and β was calculated as follows:

$$\Delta E_{1/2}=(E_{1/2})_c-(E_{1/2})_s=\frac{0\cdot0601}{n}\log\beta+p\frac{0\cdot0601}{n}\log C_x$$

Cd-TDAA system — Cd-TDAA system gives a well-defined single wave in each case. The diffusion-controlled nature of the reduction wave was indicated by the constancy of the ratio of diffusion current to the square root of the effective height of mercury column and was confirmed by the temperature, coefficients of diffusion current values $(0\cdot5\pm0\cdot1$ $mV/$deg). The slopes of the log plots (32-40 mV) coupled with the temperature cofficient of $-E_{1/2}$ values conclusively prove that the two-electron reduction is reversible.

A plot of $-E_{1/2}$ versus pH indicates breaks at pH 3·5 and 5·5. $E_{1/2}$ remains uneffected below pH 3·5. On increasing the pH from 3·5, $-E_{1/2}$ also increases. Beyond pH 7 the turbidity appears. Hence pH 6·5 was found to be most suitable for the complexation process. A decrease in i_d has also been observed on increasing the pH from 3·5 to 6·5.

The shift in $E_{1/2}$ to more negative potential indicates the formation of the complex. The curve between $-\log C_x$ versus $-E_{1/2}$ shows successive complexation. The plots of $F_1(X)$, $F_2(X)$ and $F_3(X)$ when extrapolated at $C_x=0$, gave the values of overall stability constants. The plot of $F_3(X)$ is horizontal to the x-axis indicating the formation of three complexes in all the cases with 1:1, 1:2 and 1:3 metal-ligand ratios.

The values of over all stability constants are 20, 60 and 245, 10, 55, 175 and 8, 45 and 150 at 30°, 40° and 50°C respectively. The change in free energy (ΔG), enthalpy (ΔH) and change in entropy (ΔS) have been calculated and the values are given below:

Temp. °C	(ΔG) kcal/mole	(ΔH) kcal/mole	(ΔS) cal deg^{-1} mole^{-1}
30	−3·333	—	—
40	−3·431	0·6343	9·3
50	−3·553	0·5260	6·0

The polarographic reduction of Cd^{2+} in 20% DMF and DMSO in water mixtures gives a single well-defined wave with $E_{\frac{1}{2}}=-0\cdot5900$ versus (SCE) which resembles that of simple Cd^{2+} ion. There seems to be no significant role of 20% non-aqueous solvent (DMF and DMSO) on the complexation process.

Lead-TDAA system — Pb^{2+}-TDAA system gives a two electron reduction wave which is diffusion-controlled and reversible as shown by constant values of $i_d/h_{eff}^{1/2}$, and slopes (35±5 mV) of log i/i_d-i) plots.

The plot of $-E_{\frac{1}{2}}$ versus pH shows that as pH increases from 4·3 to 6·5, a more cathodic shift in $E_{\frac{1}{2}}$ is observed. Thus pH 6·0 is found to be most suitable for the study of complexation reactions. The cathodic shift in $-E_{\frac{1}{2}}$ on increasing (TDAA) (0·0 to 0·2M) shows the formation of the complex. The plot of $-\log C_x$ versus $-E_{\frac{1}{2}}$ results to linear. It is, therefore, concluded that a single complex is being formed. The Lingane's method has been applied for calculating the stability constants; the

values are 1103·4, 900 and 740 at 30°, 40° and 50°C respectively.

The polarographic reduction of Pb^{2+} in 20% DMF and DMSO media gives a single well-defined wave with $-E_{\frac{1}{2}}=0\cdot38$ mV which also resembles the $E_{\frac{1}{2}}$ of simple metal ion. Thus no significant role of 20% non-aqueous (DMF and DMSO) media is being noted.

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Equilibrium Studies on Cu(II) & UO₂(II) Complexes of Isobutyric, β,β-Dibromoisobutyric & 4-Aminobutyric Acids

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The acidity constants and stability constants of Cu(II) and UO₂(II) complexes of isobutyric β,β′-dibromoiso-butyric and 4-aminobutyric acids have been determined pH-metrically at 31° and μ = 0·1M NaClO₄.

THE stability constants of copper and uranyl ion complexes with isobutyric, β,β′-dibromoisobutyric and 4-aminobutyric acids have been obtained by pH titration methods at 31°±0·1°C and $\mu=0\cdot1M$ (NaClO₄) and the results reported in this note.

The preparation of uranyl perchlorate[1] and copper perchlorate[2] as well as the other reagents and their estimations have been described by Ramamoorthy and Santappa[1,2]. Isobutyric acid was distilled (154°) and dibromoisobutyric acid recrystallized (99°) before use. 4-Aminobutyric acid (Fluka) was used as such.

The details of apparatus and experimental technique used to obtain Bejrrum-Calvin titration curves;, methods of calculation of the dissociation constants of the ligand carboxylic acids and stability constants of simple 1:1 complexes by Irving and Rossotti's method are the same as described by Ramamoorthy and Santappa[1]. In the case of 4-aminobutyric acid the acidity constants of the acid and basic functions were determined by the method of Albert[3] at 31° ±0·1° and the stability constant calculations were done by the algebraic method[4].

In all the cases copper and uranyl ions form only 1:1 complexes with those ligands. The pK values

TABLE 1 — PROTON-LIGAND DISSOCIATION CONSTANTS OF THE ACIDS AND STABILITY CONSTANTS OF THEIR CHELATES WITH Cu(II) AND UO$_2$(II)

Ligand	pK_1	pK_2	log K_{ML}	
			Cu(II)	UO$_2$(II)
Isobutyric acid	(4·73)[9]	—	(2·36)[5]	—
	4·76	—	2·37	(3·40)[9]
Dibromoisobutyric acid	3·26	—	2·69	3·49
4-Aminobutyric acid	4·04	10·26	6·61	9·13
Glycine	—	—	(8·62)[6]	—
β-Alanine	—	—	(7·10)[7]	(9·20)[8]

Values in parentheses are taken from literature for comparison.

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of the ligands and the equilibrium constants of 1:1 simple complexes of copper and uranyl with isobutyric acid dibromoisobutyric acid and 4-aminobutyric acid are listed in Table 1 along with other values taken from literature for comparison. The formation of higher and polynuclear complexes is ruled out by the fair constancy of stability values obtained over a wide range of pH values and concentrations of both metal and ligand. Also the superimposibility of the theoretical formation curve over the experimental curve in all these cases clearly shows the validity of the equilibria assumed.

The stability values for the complexes of the two metals with isobutyric and dibromoisobutyric acids are as expected from the pK values of the individual ligands. The higher stability in the latter case with both the metals is possibly due to the $-I$ effect (electron attracting) of the bromine atoms which is indicated from its lower pK value than isobutyric acid. The log K_{ML} value for copper-isobutyric acid obtained by pH titration method is in good agreement with that obtained by spectrophotometric method[5]. In the case of 4-aminobutyric acid-copper system, the log K value of 6·61, several magnitudes greater than isobutyric acid, indicates the bidentate nature of the ligand and this is also in good agreement with the observed behaviour of glycine[6] and β-alanine[7] with copper. The lower log K value for 4-aminobutyric acid when compared with that for β-alanine is possibly due to the lesser stability of seven-membered ring which is generally the case in the complexes formed by the 3d transition metals with a ring size greater than five. The log K value obtained for the system uranyl-4-aminobutyric acid, is comparable with that of uranyl-β-alanine system[8]. Uranyl being a bulky ion favours a six-membered ring. In the present system though a seven-membered ring is formed, the log K value is only slightly lower than for uranyl-β-alanine system, indicating that the stability of seven-membered ring is nearly of the same order as that of six-membered ring.

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Formation Constants of Co(II), Ni(II), Cu(II) Zn(II), Cd(II) & UO$_2$(II) Complexes of the Schiff Base Derived from Acetylacetone & 2-Aminoethane Sulphonic Acid

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Proton-ligand stability constants (pK_1 and pK_2) of the Schiff base derived from acetylacetone and 2-aminoethane sulphonic acid and the metal-ligand stability constants of its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO$_2$(II) have been determined in water-dioxane mixture (1:1, v/v) at 25 ± 0·1° and 35 ± 0·1° using Calvin-Bjerrum pH titration technique. The order of metal-ligand stability constants is UO$_2$(II) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II), which follows the Irving-Williams rule.

IN continuation of our work on the dissociation constants of N-acetylacetoneorthanilic acid[1] and the stability constants of its complexes with some bivalent metal ions, we report here the synthesis of a new chelating agent derived from acetylacetone and 2-aminoethane sulphonic acid (H$_2$AT), determination of its dissociation constants and the metal-ligand stability constants of its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO$_2$ (II). These studies have been carried out in water-dioxane (1:1, v/v) medium at 25°±0·1° and 35°±0·1° adopting the Calvin-Bjerrum pH titration technique[2,3]. The overall free energy changes, enthalpy and entropy changes have also been evaluated.

All the chemicals used were either BDH or Reidel reagents. The ligand was synthesized by a procedure similar to that reported earlier[4], m.p. 141°. [Found: C, 40·34; H, 6·19; N, 6·62; S, 15·31 Calc. for (C$_7$H$_{13}$NSO$_4$): C, 40·57; H, 6·28; N, 6·76; S, 15·45%].

The standard solution of the ligand was prepared in dioxane and those of metal nitrates and sodium perchlorate were prepared in doubly distilled water.