range of spectra. The previous work\textsuperscript{3,7} and the reported absorption frequencies indicate that $\text{SO}_3\text{R}$ group acts as bridging group resulting in the polymeric structure, also confirmed by X-ray diffraction data for similar compounds\textsuperscript{8,14,15}. A polymeric structure for these compounds is also suggested by the high decomposition point and low solubility in organic solvents.

Financial assistance from the CSIR, New Delhi and State Council of Science & Technology, Lucknow is gratefully acknowledged.

References

11. VOEGE, A. I., Practical organic chemistry (Longmans, London), 549.

Stability Constants of Mixed Ligand Complexes of Cd(II)-Piperidine-Tris(hydroxymethyl)methylamine

D. RAJENDRA FRASAD* & K. SARASWATHI
Department of Chemistry, Sri Venkateswara University, Tirupati 517502

Received 21 November 1977; revised 20 February 1978; accepted 21 June 1978

Cathodic reduction of the mixed cadmium(II)-piperidine(PPD)-tris(hydroxymethyl)methylamine (tris) system has been studied and the composition and stability constants have been determined. The electrode reaction is found to be reversible and diffusion controlled involving two electrons. Piperidine and tris form tetra coordinated complexes with cadmium. The log stability constants of mixed complexes [Cd XY]\textsuperscript{2+}, [Cd X\texttextsuperscript{2+}Y]\textsuperscript{2+}, i.e., [Cd (PPD) (tris)]\textsuperscript{2+} and [Cd (PPD) (tris)]\textsuperscript{2+} are found to be $6.17 \pm 0.20$ and $6.06 \pm 0.44$ respectively. The negative values for $K_{MXY}$, $K_{MY}$, $K_{XMY}$ and $K_{X}$ indicate the absence of [Cd XY]\textsuperscript{2+}, [Cd X\texttextsuperscript{2+}Y]\textsuperscript{2+} and [Cd X\textsuperscript{2+}Y]\textsuperscript{2+} type of complex species in solution.

Most of the studies regarding mixed ligand complexes reported in literature have been made employing potentiometric and spectrophotometric techniques. In the present investigation ligand displacement technique has been used in which a stronger complexing ligand piperidine has been added to Cd(II) complex with a weaker complexing ligand like tris(hydroxymethyl)methylamine (tris) and the stabilities of the resulting species determined polarographically by the method of Schaap and McMasters\textsuperscript{1}.

Reagents used were of AR grade and used as such. The $\rho K_a$ values of ligands were determined at 30° and in 1M (KNO\textsubscript{3}), and are 11.38 for piperidine and 8.32 for tris. Experimental solutions containing $1 \text{mM Cd(II)}, 1\text{mM KNO}_3+0.16\text{mM NH}_4\text{Ac}$ and varying [ligand] were prepared using air-free conductivity water. A manual polarograph with Multiflex galvanometer was used for polarographic measurements. The capillary had the following characteristics: $m = 3.933 \text{mg sec}^{-1}$ and $t = 3 \text{sec}$ per drop at 30 cm of Hg pressure in 1M KNO\textsubscript{3} in open circuit. Test solutions were deoxygenated by purified H\textsubscript{2}. Polarograms of Cd(II)-piperidine, Cd(II)-tris simple systems with varying concentrations of ligands, and Cd(II)-piperidine-tris system at four [tris] with varying [piperidine] in each case were determined. Treatment of data was done following Dford and Hum\textsuperscript{2} method for monoligand complexes and Schaap and McMasters method for mixed ligand system.

The polarograms obtained for mono-ligand and mixed-ligand complexes are well-defined single waves and are diffusion-controlled and reversible. The shift in $E_1$ is more in the presence of tris with varying [piperidine] and finally when all tris has been replaced by piperidine the magnitude of shift in $E_1$ is the same for both simple and mixed systems. Since the ligands are monodentate and form tetra-coordinated complexes with Cd(II), there is a possibility of existence of six mixed ligand complex species of the type: [CdXY]\textsuperscript{2+}, [CdXY2]\textsuperscript{2+}, [CdXY3]\textsuperscript{2+}, [CdX2Y3]\textsuperscript{2+}, [CdX3Y2]\textsuperscript{2+} and [CdX2Y2]\textsuperscript{2+}. Therefore, for a complexation with monodentate ligands X and Y, $M+\text{X}+\text{Y}\rightleftharpoons MX\text{Y}$ \textsuperscript{1}...

and consequently the data were treated by Schaap and McMasters method\textsuperscript{4}. The solution for the function $F_{00} (X, Y)$ is given by Eq. (2)

$$F_{00}(X, Y) = A + B X + C X^2 + D X^3 + E X^4$$ \textsuperscript{2}...

at each constant [Y]. The quantities $A$, $B$, $C$, $D$ and $E$ are defined by Ledens\textsuperscript{8} equation and are constant at each [Y]. The original graphical method
was extended and $F_{30}(X, Y)$ versus $[X]$ plotted at each constant [Y]. The intercept on the $F_{30}(X, Y)$ axis in the plot of $F_{30}(X, Y)$ versus $[X]$ gives $A$ (Fig. 1) so that

$$F_{10}(X, Y) = \frac{F_{30}(X, Y) - A}{(X)} = B + CX + DX^2 + EX^3$$

... (3)

Extending this, $F_{20}$ obtained seems to be quadratic, $F_{30}$ linear and $F_{40}$ horizontal, i.e. $F_{40}$ independent of $[X]$. The value of $A$, $B$, $C$, $D$ and $E$ obtained from the intercept in each set at constant $[y]$ are substituted in Ledens equation and mixed ligand complex equilibrium constants evaluated by solving the corresponding set of equations.

Formation of single ligand complexes of cadmium(II) — The formation constants of the complexes of Cd(II) with piperidine and tris were evaluated from the data of single ligand complex system by DeFord and Hume method by plotting $F_j [X]$ versus $[X]$

The formation constants of mixed complexes evaluated from the experimental data by Ledens approach are, log $K_1 = 6.27 \pm 0.26$, log $K_2 = 6.06 \pm 0.44$ which are positive values of $[Cd(PPD)(tris)]^{2+}$ and $[Cd(PPD)(tris)]^{3+}$ respectively. Log $K_3$, log $K_4$, and log $K_5$ are negative values showing the instability of $[Cd(tris)]^{2+}$, $[Cd(tris)]^{3+}$, $[Cd(tris)]^{4+}$ and $[Cd(tris)]^{5+}$ in solution. The log $E$ values which are supposed to be equivalent to log $K_a$ are not in good agreement for the $[Cd(PPD)]^{2+}$ complex. This discrepancy may arise from the contribution of tris ligand in the solution. The absence of some of the mixed ligand complex species may also be due to entropy change, steric and electrostatic factors apart from the statistical consideration which does not favour the stability of those complexes and the negative values of these complexes are also included in Table 1.

The authors are thankful to Prof. V. R. Krishnan for facilities.

Table 1 — Stability Constants of Cadmium-Piperidine-Tris Mixed Complexes

<table>
<thead>
<tr>
<th>Mixed complex</th>
<th>log $K$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (tris)</td>
<td>$3.70 \pm 0.08$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$5.07 \pm 0.01$</td>
</tr>
<tr>
<td>Cd (tris)</td>
<td>$4.00 \pm 0.04$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$5.04 \pm 0.04$</td>
</tr>
<tr>
<td>Cd (tris)</td>
<td>$4.78 \pm 0.01$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$6.17 \pm 0.26$</td>
</tr>
<tr>
<td>Cd (tris)</td>
<td>$-6.13 \pm 0.22$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$5.65 \pm 0.01$</td>
</tr>
<tr>
<td>Cd (tris)</td>
<td>$5.15 \pm 0.01$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$5.79 \pm 0.58$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$6.06 \pm 0.44$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$-6.98 \pm 0.35$</td>
</tr>
<tr>
<td>Cd (PPD)</td>
<td>$6.42 \pm 0.01$</td>
</tr>
</tbody>
</table>

and the values for both the systems are included in Table 1.

Cadmium(II)-piperidine-tris system — In the present ligand displacement techniques, the concentration of tris (weaker ligand) was kept constant at four concentrations and in each case tris was displaced by piperidine (stronger ligand) whose concentration was varied. The four concentrations of tris were so chosen that at these concentrations $1:1, 1:2, 1:3, 1:4$ complexes predominated for the simple Cd(II)-tris system and the four concentrations are $0.21\text{M}$, $0.48\text{M}$, $0.99\text{M}$ and $1.51\text{M}$. The $F_{30}(X, Y)$ versus $[X]$ at $1.51\text{M}$ tris are plotted in Fig. 1.

The plot of $E_i$ versus log $C_x$ at four concentrations of Tris has been divided into four segments indicating four piperidine molecules entering the coordination sphere.

The possible reactions that take place when solutions are mixed and later when reduced at d.m.e. are shown in Scheme 1.

References