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Raman and Infrared Studies of Complexes of Mercury(II) with Cysteine, Cysteine Methyl Ester, and Methionine

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Raman and infrared spectral data are reported for L-cysteine (free base), L-cysteine hydrochloride monohydrate, bis(cysteinato)mercury(II) hydrochloride hemihydrate [$(C_3H_6O_2NS)_2Hg\cdot HCl\cdot{}^1/_2H_2O$], L-cysteine methyl ester hydrochloride, bis(methyl-L-cysteinato)mercury(II) hydrochloride hydronitrate monohydrate [$(C_4H_8O_2NS)_2Hg\cdot HCl\cdot HNO_3\cdot H_2O$], bis(methyl-L-cysteinato)mercury(II) dihydrochloride monohydrate [$(C_4H_8O_2NS)_2Hg\cdot 2HCl\cdot H_2O$], D,L-methionine, and bis(methioninato)mercury(II). The results are discussed in terms of metal–ligand bonding for which ν(Hg–S) (310–316 cm^{-1}) and ν(C–S) (670–680 cm^{-1}) were found for the cysteine complexes whereas ν(Hg–N) at 481 cm^{-1} was observed for the methionine mercury complex. CH_3 symmetrical stretching is assigned to the range 2912–2917 cm^{-1} because the frequency does not differ significantly in methionine, methionine hydronitrate, and lithium methioninate. The structural features deduced for the solid state are compared to those determined for the same complexes in acidic aqueous solution by ^1H and ^{13}C NMR spectroscopy. The bis(methioninato)mercury(II) complex is particularly interesting in that the solid state appears to favor mercury bonding by amino N and carboxyl O whereas in solution, mercurial bonding is localized to the sulfur atom of the methioninate having an extended-chain configuration in which the amino and carboxyl moieties are remote from the mercury atom. For the mercury complexes of cysteine and cysteine methyl ester, mercurial bonding is exclusive to sulfur in both the solid and solvated states.

Introduction

The sulfur-containing α-amino acids are important in the chemistry of biological systems because of their ability to complex with a wide variety of metal ions. Unfortunately, little is known in particular about the nature of mercury complexes of amino acids such as cysteine and methionine, let alone the mechanisms by which mercurial complexes exert toxic effects, undergo biotransformation and are transported.[2] Until recently, very few mercury complexes of sulfur-containing amino acids had been isolated for characterization. Generally, solution studies have been emphasized to gain insight into the structure of complexes first by means of indirect studies such as polarography[3] and potentiometry[4] and later with proton magnetic resonance (PMR) spectroscopy[5–8] to obtain structural

Table I. Selected Vibrational Frequencies for Sulfur-Containing Amino Acids and Their Mercurial Complexes[a,b]

Raman	Ir	Assignmt
	L-Cysteine	
678 ms		C–S ν
1402 m	1400 s	CO_2^- ν_s
1512 w	1513 s	NH_3^+ δ_s
	1590 s	CO_2^- ν_a
1612 w	1610 s	NH_3^+ δ_d
2544 vs	2545 m	S–H ν
2929 s, 2954 s, 2984 s		CH ν
	L-cys·HCl·H_2O	
682 s	690 w	C–S ν
1210 m, 1225 m	1213 vs, 1227 vs	C–O ν
	1520 s, 1572 m, 1623 w, 1644 w	NH_3^+ δ
1735 m	1740 s	C=O ν
2569 vs	2565 wm	S–H ν
2949 vs, 2996 s		CH ν
	$(C_3H_6O_2NS)_2Hg·HCl·{}^1/_2H_2O$	
316 vs		Hg–S ν
670 s	675 vw	C–S ν
	1262 m	C–O ν
	1430 m	CO_2^- ν_s
	1487 s	NH_3^+ δ_s
	1606 m	NH_3^+ δ_d + CO_2^- ν_a
	1678 s	C=O ν
2930 s, 2960 s, 2982 s		CH ν
	L-Cysteine Methyl Ester Hydrochloride	
677 s	681 w	C–S ν
1251 w	1248 s	C–O ν
1520 m	1515 s	NH_3^+ δ_s
	1578 m, 1598 w	NH_3^+ δ_d
1744 m	1742 s	C=O ν
2562 s	2560 w	S–H ν
2951 vs, 2991 vs		CH ν
	$(C_4H_8O_2NS)_2Hg·HCl·HNO_3·H_2O$	
312 vs		Hg–S ν
680 s	685 w	C–S ν
	830 m	NO_3^- π
1048 s		NO_3^- ν_s
	1250 ms	C–O ν
	1512 s	NH_3^+ δ_s
	1600 m	NH_3^+ δ_d
1748 m	1742 s	C=O ν
2955 s		CH ν
	$(C_4H_8O_2NS)_2Hg·2HCl·H_2O$	
310 vs		Hg–S ν
680 s	680 w	C–S ν
	1248 s	C–O ν
	1495 s	NH_3^+ δ_s
	1582 m	NH_3^+ δ_d
1749 m	1742 s	C=O ν
2954 s		CH ν
	D,L-Methionine	
687 m, 719 ms	688 m	C–S ν
2917 vs		CH_3 ν_s
2940 m, 2985 s		CH ν
	D,L-Methionine Hydronitrate	
698 ms, 733 ms		C–S ν
2916 vs		CH_3 ν_s
2946 ms, 2966 ms		CH ν
	Lithium Methioninate, $(C_5H_{10}O_2NS)Li$	
692 m, 714 s, 746 m		C–S ν
1423 ms		CO_2^- ν_s
1580 m		CO_2^- ν_a
2882 s		CH ν
2912 vs		CH_3 ν_s
2930 s, sh, 2964 ms, 2979 s		CH ν
	$(C_5H_{10}O_2NS)_2Hg$	
481 s		Hg–N ν
656 m, 696 m, 722 w		C–S ν
1402 m	1400 s	CO_2^- ν_s
1594 w	1595 s	CO_2^- ν_a
2913 vs	2910 m	CH_3 ν_s
2942 s, sh, 2984 s		CH ν

[a] All values in cm^{-1}. [b] A full tabulation of Raman and infrared spectral data is available on microfilm from the depository of supplementary information (see paragraph at end of paper regarding supplementary material). Abbreviations: ν, stretching; ν_s, symmetric stretching; ν_a, asymmetric stretching; δ, deformation; δ_s, symmetric deformation; δ_d, degenerate deformation; π, out-of-plane deformation; s, strong; m, medium; w, weak; v, very; sh, shoulder.

information by variation of reactant concentrations and solution pH. Some infrared spectral features have been reported for five different mercurial complexes of cysteine;[9] however, no details of preparation and isolation were reported for the complexes. Some infrared features have been reported for a bis(methioninato)mercury(II) complex[10] prepared under nonaqueous conditions. A bis(methylcysteinato)mercury(II) complex has been prepared under strongly alkaline conditions.[11]

In this paper, infrared and Raman spectral data are presented for various mercury complexes of cysteine, cysteine methyl ester, methionine, and related compounds whose preparation, isolation, and characterization by complete elemental microanalysis and ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy has already been reported.[12-14] The mildest possible in vitro acidic conditions, in relation to the in vivo state, were used in the preparation of the mercury complexes for biological relevance. The purpose in undertaking this solid-state study of the mercurial complexes is to determine what structural changes, if any, occur upon dissolution of the complexes and to obtain infrared and Raman frequency data useful in the identification of such complexes and for distinguishing the nature of metal–ligand bonding. These concerns are especially appropriate in view of an earlier report of direct sulfur–mercury bonding in solutions of mercury complexes of methionine.[15]

Experimental Section

The amino acids and derivatives used in this work were the best grade obtainable from the Sigma Chemical Co.

Bis(cysteinato)mercury(II) hydrochloride hemihydrate may be prepared in any of four ways to obtain identical product[14] some of which was used in this study.

Bis(methyl-L-cysteinato)mercury(II) hydrochloride hydronitrate monohydrate and bis(methyl-L-cysteinato)mercury(II) dihydrochloride monohydrate were samples prepared as reported.[12]

Bis(methioninato)mercury(II) was taken from identical material prepared by either of two described methods.[13] The D,L-methionine hydronitrate and lithium D,L-methioninate were also taken from previously prepared material.[13]

The Raman spectra were recorded with a Jarrell-Ash Raman spectrometer (Model 25-300) using an argon ion laser operated at 488.0 nm and 180–200 mW (Coherent Radiation Model 54) as the excitation source. Preliminary experiments using a 514.5-nm laser line indicated that the solid mercury complex bis(methyl-L-cysteinato)mercury(II) hydrochloride hydronitrate monohydrate was decomposed in the laser beam at ~100 mW. All the results reported in this work were obtained using the 488.0-nm line. Plasma lines were removed by a laser line narrow-band filter with a bandwidth at half-height of 1 nm. Samples were sealed in capillary tubes (1.5–2-mm o.d.) which were placed at an angle of approximately 45° with the laser beam. For most of the samples, duplicate spectra were recorded. These spectra are identical with each other indicating the samples are stable to the excitation line.

Infrared spectra were obtained using a Perkin-Elmer Model 621 spectrometer using Fluorolube mulls and NaCl windows from 4000 to 1340 cm^{-1} and Nujol mulls with CsI windows from 1340 to 200 cm^{-1}.

Results and Discussion

Cysteine. Raman and infrared results for cysteine ($HSCH_2CH(NH_2)CO_2H$, cys), cys·HCl·H_2O, and the bis(cysteinato)mercury(II) complex $(C_3H_6O_2NS)_2Hg·HCl·{}^1/_2H_2O$ are summarized in Table I. The infrared frequencies for cysteine are in good agreement with those reported in the literature.[9] Upon deuterium substitution, a number of bands shift down by a factor of about 1.4. Among these bands, we

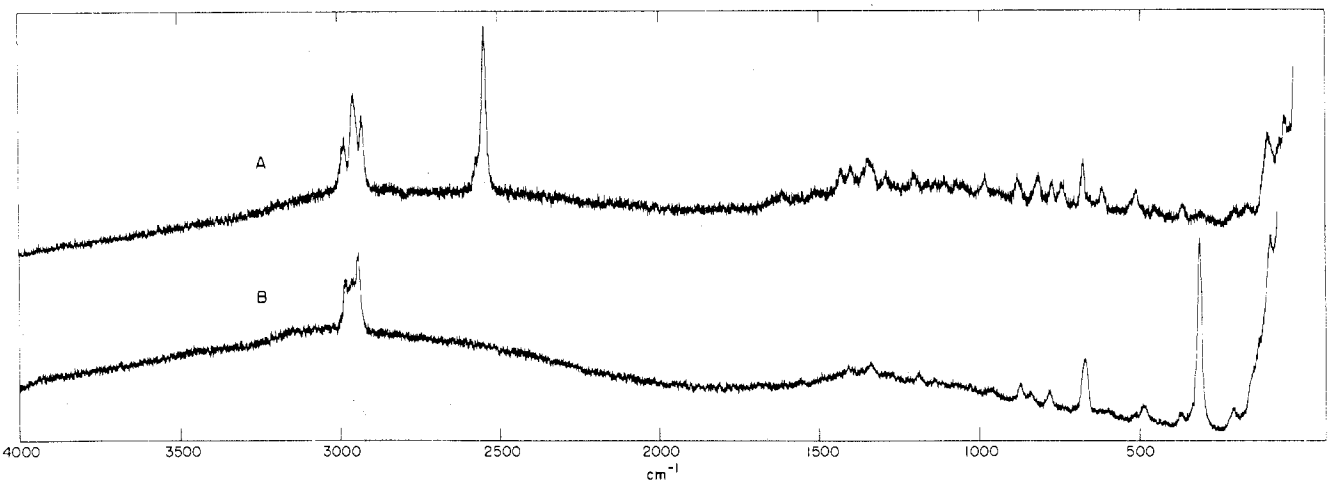


Figure 1. Raman spectra for (A) cysteine and (B) bis(cysteinato)mercury(II) hydrochloride hemihydrate, $(C_3H_6O_2NS)_2Hg\cdot HCl\cdot{}^1/_2H_2O$.

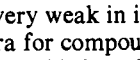
are particularly interested in the bands at 2545 cm^{-1} (shifted to 1848 cm^{-1} upon deuteration), 1610 cm^{-1} (to 1180 cm^{-1}), and 1513 cm^{-1} (to 1145 cm^{-1}). These bands are assigned to SH stretching, NH_3^+ degenerate bending, and NH_3^+ symmetric bending modes, respectively, by comparison with the literature.[9,16] The CO_2^- group is characterized by the bands at 1590 and 1400 cm^{-1} ascribed to $-CO_2^-$ asymmetric and symmetric bending modes. This evidence for the zwitterion form of cysteine (free base) in the solid state is consistent with X-ray crystallographic work.[17]

The Raman spectrum of cysteine contains a very prominent band at 2544 cm^{-1} due to HS stretching and a strong band at 678 cm^{-1} due to CS stretching. The band due to CS stretching is very weak in infrared spectra but very strong in Raman spectra for compounds containing the C–S bond.[18,19]

The Raman and infrared spectra of $cys\cdot HCl\cdot H_2O$ show the presence of the bands at 1735 cm^{-1} (R) and 1740 cm^{-1} (ir) characteristic of C=O stretching which indicate that the carboxylic acid group is not dissociated. Four infrared bands are present at 1520, 1572, 1623, and 1644 cm^{-1}, all of which shift upon deuteration. These bands are attributed to the NH_3^+ group hydrogen bonding with the environment which removes the degeneracy of the bending mode.

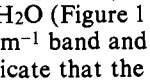
Very significant changes occur in the Raman spectrum of $(C_3H_6O_2NS)_2Hg\cdot HCl\cdot{}^1/_2H_2O$ compared to those of cysteine and $cys\cdot HCl\cdot H_2O$ (Figure 1 and Table I). The disappearance of the 2550-cm^{-1} band and the presence of a strong band at 316 cm^{-1} indicate that the H–S bond in cysteine is now replaced by the Hg–S bond in the complex. Of the three infrared bands attributable to NH bending and carboxyl stretching modes, the band at 1487 cm^{-1} disappears upon deuteration, the 1606-cm^{-1} band decreases in intensity, and the 1678-cm^{-1} band remains unchanged in intensity. This feature suggests that the 1606-cm^{-1} band is partly due to the N–H bending and partly due to the carboxylate stretching occurring at the same frequency. The 1487-cm^{-1} band is assigned to the symmetric deformation and the 1606-cm^{-1} band to the degenerate deformation modes of $-NH_3^+$. These assignments are supported by the fact that the 1487-cm^{-1} band is too low to be assigned to an $-NH_2$ bending mode; frequencies in the range 1547–1583 cm^{-1} have been observed for the $-NH_2$ bending vibration for a number of zinc–cysteine complexes in which N is the ligating atom.[9] The observation of the 1487, 1606 cm^{-1} doublet due to $-NH_3^+$ in the spectrum of the mercury–cysteine complex suggests that the N atom is not a ligating site in the complex in the solid state.

The positions of the two bands of the carboxyl group are of particular interest in the understanding of its coordination to Hg(II). These frequencies, namely 1606 and 1678 cm^{-1}, suggest that the carboxyl groups interact with Hg(II) in the complex. In recent Raman studies of solid $Hg(OAc)_2$[20] and its solutions,[21] a fairly strong band at ~280 cm^{-1} has been observed which is attributed to bonding between Hg(II) and the carboxylate group. The marked Raman intensity of this band implies that the mercury–carboxylate bonding is of considerable covalent character.[22] The absence of this band in the Raman spectrum of the mercury(II)–cysteine complex suggests that the interaction between Hg(II) and the carboxylate group in this compound is mainly electrostatic. Although the 1606-cm^{-1} band can reasonably be assigned to the asymmetric stretching of a



unit in which the carboxylate ion is perturbed by electrostatic force, it is unlikely that pure electrostatic force can cause a highly asymmetric structure of the carboxylate group to give rise to a band at 1678 cm^{-1}. This frequency is 100 cm^{-1} higher than the stretching frequency observed for crystalline sodium acetate[23] in which the carboxylate ion is expected to be almost symmetrical.[24]

We attribute the 1678-cm^{-1} band to C=O stretching of the



group in the complex (cf. 1740 cm^{-1} for $cys\cdot HCl\cdot H_2O$). The lowering of the C=O stretching frequency is explained in terms of an interaction of the O atom of the C=O group with the metal. It has been noticed that for a number of amide–metal complexes, coordination of the O atom of the C=O group results in a significant downward shift of the C=O stretching frequency.[25-29] The same frequency-lowering effect is expected to occur in the mercury(II)–cysteine complex. It is noteworthy that the structure proposed is in agreement with the empirical formula $(C_3H_6O_2NS)_2Hg\cdot HCl\cdot{}^1/_2H_2O$ and that for 2 mol of cysteinate there is 1 mol of proton.

Cysteine Methyl Ester. The spectral results of solid cysteine methyl ester hydrochloride and its complexes $(C_4H_8O_2NS)_2Hg\cdot HCl\cdot HNO_3\cdot H_2O$ (Porter's complex)[30] and $(C_4H_8O_2NS)_2Hg\cdot 2HCl\cdot H_2O$ are summarized in Table I. The NH_3^+ group in cysteine methyl ester hydrochloride is evidenced by the strong band at 1515 cm^{-1} and the weaker bands near 1600 cm^{-1}. All these bands shift down by a factor of ~1.4 upon deuteration. The carboxyl group exhibits bands at 1742 (s) and 1248 cm^{-1} (s) in infrared spectra and at 1744 (m) and 1251 cm^{-1} (w) in Raman spectra, typical for an ester group.

For the complexes, Raman spectra indicate the absence of

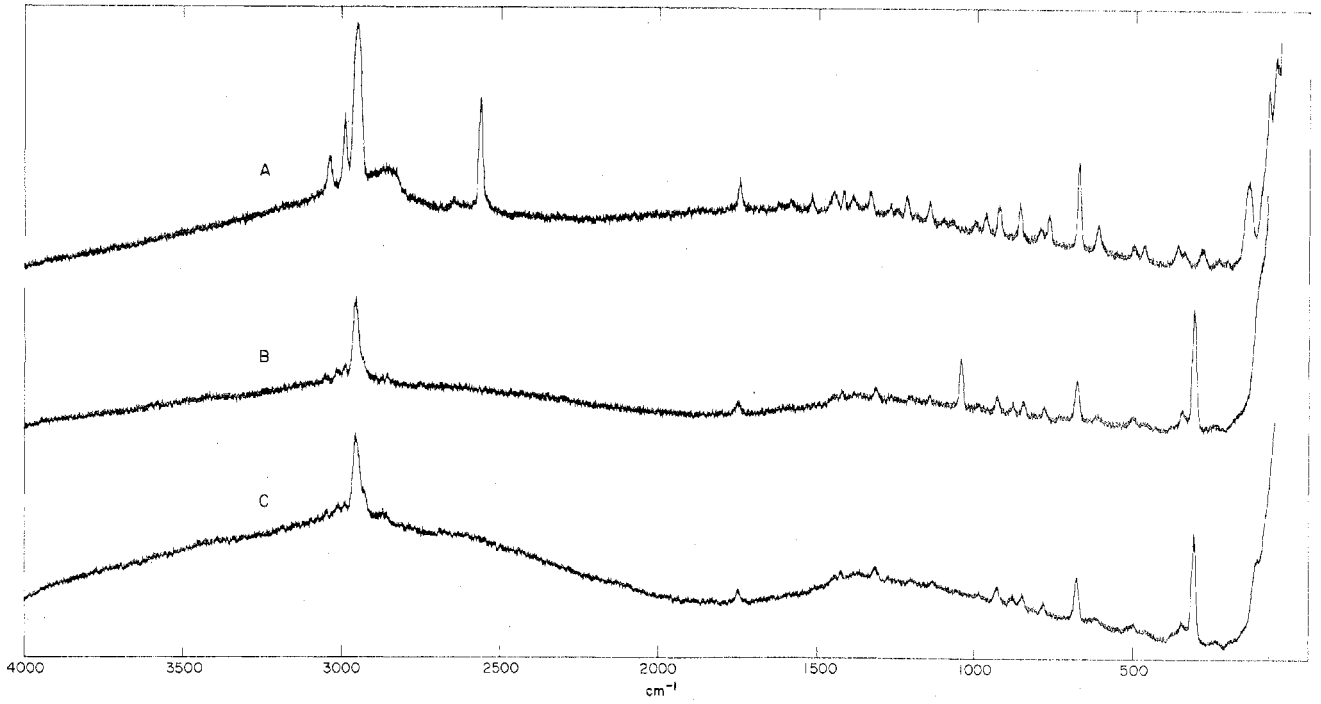


Figure 2. Raman spectra for (A) L-cysteine methyl ester hydrochloride, (B) bis(methyl-L-cysteinato)mercury(II) hydrochloride hydronitrate monohydrate, $(C_4H_8O_2NS)_2Hg\cdot HCl\cdot HNO_3\cdot H_2O$, and (C) bis(methyl-L-cysteinato)mercury(II) dihydrochloride monohydrate, $(C_4H_8O_2NS)_2Hg\cdot 2HCl\cdot H_2O$.

the strong band at 2562 cm^{-1} due to H–S stretching in the parent compound and the appearance of a strong band at 310 cm^{-1} attributed to Hg–S stretching (Figure 2). The complexes are also devoid of S–H absorption in infrared spectra. These results suggest that, as in the mercury(II)–cysteine complex, the S atom is involved in coordination in the mercury(II)–cysteine methyl ester complexes. In infrared spectra the observation of the strong band corresponding to C=O stretching of the ester group having identical frequency with that for cysteine methyl ester suggests that the C=O group is not involved in coordination in the solid state. The bands in the 1495–1600-cm^{-1} region, characteristic of NH_3^+ symmetric and degenerate bending modes, indicate that the N atom is not a coordinating site in the complexes. The extended-chain configuration in which cysteine methyl ester coordinates only through its S atom is consistent with the structure suggested by an NMR study of aqueous solutions of the two complexes.[12]

The presence of nitrate ion in Porter's complex is evidenced by the observation of medium to strong bands at 1048 (Raman) and 830 cm^{-1} (infrared). These bands are absent in the spectra of the parent compound and the complex $(C_4H_8O_2NS)_2Hg\cdot 2HCl\cdot H_2O$. The positions of these bands indicate that the nitrate ion is not coordinating to Hg(II).[31] Excepting the absence of nitrate bands, the spectra of the complex $(C_4H_8O_2NS)_2Hg\cdot 2HCl\cdot H_2O$ are very similar to those of Porter's complex, $(C_4H_8O_2NS)_2Hg\cdot HCl\cdot HNO_3\cdot H_2O$ (Table I and Figure 2). It may thus be concluded that the two complexes are isostructural in which chloride ion, like nitrate ion, does not coordinate to Hg(II).

Methionine. Spectral results of methionine, methionine hydronitrate, lithium methioninate, and the bis(methioninato)mercury(II) complex, $(C_5H_{10}O_2NS)_2Hg$, are tabulated in Table I. Fairly strong Raman bands were observed in the CS stretching region (~700 cm^{-1}). The spectra in this region are more complicated than those of cysteine, cysteine methyl ester, and their mercury complexes (Table I) because of the presence of the CH_3–S group. The positions of these bands are very sensitive to the composition and structure of the compounds containing methionine (Table I).

In the CH stretching region, the strongest band at 2912–2917 cm^{-1}, which is much lower in frequency than those observed for compounds not containing S–CH_3 (Table I), can be identified as the CH_3 symmetric stretching of this unit. In agreement with this assignment is the fact that the frequency of this band does not differ significantly in methionine, methionine hydronitrate and lithium methioninate while the other CH stretching bands do. In these compounds, the major structural changes occur at the amino and carboxylate group and it is reasonable to expect that the methyl group linked to the S atom is the one least affected. The small variation in frequency of this band thus supports the above assignment.

A comparison is made between the Raman spectra of $(C_5H_{10}O_2NS)Li$ and $(C_5H_{10}O_2NS)Hg$ in Figure 3. It can be seen that the band at 2912 cm^{-1} is almost unaffected upon coordination of methioninate to Hg(II) suggesting that the S atom is not a ligating site in the solid state.

A strong band at 481 cm^{-1} is observed for $(C_5H_{10}O_2NS)_2Hg$ which is absent in the spectra of $(C_5H_{10}O_2NS)Li$, methionine, and methionine hydronitrate. This band is assigned to Hg–N stretching in agreement with previous observations that Hg–N stretching bands for a number of compounds occur in the range 400–700 cm^{-1}.[32,33] In the light of our previous argument that the methyl group in the complex is almost unaffected and the fact that Hg–S stretching vibration occurs at ~310 cm^{-1} for Hg(II) complexes of cysteine and cysteine methyl ester, the possibility of assigning the band at 481 cm^{-1} to Hg–S stretching vibration is ruled out. Since covalent interaction between Hg(II) and carboxylate group gives a band at ~280 cm^{-1}, this band at 481 cm^{-1} cannot be ascribed to Hg–O stretching either.

The band at 1400 cm^{-1} characteristic of CO_2^- symmetrical stretching vibration for $(C_5H_{10}O_2NS)_2Hg$ is slightly lower than that for $(C_5H_{10}O_2)Li$ (1423 cm^{-1}) while the band due to asymmetric stretching for $(C_5H_{10}O_2NS)_2Hg$ is slightly higher (1595 cm^{-1} vs. 1580 cm^{-1}). This feature suggests that weak bonding exists between the carboxylate group and Hg(II) which is essentially ionic in nature. A structure basically in agreement with the one proposed above has also been suggested by McAuliffe et al.[10] in their recent infrared study. These authors studied a large number of metal complexes of

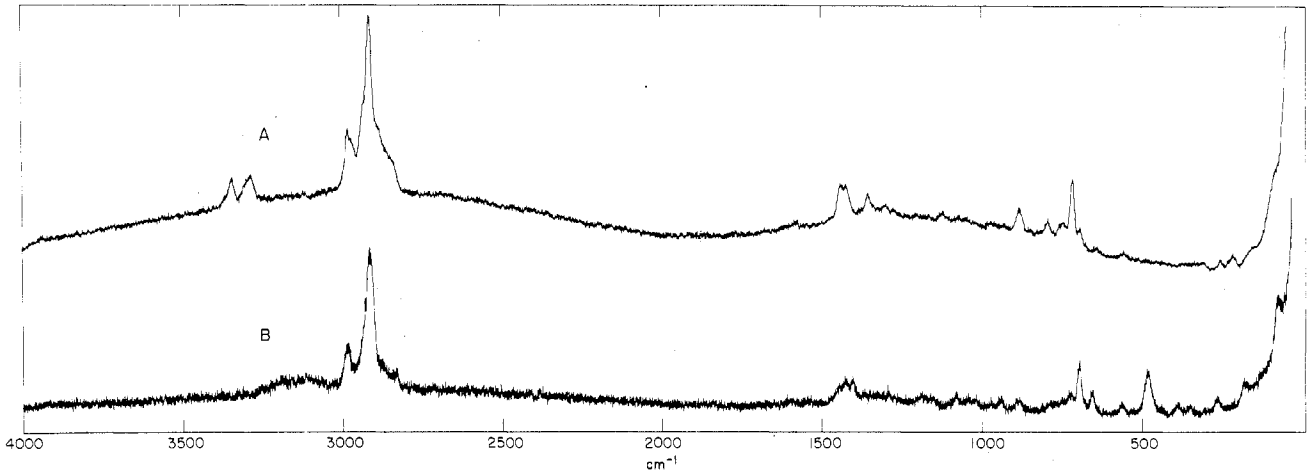


Figure 3. Raman spectra for (A) lithium methioninate, $(C_5H_{10}O_2NS)Li$, and (B) bis(methioninato)mercury(II), $(C_5H_{10}O_2NS)_2Hg$.

methionine and suggested that for the divalent metal complexes $(C_5H_{10}O_2NS)_2M^{II}$, the ligand is both chelating and bridging, coordinating through its N atom and both of the oxygen atoms of the COO^- group. The argument that N is ligating to Hg(II) was based on indirect evidence, namely, the frequencies of the $-NH_2$ bands which become less indicative if extensive hydrogen bonding is present in the system (see below). The inference that both oxygen atoms ligate to the metal was based on the observation that the bands due to NH_2 stretching modes are sharp (half-widths < 50 cm^{-1}) for some of the transition metal complexes—an indication that there is no oxygen atom available for hydrogen bonding to $-NH_2$. This was not observed in Raman and infrared spectra in the present study of the mercury complex. Figure 3 indicates that the $-NH_2$ group is strongly hydrogen bonded. This observation supports our previous conclusion that the $-CO_2^-$–Hg^{II} bond is essentially ionic. It further suggests that the $-CO_2^-$ group probably uses only one of its two oxygen atoms in coordination; the other oxygen atom with considerable negative local charge interacts with the amino group resulting in the broad contour in the 3150-cm^{-1} region.

The above indication of strong bonding by amino N and weaker bonding by carboxyl oxygen to mercury in the bis(methioninato)mercury(II) complex in the solid state is particularly interesting in that it permits one to infer that mercurial coordination alters on dissolution of the complex.[13] It would therefore appear that dissolution of the bis(methioninato)mercury(II) complex upon acidification is accomplished through protonation of the amino group with reassociation of the carboxyl hydrogen resulting in disruption of the nitrogen–oxygen bonding to mercury that prevailed in the solid state. On increasing the pH to slightly alkaline, it is reasonable to expect the reinvolvement of nitrogen–oxygen bonding to mercury as dissociation of the carboxyl group occurs, and this would appear to be the state alluded to by Natusch and Porter.[15] It had been a prevalent view[4a,5] that substituted mercapto groups would have little or no involvement in chelation with mercuric ion until PMR evidence was first presented by Natusch and Porter[15] for the direct detection of mercury(II)–thioether bonding in complexes of methionine and *S*-methylcysteine. More recently, not only has mercurial bonding to the substituted sulfur of these compounds been substantiated,[8,13,14] but evidence has been provided by ^{13}C NMR to indicate that, in the solvated state, mercurial bonding is exclusive to sulfur and that the amino and carboxyl moieties are remote from mercury on account of an extended molecular chain configuration.[13,14]

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Registry No. L-Cysteine, 52-90-4; L-cys·HCl, 52-89-1; $(C_3H_6O_2NS)_2Hg\cdot HCl$, 52700-45-5; L-cysteinemethyl ester hydrochloride, 18598-63-5; $(C_4H_8O_2NS)_2Hg\cdot HCl\cdot HNO_3$, 55057-00-6; $(C_4H_8O_2NS)_2Hg\cdot 2HCl$, 21496-19-5; D,L-methionine, 59-51-8; D,L-methionine hydronitrate, 55012-65-2; $(C_5H_{10}O_2NS)Li$, 52183-86-5; $(C_5H_{10}O_2NS)_2Hg$, 31210-58-9.

Supplementary Material Available. A full tabulation of Raman and infrared spectral data of the compounds listed in Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40699W.

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Isocyanide Complexes and (Alkoxy)(*N*-alkylimino)methyl Derivatives of Silver and Their Reactions

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Isocyanide and silver chloride give $[(RNC)AgCl]_n$ complexes. These, or a mixture of Me_2SAgNO_3 and isocyanide, react with alcoholic potassium hydroxide affording $[(R'O)(RN{=})CAg]_3$, from which transfer of the organic group on other metals can be accomplished yielding HgY_2, ClHgY, $[AuY]_3$, and $(Ph_3P)_2PtClY$, where Y is $(EtO)(p\text{-}CH_3C_6H_4N{=})C-$.

Introduction

Among the isocyanide complexes of group 1B metals much data are available[2,3] on the preparation and reactivity of copper and gold complexes, while information about silver derivatives is lacking. In the field of gold chemistry, the preparation and reactions of neutral and cationic isocyanide derivatives, RNCAuCl and $[(RNC)_2Au]^+$, respectively, were recently described.[4]

Starting from these species, nucleophilic attack by an alcohol or by an amine afforded "carbene" complexes, according to the reaction patterns (1)–(4), which are in agreement with later

$$RNCAuCl + R'OH = \underset{A}{(RNH)(R'O)CAuCl} \quad (1)^{4-6}$$

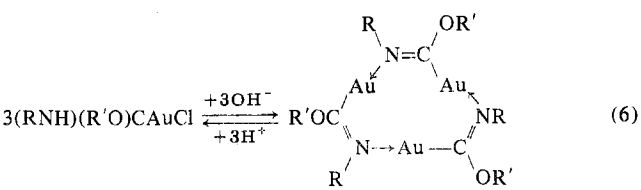
$$RNCAuCl + R'NH_2 = \underset{B}{(RNH)(R'NH)CAuCl} \quad (2)^{5,7}$$

$$[(C_6H_{11}NC)_2Au]^+ + ArNH_2 = [(C_6H_{11}NH)(ArNH)CAu(CNC_6H_{11})]^+ \quad (3)^{8,9}$$

$$[(RNC)_2Au]^+ + 2R'NH_2 = [\{(RNH)(R'NH)C\}_2Au]^+ \quad (4)^{8,9}$$

$$[(RNC)_2Au]^+ + 2R'OH = [\{(RNH)(R'O)C\}_2Au]^+ \quad (5)^{8,9}$$

reports by other authors,[10,11] or to reaction pattern (5), in place of which other authors[10] found either no reaction or dealkylation of the isocyanide (sealed tube, 60–100°). Further reaction of the carbene complexes A or B takes place according to the reaction pattern (6) or (7), affording cyclic trimers (C)[11,12] or polymers (D).[7] In addition, both reactions 6 and



(6)

$$n(RNH)(R'NH)CAuCl \underset{+nH^+}{\overset{+nOH^-}{\rightleftharpoons}} \underset{D}{[(RN{=})(R'NH)CAu]_n} \quad (7)$$

7 are reversible: indeed protonation[11,12] of C or D affords the carbene complex A or B, respectively.

In order to get a complete picture inside group 1B, it was decided to extend some of these reactions to silver. The (RNC)AgCl compounds were isolated, but they did not give carbene derivatives, type A or B, while the $[AgC(OR){=}NR']_3$ complexes analogous to C were obtained. These (alkoxy)(alkylimino)methylsilver compounds were found to be useful intermediates for the transfer of the $(R'N{=})(RO)C-$ group to different metals. A preliminary account of this work has already appeared.[13]

Experimental Section

Reactions were carried out under nitrogen and in the dark because the crude products are often air or (especially) light sensitive. The $(RO)(ArN{=})CAg$ compounds can be obtained from Me_2SAgNO_3 or from (ArNC)AgCl according to the procedures described below for compounds VI and VII. Evaporation was always carried out under reduced pressure. Before each reaction solid *p*-tolyl isocyanide (mp ca. 19°) was allowed to thaw at room temperature; it was then measured volumetrically. Analytical data are reported in Table I; NMR data, in Table II.

The starting material, $(Me_2S)AgNO_3$ (I), mp 120–123°, was obtained as a white precipitate (50% yield) from aqueous silver nitrate (15 g, saturated solution) and dimethyl sulfide (70 ml).

(*p*-Tolyl isocyanide)chlorosilver(I) (II). Silver chloride (1.5 g, 10.47 mmol) was suspended in chloroform (40 ml) and *p*-tolyl isocyanide was added (2.6 and, shortly afterward, 0.2 ml, 21 mmol), under stirring. To the filtered solution petroleum ether was added (50 ml). After the volume was halved by evaporation, addition of more petroleum ether (30 ml) gave a white compound (1.31 g; 48% on silver). The compound is insoluble in chloroform, dichloromethane, acetone, benzene, alcohol, acetonitrile, and diethyl ether; $\nu(C{\equiv}N)$ at 2160 cm^{-1}, Nujol mull.

(Cyclohexyl isocyanide)chlorosilver(I) (III), was obtained similarly (48%). It was insoluble in common organic solvents and showed $\nu(C{\equiv}N)$ at 2180 cm^{-1}, Nujol mull. Methyl or *p*-nitrophenyl isocyanide did not react under the same conditions, while reaction of $(Me_2S)AgNO_3$ with methyl isocyanide gave an insoluble compound which analyzed as $(MeNC)_2(AgCl)_5$ and which was not further investigated.

(*n*-Propoxy)(*N*-*p*-tolylimino)methylsilver(I) Trimer (VI). To a stirred 1-propanol (30 ml) suspension of compound II (405 mg, 1.55 mmol), *p*-tolyl isocyanide (0.21 ml, 1.6 mmol) and, later, potassium hydroxide in 1-propanol (15.8 ml, 5.5 g/l., 1.55 mmol) were added. A brownish precipitate was filtered and extracted with chloroform (30 ml). 1-Propanol (30 ml) was added and the solution was concentrated to yield a white solid (ca. 200 mg), soluble in chloroform and dichloromethane and insoluble in acetone and acetonitrile. Molecular weight: found, 882 (cryoscopy in 3.45% w/w benzene solution), 864 (vapor-phase osmometry, chloroform solution); required, 851.4.

Compounds IV and V were prepared analogously. The methoxy derivative, IV, was insoluble and the ethoxy derivative, V, was sparingly soluble in $CHCl_3$ and C_6H_6. For this reason and for the rather limited stability of the solution, no molecular weight determination was carried out for these two compounds.