# Polynuclear and Mononuclear Complex Formation between Indium(III) and Sulfhydryl-containing Bidentate Ligands

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The various physico-chemical studies were made on the complex-formation equilibria between In(III) and sulfhydryl-containing bidentate ligands, such as 2-aminoethanethiol (2-mercaptoethylamine, MEA), 3-mercaptopropionic acid (MPA), and mercaptoacetic acid (thioglycolic acid, TGA). The insoluble and stable complex, $InL_3$, was formed during the titration of the MEA–In(III) solution. The complex formation of In(III) with MPA and TGA was investigated by potentiometric titration over a wide range of the metal concentration. Calculation of the titration data of the MPA–In(III) system indicated that MPA formed the $In_2L_2$, $In_3L_4$, and $In_3(OH)L_4$ species together with the mononuclear species. In the higher concentration, non-charged species, $In_3(OH)L_4$, was precipitated. In the alkaline solution, the carboxyl group was eliminated from the coordination sphere and the $InL_4$ species was formed. These observations in the MPA–In(III) system were similar to those of the cysteine case. Since TGA forms the stable complex with five-membered chelate ring, the $InL_4$ or hydrolyzed species were not formed even in the alkaline solution. Calculation indicated the formation of the $InL_3$, $In_2L_3$, and $In_3L_6$ species in the TGA system.

Keywords——In(III) complex; 2-aminoethanethiol; 3-mercaptopropionic acid; mercaptoacetic acid; sulfur-bridged polynuclear complex; potentiometric titration; non-linear least-squares computer calculation; IR spectra; UV spectra; PMR spectra

Metal ions involving an almost filled d electron shell readily form the sulfur–bridged polynuclear complexes. Examples include the complexes of 2-aminoethanethiol(2-mercapto-ethylamine, MEA) with Ni(II), Pd(II), Co(II), and Cd(II),[2] of mercaptoacetic acid(thiogly-colic acid, TGA) with Ni(II)[3,4] and Zn(II),[3] and of 3-mercaptopropionic acid(MPA) with Co(II).[5] The preceding paper has clarified that In(III) forms the sulfur-bridged trimeric complex with a terdentate ligand, cysteine, under certain conditions.[6] Sarin and Munshi calculated the stability constants of the In(III) complexes with sulfhydryl-containing bidentate ligands, such as TGA[7] and MPA,[8] from potentiometric data on the assumption that only the mononuclear species is present. The validity of this assumption should be tested by pH measurements over a wide range of the metal ion concentration.

The present work was carried out in order to re-examine the complex formation of In(III) with MEA, MPA, and TGA.

## Experimental

**Materials**——TGA and MPA (Dojindo Laboratories, Kumamoto) were purified by vacuum distillation as described by Leussing and Kolthoff,[9] and by Yamaguchi and Ueno,[10] respectively. The distilled reagents

1) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606 Japan.*
2) D.C. Jicha and D.H. Busch, *Inorg. Chem.*, 1, 872 (1962).
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9) D.L. Leussing and I.M. Kolthoff, *J. Electrochem. Soc.*, 100, 334 (1953).
10) K. Yamaguchi and K. Ueno, *Talanta*, 10, 1195 (1963).

were stored at 0° under nitrogen atmosphere. TGA, MPA, and MEA·HCl were dissolved in air-free water and standardized by the iodometry of the sulfhydryl group.[9] The standard metal ion solution for pH titration was prepared and standardized in the manner previously described.[6] The carbonate-free standard KOH solutions were made by removing the carbonate with $Ba(OH)_2$, followed by the treatment with cation exchanger, Dowex 50 W×8 (100—200 mesh). The amount of the barium ion in the solutions was confirmed to be negligible with calcein. Standardization of the solutions was made by a conventional method. All other reagents used were of a reagent grade.

　　Spectral Measurements——The infrared (IR) spectra were measured by the use of a Hitachi grating infrared spectrophotometer, model 215. The optical spectra were recorded with a Shimadzu recording spectrophotometer, model Double 40-R. Sample solutions were titrated with 1 M KOH. The proton magnetic resonance (PMR) spectra were obtained by the use of a Varian A-60 nuclear magnetic resonance (NMR) spectrometer, and the chemical shifts were determined with sodium 3-(trimethylsilyl)propionate-2,2,4,4-$d_4$ as the internal standard.

　　Titration Procedure——Mixtures of the metal ion and ligands were titrated with standard carbonate-free KOH solutions (1.001 and 0.1003 M) under nitrogen atmosphere. Four titrations were performed with the total metal ion concentrations of 0.004, 0.002, 0.001, and 0.0005 M where no hydrolytic polymerization of the In(III) ion occurs below pH 3.[11] An initial concentration of total ligand was five times of that of the metal ion. Total volume was adjusted to 20.00 ml. In order to keep the activity coefficient as constant as possible, all solutions were prepared in 0.5 M $KNO_3$. The pH was measured at 20±0.05° as described previously.[12] A non-linear least-squares computer program[12] was used for the calculation of the formation constants $(\beta_{pqr}=[M_pH_qL_r]/[M]^p[H]^q[L]^r)$. The values of $pK_w=14.165$ and $f_{\pm}=0.93$ were obtained from the titration data for 0.025 M $HNO_3$ ($I=0.5$ ($KNO_3$), 20°) and used in the calculation. The calculations were carried out on a FACOM M-190 computer, Kyoto University.

## Results and Discussion

### Proton-Ligand Systems

　　The proton-ligand systems were studied by titrating solutions containing the protonated ligands (0.025 M) in the presence of 0.5 M $KNO_3$ with standard 1 M KOH. The acid dissociation constants were refined by the non-linear computer program, using the recently reported values shown in Table I. The resulting values summarized in Table I were used for the evaluation.

TABLE I. Acid Dissociation Constants

|  | Ionic strength | Temp. (°C) | $pK_{a_1}$ | $pK_{a_2}$ | Ref. |
|---|---|---|---|---|---|
| 2-Aminoethanethiol | 0.5M $KNO_3$ | 20 | 8.39 | 10.81 | This work |
|  | 0.1M $KNO_3$ | 25 | 8.19 | 10.73 | 13 |
| 3-Mercaptopropionic acid | 0.5M $KNO_3$ | 20 | 4.20 | 10.31 | This work |
|  | 0.1M $NaClO_4$ | 25 | 4.14 | 10.32 | 8 |
| Mercaptoacetic acid | 0.5M $KNO_3$ | 20 | 3.52 | 10.19 | This work |
|  | 0.1M $NaClO_4$ | 20 | 3.516 | 10.203 | 3 |
|  | 0.5M $KNO_3$ | 25 | 3.548 | 10.048 | 4 |

of the formation constants of the In(III) complexes. Estimated standard deviations for each $pK_a$ values were less than 0.01.

### 2-Aminoethanethiol-In(III) System

　　Insoluble complex was formed during the titration of the MEA–In(III) solution. Hence, only the lower pH region of the titration curve was used for the calculation in order to preclude error due to the precipitation. The obtained value of log $K_1=13.94\pm0.08$ is slightly lower than that(14.12) of the corresponding cysteine complex(S N O coordination). The precipitate was isolated and dried under reduced pressure over $P_2O_5$. In its IR spectrum, the SH(2500

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12) N. Kojima, Y. Sugiura, and H. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 1294 (1976).
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$cm^{-1}$) and $NH^+_3$(1950 $cm^{-1}$) absorptions of the ligand disappeared, indicating the coordination to In(III) through sulfur and nitrogen atoms. The charge-transfer band[12] based on the $In<^S_N)$ bond was observed at 215 nm (shoulder). These results and elemental analysis indicate the formation of the non-charged octahedral complex, $InL_3$, at the end of the titration: Found: C, 20.89; H, 5.13; N, 12.31; In, 32.22%. Calcd. for $[In(SCH_2CH_2NH_2)_3]$: C, 21.00; H, 5.29; N, 12.24; In, 33.45%.

### 3-Mercaptopropionic Acid–In(III) System

When the total concentration of the metal ion exceed 0.1 M, a white precipitate was observed during the titration of the 5:1 ligand–In(III) solution. Under the metal ion concentration of 0.2 M, the precipitate was formed at pH 2.7 and redissolved at pH 4. It was distinguishable from the precipitate of $In(OH)_3$, which occurred at pH 3.4 in 0.2 M indium sulfate solution. The product was isolated at pH 3, where the carboxyl group of the free ligand is almost protonated. IR data summarized in Table II indicate the coordination of the

TABLE II. Infrared Spectra of 3-Mercaptopropionic Acid (MPA)
and Isolated MPA-In (III) Complex ($cm^{-1}$)[a]

|  | SH str. | C=O str. | COO⁻ as. str | COO⁻ sym. str. | CO str.+OH bend |
|---|---|---|---|---|---|
| MPA | 2560(w) | 1710(s) |  |  | 1420(m) |
| MPA-In |  |  | 1530(s) | 1430(s) |  |

*a*) Intensity designations: s, strong; m, medium; w, weak.

ligand to In(III) through the carboxyl and sulfhydryl groups. Moreover, *N*-acetyl-DL-penicillamine, whose methyl groups sterically hinder the formation of sulfur bridge, formed no precipitate. These observations suggest that the insoluble complex is neither a non-charged protonated (for example, In(HL)L) nor 1:1 hydrolyzed species(for example, In(OH)L), but some non-charged sulfur-bridged polynuclear species. Elemental analysis on the isolated complex showed that the metal to ligand ratio was 1:1.3: Found: C, 18.14; H, 2.55; In, 43.57%. Calcd. for $[In_3(SCH_2CH_2CO_2)_4(OH)]$: C, 18.53; H, 2.20; In, 44.28%. Since absorption maximum of the charge-transfer band based on the $In<^S_O)$ bond appears at <200 nm,
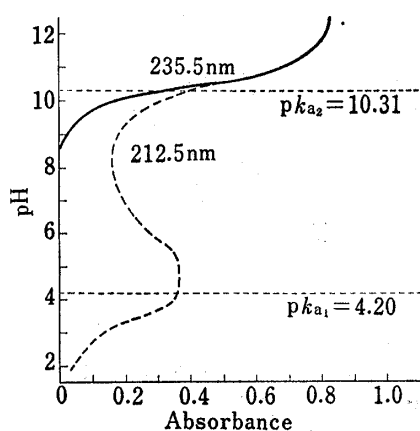


Fig. 1. Spectrophotometric Titration Curves for Mercaptoacetic Acid (0.00016M) with (Dotted Line) or without (Solid Line) In (III) (0.000032M)
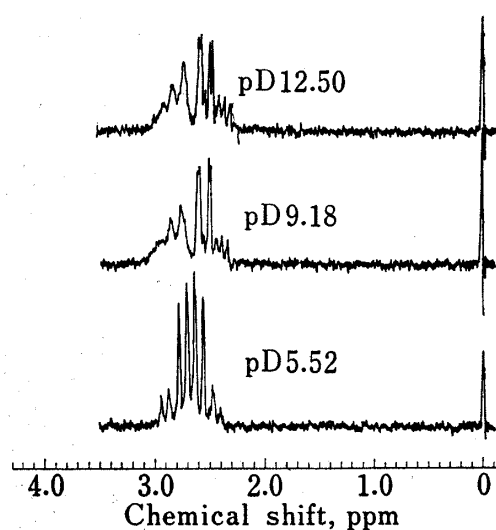


Fig. 2. PMR Spectra of the 3-Mercaptopropionic Acid (0.5M)-In(III) (0.1M) System

absorbance at 212.5 nm was plotted against pH(Fig. 1, dotted line). The absorption at 235.5 nm is based on the form of $RS^-$ ion. Although no precipitate occurred in the low concentration, the absorbance increased at about pH 4, which corresponds to the pH region of the precipitate formation in the highly concentrated solution. The increase of the absorbance is based on the turbidity which suggests the formation of the polynuclear species even in the solution of the lower concentration.

Figure 2 shows the PMR spectra of the 5:1 MPA–In(III)(0.1 M) system. The signals of the two methylene groups, which are symmetrical over the wide pD region in the metal-free solution, became unsymmetrical in the metal solution with an increase in the pD, indicating non-equivalence of the groups in the alkaline solution. This observation suggests the elimination of the carboxyl group from the coordination sphere, since the sulfhydryl group coordinates to In(III) more strongly than the carboxyl group. Figure 3 shows the titration curves of the 4:1 and 5:1 MPA–In(III)(0.1 M) solutions. The pH inflections at about pH 6 indicate the
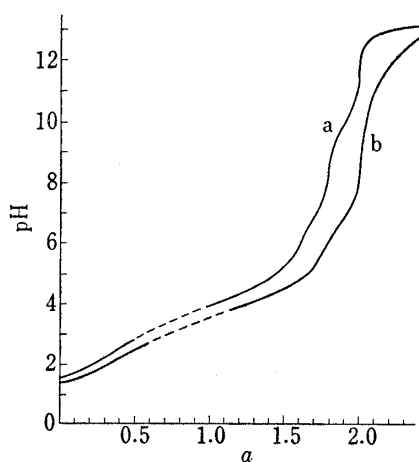


Fig. 3. Titration Curves of 3-Mer-
captopropionic Acid(0.5M(a) and
0.4M(b)) with In(III) (0.1M)
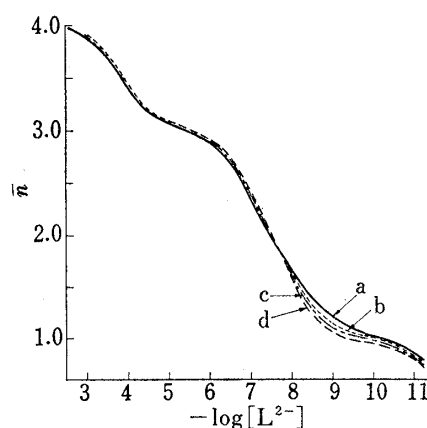
Dotted lines indicate the precipitations.



Fig. 4. Formation Curves of the
In(III) Complex with 3-Mercapto-
propionic Acid

Total metal concentrations are 0.004(a),
0.002(b), 0.001(c), and 0.0005M(d), respe-
ctively.

formation of the $InL_3$ species. Additional proton liberation in the higher pH region($>$pH 6) is related to the unsymmetric PMR signals and indicates the coordination of the fourth molecule of the ligand. The $OH^-$ ion does not coordinate because the last pH inflections appear at $a=2$. The pH inflection at $a=2$ in the 4:1 solution indicates the absence of the $InL_5$ species, which was formed in the reaction of In(III) with more bulky ligand, $N$-acetyl-L-cysteine. The pH inflections at $a=1.6$, 1.8, and 2.0 in the 5:1 solution reflect the formation of the $InL_3$ and $InL_4$ species and the dissociation of the sulfhydryl group of the free ligand, respectively. The structure of the $InL_4$ species is proposed as shown in Chart 1.



Chart 1
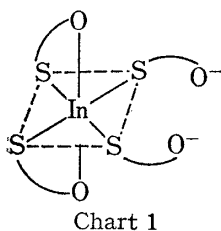
Potentiometric titrations over a wide range of the metal ion concentration were carried out to check on the formation of polynuclear species. The formation curves were calculated without assuming the formation of any hydrolyzed and protonated complexes (Fig. 4). The value of $\bar{n}_{max}=4$ supports the formation of the $InL_4$ species mentioned above. Sarin and Munshi[8] also overlooked this region. Failure in superimposing the curves one another for $\bar{n}<2$, where the precipitate is formed at the higher concentration, suggests the formation of the protonated, hydrolyzed, and/or polynuclear complexes. If a so-called "core plus links"

system[14] of general formula $In(InL_t)_n$ forms in the solution, the value of $t=2$ can be calcu-lated from the spacing of the curves.

Among the possible species of about 20, the chemical models of Trials 1—7 (Table III)

TABLE III.  Values (Logarithmic Units) of the Formation Constants in the Successive Trials
for the 3-Mercaptopropionic Acid(0.02M)–In(III) (0.004M) System[a]

| Trial | Complex species | | | | | | | | | Std.Dev. in Titre (ml) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | InL | $InL_2$ | $InL_3$ | $InL_4$ | In(OH)L | $In(OH)L_3$ | $In_2I_2$ | $In_3L_4$ | $In_3(OH)L_4$ | |
| 1 | 11.739 (0.084) | 20.03 (0.12) | 26.76 (0.20) | | | 17.73 (0.26) | | | | 0.017 |
| 2 | 11.722 (0.086) | 19.82 (0.35) | 26.80 (0.20) | | 7.38 (0.53) | 17.78 (0.26) | | | | 0.017 |
| 3 | 11.723 (0.013) | 20.015 (0.020) | 26.732 (0.029) | 30.610 (0.038) | | | | | | 0.0028 |
| 4 | 11.704 (0.008) | 19.793 (0.036) | 26.772 (0.017) | 30.644 (0.023) | 7.380 (0.050) | | | | | 0.0017 |
| 5 | | 19.956 (0.034) | 26.530 (0.046) | 30.398 (0.080) | | | 25.774 (0.046) | | | 0.0058 |
| 6 | | 19.08 (0.29) | 26.618 (0.036) | 30.477 (0.045) | 7.664 (0.047) | | 25.728 (0.027) | | | 0.0033 |
| 7 | | 19.915 (0.026) | 26.666 (0.026) | 30.528 (0.034) | | | 25.767 (0.019) | 48.606 (0.079) | 44.03 (0.20) | 0.0024 |

$a$ )  Standard deviations in parentheses.

gave relatively good data fits.  As can be seen in Trials 1 and 2, the $In(OH)L_3$ species did not give better fit.  Accordingly, the $InL_4$ species is acceptable in the alkaline solution, as predicted.  Although Trial 4 gave the best fit of all Trials investigated, the presence of the non-charged In(OH)L species was indicated over the wide pH range.  This is incompatible with the fact that the insoluble complex is formed in the narrow pH region.  Inclusion of the polynuclear complexes with the $InL_2$ "core", gave a fairly good fit to the experimental data (Trial 7).  Since the introduction of InL into Trial 7 led to non-convergence, the InL species was ignored.  The fit was not improved by inclusion of the series of the $In(InL_2)_n$ complexes. The species-distribution as a function of pH was calculated from Trial 7(Fig. 5).  The pH range where the $In_3(OH)L_4$ species is formed, seen in Fig. 5, is reasonable and the species is consistent with the result of elemental analysis of the precipitate.  This complex is considered to precipitate at the higher concentration because it is non-charged.  In addition, the effect of the hydrolysis of the In(III) ion is negligible since the amount of the free metal ion is negligibly small at pH 3.  Actually, the result was not affected by the introduction of the hydrolysis constants of In(III) to the calculation.

These results are analogous to those obtained in the cysteine-In(III) system, where the insoluble trimer is formed, and the coordination of S N O type is coverted to that of S N type in the alkaline solution.[6]

### Mercaptoacetic Acid–In(III) System

In the mercaptosuccinic acid–In(III) system, the species formed at the end of the titra-tion was not $InL_2$(O S O coordination type) but $InL_3$ which has five-membered chelate ring (S O type).  Hence, the five-membered ring is more favorable than the six-membered.  Figure 6 indicates that the TGA complex which is a five-membered chelate is stable.  The $\bar{n}$ value is already more than 1 before addition of alkali, indicating the complexation.  Moreover, the $InL_4$ species was absent even in the alkaline solution.

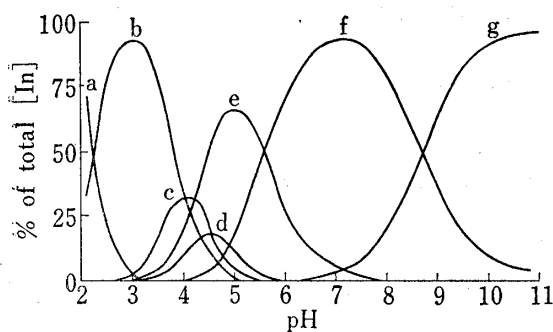14) L.G. Sillen, *Acta Chem. Scand.*, **8**, 299 (1954).

Fig. 5.  Variation with pH of the Percentage
of In(III) Bound in the Form of the Various
Complexes in the 3-Mercaptopropionic Acid
(0.02M)-In(III) (0.004M) System

(a), In$^{3+}$; (b), In$_2$L$_2$; (c), In$_3$L$_4$; (d), In$_3$(OH)L$_4$;
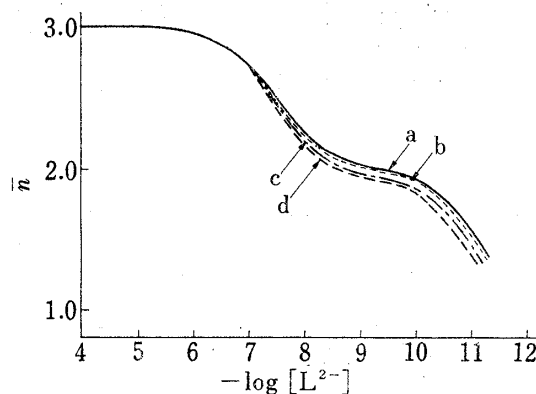(e), InL$_2$; (f), InL$_3$; (g), InL$_4$.



Fig. 6.  Formation Curves of the In(III)
Complex with Mercaptoacetic Acid

Total metal concentrations are 0.004 (a), 0.002 (b),
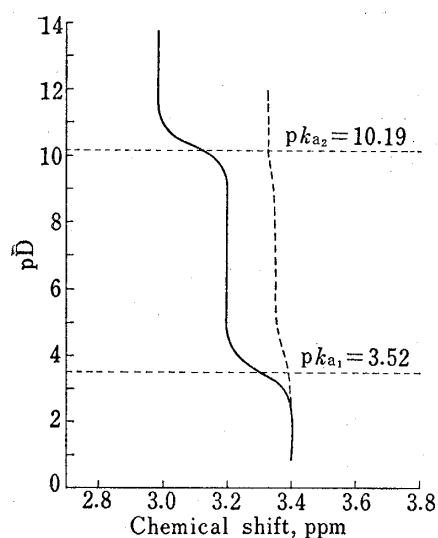0.002 (b), 0.001 (c), and 0.0005M (d), respectively.



Fig. 7.  Chemical Shift Behavior of
Mercaptoacetic Acid (0.5M) with
(Dotted Line) or without(Solid
Line) In(III) (0.16M)

A set of parallel curves cannot be reproduced by
the simple chemical model of InL, InL$_2$, and InL$_3$.  Al-
though in the region of $\bar{n}>2.5$ the mononuclear InL$_3$
species might be formed, the formation of polynuclear
or hydrolyzed species is suggested in the lower $\bar{n}$
region.  The data fit was not improved by the introduc-
tion of the hydrolyzed species, such as In(OH)L and
In(OH)L$_2$.  The calculated value of $t$ was 3 in the In-
(InL$_t$)$_n$ complex.  Among the series of the polynuclear
In(InL$_3$)$_n$ species, the In$_2$L$_3$ and In$_3$L$_6$ complexes fitted
the data whereas the inclusion of the species of $n \geqq 3$
did not significantly improve the fit.  The possible
species and their formation constants are as follows:
InL$_3$(30.59±0.05), In$_2$L$_3$(37.95±0.05), and In$_3$L$_6$(74.10
±0.08).  The formation constant of InL$_3$ is more stable
by 4 log units than that(26.67) of the corresponding
MPA complex.

As shown in Fig. 7 (dotted line), the chemical
shifts of the methylene protons are almost constant
at various pD values.  The result indicates that the
carboxyl group coordinates to the metal ion in the polynuclear species.

In conclusion, the re-examination of the complex formation between the sulfhydryl-
containing bidentate ligands and In(III) revealed the presence of the polynuclear complex
species together with the mononuclear species.