# Ternary Coordination Complexes Formed by Copper(II) with Thio- or Dithiodialkanoic Acids and Some Selected Ethyl-substituted Malonic Acids*

D. N. Shelke
*Chemistry Department, Marathwada University, Aurangabad 431004, India*

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Binary and ternary complexes formed by copper(II) with thio- or dithiodialkanoic acids and ethyl-substituted malonic acids have been investigated potentiometrically in an aqueous solution and the relevant stability constants have been evaluated using computer technique. Thio- and dithiodialkanoic acids were thiodiacetic, dithiodiacetic, 3,3′-thiodipropionic, and 3,3′-dithiodipropionic acids. The results are discussed in terms of substituent influences upon the chelation of the malonate dianions to the systems copper(II)–thiodialkanoic acids. It is suggested that in the mixed copper chelates containing thiodiacetic acid, the geometrical characteristics of the more basic ligand, governs the coordination of the other ligand.

The study of the coordination chemistry of transition metal complexes with thiodialkanoic (CT) acid ligands has received much attention in recent years and the applications of such complexes to a wide variety of problems of structure, bonding and mechanism are considerable. Initially the major attention was focussed to tridentate thiodialkanoic acids but now, with the advent of X-ray data, interest has been extended to ligands of greater or smaller denticity[1–3]. As part of our interest[4] in the bonding sites of thiodialkanoic aicds in mixed-ligand complexes, we have examined the coordinating tendencies of thiodialkanoic acids to the metal ions on the basis of thermodynamic parameters. We report here, in addition to a few data for binary complexes already reported[5–7], the equilibrium studies on mixed-ligand complex formation occurring, when copper(II) is mixed with thiodialkanoic acids and ethyl-substituted malonic acids. The mode of bonding in the ternary complex species involved is also examined.

## Experimental

The ligands thiodiacetic acid (AT), dithiodiacetic acid (ADT), 3,3′-thiodipropionic acid (PT), 3,3′-dithiodipropionic acid (PDT), ethylmalonic and diethylmalonic (L) acids were obtained from Fluka (purum) or B.D.H. (AnalaR) and were used without purification. Metal ion was added as copper perchlorate and the concentration was estimated by EDTA titration.[8] All solutions were prepared in glass distilled water (pH=6.8 and conductivity=$1.6\times10^{-6}$ Mho). Details regarding other chemicals and the measurements have been described previously.[9,10]

Copper complex formation constants were evaluated from potentiometric titration curves of thiodialkanoic (CT) and ethyl-substituted malonic acids in the absence and presence of copper(II). Changes in pH were followed using glass and calomel electrodes and a ELICO Digital pH meter (L1-10 No. 1275). The accuracy of the pH meter was ±0.01 pH Unit. The glass electrode was calibrated in terms of hydrogen ion concentrations and titrations were carried out at 30 °C with an ionic background of 0.10 mol dm$^{-3}$ ($NaClO_4$). Calculations were made with the aid of a computer programme[11] and carried out at the Tata Institute of Fundamental Research, Bombay.

## Results and Discussion

The protonation constants of the thiodialkanoic acids and ethyl-substituted malonic acids and the formation constants of copper(II) mono- and bis-complexes with these acids are presented in Table 1. The errors in the data obtained for the formation constants of binary and ternary systems were estimated to be 1±0.05 log units. Besides the direct experimental errors, the standard deviation of the equilibrium constants were between 0.01 and 0.05 for the systems studied. A representative data *i.e.*, copper(II)–ADT–ethylmalonic acid system, explains adequately the precision of the work (Table 2).

The overall stability constants $\beta^{Cu}_{Cu(CT)L}$ of the ternary complexes, together with the stability constants $K^{Cu(CT)}_{Cu(CT)L}$ and $K^{CuL}_{CuL(CT)}$, according to the following expression:

$$Cu + CT + L \rightleftharpoons Cu(CT)L\ ,$$

$$\beta^{Cu}_{Cu(CT)L} = \frac{[Cu(CT)L]}{[Cu][(CT)][L]}\ ,$$

$$Cu(CT) + L \rightleftharpoons Cu(CT)L\ ,$$

$$K^{Cu(CT)}_{Cu(CT)L} = \frac{[Cu(CT)L]}{[Cu(CT)][L]}\ ,$$

$$CuL + (CT) \rightleftharpoons CuL(CT)\ ,$$

$$K^{CuL}_{CuL(CT)} = \frac{[CuL(CT)]}{[CuL][(CT)]}\ ,$$

Table 1. Logarithms of acidity constants of thiodialkanoic acids (CT) and substituted malonic acids (L) and logarithms of stability constants of their binary complexes with copper(II) at $\mu=0.1$ mol dm$^{-3}$ and 30±0.1 °C

| Ligand | Log ${}^{H}_{H(CT)}$ | Log ${}^{H(CT)}_{H(CT)_2}$ | Log $K^{Cu}_{Cu(CT)}$ | Log $K^{Cu(CT)}_{Cu(CT)_2}$ |
|---|---|---|---|---|
| AT[a)] | 4.28 | 3.08 | 4.58 | 3.20 |
| PT[a)] | 4.93 | 3.87 | 2.55 | — |
| ADT | 3.81 | 2.88 | 3·46 | — |
| PDT | 4.60 | 3.90 | 1.61 | — |
| Ethyl-malonic | 5.48 | 2.85 | 4.95 | 2.82 |
| Diethyl-malonic | 6.96 | 2.02 | 4.94 | 2.74 |

a) From Refs. 4—7.

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Table 2. Logarithms of equilibrium constants of copper(II)-ADT (CT)-ethylmalonic (L) acid system at $C_M = C_{CT} = C_L$, $\mu = 0.1$ mol dm$^{-3}$, and $30 \pm 0.1$ °C

| pH | $[H^+] \times 10^4$ | $\log K^{Cu}_{Cu(CT)L}$ | $\log \beta^{Cu}_{Cu(CT)L}$ | $\log K_r$ | $\log K^{Cu(CT)}_{Cu(CT)L}$ | $\log K^{CuL}_{CuL(CT)}$ |
|---|---|---|---|---|---|---|
| 3.90 | 1.151 | −3.642 | 8.118 | 1.838 | 3.168 | 4.658 |
| 3.95 | 1.349 | −3.643 | 8.117 | 1.837 | 3.167 | 4.657 |
| 4.00 | 1.203 | −3.644 | 8.116 | 1.836 | 3.166 | 4.656 |
| 4.05 | 1.072 | −3.645 | 8.114 | 1.835 | 3.165 | 4.655 |
| 4.10 | 0.955 | −3.646 | 8.114 | 1.834 | 3.164 | 4.654 |
| 4.15 | 0.852 | −3.647 | 8.112 | 1.833 | 3.162 | 4.652 |
| 4.20 | 0.759 | −3.649 | 8.111 | 1.831 | 3.161 | 4.651 |
| 4.25 | 0.676 | −3.645 | 8.113 | 1.834 | 3.165 | 4.654 |
| Average |  | −3.646 | 8.117 | 1.835 | 3.165 | 4.654 |

Table 3. Logariths of stability constants of the ternary complexes Cu(CT)L at $\mu = 0.1$ mol dm$^{-3}$ and $30 \pm 0.1$ °C

| System | $\log \beta^{Cu}_{Cu(CT)L}$ a) | $\log K^{Cu(CT)}_{Cu(CT)L}$ | $\log K^{CuL}_{CuL(CT)}$ |
|---|---|---|---|
| AT-ethylmalonic | 8.93 (1) | 3.98 | 4.35 |
| AT-diethylmalonic | 9.07 (3) | 4.13 | 4.49 |
| PT-ethylmalonic | 7.13 (2) | 2.18 | 4.58 |
| PT-diethylmalonic | 7.16 (4) | 2.22 | 4.61 |
| ADT-ethylmalonic | 8.11 (1) | 3.16 | 4.65 |
| ADT-diethylmalonic | 8.29 (2) | 3.35 | 4.83 |
| PDT-ethylmalonic | 6.42 (3) | 1.48 | 4.81 |
| PDT-dimethyl-malonic | 6.54 (2) | 1.60 | 4.93 |

a) The figures in parentheses are the standard deviations of the last decimal figure.

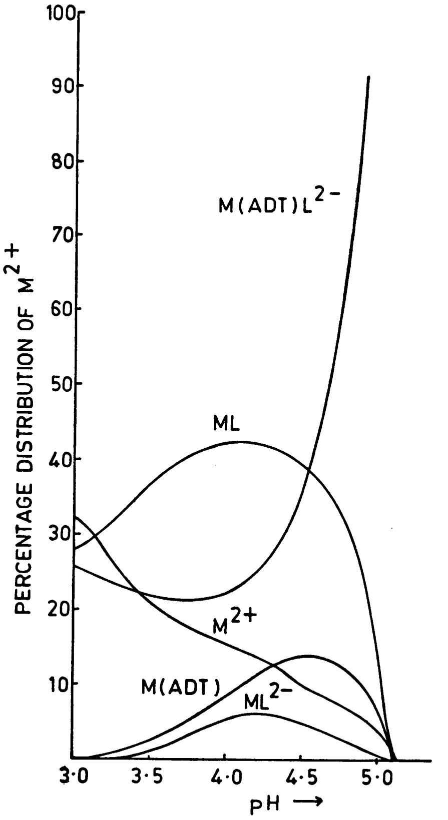


Fig. 1. Percentage distribution of various species present in ternary copper(II)–dithiodiacetic (ADT), ethylmalonic (L) acid system as a function of pH, $M_2^+$= copper ion$_{free}$, ML=copper ion-ethylamlonic, $ML_2^{2-}$= copper ion–(ethylmalonic)$_2$, M(ADT)=copper ion-dithiodiacetic and M (ADT)$L^{2-}$=copper ion-dithiodiacetic-ethylmalonic, $\mu = 0.1$ mol dm$^{-3}$ (NaClO$_4$), Temp=$30 \pm 0.1$ °C, $C_M = C_L = C_{ADT} = 2.0 \times 10^{-3}$ mol dm$^{-3}$.

are presented in Table 3. The percentage distribution of the complexes formed in the copper(II)–dithiodiacetic–(ADT)–ethylmalonic (L) acid systems as a function of pH, is presented in Fig. 1.

In our earlier studies on mixed-ligand complexes, the tridentate nature of AT with copper(II) ion, has been reported.[5] These conclusions have been amply confirmed in subsequent studies involving tridentate thiodialkanoic acids particularly, copper(II) complex of AT.[12,13] The bonding nature of PT with copper (II) through the oxygen of the carboxylato group has been confirmed by Krebs *et al.*[14] by X-ray measurements. The structure consists of centrosymmetric complex unit in which the central Cu$^{II}$ is in tetragonal planar arrangement, of two *trans*-coordinated water molecules and the carboxylato groups of two organic ligands. In view of the above, our potentiometric studies and observed stability constants (Table 1) suggest that PT and PDT bond through the oxygen atom of the carboxylato group whereas AT is coordinated through both oxygen atoms of the carboxylato groups and the sulfur atom. The stability constants obtained for ethylmalonic and diethylmalonic acids are also understandable.

Consequently, no simple relation exists between the stability of the ternary complexes and the basic properties of the dialkanoic acids. In these systems we note the sole formation of the 1 : 1 : 1 ternary species, with stability constant values higher than 0.6 would be expected from statistical considerations[15,16] as is apparent from Table 4, on examining the values of the stabilization parameters log $K_r$ and Δ log $K$, defined by the following expressions:

$$\mathrm{Cu(CT)_2} + \mathrm{CuL_2} \rightleftharpoons 2\mathrm{Cu(CT)L}\ ,$$

$$\log K_r = 2\log \beta^{Cu}_{Cu(CT)L} - (\log \beta^{Cu}_{Cu(CT)_2} + \log \beta^{Cu}_{CuL_2})$$

$$\mathrm{Cu(CT)} + \mathrm{CuL} \rightleftharpoons \mathrm{Cu(CT)L} + \mathrm{Cu}$$

$$\Delta \log K = \log \beta^{Cu}_{Cu(CT)L} - (\log K^{Cu}_{Cu(CT)} + \log K^{Cu}_{CuL}).$$

These results are of the same order of magnitude as

TABLE 4. STABILIZATION PARAMETERS $\Delta \log K$ AND $\log K_r$ FOR TERNARY COMPLEX FORMATION AT $\mu=0.1\ \mathrm{mol\ dm^{-3}}$ AND $30\pm0.1\ ^{\circ}\mathrm{C}$

| System | $-\Delta \log K$ | $\log K_r$ |
|---|---|---|
| AT-ethylmalonic | 0.60 | 2.31 |
| AT-diethylmalonic | 0.46 | 2.55 |
| PT-ethylmalonic | 0.37 | 1.76 |
| PT-diethylmalonic | 0.33 | 1.87 |
| ADT-ethylmalonic | 0.30 | 1.83 |
| ADT-diethylmalonic | 0.11 | 2.09 |
| PDT-ethylmalonic | 0.14 | 1.99 |
| PDT-diethylmalonic | 0.01 | 2.19 |

those for previously studied complexes of copper(II) with thiodialkanoic acids and O–O donor ligands[17] and the following important conclusions may be drawn from the tabulated data.

(a) The $\Delta \log K$ values which are greater than —0.6 (Table 4) indicates the preferential formation of ternary complexes compared to the binary ones. This tendency to form mixed-ligand chelates is the same in the case of PT–ethylmalonic, PT–diethylmalonic and ADT–ethylmalonic acid system wherein $\Delta \log K$ are —0.37, —0.33, and —0.30 respectively.

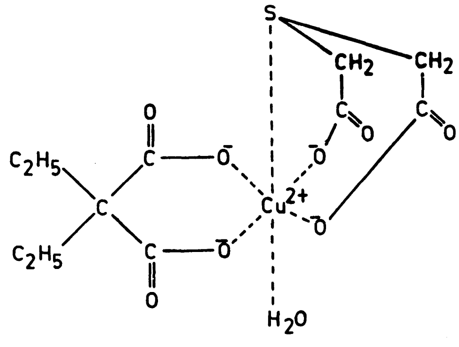
(b) In the systems under investigation, the values of $\log K_r$ are significantly greater than 0.6 log units, demonstrating that the mixed-ligand complexes are more stable than the binary ones.[15]

(c) The introduction of two substituents increases the stability of ternary complexes in proportion to the size of the alkyl groups[18] (Table 3).

(d) The values of $\log K^{\mathrm{Cu(CT)}}_{\mathrm{Cu(CT)L}}$ and $\log K^{\mathrm{CuL}}_{\mathrm{CuL_2}}$ (Table 3) show the preferential formation of the ternary over the binary complexes. A comparison of $\log K^{\mathrm{CuL}}_{\mathrm{CuL(CT)}}$ with $\log K^{\mathrm{Cu(CT)}}_{\mathrm{Cu(CT)_2}}$ values, especially in the systems involving thiodiacetic acid as a secondary ligand, reveals the preferential formation of the ternary complexes over the corresponding binary bis ones.

(e) AT forms mixed complexes of exceptionally high stability with ethylmalonic and diethylmalonic acid because the ligand is coordinated through the thio group and two carboxyl groups. The highest value of $\log K_r$ for the AT–diethylmalonic acid system (2.55) accompanied by the highest stability for a $\log \beta^{\mathrm{Cu}}_{\mathrm{Cu(CT)L}}$ is due to the respective tridentate and bidentate nature of the two ligands. The bidentate diethylmalonic acid ligand occupies an equatorial position while the AT assumes an equatorial-axial coordination as shown in structure (I). The equatorial-axial coordination of AT with $\mathrm{Cu^{II}}$ has been recently reported on the studies of mixed-ligand complexes from X-ray data.[19]

(f) It can be seen from the experimental values of $\beta=^{\mathrm{Cu}}_{\mathrm{Cu(CT)L}}$ and the stabilization parameters $\Delta \log K$ and $\log K_r$ (Tables 3, 4) that the inductive effect of the alkyl group has no great influence on the stability of these systems. The presence of one or two substituents affects the reciprocal coplanarity of the two carboxylato group in different ways, giving rise to a different stability order in both binary and ternary complexes. In particular the presence of two bulky substituents as in the case of Cu(CT) DEt-mal. seems especially to favour the formation of the ternary species, probably by forcing the two carboxylato groups into the best position of chelation.



(Structure I)

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