes a privileged complexing site for iron. This assumption is confirmed by the study of the solid complexe (A). At pH 8-9, the amino and thiol groups are the only ones implicated in the coordination with iron (compounds B and C) owing to the powerful electron giving character of nitrogen and the weak electronegativity and the great polarizability of sulphur atoms.

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