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[CONTRIBUTION FROM THE INFRARED SPECTROSCOPY LABORATORY, FISK UNIVERSITY]

Infrared Spectroscopy of Compounds Having Biological Interest. II. A Comprehensive Study of Mercapturic Acids and Related Compounds[1]

BY NELSON FUSON, MARIE-LOUISE JOSIEN AND ROBERT L. POWELL

An analytical study has been made of the rock salt region infrared spectra of eight of the nine known mercapturic acids and of several corresponding S-substituted cysteines. The results are of practical value in the identification of these compounds, *e.g.*, among the metabolites from feeding experiments. The mercapturic acid spectra in the 3500–1500 cm.$^{-1}$ region contain all the key bands characteristic of α-amido acids; the S-substituted cysteine spectra are similarly characteristic of α-amino acids. The 1500–650 cm.$^{-1}$ region enables some comments to be made on the particular S-substituent involved. A prominent band has been found in the S-substituted cysteines at 860 cm.$^{-1}$; it may be interpreted as a carboxylate ion deformation vibration. Of particular interest is a strong band *ca.* 1225 cm.$^{-1}$ which is present in the N-acetylated cysteines. A study of the literature has shown that this band is also present in amino acids, amino acid hydrochlorides and dicarboxylic amino acids and may be considered as an additional key band for these compounds. It has tentatively been assigned to the COH group in the un-ionized carboxyl radical.

Introduction

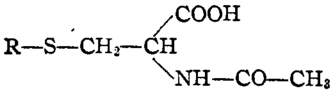
The synthesis of mercapturic acids in the animal body is one of the biochemical adaptations known as a detoxication mechanism.[2] In order to apply the techniques of infrared spectrometry to the detection of mercapturic acids in extracts from the urines of animals fed toxic compounds a preliminary study has been made of the spectra of model compounds. This paper will summarize the results.

Experimental

Ten amido acids, consisting of eight of the nine known mercapturic acids[3] and two acetylcysteines, and five amino acids, all being S-substituted non-acetylated cysteines, have been studied. As far as we know the infrared spectra of these compounds are reported here for the first time. Figure 1 is a line diagram showing all the spectra obtained.[4] The spectra reported were obtained on a single beam, automatic recording, rock salt prism infrared spectrometer recently described in the literature.[5] The compounds were all studied in the crystalline solid state in Nujol mulls. Usually about 5 mg. of compound were sufficient to obtain a satisfactory spectrum. The six micron region of the spectrum of all the mercapturic acids was also obtained in about 0.05 molar dioxane solution with a cell 0.15 mm. thick.

Analysis of the 3400–1500 Cm.$^{-1}$ Region for the Mercapturic Acids

The schematic structure of a mercapturic acid (S-substituted acetylcysteine) is



$$\mathrm{R{-}S{-}CH_2{-}\overset{\nearrow COOH}{\underset{\searrow NH{-}CO{-}CH_3}{CH}}}$$

The infrared spectroscopy of amido acids, the category into which fall mercapturic acids, has been developed during recent years as one of the necessary approaches to the study of the structure of the penicillin molecule.[6,7]

Key Bands.—Seven bands have been given[7] as characteristic of all amido acids. The band of medium intensity at about 3333 cm.$^{-1}$ is due to the stretching vibrations of the N–H bond con-

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[1] A short reference to the work described in this paper was made by H. D. West, N. Fuson, M. L. Josien, R. L. Powell and L. A. Black (*Federation Proc.*, **10**, 269 (1951)) at the 42nd Annual Meeting of the American Society of Biological Chemists at Cleveland, Ohio, April 29–May 3, 1951. A part of the research described in this paper formed the thesis submitted by R. L. Powell to the Graduate School Faculty of Fisk University in May, 1951, in partial fulfillment of the requirements of the M. A. degree.

[2] R. T. Williams, "Detoxication Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 2, 8.

[3] *Ibid.*, p. 67; also J. A. Stekol, *J. Biol. Chem.*, **138**, 225 (1941).

[4] For tables of wave lengths and intensities for all spectra recorded in this work order Document 3335 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

[5] M. L. Josien, N. Fuson and A. S. Cary, THIS JOURNAL, **73**, 4445 (1951).

[6] H. W. Thompson, R. R. Brattain, H. M. Randall and R. S. Rasmussen, "Infrared Spectroscopic Studies of Penicillin," being Chapter XIII of the Monograph "The Chemistry of Penicillin," Princeton University Press, Princeton, New Jersey, 1949.

[7] H. M. Randall, R. G. Fowler, N. Fuson and R. Dangl, "The Infrared Determination of Organic Groups," D. Van Nostrand and Co., Inc., New York, N. Y., 1949, Chapter II. (This book will be referred to hereafter as RFFD.)

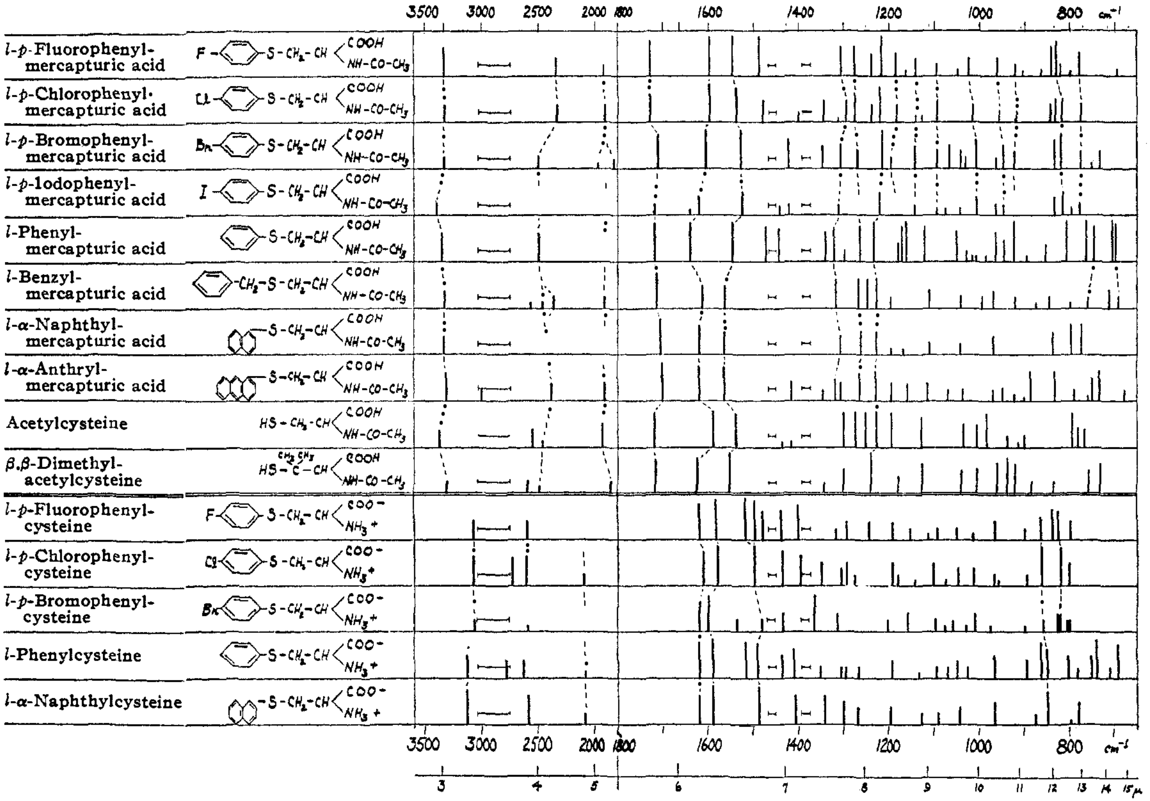

Fig. 1.—Line diagram of spectra between 3500–650 cm.$^{-1}$. Relative intensities are indicated by the height of the vertical line. Dotted lines tie together related bands which are discussed in the text. The horizontal lines indicate Nujol interference.

tained in the amide structure. The 2900 cm.$^{-1}$ band is produced by C–H stretching vibrations. The explanation for the bands at 2500 and 2000 cm.$^{-1}$ is still to be given but they may result from overtone or combination bands of vibrations of the amido acid skeleton. They are not always present and thus may be looked for only as an additional confirmation when the other key bands are found. The strong band at 1725 cm.$^{-1}$ is assumed to result from the C=O stretching vibration of the carboxyl group. The two strong bands at 1640 and 1540 cm.$^{-1}$ are assigned to the monosubstituted amide group.

The positions of the latter three bands are much influenced by the state of the compound when its spectrum is being made. Band shifts in going from solid to solution have shown much variety, particularly in the case of the two amide bands.[6] Many solvents, including chloroform, methanol, carbon tetrachloride, tetrachloroethane, methyl cellosolve and dioxane have been used in the study of this shifting.[6,8] While the higher frequency member of the six micron amide band pair, sometimes referred to as Amide I,[7] is generally attributed to the carbonyl linkage in the peptidic group, the explanation for the lower frequency member of this pair, Amide II, is still a controversial matter.[7,9,10,11]

New Results.—Table I lists six[12] characteristic band frequencies in the 4000–1500 cm.$^{-1}$ region for the eight mercapturic acids and two acetylcysteines studied.[13] Ranges for each of these bands, based on our examination of the published infrared spectra of fifteen α-amido acids in the solid state,[14] are also given in Table I, as are ranges for dioxane solution spectra in the six micron region.[6]

Discussion.—The band frequencies of these ten new α-amido acid spectra generally fall within the ranges given and thus lend even more significance to these key bands.

The 1900 cm.$^{-1}$ band is absent from the spectra of three compounds. The *ca.* 2500 cm.$^{-1}$ band is present in all but two of the spectra though in several cases it falls below the range given. However, both these bands are present in the two substituted cysteines which contain no benzene ring, so presumably the origin of these bands is not associated with vibrations of the aromatic part of the mercapturic acid molecule.

The location of the acid C=O band at or below 1620 cm.$^{-1}$ is characteristic of α-amido acids, RFFD having shown[7] that the corresponding bands for other amido acids are all found to lie on the high frequency side of 1620 cm.$^{-1}$. It should be mentioned that occasionally an α-amido acid carbonyl

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[8] J. H. Hunter, J. W. Hinman and H. E. Carter, "Methyl Benzylpseudopenicillinate," Chapter XXIV, page 914, of "The Chemistry of Penicillin," ref. 6.

[9] B. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

[10] G. B. B. M. Sutherland, *Discussions Faraday Soc.*, **9**, 274 (1950).

[11] H. Lenormand, "Spectre Infra-rouge et Structure de la Liaison Peptidique," These, Paris, 1949, pp. 52-55, 80-88.

[12] The CH stretching band is omitted from the table since, in our study, it was masked by Nujol bands.

[13] We have found the spectrum of only one other acetylcysteine reported in the literature, namely, N-acetoacetyl-β,β-dimethylcysteine (RFFD, page 67). Its bands in this region, located at 3434, 2457, 1940, 1724, 1613 and 1553 cm.$^{-1}$, also fit the key band ranges given in Table I.

[14] RFFD, Chapter VII.

TABLE I

FREQUENCIES (CM.$^{-1}$) OF KEY BANDS FOR MERCAPTURIC ACIDS AND ACETYLATED CYSTEINES

Assignment	N–H	.....	.....	Acid C═O		Amide I		Amide II		Source[g]
Sample state	Solid	Solid	Solid	Solid	Soln.	Solid	Soln.	Solid	Soln.	
α-Amido acid[a] key band ranges	3390–3260	2640–2430[b]	1945–1835[c]	1724–1695[d]	..	1621–1600[e]	1700–1680[f]	1565–1508	1530–1510[f]	
l-*p*-Fluorophenylmercapturic acid	3333	2353	1931	1730	..	1597	1686	1546	1531	1
l-*p*-Chlorophenylmercapturic acid	3333	2360	1912	1730	1757	1597	1686	1538	1527	1
l-*p*-Bromophenylmercapturic acid	3333	2500	1835	1709	1757	1603	1689	1527	1529	1
l-*p*-Iodophenylmercapturic acid	3390	..	..	1718	1764	1621	1686	1524	1531	1
l-Phenylmercapturic acid	3344	2530	..	1718	1754	1639	1686	1546	1531	1, 2
l-Benzylmercapturic acid	3322	2353	1916	1712	1754	1613	1686	1563	1531	3
l-α-Naphthylmercapturic acid	3333	..	..	1706	1748	1618	1686	1563	1531	1
l-α-Anthrylmercapturic acid	3311	2370	1919	1701	1764	1618	1689	1563	1527	4
dl-Acetylcysteine	3367	2451	1931	1718	1751	1587	1689	1536	1527	1, 5
β.β-Dimethylacetylcysteine	3300	2481	1859	1715	1745	1623	1692	1553	1527	5

[a] These frequency ranges for the infrared bands characteristic of the α-amido acids are based on the spectra of solid crystalline samples of the following 15 α-amido acids published by RFFD, p. 127–146: α-acetamido-β,β-dimethylacrylic acid, α-benzamido-β,β-dimethylacrylic acid, phenacetamidoallylmalonic acid, *dl*-N-phenacetylalanine, *dl*-N-phenacetyl-β-phenylalanine, α-phenacetamido-α-methyl-*n*-butyric acid, α-acetamidoisobutyric acid, α-phenacetamidoisobutyric acid, α-phenacetamido-*n*-caproic acid, hippuric acid, *d*-N-phenacetylisoleucine, phenaceturic acid, α-phenacetamido-β,β-dimethoxypropionic acid, α-phenacetamido-*n*-valeric acid and *dl*-N-phenacetylvaline. [b] Sometimes multiple and/or broad; missing entirely in one case. [c] Sometimes multiple; missing entirely in six cases. [d] In only one case did this band fall outside the range given (hippuric acid, 1740 cm.$^{-1}$). [e] In only three cases did this band fall outside the range listed (α-benzamido-β,β-dimethylacrylic acid and *dl*-N-phenacetylalanine 1645 cm.$^{-1}$; and *dl*-phenacetyl-β-phenylalanine, 1665 cm.$^{-1}$). [f] Data from dioxane solution work on monosubstituted amides (not necessarily α-amido acids) by Thompson and Richards at Oxford; reported in "The Chemistry of Penicillin," ref. 6, p. 388. The number of compounds studied is not given. [g] (1) Harold D. West, Biochemistry Department, Meharry Medical College, Nashville, Tennessee; (2) S. H. Zbarsky, University of British Columbia, Vancouver, Canada; (3) J. A. Stekol, Lankenau Hospital Research Institute and Institute for Cancer Research, Philadelphia, Pennsylvania. (4) E. Boyland, Chester Beatty Institute, Royal Cancer Hospital, London, England. (5) Werner E. Bachmann, University of Michigan, Ann Arbor, Michigan.

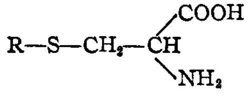
group band falls above 1620 cm.$^{-1}$, *e.g.*, phenylmercapturic acid and the three compounds mentioned in footnote (*e*) of Table I.

The mercapturic acids not being soluble in nonpolar solvents such as carbon disulfide and carbon tetrachloride, solution spectra in the six micron region were obtained in dioxane, though it is known[15] that dioxane causes anomalies in solution spectra of some types of compounds. The shifts observed for the acid carbonyl band and for the two amide bands are in general agreement with results in the literature.[6] In solution the acid carbonyl band shifts from 30 to 60 cm.$^{-1}$ to higher wave numbers; solvent absorption in the region of this band made its exact location difficult. The amide II band in solution seemed to be stabilized at about 1530 cm.$^{-1}$, the shift in going from solid to solution being generally to lower wave numbers. Solvent background interference in this region again caused difficulties, in some cases the uncertainty being as large as ±6 cm.$^{-1}$. The amide I band is found to shift to higher wave numbers when in solution. This shift is an especially large one, in some cases being as much as 100 cm.$^{-1}$. The solid spectrum amide I band position varied over a range of 50 cm.$^{-1}$ for the ten compounds studied, whereas the solution spectrum amide I band is remarkably constant in position, varying only within a range of 6 cm.$^{-1}$. This band fell in a transparent region of the solvent background and thus could be located in each case with an accuracy of ±3 cm.$^{-1}$. It may be concluded from this solution study that the rather wide range of acid carbonyl and amide band positions for different compounds in the solid state is a result primarily of intermolecular forces arising from the crystal lattice.

One band of significance which is not listed in Table I falls in this spectral region in two compounds studied. This weak band *ca.* 2570 cm.$^{-1}$, appearing only in acetylcysteine and β,β-dimethylacetylcysteine, is properly located to be assigned to the stretching vibration of S–H, a group present only in these two compounds.

Analysis of 3400–1500 Cm.$^{-1}$ Region for the S-Substituted Cysteines

An S-substituted, non-acetylated cysteine is an amino acid whose schematic structure is



$$R{-}S{-}CH_2{-}CH(COOH)(NH_2)$$

The infrared spectra of amino acids have also been studied[7,16,17,18] though not as widely as the amido acids. We have considered seven key bands for the amino acids in this region. Six of them have been given by RFFD[7] as follows: the strong C–H stretching vibration band at about 2900 cm.$^{-1}$; two weak unassigned bands or groups of bands *ca.* 2600 and 2100 cm.$^{-1}$ which are present in most but not all amino acids; the strongest band in the spectrum, at 1580 cm.$^{-1}$, associated with the carboxylate ion; the remaining two bands in the six micron region, the amino acid I band near 1620 cm.$^{-1}$ and the amino acid II band near 1520 cm.$^{-1}$. RFFD[14] assigns the former to δNH_3^+, and leaves the latter unassigned. Lenormand,[18] on the other hand, exactly reverses these two statements.

The seventh band, which we take to be an important key band even though not referred to in RFFD, appears at about 3070 cm.$^{-1}$. It has been assigned by Freymann and Thompson[19] to the

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(15) W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

(16) N. Wright, *J. Biol. Chem.*, **127**, 137 (1939).

(17) C. Duval and J. Lecomte, *Bull. soc. chim. France*, **10**, 187 (1943).

(18) H. Lenormand, *J. chim. phys.*, **43**, 333 (1946).

(19) M. Freymann and R. Freymann, *Proc. Indian Acad. Sci.*, **8A**, 301 (1938); H. W. Thompson, D. L. Nicholson and L. N. Short, *Discussions Faraday Soc.*, **9**, 222 (1950).

TABLE II

FREQUENCIES (CM.$^{-1}$) OF KEY BANDS FOR S-SUBSTITUTED NON-ACETYLATED CYSTEINES[a]

Assignment ⟶	N-H	....	....	Amino acid I	Carboxylate ion	Amino acid II
α-Amino acid[b] key band ranges	3130–3030	2760–2530[c]	2140–2080[d]	1640–1610[e]	1600–1560[f]	1550–1490
l-*p*-Fluorophenylcysteine	3077	2597	..	1618	1582	1517, 1495, 1477
l-*p*-Chlorophenylcysteine	3077	2732, 2604	2096	1610	1577	1498 (broad)
l-*p*-Bromophenylcysteine	3058	2584	..	1618	1597	1534, 1477
l-Phenylcysteine	3125	2778, 2632	2083	1618	1587	1515, 1488
l-α-Naphthylcysteine	3125	2591	2083	1618	1587	1486

[a] All the compounds are from Harold D. West, Biochemistry Department, Meharry Medical College, Nashville, Tennessee. [b] These frequency ranges for infrared bands characteristic of α-amino acids are based on a study of the spectra of solid crystalline samples of the following thirteen α-amino acids published by RFFD, p. 119–123: *dl*-alanine, *dl*-β-phenylalanine, *dl*-α-amino-α-methylbutyric acid, α-aminoisobutyric acid, *dl*-α-amino-*n*-caproic acid, cystine, N-phenylglycine, *d*-isoleucine, *l*-proline, sarcosine, *l*-tyrosine, *dl*-α-amino-*n*-valeric acid, *dl*-valine. Frequencies published by Lenormand (see reference (18)) for amino acids in the 5–8 micron region are in general agreement with these ranges. [c] A pair of bands are present in this region in ten out of the thirteen cases. Very weak bands occasionally fall between 2500 and 2200 cm.$^{-1}$. [d] A single band is present in this region in eleven out of the thirteen cases. [e] In only one case, N-phenylglycine, did this band fall outside the range given. In this case it was masked by the very strong carboxylate ion band at 1567 cm.$^{-1}$. [f] In only one case (sarcosine, 1616 cm.$^{-1}$) did this band fall outside the range given.

N–H stretching vibration, its position being much shifted as compared to that of the NH band in amido acids. In order to explain its low frequency these authors have discussed the possible influence of the electrical charge of the NH_3^+ group.

Table II contains the six[12] characteristic frequencies of each of the S-substituted non-acetylated cysteines studied; ranges for each of these bands, based on our examination of the published spectra of thirteen α-amino acids in the solid state,[14] are also included.

A study of this Table suggests the following comments. The band frequencies found fall within the ranges given by previous authors. The band *ca.* 2100 cm.$^{-1}$, which Thompson[19] suggests to be associated with the NH_3^+ group, has been found in three cases out of five. It is interesting to note that this region is clear in the amido acids, a band appearing instead *ca.* 1900 cm.$^{-1}$ in the latter. The position of the amino acid I band in the S-substituted cysteines is very constant. The amino acid II band region is a very complicated one with several strong bands. Lack of sufficient resolution possibly accounts for the varying number of bands in this region of the spectrum of the five different substituted cysteines.

In closing this section on amino acids, it should be stated that, confirming a conclusion of Lenormand,[18] we find also that the presence of a sulfur atom in an amino acid does not appreciably affect its spectrum in the 3 to 7 μ region.

Analysis of the 1500–650 Cm.$^{-1}$ Region

Before discussing the major points of interest in the "finger-print" region of the spectra of the mercapturic acids and cysteines, a few remarks on unassigned bands should be made. An unassigned band occurs at 1190 cm.$^{-1}$ in all the compounds studied, with the exception of phenylmercapturic acid, whose spectrum was quite weak. It may be that one of the two bands occurring at 1440 and 1406 cm.$^{-1}$ for almost all of the non-acetylated cysteines corresponds to Edsall's[20] assignment of a 1400 cm.$^{-1}$ Raman band to the carboxylate ion group.

It was not found possible to assign any band to the weak C–S–C stretching vibration[21] of the mercapturic acids.

Substituted Benzene Rings.—Most of the compounds examined contained benzene rings in various degrees of substitution. These structures prove to be responsible for some of the more intense low wave number bands. Table III lists our assignments, using as a guide the most recently published ranges[22,23] for the bands associated with substituted benzene. Colthup[22] and Lecomte[24] give additional assignments between 1250–950 cm.$^{-1}$; in this region the spectrum lines in the compounds we analyzed are so numerous that it was not meaningful for identification purposes to try to make any of these assignments.

TABLE III

FREQUENCIES (CM.$^{-1}$) OF BANDS ASSIGNED TO SUBSTITUTED BENZENE RING STRUCTURES[a]

Monosubstituted	(770–725)	(720–675)
Phenylmercapturic acid	747	698
Benzylmercapturic acid	762	694
Phenylcysteine	750	690
para-Disubstituted	(860–800)	
l-*p*-Fluorophenylmercapturic acid	824	
l-*p*-Chlorophenylmercapturic acid	817	
l-*p*-Bromophenylmercapturic acid	820	
l-*p*-Iodophenylmercapturic acid	816	
l-*p*-Fluorophenylcysteine	824	
l-*p*-Chlorophenylcysteine	818	
l-*p*-Bromophenylcysteine	817	
ortho-Disubstituted	(775–725)	
l-α-Anthrylmercapturic acid	750	
1,2,3-Trisubstituted	(800–760)	(750–690)
l-α-Anthrylmercapturic acid	791	733
1,2,3,4-Tetrasubstituted	(890)	
l-α-Anthrylmercapturic acid	887	
α-Substituted naphthylenes (special case)	(810–775)	(780–750)
l-α-Naphthylmercapturic acid	800	775
l-α-Naphthylcysteine	794	778
l-α-Naphthyicysteine HCL	786	758

[a] Band ranges (shown in parentheses) for each structure group are taken from Colthup[22] and Cole and Thompson[23] in all cases but that of the tetrasubstituted benzene ring. In this case the range listed is that reported by H. W. Thompson, *J. Chem. Soc.*, 219 (1950).

A comparison between the spectra of the mercapturic acids and of the corresponding aromatic

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(20) J. D. Edsall, *J. Chem. Phys.*, **5**, 508 (1937).

(21) N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

(22) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 396 (1950).

(23) A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).

(24) Lecomte, *J. phys. radium*, VII, **8**, 489 (1937); **9**, 13 (1938).

group on the sulfur atom[25] shows, as is to be expected, a decreasing correlation in the 1400–900 cm.$^{-1}$ region with decreasing size of the aromatic substituent, this being because the introduction of an additional substitution on a single benzene ring modifies the vibrational modes of the substructure more than will one additional substitution on a polycyclic subgroup.

Several bands occur in approximately the same place in each of the halogenated phenylmercapturic acids as may be seen in Fig. 1. No assignments have yet been made for these persistent bands.

No bands were assigned to the carbon–halogen stretching vibration in the spectra of the halogenated phenylmercapturic acids. Nevertheless, it is interesting to speculate as to whether the 839 cm.$^{-1}$ band in *p*-fluorophenylmercapturic acid and the companion band at 838 cm.$^{-1}$ in *p*-fluorophenylcysteine might be due to the C–F stretching frequency. Likewise, it is possible that the 1295 cm.$^{-1}$ band in *p*-chlorophenylmercapturic acid and *p*-chlorophenylcysteine might be the first overtone of the C–Cl stretching frequency. These speculations are based on assignments made by Lecomte[24] for monohalogenated benzenes.

The 1225 Cm.$^{-1}$ Band in N-Acetylated Cysteines.—A striking difference between the spectra of the N-acetylated cysteines (which include the eight mercuric acids) and the spectra of the corresponding S-substituted non-acetylated cysteines is the presence of a strong band *ca.* 1225 cm.$^{-1}$ in the former only (see Fig. 1). This band is very constant in position. For the four halogenated mercapturic acids it is located at 1217 ± 3 cm.$^{-1}$; for the other mercapturic acids, at 1230 ± 3 cm.$^{-1}$.

A preliminary study[26] indicates that the 1225 cm.$^{-1}$ band, which is also present in amido acids, amino acid hydrochlorides and in dicarboxylic amino acids, may be assigned to some vibration of the C–O–H group. Various arguments may be put forward in support of an assignment either to the C–O stretching or bending vibration or to the O–H bending vibration, but without deuterium substitution experiments it is impossible to localize the assignment any more precisely.

The 860 Cm.$^{-1}$ Band in S-Substituted Non-acetylated Cysteines.—A rather prominent band at 860 cm.$^{-1}$ in the S-substituted cysteines is absent in the mercapturic acids. Among the possible explanations for this band would be that of a deformation vibration associated with the carboxylate ion which is reported to be found in the 930–870 cm.$^{-1}$ region.[17] A study similar to that made on the 1225 cm.$^{-1}$ band is not possible, the RFFD spectra not having been published below 1100 cm.$^{-1}$. Wright[16] gives spectra of a number of amino acids most of which have a band of medium intensity in this region, but no amino acid hydrochloride spectra are at present available for comparison purposes.

Acknowledgments.—We are particularly greatful to Dr. Harold D. West who made this study possible not only through suggesting the problem but also by his generosity in preparing all the unavailable compounds we needed.[27] We would like to express our thanks to Dr. E. Boyland, Dr. J. A. Stekol, and Dr. S. H. Zbarsky for supplying us with samples. We would also like to acknowledge the gift of several compounds from the late Dr. Werner E. Bachman. This investigation has been supported by a Frederick Gardner Cottrell Grant from the Research Corporation.

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[25] Unpublished data recently obtained in this Laboratory.

[26] M. L. Josien and N. Fuson, *Compt. rend.*, **232**, 2016 (1951).

[27] Details of preparation are to be published elsewhere.

NASHVILLE, TENN. RECEIVED MAY 31, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Visible and Ultraviolet Absorption Spectrum of the Tetrachloroferrate(III) Ion in Various Media[1]

BY HAROLD L. FRIEDMAN

A comparison is made of the ultraviolet and visible absorption spectra of the following systems: solutions of ferric chloride in concentrated aqueous hydrochloric acid, the ether extracts of these solutions, anhydrous ether solutions of $KFeCl_4$ and solid $KFeCl_4$. The similarity of the spectra provides evidence that the principal iron-containing species in each of these systems is the $FeCl_4^-$ ion with coördination number four for iron. This conclusion is supported by other spectral observations and is shown to be consistent with the known properties of these systems including the high solubility of $KFeCl_4$ in ether.

This paper presents the results of the beginning of an investigation of the properties of solutions of electrolytes in solvents of low dielectric constant. The electrolytes discussed in this paper all have the type formula $M'M'''Cl_4$, where M' is a monovalent element or group and M''' a trivalent metal.

It has been shown that trivalent iron is extracted from aqueous hydrochloric acid by various ethers[2,3,4,5] as the compound $HFeCl_4 \cdot nH_2O$, with n equal to about 4.5. Similarly, trivalent gallium is extracted from aqueous hydrochloric acid by diisopropyl ether as the compound[6] $HGaCl_4$ with undetermined hydration. The following ob-

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[1] Presented in part before the 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950.

[2] S. Kato and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **36**, 82 (1939).

[3] J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

[4] N. H. Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948).

[5] R. J. Myers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3767 (1950).

[6] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **71**, 4035 (1949).