**Table I.** Donor and Solvating Tendencies of Some Solvents

| Solvent | $K_{as}$ (salt) | $Z^a$ | Dielectric constant, $\epsilon$ | $-\Delta H$, kcal. mole$^{-1}$ | | $Dq,^b$ cm.$^{-1}$ |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | $C_6H_5OH^g$ | $I_2$ | |
| CH$_3$OH | 26 (Bu$_4$NBr)$^{c,k}$ | 83.6$^e$ | 33.5 (25°) | ... | 1.9$^p$ | 850$^h$ |
| (CH$_3$)$_2$SO | 0 (Bu$_4$NBr)$^l$ | 71.1$^e$ | 48.9 (25°) | 6.5 | 4.4$^q$ | 773$^i$ |
| CH$_3$C(O)NHCH$_3$ | 0 (Et$_4$NBr)$^{c,m}$ | 77.9$^f$ | 175.7 (40°) | 4.7$^d$ | ... | 752$^j$ |
| CH$_3$C(O)N(CH$_3$)$_2$ | 20 (Et$_4$NBr)$^n$ | 66.9$^f$ | 38 (25°) | 6.4 | 4.0$^r$ | 769$^j$ |
| OP(OC$_2$H$_5$)$_3$ | 1600 (Et$_4$N picrate)$^o$ | ... | 13 (25°) | 6.2 | ... | ... |

$^a$ The $Z$ value is the transition energy in kcal. at 25°, 1 atm. pressure, for the charge-transfer transition of 1-ethyl-4-carbomethoxypyridinium iodide. The larger values correspond to better solvating solvents. $^b$ The $Dq$ value for the octahedral nickel(II) complex of this ligand. For comparison, the $Dq$ value for chloride ion is 720. $^c$ Bu stands for $n$-butyl and Et for ethyl. $^d$ This value was obtained from the phenol frequency shift, see footnote $g$ below, and represents the enthalpy for unassociated amide complexing to phenol. $^e$ See ref. 11. $^f$ This work. $^g$ See M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962). $^h$ V. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965). $^i$ D. W. Meek, R. S. Drago, and T. S. Piper, *ibid.*, **1**, 285 (1962). $^j$ See ref. 13. $^k$ H. Sodek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950). $^l$ P. G. Sears, G. R. Lester, and L. R. Dawson *J. Phys. Chem.*, **60**, 1433 (1956). $^m$ C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1418 (1955). $^n$ G. R. Lester, T. A. Glover, and P. G. Sears, *J. Phys. Chem.*, **60**, 1076 (1956). $^o$ C. M. French, P. B. Hart, and D. F. Muggleton, *J. Chem. Soc.*, 3582 (1959). $^p$ H. Tsubomura and R. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). $^q$ R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963). $^r$ R. S. Drago, *et al.*, *ibid.*, **83**, 3572 (1961).

solvating ability of the solvent. In the best solvating solvent, NMA, the principal species are FeS$_6^{3+}$ and chloride ion (see eq. 1). In DMSO the principal species are FeS$_5$Cl$^{2+}$ and chloride ion. Even though methanol is estimated to be the best donor solvent of those studied, both FeS$_5$Cl$^{2+}$ and FeS$_4$Cl$_2^+$ exist. This result correlates with the low dielectric constant of methanol and extensive ion pairing of Bu$_4$NBr in this solvent. In the poorer solvating solvents, DMA, (CH$_3$O)$_3$PO ($\epsilon$ = 20.60 at 20°),[4] (C$_2$H$_5$O)$_3$PO, POCl$_3$ ($\epsilon$ = 14 at 22°), C$_6$H$_5$POCl$_2$, and possibly in many other oxyhalide solvents, the principal species are FeS$_4$Cl$_2^+$ and FeCl$_4^-$.

It is interesting that the above interpretation has been so simple. This is probably due to the fact that we have selected systems where the difference in solvation energies is large enough to overcome any entropy differences that exist between the systems studied. When very similar systems are compared or when there are very large entropy differences between the systems compared, which counteract the enthalpy, such an interpretation may not be possible.

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# Infrared Spectra of Complexes of L-Cysteine and Related Compounds with Zinc(II), Cadmium(II), Mercury(II), and Lead(II)[1]

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*Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received September 14, 1964*

Complexes of L-cysteine, S-methyl-L-cysteine, methyl L-cysteinate, and 3-mercaptopropionic acid with Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, and Hg$^{2+}$ have been prepared under solution conditions of varying acidity. Infrared spectra of solid compounds have been employed to assist in determining which groups are coordinated to the metal. Among the new solid species formed are a number of complexes which are believed to be trinuclear, of the form [M$_3$L$_4$]$^{2+}$-MCl$_4^{2-}$. The infrared spectra in D$_2$O solution of complexes of the form Na$_2$[ML$_2$], where L is (SCH$_2$CHNH$_2$-CO$_2$)$_2^-$ or (SCH$_2$CH$_2$CO$_2$)$^{2-}$, and [ML$_2$], where L is (SCH$_2$CHNH$_2$CO$_2$CH$_3$), have been obtained. From the shifts in the carboxylate or carbonyl frequencies as a function of M, it appears that the order of strength of coordination to either oxygen or the amino group is in the order Zn > Cd > Hg > Pb. The over-all driving force for complex formation is in the reverse order because metal–sulfur bonding is of overriding importance.

Cysteine, which figures prominently in discussions of metal ion binding to protein, has three possible coordination sites, namely sulfhydryl, amino, and carboxylate groups. This provides three possible combinations for forming a chelate ring with a divalent

metal ion. Li, *et al.*,[3] determined the formation constants of the complexes formed by lead(II), cadmium(II), zinc(II), and nickel(II) ions with cysteine and related compounds. The sites of binding to zinc and nickel ions were suspected to be the amino and sulfhydryl groups. Little work has been done, however, by way of isolation and characterization of solid complexes. The solid complexes of cysteine with zinc(II) and cadmium(II) have not yet been recorded; complexes with mercury(II)[4,5] and lead(II)[6,7] ions are reported in the literature preceding 1935. The only cysteine complexes which have been isolated and studied extensively are those with cobalt(II) and cobalt(III), first prepared by Schubert,[8] in which nitrogen and sulfur serve as donors.[9] For transition metal ions such as Cu(II) and Fe(II), the ready oxidation of cysteine to cystine complicates study of the complexes.[10] For example, cysteine is readily oxidized by Cu(II) ion in an alkaline solution; excess cysteine reacts with Cu(I) ion.[11] While considerable attention has been devoted to transition metal ion complexes with respect to oxidation–reduction reactions, less is known about complexes of nontransition metals.

The present investigations were carried out to obtain further information about metal ion interactions with cysteine. Salient features of the infrared spectra of complexes formed—Zn(II), Cd(II), Hg(II), and Pb(II) ions with cysteine and related ligands—are reported.

## Results and Discussion

*Spectra of Solid Complexes.* A dilute solution of zinc(II) chloride and cysteine in the slightly acid pH range yields a complex of empirical formula $ZnSCH_2CH(NH_2)CO_2$ (I). The infrared spectrum shows no S–H absorption. Bands at 3317 and 3260 cm.$^{-1}$ can be ascribed to coordinated $NH_2$.[12] Cadmium, lead, and mercury also form 1:1 complexes with cysteine. The spectra are similar, but the carboxylate asymmetric stretching frequency varies somewhat with the metal ion (1604, 1584, and 1598 cm.$^{-1}$ in the Cd(II), Pb(II), and Hg(II) complexes, respectively). Treatment of I with 2 equiv. of aqueous hydroxide yields the solid complex $Zn(SCH_2CHNH_2CO_2)_2Na_2 \cdot 4H_2O$ (II). II is also devoid of S–H absorption; although the $NH_2$ stretching absorptions are obscured by the presence of water of hydration, the appearance of other $NH_2$ ($ND_2$) bands in the spectrum indicates $NH_2$ coordination. The carboxylate frequencies are in the range expected for noncoordinated $-CO_2^-$. The coordination of cysteine to zinc in II is thus assigned as



II
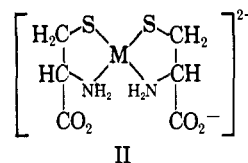
A 2:1 complex (III) is formed between methyl cysteinate and zinc. The infrared spectrum (Table I) shows no S–H absorptions; the carbonyl absorption occurs at 1744 cm.$^{-1}$, characteristic of an uncoordinated ester carbonyl group.[13] The spectrum therefore indicates that coordination occurs through sulfur and amino groups. S-Methylcysteine also forms a 2:1 complex (IV) with zinc. Indication of binding through the amino group is seen in the close similarity of the $-NH_2$ frequencies to those in I and III (Table I). The frequencies assigned to the carboxylate group are not far below those found in I, in which there is surely carboxylate coordination to zinc. These results are consistent with structure IV.



IV
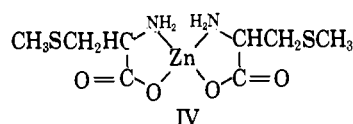
Cysteine forms another set of complexes with zinc(II) and cadmium(II) chlorides and bromides in acid aqueous solution, pH ~2. Elemental analysis yields the general empirical formula $MSCH_2CH(NH_3)CO_2X$, where M is $Zn^{2+}$ or $Cd^{2+}$ and X is $Cl^-$ or $Br^-$. The characteristic infrared absorption frequencies of the solid complexes are tabulated in Table II. The spectra contain bands corresponding to $-NH_3^+$ and to carboxylate ion. No S–H absorption is seen. The $-NH_3^+$ group is characterized by the doublet arising from the symmetric and degenerate bending modes at around 1510 and 1600 cm.$^{-1}$, respectively.[14] Coordination of carboxylate oxygen is evidenced by the high frequency of the asymmetric carboxylate stretching mode (Table II) in the complexes as compared with the zwitterionic free acid and the 1:1 complexes (*vide supra*).

The zinc and cadmium chloro complexes exhibit absorption at 281 and 252 cm.$^{-1}$, respectively. This region is free in the spectrum of the zinc bromide complex. The observed absorptions correspond very well to those found for the $ZnCl_4^{2-}$ and $CdCl_4^{2-}$ ions.[15,16] The zinc and cadmium chloride compounds are easily converted to the corresponding 1:1 complexes by heating in water. On the basis of the infrared spectra and their general behavior, the following structure (A) seems most reasonable

Structures analogous to these have been proposed by Busch and co-workers[17] for some mercaptoethylamine

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**Table I.** Some Characteristic Infrared Bands of Zinc Cysteine Complexes

| I[a] | | II[b] | | III[c] | | IV[d] | | |
| H | D | H | D | H | D | H | D | |
|---|---|---|---|---|---|---|---|---|
| 3317 m | 2477 m | 3405 | 2498 s | 3288 ms | 2457 ms | 3315 m | 2478 m | $NH_2$ ($ND_2$) stretch. |
| 3260 m | 2424 m | 3350 br | 2383 s | 3180 m | 2362 m | 3282 ms | 2450 m | (+ $H_2O$ stretch.) |
| | | 3160 | 2322 sh | 3111 m | 2317 ms | 3124 m | 2318 m | |
| ... | ... | ... | ... | 1744 vs | 1744 vs | ... | ... | C=O stretch. |
| 1634 vs | 1628 vs | 1588 vs | 1589 vs | ... | ... | 1622 vs | 1619 vs | $COO^-$ asym. stretch |
| 1583 s | ... | 1547 s | ... | 1575 s | ... | ? | ... | $NH_2$ bend. |
| 1418 vs | 1410 vs | 1404 vs | 1403 vs | ... | ... | 1411 s | 1414 s | $COO^-$ sym. stretch |
| 1244 ms | ... | 1252 ms | ... | 1279 s | ... | 1264 m | ... | $NH_2$ wagging |
| | 1219 m | | | | | | | |
| ... | 1194 m | ... | 1171 m | ... | 1199 s | ... | 1180 s | $ND_2$ bend. |
| | 1167 s | | 1160 m | | | | | |
| 1148 m | ... | 1095 m | ... | 1137 s | ... | 1159 ms | ... | $NH_2$ twist. |
| ... | 886 ms | ... | 947 w | ... | 952 w | ... | 949 ms | $ND_2$ wagging |
| 850 m | ... | 908 m | ... | 904 m | ... | 915 m | ... | $NH_2$ rocking |
| 811 m | 824 ms | 867 ms | 870 ms | 862 ms | 871 m | 828 m | 865 ms | + $CH_2$ rocking |
| ... | 804 m | ... | 813 m | ... | 831 ms | ... | 815 s | $ND_2$ twist. |

[a] I = $Zn_2(SCH_2CH(NH_2)CO_2)_2$. [b] II = $Zn(SCH_2CH(NH_2)CO_2)Na_2 \cdot 4H_2O$. [c] III = $Zn(SCH_2CH(NH_2)CO_2CH_3)_2$. [d] IV = $Zn(CH_3SCH_2CH(NH_2)CO_2)_2$.

**Table II.** Some Characteristic Infrared Bands of L-Cysteine and Bis(L-cysteine)–Metal Halide Complexes

| L-Cysteine | | $[M\{M(SCH_2CH(NH_3)CO_2)_2\}_2]MX_4$ | | | | |
| H | D | H[a] | D[a] | H[b] | H[c] | |
|---|---|---|---|---|---|---|
| 3012 s,br | 2388 m | 3435 sh | 2565 ms | 3100 s,br | 3200 s | $NH_3^+$ ($ND_3^+$) stretch. |
| | 2225 s | 3336 s | 2478 ms | | 3120 s | (+$H_2O$ stretch.) |
| | | 3080 s,br | 2355 sh | | | |
| | | | 2312 ms | | | |
| | | | 2227 ms | | | |
| 2568 s | 1856 m | ... | ... | ... | ... | SH (SD) stretch. |
| 1615 vs | ... | 1599 s | ... | 1604 vs | 1581 s | $NH_3^+$ deg. deform. |
| 1590 vs | 1598 vs | 1663 vs | 1651 vs | 1642 vs | 1616 vs | $COO^-$ asym. stretch. |
| 1519 vs | ... | 1517 vs | ... | 1520 vs | 1507 | $NH_3^+$ sym. deform. |
| 1400 s | 1398 s | 1403 s | 1400 s | 1394 vs | 1425 s | $COO^-$ sym. stretch. |
| ... | 1180 s | ... | 1180 s | ... | ... | $ND_3^+$ deg. + sym. |
| ... | 1163 sh | ... | 1151 sh | ... | ... | deformations |
| 1143 m | ... | 1137 ms | ... | 1136 ms | 1145 ms | $NH_3^+$ rocking |
| 1068 m | ... | 1100 w | ... | 1090 m | 1075 m | |
| 1047 sh | 1027 w | 1043 ms | 1069 m | 1057 m | 1038 ms | C–N, C–C stretch. |
| 988 m | 967 w | 972 w | 1015 m | 960 m | 966 m | |
| 945 m | ... | ... | ... | ... | ... | SH bending? |
| ... | 808 m | ... | 812 ms | 811 m | 801 ms | $ND_3^+$ rocking + |
| 778 w | 777 m | 798 ms | 766 s | ... | ... | $CH_2$ rocking |
| ... | ... | 281 vs | d | ... | 252 s | $MX_4^{2-}$ stretch. |

[a] M = Zn (tetrahydrate), X = Cl. [b] M = Zn (anhydrous), X = Br. [c] M = Cd (anhydrous), X = Cl. [d] Not determined.



M = $Zn^{2+}$, X = $Cl^-$
M = $Zn^{2+}$, X = $Br^-$
M = $Cd^{2+}$, X = $Cl^-$

A
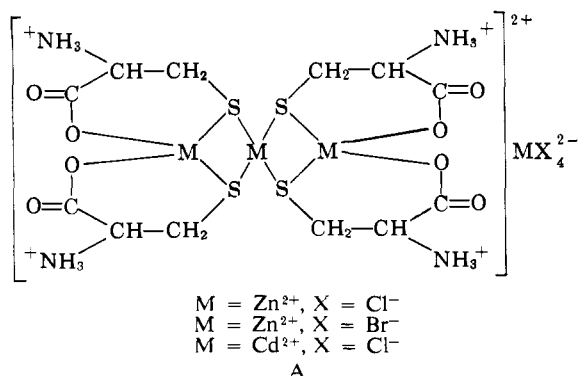
complexes. Unfortunately, the very low solubility of our compounds in all solvents precludes conductivity measurements which might be of utility in more firmly establishing that the proposed structures are correct. At the moment, the best that can be said is that the trinuclear ion structure is consistent with the infrared spectral data, whereas other structures which have occurred to us are not.

In addition to the 1:1 complex mentioned earlier, mercury forms a number of other cysteine complexes from solutions at various pH values. The empirical formulas of these species are given in Table III, along with very brief comments on the infrared spectra. It is not possible to make any definitive statements about the structures in any of these cases. The complexes described are consistent with the indications from polarographic studies of the equilibria between cysteine and mercury as a function of pH.[18] In connection with compound VI, it might be remarked that the presence of $NH_3^+$ as well as of coordinated *and* free carboxylate precludes the structure proposed earlier by Shinohara.[5]

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| Compound[a] | | pH[b] | Infrared spectra, cm.$^{-1}$ |
|---|---|---|---|
| V | $Hg_2[SCH_2CH(NH_2)CO_2]_2$ | 8 | COO⁻ 1598, 1394<br>NH₂ 1584, 1280; ND₂ 1204 |
| VI | $Hg_2[SCH_2CH(NH_2)CO_2]_2HCl$ | 6 (excess HCl) | CO₂⁻ 1593, 1398<br>NH₃⁺ 1639, 1491; ND₃⁺ 1170, 1139<br>NH₂ 1568, 1243; ND₂ 1194 |
| VII | $Hg_4[SCH_2CH(NH_2)CO_2]_2Cl_2$ | 6 (excess HgCl₂) | CO₂⁻ 1590 |
| VIII | $Hg[SCH_2CH(NH_3)CO_2]_2$ | 2 (excess cysteine) | CO₂⁻ 1580, 1404<br>NH₃⁺ 1618, 1530; ND₃⁺ 1173, 1135 |
| IX | $Hg_3[SCH_2CH(NH_3)CO_2H)_2Cl_6 \cdot 2H_2O$ | 2 (excess HgCl₂, HCl) | C=O 1733; NH₃⁺ 1601, 1518<br>–Hg–Cl 331 |

[a] Empirical formulas were established on the basis of carbon, hydrogen, nitrogen, and, where appropriate, chlorine analyses. [b] This refers to the pH of the solution from which the complex precipitated.

**Table IV.** Infrared Spectra of Complexes of Cysteine and Related Compounds in Alkaline Aqueous Solution

| | | HSCH₂CH-<br>(NH₃⁺)CO₂⁻ | –SCH₂CH-<br>(NH₂)CO₂⁻ | +Pb²⁺ | +Hg²⁺ | +Cd²⁺ | +Zn²⁺ |
|---|---|---|---|---|---|---|---|
| $\nu_{COO^-}$ | Asym.[a] | 1625 | 1576 | 1583 | 1583 | 1588 | 1592 |
| | Sym.[a] | 1402 | 1414 | 1403 | 1404 | 1405 | 1408 |

| | | HSCH₂CH-<br>(NH₃⁺)CO₂CH₃ | –SCH₂CH-<br>(NH₂)CO₂CH₃ | | +Pb²⁺ | +Cd²⁺ | +Zn²⁺ |
|---|---|---|---|---|---|---|---|
| $\nu_{C=O}$ | | 1749 | 1726 | | 1730 | 1731 | 1736 |

| | | –SCH₂CH₂CO₂⁻ | | +Pb²⁺ | +Hg²⁺ | +Cd²⁺ | +Zn²⁺ |
|---|---|---|---|---|---|---|---|
| $\nu_{COO^-}$ | Asym.[b] | 1558 | | 1561 | 1565 | 1567 | 1572 |
| | Sym.[b] | 1407 | | 1405 | 1405 | 1404 | 1404 |

[a] 1.0 $M$ ligand + 0.5 $M$ MCl₂ in 2.0 $M$ NaOD. [b] 1.0 $M$ ligand + 0.5 $M$ MCl₂ in 1.0 $M$ NaOD.

Solid 1:1 complexes of zinc, cadmium, lead, and mercury with mercaptopropionic acid were isolated. We will report here, however, only the spectra of the 2:1 complexes in alkaline aqueous solution.

*Aqueous Solution Spectra.* The sodium salts of 2:1 cysteine and mercaptopropionic acid complexes are quite soluble in water. The spectra of the carboxylate absorptions in D₂O solutions of these complexes provide a number of interesting comparisons. The data are given in Table IV. A special effort was made to ensure that the frequencies reported are relatively accurate to within 1 cm.$^{-1}$.

The asymmetric carboxylate frequency for the cysteine complexes shifts in the order $Zn^{2+} > Cd^{2+} > Hg^{2+} \sim Pb^{2+}$, with the values for the complexes intermediate between those characterizing the zwitterionic and anionic forms of the free acid. An increase in carboxylate frequency results from appearance of positive charge at the amino nitrogen, because of inductive electron withdrawal from the carboxylate group. Since cysteine is almost certainly coordinated through the amino and sulfide groups in alkaline solution, the shift in carboxylate frequency in the complexes can be taken as a measure of the strength of coordination through the amino group. If the carboxylate frequency shifts are indeed due to inductive electron withdrawal, it follows that the symmetric carboxylate frequency should also shift to higher values upon complex formation. The expected trend is observed in the metal complexes themselves, but the values for the zwitterionic and anionic free acid forms are inverted from the expected order. The reasons for this are not clear, although one may conjecture

that intramolecular hydrogen bonding in the zwitterionic form is involved.

The carbonyl frequency in methyl cysteinate shifts to higher frequency upon complex formation or protonation of the amino group, as expected. The results again support an order of strength for amino coordination: $Zn^{2+} > Cd^{2+} > Pb^{2+}$.

The carboxylate groups are no doubt coordinated in the mercaptopropionic acid complexes. The asymmetric carboxylate frequency is shifted to higher values in the order $Zn^{2+} > Cd^{2+} > Hg^{2+} > Pb^{2+}$, which represents a reasonable order of strength of carboxylate interaction. The symmetric carboxylate frequency exhibits very little or no shift in the series.

The association of the carboxylate frequency shift with the strength of the coordinative bond to the amino or carboxylate group in the forgoing examples is potentially capable of general utility. The over-all formation constants for cysteine binding[3a] are in the order $Pb^{2+} > Hg^{2+} > Cd^{2+} > Zn^{2+}$, an order which reflects the predominating influence of binding to sulfur. The aqueous infrared spectral data permit an assessment of the other half of the chelate bonding, to the amino or carboxyl group, in the presence of the binding at sulfur. Finally, it should be noted that the asymmetric carboxylate frequency increases by roughly the same amount in the corresponding mercaptopropionic and cysteine complexes. In the first instance coordination is almost certainly through the carboxylate, and in the latter case it just as surely is not. It is clear that care must be exercised in evaluating carboxylate frequency shifts in complexes

when more than one reasonable possibility exists for carboxylate coordination.[19]

## Experimental

Infrared spectra of solids were obtained as Nujol mulls or KBr disks. A Beckman IR-7 instrument was employed for the 4000–650-cm.$^{-1}$ region. A Beckman IR-5A with CsBr optics and a Perkin-Elmer 521 were employed in studying the 650–250-cm.$^{-1}$ region. All spectrometers were frequency calibrated using $H_2O$ vapor, gaseous HCl, and polystyrene film. For purposes of comparison, the relative frequencies of the carboxylate absorptions in the aqueous spectra were determined to within one wave number, by employing slow scanning speeds and making repeated observations. The frequencies reported for the solid spectra are reproducible to within 2 cm.$^{-1}$ in the 650–2000-cm.$^{-1}$ range, and 5 cm.$^{-1}$ in the 2000–4000-cm.$^{-1}$ range.

Aqueous solution spectra were obtained using IRTRAN-2 plates. A drop of solution was placed between two plates with no spacer. No pressure is exerted on the plates to clamp them in position; by gentle finger pressure a convenient path length of about 0.025 mm. can be arrived at.

All reagents were of analytical reagent grade. L-Cysteine and its hydrochloride, methyl cysteinate hydrochloride, and S-methylcysteine were obtained from Sigma Chemical Co. 3-Mercaptopropionic acid was obtained from Evans Chemicals, Inc., and purified by vacuum distillation.

Deuterium oxide of 99.5% isotopic purity was employed. Deuteration of solid samples was achieved by preparing each sample from $D_2O$ or NaOD solutions, after first deuterating cysteine by recrystallization from $D_2O$.

*Zinc(II) Bis(L-cysteinato)zincate(II), $Zn[Zn(SCH_2CHNH_2CO_2)_2]$ (I).* An aqueous solution of 2.73 g. of zinc chloride (0.02 mole) was added with stirring to a solution of 4.84 g. of L-cysteine (0.04 mole) in 100 ml. of water. The solution was brought to pH 6.0 with dilute ammonium hydroxide solution. A white amorphous precipitate appears at pH around 4.0. Stirring was continued for 1 hr. and the precipitate filtered and washed several times with water. The white powder obtained was heated in 100 ml. of boiling water for 1 hr. with vigorous stirring, and the hot suspension was filtered. After washing with 50 ml. of hot water and absolute ethanol, the white powder was dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_6H_{10}N_2O_4S_2Zn_2$: C, 19.53; H, 2.73; N, 7.59. Found: C, 19.70; H, 2.96; N, 7.29.

Alternatively, this compound can be prepared by warming 0.02 mole of L-cysteine in 100 ml. of water with 0.01 mole of freshly precipitated zinc hydroxide at 60–70° for 2 hr. The white powder obtained is treated in the same way as described above.

*Sodium Bis(L-cysteinato)zincate(II) Tetrahydrate, $Na_2[Zn(SCH_2CHNH_2CO_2)_2]\cdot 4H_2O$ (II).* To a suspension of 2.54 g. of $Zn_2(SCH_2CHNH_2CO_2)_2$ (0.01 mole) in 50 ml. of water was added .with stirring 10 ml. of 2.0 N sodium hydroxide solution (0.02 mole).

(19) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).

Stirring was continued for 1 hr. and the colloidal precipitate of zinc hydroxide filtered out. The filtrate was evaporated to dryness under reduced pressure at room temperature; the white residue was recrystallized from 1:1 ethanol–water. The fine white needles were dried *in vacuo* over $P_2O_5$. *Anal.* Calcd. for $C_6H_{18}N_2S_2O_8ZnNa_2$: C, 17.09; H, 4.30; N, 6.64. Found: C, 16.82; H, 4.71; N, 6.62.

The same compound was isolated from a solution of 0.02 mole of L-cysteine and 0.01 mole of zinc chloride in 20 ml. of 2.0 N sodium hydroxide (0.04 mole). A white precipitate which at once appears is soon dissolved by stirring. The solution was evaporated to dryness and the residue recrystallized from ethanol–water repeatedly.

*Tetrakis(L-cysteinato)trizinc(II) Tetrachlorozincate-(II), $[Zn\{Zn(SCH_2CHNH_3CO_2)_2\}_2][ZnCl_4]$.* L-Cysteine (4.84 g., 0.04 mole) was dissolved in 50 ml. of warm water and to it was added with stirring a warm solution of 5.46 g. of zinc chloride (0.04 mole) in a small amount of water. After 2 hr., formation of white crystals was observed. The pH of the solution was around 2.0. Stirring was continued for an additional 3 hr.; the crystals were filtered and washed with water and absolute ethanol and dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_{12}H_{24}N_4S_4O_8Cl_4Zn_4\cdot 4H_2O$: C, 15.08; H, 3.37; N, 5.86; Cl, 14.83. Found: C, 14.90; H, 3.54; N, 5.92; Cl, 14.63.

The anhydrous compound was obtained by drying *in vacuo* at 70° over $P_2O_5$ under continuous pumping. *Anal.* Calcd. for $C_{12}H_{24}N_4S_4O_8Cl_4Zn_4$: C, 16.31; H, 2.74; N, 6.34. Found: C, 16.35; H, 2.98; N, 6.12.

This compound was converted to I by heating in water at 100° for 1 hr.

The corresponding bromide salt was isolated with some difficulty from a concentrated solution of 2.42 g. of L-cysteine (0.02 mole) and 4.5 g. of zinc bromide (0.02 mole) in 20 ml. of water. Stirring was continued for several hours; several drops of 2.0 N sodium hydroxide solution were added to promote precipitation (pH 2.0). By allowing the solution to stand overnight, white crystals were deposited; these were filtered, washed several times with water and absolute ethanol, and dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_{12}H_{24}N_4S_4O_8Br_4Zn_4$: C, 12.71; H, 2.84; N, 4.94. Found: C, 12.69; H, 2.86; N, 5.22.

*Tetrakis(L-cysteinato)tricadmium(II) Tetrachlorocadmate(II), $[Cd\{Cd(SCH_2CHNH_3CO_2)_2\}_2][CdCl_4]$.* L-Cysteine (4.84 g., 0.04 mole) was dissolved in 100 ml. of warm water and to it was added with stirring a warm solution of 7.32 g. of cadmium chloride (0.04 mole) in a small amount of water. A white precipitate appeared almost immediately. Stirring was continued for 2 hr. and the precipitate was filtered, washed several times with water and finally with absolute ethanol, and dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_{12}H_{24}N_4S_4O_8Cl_4Cd_4\cdot 4H_2O$: C, 12.60; H, 2.82; N, 4.90; Cl, 12.39. Found: C, 12.70; H, 2.67; N, 4.77; Cl, 12.28.

The anhydrous compound was obtained by drying *in vacuo* at 70° over $P_2O_5$ under continuous pumping. *Anal.* Calcd. for $C_{12}H_{24}N_4S_4O_8Cl_4Cd_4$: C, 13.44; H, 2.26; N, 5.23. Found: C, 13.58; H, 2.39; N, 5.21.

*Bis(methyl-L-cysteinato)zinc(II), Zn(SCH₂CHNH₂-*
$Bis(methyl$-L-$cysteinato)zinc(II),$ $Zn(SCH_2CHNH_2$-$CO_2CH_3)_2$ *(III).* Methyl L-cysteinate hydrochloride (1.72 g., 0.01 mole) was dissolved in a solution of 0.8 g. of sodium hydroxide (0.02 mole) in 50 ml. of water at 0°; to it was added with vigorous stirring a cold aqueous solution of 0.68 g. of zinc chloride (0.005 mole). The white precipitate formed was quickly filtered, washed three times with cold water, and recrystallized from a small amount of hot water. The white fine crystals were dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_8H_{16}N_2S_2O_4Zn$: C, 28.79; H, 4.83; N, 8.39. Found: C, 28.84; H, 4.81; N, 8.59.

$Bis(S$-$methyl$-L-$cysteinato)zinc(II),$ $Zn(CH_3SCH_2$-$CHNH_2CO_2)_2$ *(IV).* S-Methyl-L-cysteine (1.35 g., 0.01 mole) was dissolved in a solution of 0.4 g. of sodium hydroxide (0.01 mole) in 50 ml. of water; to it was added with stirring an aqueous solution of 0.68 g. of zinc chloride (0.005 mole). A white precipitate began to form soon after the addition. After stirring for 2 hr., the precipitate was filtered, washed several times with water until the filtrate gave a negative chloride test, and dried *in vacuo* over $CaCl_2$. *Anal.* Calcd. for $C_6H_{16}N_2S_2O_4Zn$: C, 28.79; H, 4.83; N, 8.39. Found: C, 28.63; H, 5.09; N, 8.30.

# Synthesis, Structure, and Bonding of Complexes of Dimethyl- and Diphenyltin Ions With Bidentate Ligands[1]

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*A series of coordination compounds of the general type $R_2SnL_2$ (R = methyl or phenyl; HL = 2,4-pentane-dione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-pro-panedione, picolinic acid, and 8-hydroxyquinoline) has been synthesized. Data are also reported for solutions of the complex with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Studies of the infrared and Raman crystal and solution spectra together with proton n.m.r. measurements indicate that the bis(2,4-pentanediono)dimethyltin complex has the trans configuration, and vibrational assignments are made for this complex. The same structure is indicated by the infrared and n.m.r. spectra for the other complexes with β-diketones. For these trans octahedral complexes, a direct correlation is observed between the tin–methyl proton coupling constants and tin–oxygen bond strength deduced from the spectral data. The vibrational spectra and proton chemical shifts of the chelated acetylacetonato ligands are very similar to those observed in other acetylacetonates. The structure and bonding in these complexes is compared with that for the trans-aquodimethyltin(IV) cation and the trans-tetrahydroxidodimethylstannate(IV) anion where the structures have been established. The picolinato and 8-hydroxyquinolinato ligands appear to be coordinated primarily through the oxygen atoms.*

## Introduction

Several years ago, it was noted that the dimethyltin cation $[(CH_3)_2Sn(aq)]^{+2}$ was rather stable and behaved in aqueous solution very much like the tin(II) ion.[3]

More recently, there has been some discussion in the literature concerning the existence of cations of the type $R_2Sn^{+2}$ in various compounds. It was suggested that dimethyltin formate contained linear $CH_3$–Sn–$CH_3^{+2}$ ions, since but one infrared active vibration was observed in the tin–carbon stretching region.[4] It was also suggested that interactions between the dimethyltin cation and the formate anions were very weak, because there were only slight differences in the carbonyl stretching region between the infrared spectra of sodium formate and dimethyltin formate. It was pointed out by Beattie and Gilson that the effective symmetry of a free and of a bridging carboxylate ion is the same, and the bands in the carbonyl stretching region could be explained equally well with a model involving bridging carboxylate groups.[5]

The question of whether dialkyltin cations exist or not is essentially one of semantics. In solution $[(CH_3)_2Sn(aq)]^{+2}$ behaves much like other divalent cations. On the other hand, most multivalent ions in complexes containing nitrogen or oxygen donor atoms form bonds with sufficient covalent character to give metal–ligand vibrations detectable in the Raman and infrared spectra. Using this as a criterion for the nonexistence of free ions, one is hard pressed to find free cations in compounds with other than alkali or alkaline earth ions.

Recent Raman, infrared, and n.m.r. studies on aqueous solutions of dimethyltin compounds have shown that the linear $CH_3$–Sn–$CH_3^{+2}$ structure exists in these solutions.[6] It would be expected that four water oxygens would coordinate to the tin atom in a

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