Structure and Stability of Carboxylate Complexes. Part 18.[1] Stability Constants of the Copper(II) Complexes of Some Thiodialkanoates

By **Francis J. C. Rossotti**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR
Richard J. Whewell,* Schools of Chemical Engineering, University of Bradford, Bradford BD7 1DP

Potentiometric studies of the complexation of Cu^{II} with 2,2′-thiodiacetate, 3,3′-thiodipropanoate, and 4,4′-thiodibutanoate have been carried out at 25.0 °C in a 3 mol dm^{-3} (sodium) perchlorate medium. Two different titration techniques are used which enable alternative methods of calculation of the results to be applied. The results show the formation of 1 : 1 complexes with both the ligand and the monoprotonated ligand in each case, and in addition the 1 : 2 species in the case of thiodiacetate. Combined potentiometric and spectroscopic evidence shows that, in both thiodibutanoate species, the ligand is unidentate through an oxygen-donor atom; the protonated species show increasing bidentate behaviour as the potential chelate-ring size is decreased from seven to five members. In the remaining unprotonated species the ligands are bi- (thiodiacetate) and tri-dentate (thiodipropanoate).

FOLLOWING extensive work on the copper(II) complexes of substituted alkanoates[2] containing one or more oxygen-donor atoms, a number of copper alkanoate systems with one sulphur-donor atom have been studied.[3] This paper reports equilibria between Cu^{II} and the potentially tridentate ligands $S[(CH_2)_xCO_2^-]_2$.

A number of studies of copper thiodiacetate ($x = 1$) has been reported in the literature,[4-8] and cover similar ranges of free-ligand concentration. No two of these studies are even in agreement over the stoicheiometry of the complex species formed, since the species reported are: BA,BA_2;[4] BA;[5] BA,BA_2,BA_3,BA_4;[6] BA,B(HA);[7] and BA,BA_2,B(HA), where B represents the Cu^{II} ion and H_2A the thiodiacid.[8] It is therefore of interest to study the equilibria rigorously and if possible to identify the donor atoms bonding to copper.

EXPERIMENTAL

2,2′-Thiodiacetic acid (B.D.H.) and 3,3′-thiodipropanoic acid (Koch–Light) were recrystallised from water with animal charcoal. 4,4′-Thiodibutanoic acid was prepared according to Gabriel[9] from chlorobutyronitrile and potassium hydrogensulphide, and similarly recrystallised. The purity of the three acids, estimated by potentiometric titation, exceeded 99.5%. AnalaR inorganic reagents were used where available. Working solutions contained $(3 - 2B)$ mol dm^{-3} sodium ion, where B is the concentration of copper(II) ions, in a perchlorate medium.

The apparatus and procedures for potentiometric titration have essentially been described elsewhere.[10,11] In these experiments, the potential of cell (I) was measured at 25.0 ± 0.1 °C with a Radiometer PHM4 pH meter to a precision of 0.1 mV. In titrations including copper, hydrolysis[12] was avoided by maintaining the hydrogen-ion concentration $h > 10^{-4.8}$ mol dm^{-3}. The small corrections for junction potentials[13] were described by equation (1).

$$\begin{array}{c|l:l:l|l} \text{Glass} & \text{Test} & 3\text{ mol dm}^{-3} & 2.99\text{ mol dm}^{-3}\ \text{Na[ClO}_4] & \text{Ag,AgCl} \\ \text{electrode} & \text{solution} & \text{Na[ClO}_4] & 0.01\text{ mol dm}^{-3}\ \text{Ag[ClO}_4] & \end{array} \qquad \text{(I)}$$

$$E_j/\text{mV} = 16.5\ (h/\text{mol dm}^{-3}) \qquad (1)$$

Titration Procedure.—A value of $E^\ominus$ for cell (I) was obtained by titration of perchloric acid (0.01 mol dm^{-3}) with sodium hydroxide (0.06 mol dm^{-3}) in the presence of the appropriate concentration of sodium perchlorate and copper perchlorate when necessary. The titration was discontinued at $h \approx 10^{-3}$ mol dm^{-3}. Calculations using Gran's equation are described elsewhere.[10]

At least two determinations of the protonation constants of the ligands were carried out as described,[10] with initial concentrations of 0.01 and 0.02 mol dm^{-3} thiodiacid. ' Standard ' copper titrations consisted of the addition of partially neutralised thiodiacid (0.02—0.15 mol dm^{-3}) to the copper-containing solution (0.01—0.05 mol dm^{-3}) remaining after the electrode calibration. The limited solubility of copper thiodibutanoate necessitated work at the lower ends of these concentration ranges. Adjustment of the degree of neutralisation of the titrant between 0 and 95% enabled the formation of protonated species B(HA) to be favoured or discouraged relative to the unprotonated species BA. For ' überschuss '[14,15] titrations a solution of $Cu[ClO_4]_2$ and partially neutralised acid was added to the solution after calibration, in such a way as to maintain a constant concentration of copper at a value 15—30 times that of the ligand concentration.

CALCULATION AND RESULTS

The nomenclature of Rossotti and Rossotti[15] is followed; in particular A, B, and H represent the total concentrations of ligand, copper, and dissociable proton, and a, b, and h those of the free ligand, copper ion, and proton respectively.

Protonation Constants.—Values of two overall protonation constants, equation (2), were obtained from the formation

$$\beta_j^{\mathrm{H}} = [\mathrm{H}_j\mathrm{A}]h^{-j}a^{-1} \qquad (2)$$

curves j(log h), equation (3), by using normalised-curve[15] and numerical analytical[16] methods. The formation

$$\bar{j} = (H - h + K_{\mathrm{w}}h^{-1})A^{-1} = (\sum_{j=1} j[\mathrm{H}_j\mathrm{A}])A^{-1} \qquad (3)$$

curves are shown in Figure 1, and the results in Table 1, together with values quoted by other workers.

Copper Complex Stability Constants.—The methods of calculation used have been described elsewhere[11] and only a summary is included here.

' Standard ' titrations. The formation function ($\bar{n}$) and free-ligand concentration, calculated on the assumption that a series of mononuclear species BA_n are formed, gave formation curves levelling off close to $\bar{n} = 2$ (thiodiacetate) and not rising above $\bar{n} = 1$ (thiodipropanoate). Species BA_n with $n \geqslant 3$ are thus not formed under the conditions

studied. Titrations with thiodibutanoate did not exceed $\bar{n} = 0.25$ in view of the limited solubility of the copper complex.

TABLE 1

Protonation constants of the thiodialkanoates. The errors (1σ) quoted are those generated by LINEFITTING [16]

	log β_1^H	log β_2^H	Conditions
(*a*) Thiodiacetate			
This work	4.349 ±0.005	7.808 ±0.01	25 °C, 3.0 mol dm^{-3} Na[ClO$_4$]
Ref. 4	4.29	7.55	30 °C, 0.1 mol dm^{-3} KCl
Ref. 5	4.13	7.28	25 °C, 0.1 mol dm^{-3} Na[ClO$_4$]
Ref. 7	4.35	7.65	20 °C, 0.1 mol dm^{-3} Na[ClO$_4$]
Ref. 8	4.14	7.26	25 °C, 0.1 mol dm^{-3} Na[ClO$_4$]
(*b*) Thiodipropanoate			
This work	4.975 ±0.005	9.334 ±0.01	25 °C, 3.0 mol dm^{-3} Na[ClO$_4$]
Ref. 5	4.66	8.50	25 °C, 0.1 mol dm^{-3} Na[ClO$_4$]
Ref. 7	4.91	9.00	20 °C, 0.1 mol dm^{-3} Na[ClO$_4$]
(*c*) Thiodibutanoate			
This work	5.312 ±0.005	10.010 ±0.01	25 °C, 3.0 mol dm^{-3} Na[ClO$_4$]

The formation curves thus generated were different for titrations performed with solutions having different concentrations. The discrepancies between the formation curves were systematic with hydrogen-ion concentration, suggesting the formation of a protonated species such as B(HA). Preliminary calculations based on the species BA, BA$_2$, and B(HA) were carried out by the iterative method of Irving and Stacey [17] using the formation function in equation (4) and constants defined in (5) and (6). Mathematical difficulties were encountered since the fraction of copper complexed as B(HA) was low.

$$\bar{n} = \frac{(\beta_1 + \beta_{111}h)a + 2\beta_2 a^2}{1 + (\beta_1 + \beta_{111}h)a + \beta_2 a^2} \qquad (4)$$

$$\beta_n = [BA_n]b^{-1}a^{-n} \qquad (5)$$

$$\beta_{111} = [B(HA)]b^{-1}h^{-1}a^{-1} \qquad (6)$$

More satisfactory calculations were performed when the matrix computations of the Irving–Stacey method were replaced by the REFBAH approach.[11] Initial values of β_{111} were used to generate a reduced formation curve $\bar{r}_n$(log a), equation (7), relating only to species BA$_n$, and, conversely, initial values of β_n were used to generate a reduced formation curve $\bar{r}_{111}$(log[HA]), equation (8), relating only to the species B(HA). The reduced formation curves were treated by normalised-curve methods [15] to give improved values of the stability constants. Since good initial estimates of the constants were available from the Irving–Stacey calculations the value of β_2 was not eliminated from a small term in the equation for the free-ligand concentration associated with equation (7).

$$\bar{r}_n = \frac{A - \sum_0^2 [H_jA] - [B(HA)]}{B - [B(HA)]} = \frac{\sum_1^2 n[BA_n]}{\sum_0^2 [BA_n]} \qquad (7)$$

$$\bar{r}_{111} = \frac{[B(HA)]}{b + [B(HA)]} = \frac{B - \sum_0^2 [BA_n]}{B - \sum_1^2 [BA_n]} \qquad (8)$$

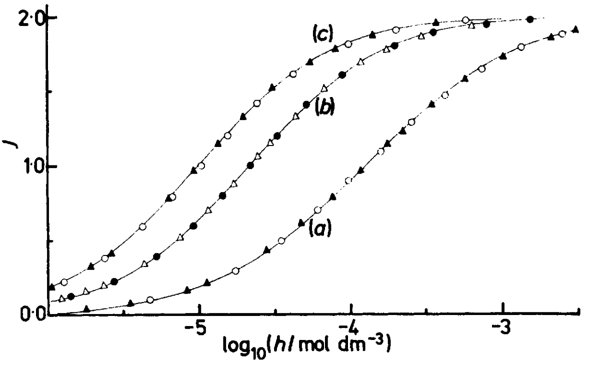

FIGURE 1 Formation curves for the proton complexes of thiodiacetate (*a*), thiodipropanoate (*b*), and thiodibutanoate (*c*). Concentration of thiodiacid: 0.01 (○) or 0.02 mol dm^{-3} (▲). The lines drawn were calculated from the constants in Table 1

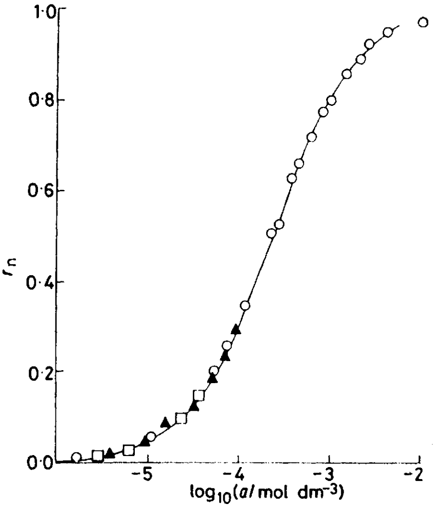

FIGURE 2 Reduced formation curve for the BA$_n$ species of copper thiodipropanoate. The degree of neutralisation of the titrant was adjusted to give pH values of *ca.* 3 (□), 4 (▲), or 5 (○). Randomly selected points from seven titrations are shown; the line drawn was calculated from the constant β_1 in Table 2

The final values of the constants were marked not only by the achievement of mutual consistency in the REFBAH treatment, but also by the reproducibility and midpoint symmetry of the final reduced formation curves. The results are entirely consistent with the formation of two complexes BA and B(HA) in all the three systems, together with the species BA$_2$ in the case of thiodiacetate. The reduced curves for copper thiodipropanoate are shown in Figures 2 and 3, and values of the constants obtained for the three systems are given in Table 2. In view of small discrepancies between copper thiodiacetate formation curves at $\bar{r}_n > 1.5$, the possibility of the higher species B(HA)$_2$ and BA(HA) was investigated briefly; no evidence was found for the former species, but a highly tentative estimate of log ($\beta_{112} = [B(HA)A]b^{-1}h^{-1}a^{-2}$) = 10.8 for the latter results in an improvement in the formation curve $\bar{r}_n$-(log a).

' *Uberschuss* ' *titrations*. Conventional [11,14] calculation generated a curve g(log h), equation (9), which may be solved for two conditional stability constants using the procedures adopted for β_1^{H} and β_2^{H} above and values of β_1 and β_{111} may then be calculated from these. Under the conditions of excess of metal ion employed, only species BA and B(HA) are considered, and approximations $a \ll A$, $b \approx B =$ constant are necessary. The calculation method was less satisfactory for thiodiacetate than for the

$$g = (H - h + K_{\mathrm{w}}h^{-1})A^{-1}$$
$$= \frac{(\beta_1^{\mathrm{H}} + \beta_{111}b)(\beta^1 b)^{-1}h + 2\beta_2^{\mathrm{H}}(\beta_1 b)^{-1}h^2}{1 + (\beta_1^{\mathrm{H}} + \beta_{111}b)(\beta_1 b)^{-1}h + \beta_2^{\mathrm{H}}(\beta_1 b)^{-1}h^2} \quad (9)$$

other ligands, since strong complexation makes the numerator of equation (9) very susceptible to both random and systematic errors, and the determination of approximately equal conditional constants was less reliable than in the other systems. The above calculations were verified using the REFBAH approach.

TABLE 2

Stability constants of the copper thiodialkanoates. The errors quoted were estimated visually from normalised curves. For conditions of titrations see Table 1

	log β_{111}	log β_1	log β_2
(*a*) Thiodiacetate			
This work			
(REFBAH)	6.35 ± 0.10	4.63 ± 0.03	7.86 ± 0.04
(überschuss)	6.50 ± 0.10	4.69 ± 0.04	
Ref. 4		4.5	7.3
Ref. 5		4.3	
Ref. 6 *		4.18	7.08
Ref. 7	7.53	4.57	
Ref. 8	6.77	4.65	7.50
(*b*) Thiodipropanoate			
This work			
(REFBAH)	6.80 ± 0.06	3.64 ± 0.01	
(überschuss)	6.73 ± 0.06	3.66 ± 0.05	
Ref. 5		3.0	
Ref. 7	6.56	2.53	
(*c*) Thiodibutanoate			
This work			
(REFBAH)	7.11 ± 0.05	2.50 ± 0.02	
(überschuss)	7.06 ± 0.10	2.68 ± 0.10	

* At 20 °C and 1.0 mol dm^{-3} Na[ClO$_4$]; log β_3 8.6, log β_4 11.9.

DISCUSSION

Protonation Constants.—The results in Table 1 closely resemble those of other workers. The ratio $K_1^{\mathrm{H}} : K_2^{\mathrm{H}}$ of the stepwise protonation constants, equation (10), is 7.8 for thiodiacetate, but for both thiodipropanoate and

$$K_j^{\mathrm{H}} = [\mathrm{H}_j\mathrm{A}][\mathrm{H}_{j-1}\mathrm{A}]^{-1}h^{-1} \quad (10)$$

thiodibutanoate is 4.1 : 1, close to the statistically expected value. A similar trend [18] of decreasing ratio with increasing x is noted for the series $\mathrm{HO_2C[CH_2]}_x\mathrm{CO_2H}$, but carboxyl interactions persist to considerably higher values of x.

If the values of K_1^{H} (Table 1) are adjusted by a statistical factor of two and compared with the corresponding constants of the monobasic acids [3] (Table 3) then considerable similarity emerges. Thus log K_1^{H} (corrected) for $\mathrm{S[(CH_2)}_x\mathrm{CO_2H]_2}$ is 4.05, 4.68, and 5.01 for $x = 1$, 2, and 3 respectively, and for $\mathrm{MeS[CH_2]}_x\mathrm{CO_2H}$ log K_1^{H} is 4.01, 4.68, and 4.99. Both series tend with increasing x towards the value for an unsubstituted alkanoate such as butanoate [2] (log K_1^{H} 5.13).

Copper Complex Stability Constants.—Work of other authors. Only by carrying out titrations with varying concentrations B and A can species other than the simple mononuclear series BA_n be identified. The absence of such detailed studies readily explains the discordant stability constants quoted in refs. 4 and 5.

The species B(HA) has been identified in both refs. 7 and 8, the latter work being carried out after our study had been completed. Particular discrepancies can, however, be seen between our values and those from überschuss titrations by Campi *et al.*[7] for log β_{111} of copper thiodiacetate and log β_1 of copper thiodipropanoate. No explanation of these discrepancies can be offered, since we have found that überschuss titrations processed in several different ways give results consistent with ' standard ' titrations treated by REFBAH.

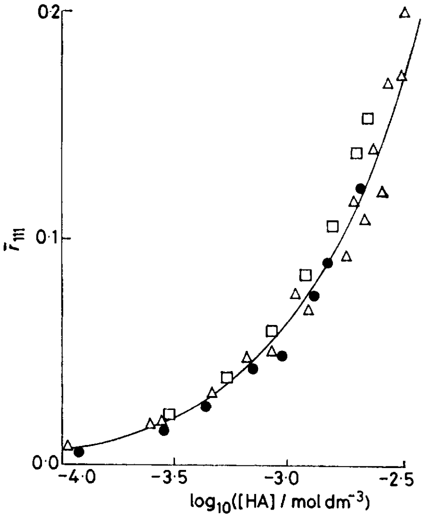

FIGURE 3 Reduced formation curve for the B(HA) species of copper thiodipropanoate. Final pH values were 2 (●), 3 (□), or 4 (△). Randomly selected points from six titrations are shown; the line drawn was calculated from the constant β_{111} in Table 2

Sandell[6] is unique in postulating the existence of species BA_n with $n > 2$ in the thiodiacetate system. At $a = 10^{-2}$ mol dm^{-3} a value of $\bar{n} \approx 3.5$ was found to be compared with $\bar{n} = 1.9$ in our work. He avoided the formation of B(HA) by adding ligand in the salt form, thus by implication working at pH > 6. Free copper-ion concentrations were measured with a copper-amalgam electrode. We note, however, that for $\mathrm{MeOCH_2CO_2^-}$, $\mathrm{EtOCH_2CO_2^-}$, and $\mathrm{EtSCH_2CO_2^-}$ Sandell reports four, three, and three copper complexes respectively. Work in Oxford [2,3] shows that the complexity of these copper systems can be fully represented by two complexes, and the evidence for higher complexation is thought to be a spurious effect arising from incomplete control of activity coefficients in media of high ionic strength.

Structure of the Complexes.—When metal complexes are formed from a series of related ligands of uniform denticity a linear increase in log β_1 with increasing log

K_1^H is frequently found, as for example in ref. 10. The trend of log β_1 for the thiodialkanoates is contrary to that of log K_1^H, indicating the importance of features other than simple inductive effects in the ligand molecule, in particular, interaction between the copper and the sulphur-donor atom. The same reversed trend is noted for reaction (11) for which values of log K_{111} are shown in

$$B + HA \rightleftharpoons B(HA) \qquad (11)$$

Table 3, and for the stability constants (Table 3) of the monoalkanoates $MeS[CH_2]_xCO_2^-$. These monoalkanoates have been shown [3,19] to behave as bidentate ($x = 1$), partially bidentate ($x = 2$), and unidentate ($x = 3$) ligands towards copper, and the trend in favourability of five- > six- ≫ seven-membered chelate-ring formation is clear.

TABLE 3

Derived stability constants for copper thiodialkanoates calculated from the REFBAH results, together with constants of related systems [3] [3.0 mol dm^{-3} (sodium) perchlorate, 25.0 °C] for comparison

	$S[(CH_2)_xCO_2^-]_2$		
$x =$	1	2	3
log K_2^H	3.46	4.35	4.70
log ($K_{BA}^H = \beta_{111}\,\beta_1^{-1}$)	1.72	3.16	4.61
log ($K_{111} = \beta_{111}K_1^{H^{-1}}$)	2.0	1.8	1.8
	$MeS[CH_2]_xCO_2^-$		
$x =$	1	2	3
log K_1^H	4.01	4.68	4.99
log β_1	2.96	2.04	1.83
log β_2	5.48	3.50	2.81

Differing copper–ligand interactions in the thiodialkanoates can be displayed by the effect of copper complexation on the protonation of the second carboxyl group of the ligand. Values of log K_{BA}^H for reaction (12)

$$BA + H \rightleftharpoons B(HA) \qquad (12)$$

are shown in Table 3 for comparison with the ligand-protonation constants. The constant K_{BA}^H for copper thiodibutanoate is close to K_1^H, and very close to K_2^H, for the thiodibutanoate ligand. Protonation is virtually unaffected by copper complexation, and unidentate *O*-donor behaviour of thiodibutanoate towards copper is suggested. Similarly K_{111} for the partially protonated (HA) thiodibutanoate ligand is close to β_1 for the corresponding monoalkanoate, again indicating unidentate complexation in the copper–thiodibutanoate B(HA) species.

The hydrogen thiodialkanoate ligands HA are potentially bidentate, and the reversed trend in K_{111} noted above suggests increasing bidentate behaviour as the number of carbon atoms (x) separating the sulphur atom from the carboxyl decreases, in parallel with the behaviour of the monoalkanoate ligands.

The values of β_1 for the (potentially tridentate) thiodialkanoates themselves indicate an increase in denticity from 1 as x is decreased below 3. Precise denticity is difficult to infer from potentiometric evidence alone, but some indication can be gained from a study of the exchange reaction (13). When $x = 3$ and both ligands

$$[Cu\{O_2C(CH_2)_xSMe\}_2] + S[(CH_2)_xCO_2^-]_2 \rightleftharpoons 2MeS[CH_2]_xCO_2^- + [Cu\{S[(CH_2)_xCO_2]_2\}] \qquad (13)$$

are unidentate the equilibrium favours the monoalkanoate as expected. For $x = 2$, however, the equilibrium favours the dialkanoate (by 0.14 log units) despite the partial chelation occurring in the monoalkanoate system. Tridentate behaviour of thiodipropanoate is thus feasible. In contrast, when $x = 1$, the equilibrium favours the monoalkanoate.

Spectroscopic Evidence.—The visible spectrum of copper is altered by its environment, and the broad effects of substituting various donor atoms for one or more of the six O atoms of the hexa-aquacopper(II) species have been established.[19] The value of $\lambda_{max.}$ for a solution containing largely the copper thiodipropanoate complex BA was found to be 721 ± 5 nm, clearly indicative of the participation of one sulphur atom in bonding, but at a wavelength slightly lower than expected from measurements on monoalkanoate systems. Participation of sulphur is also shown by a copper thiodiacetate solution with $\lambda_{max.} = 714 \pm 5$ nm. The greenish hue observed in copper thiodiacetate and thiodipropanoate solutions was absent in solutions of copper thiodibutanoate and $\lambda_{max.}$ for this last complex is equal to that of $[Cu(OH_2)_6]^{2+}$ at 800 nm. This suggests that only oxygen-donor atoms are involved in the thiodibutanoate complex.

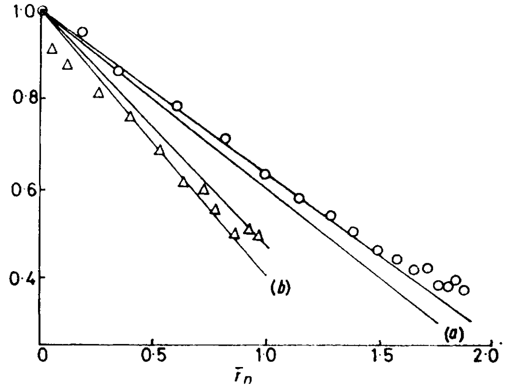

FIGURE 4 Variation of ρ with the reduced degree of formation of copper thiodiacetate (○) and thiodipropanoate (△) complexes. The choice of high pH values (3—5) minimised B(HA) formation. The lines drawn indicate the spread of values of ρ encountered for bi- (*a*) and tri-dentate (*b*) copper–amino-acid complexes

Studies of the broadening of the n.m.r. line due to the proton of inner-sphere water have been used to determine the denticity of several ligands [19,20] bound to Cu^{II}. Titrations of aqueous $Cu[ClO_4]_2$ with ligand were carried out by Dr. M. R. Harrison under conditions favourable to the formation of BA_n rather than B(HA). The dependence of the variable ρ, defined from linewidths (Δν) by equation (14), on $\bar{r}_n$ [equation (6)] is shown in Figure 4. Comparison with previous experiments with bi- and tri-dentate amino-acids points with certainty to the tridentate behaviour of thiodipropanoate, and to bidentate behaviour in the case of thiodiacetate.

$$\rho = \frac{\Delta\nu(\text{expt.}) - \Delta\nu(\text{water})}{\Delta\nu[\text{Cu(ClO}_4)_2] - \Delta\nu(\text{water})} \qquad (14)$$

These values of denticity are somewhat surprising in view of the considerably greater stability of copper thiodiacetate as compared with copper thiodipropanoate. However, the monoalkanoate studies have revealed the considerable thermodynamic advantage of a five-membered over a six-membered chelate ring.[2,3] Construction of Catalin molecular models shows that the closure of the second five-membered ring in copper thiodiacetate would cause considerable strain, whereas thiodipropanoate is quite capable of forming two six-membered chelate rings. For the crystalline state, *X*-ray studies have shown that thiodiacetate is indeed a tridentate ligand with respect to both cadmium(II) [21] and neodymium(III) [22] and that the analogous *O*-ligand oxydiacetate is tridentate towards Cu^{II} itself.[23] Nevertheless, it is quite feasible for the denticities of the ligands to be lower in solution.

The Complex BA_2.—Only in the case of thiodiacetate is this complex evident, and the stepwise formation constant $\log(\beta_2\beta_1^{-1}) = 3.23$ is lower by 1.4 log units than $\log \beta_1$. The formation of the second complex is thus considerably less favoured than would be expected on a statistical basis for copper thiodiacetate, and BA_2 formation for the larger homologues is yet more difficult. It is likely that the approach of a second ligand is sterically hindered, and that when the one relatively planar five-membered ring of copper thiodiacetate is replaced by two bulkier buckled six-membered rings of copper thiodipropanoate such approach is effectively prevented. There are precedents for the reduction of ligand denticity when a second ligand co-ordinates (as in some iminodiacetates [4,24]), but changes of this sort do not appear to occur in the thiodialkanoate system under the conditions studied.

[8/722 *Received, 18th April,* 1978]

REFERENCES

[1] Part 17, *J.C.S. Dalton*, 1977, 1229.

[2] F. J. C. Rossotti, J. D. E. Carson, J. J. Clarke, K. B. Dillon, J. N. Knight, D. L. Martin, and V. M. Moxham, unpublished work.

[3] P. Ebden, M. R. Harrison, and F. J. C. Rossotti, unpublished work.

[4] R. M. Tichane and W. E. Bennett, *J. Amer. Chem. Soc.*, 1957, **79**, 1293.

[5] M. Yasuda, K. Yamasaki, and H. Ohtaki, *Bull. Chem. Soc. Japan*, 1960, **33**, 1067; K. Suzuki, C. Karaki, S. Mori, and K. Yamasaki, *J. Inorg. Nuclear Chem.*, 1968, **30**, 167.

[6] A. Sandell, *Acta Chem. Scand.*, 1961, **15**, 190.

[7] E. Campi, G. Ostacoli, N. Cibrario, and G. Saini, *Gazzetta*, 1961, **91**, 361.

[8] J. Podlaha and J. Podlahova, *Inorg. Chim. Acta*, 1970, **4**, 521.

[9] S. Gabriel, *Ber.*, 1890, **23**, 2492.

[10] F. J. C. Rossotti, and R. J. Whewell, *J.C.S. Dalton*, 1977, 1223.

[11] F. J. C. Rossotti and R. J. Whewell, *Proc. 3rd Symp. Co-ordination Chem.*, Debrecen, Akademiai Kiado, Budapest, 1970, **1**, 233.

[12] C. Biedermann, *Arkiv. Kemi*, 1956, **9**, 175.

[13] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.

[14] G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 947; N. C. Li, A. Lindenbaum, and J. M. White, *J. Inorg. Nuclear Chem.*, 1959, **12**, 122.

[15] F. J. C. Rossotti and H. S. Rossotti, ' The Determination of Stability Constants,' McGraw-Hill, New York, 1961.

[16] G. L. Cumming, J. S. Rollett, F. J. C. Rossotti, and R. J. Whewell, *J.C.S. Dalton*, 1972, 2652.

[17] H. M. N. H. Irving and M. H. Stacey, *J. Chem. Soc.*, 1961, 2019.

[18] N. Bjerrum, *Z. phys. Chem.*, 1923, **106**, 219.

[19] M. R. Harrison and F. J. C. Rossotti, *Chem. Comm.*, 1970, 175.

[20] F. J. C. Rossotti and H. Sunshine, *Chem. Comm.*, 1968, 447.

[21] S. H. Whitlow, *Acta Cryst.*, 1975, **B31**, 2531.

[22] T. Malmborg and A. Oskarsson, *Acta Chem. Scand.*, 1973, **27**, 2923.

[23] S. H. Whitlow and G. Davey, *J.C.S. Dalton*, 1975, 1228.

[24] M. B. Jones and L. Pratt, *J.C.S. Dalton*, 1976, 1207.