

both in the presence and in the absence of monomer, the quantum yields for the complex disappearance are reported for the first time.

Supplementary to the spectrophotometric studies, gasometric studies of the nitrogen evolution were also made. Solutions of the monoazido complex were irradiated at  $\lambda = 365 \text{ m}\mu$  and the amount of nitrogen evolved was measured (in a dilatometer devised by us) and plotted against time (Fig. 1 B). The average quantum yield obtained was  $\sim 0.135$ . The evolution of nitrogen ceased completely only after three days.

The low quantum yields for photoredox decomposition and the small change of the quantum yield with the increase of wavelength of the irradiating light may be understood in terms of (a) the excitation of the complex in the primary photochemical act and (b) the postulate that electronically excited states of moderately long lifetime (which can undergo internal conversion before reactive deactivation) are intermediates in photochemical reactions of cobalt (III)<sup>4</sup>. Inefficiencies observed in the photoaquation and photoreduction of cobalt (III) complexes are the result of competing reactions of the electronically excited states of the complexes.

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#### COMMENTS ON THE PAPER "A NEW APPROACH TO THE ELOVICH EQUATION" BY VISWANATH ET AL.<sup>1</sup>

R. P. VISWANATH *et al.*<sup>1</sup> have recently analysed the kinetics of chemisorption of hydrogen on iron oxide. Over a wide range of temperature and pressure the chemisorption followed the Elovich equation<sup>2,3</sup>,

$$q = \frac{1}{a} \ln(t + t_0) - \frac{1}{a} \ln t_0$$

where  $q$  = amount chemisorbed at time  $t$ , and  $a$  and  $t_0$  are constants. If  $q = 0$  at  $t = 0$  then  $t_0 = 1/a$  where  $a$  is the rate of chemisorption at  $t = 0$ .

I have recently emphasised<sup>4</sup> that the role of  $t_0$  is purely mathematical and that no physical significance can be attached to the value of  $t_0$ . Viswanath *et al.*<sup>1</sup> questioned this statement in the case of their measured chemisorption on iron oxide because plots of  $q$  against  $\log(t + t_0)$  intersected the  $\log(t + t_0)$  axis at  $\log(t_0)$ . They concluded that this indicated an induction period for the chemisorption and that  $t_0$  was the length of this induction period which preceded the chemisorptions.

It should be pointed out that the intersection of integrated Elovich plots at  $\log(t_0)$  on the  $\log(t + t_0)$  axis is precisely what *must* occur if Elovich kinetics apply with  $q = 0$  at  $t = 0$ . The data of Viswanath *et al.* cannot therefore be taken as evidence of a mechanistic significance for  $t_0$  but do indicate that this chemisorption is accurately described by the Elovich equation for the entire course of the reaction. The data are thus of particular interest since it has been shown<sup>5</sup> that the majority of chemisorptions obey Elovich kinetics only after an initial process which follows different kinetics.

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Dundee, Scotland, October 16, 1971.

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#### $\gamma$ -PICOLINE COMPLEX OF COPPER (II) IODIDE

DIVALENT copper ion having a non-spherical  $3d^9$  non-bonding shell is subjected to Jahn-Teller distortions and hence exhibits square planar configuration as a limit to axial octahedral distortion. Several complexes of copper (II) have been reported<sup>1-3</sup> earlier by us. In this communication, a copper (II) iodide complex with  $\gamma$ -picoline having the composition  $[\text{Cu}(\gamma\text{-pic})_3\text{I}_2 \cdot \text{H}_2\text{O}]$  is described.

To an aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , excess  $\gamma$ -picoline was added and the mixture shaken till a deep blue solution was obtained. The solution was warmed and potassium iodide



was added gradually in small quantities with thorough shaking till a blue precipitate appeared. The precipitate was filtered, washed thoroughly with methanol till the blue tint was removed leaving behind a green amorphous complex. It was washed with ether and dried *in vacuo*. The purity of the isolated compound was established by estimating metal and halogen by standard methods. (Found: Cu, 10.13%; I, 41.05% [Cu( $\gamma$ -pic)<sub>3</sub>I<sub>2</sub>·H<sub>2</sub>O] requires Cu, 10.34%; I, 41.38%.) Conductance measurement was carried out in 0.001 M acetone solution using a Toshniwal Conductivity Bridge and magnetic susceptibility was determined on solid specimens using Gouy method. I.R. spectra were recorded on Nujol mulls using a Unicam SP-200 spectrophotometer. Chloroform solution (0.01 M) of the compound was used to record the electronic spectra in the visible range. I.R. and electronic spectral data are given below:

* I. R. spectra (cm <sup>-1</sup> )	Electronic spectra
728s, 825vs, 970w, 1040s, 1075s, 1235s, 1520m, 1630s, 3500br (742s, 823s, 1015vs, 1060m, 1235s, 1430w, 1460w, 1610vs)	$\gamma_{\max.}$ (cm <sup>-1</sup> ) ( $\epsilon$ ) 14,800 (31)

\*The free ligand ( $\gamma$ -picoline) absorption bands are given in parenthesis.

Cupric iodide is unstable and gets converted to cuprous iodide and iodine. Complexes of copper (II) iodide are known with chelating ligands<sup>4-6</sup>. The nature of the compounds CuI<sub>2</sub>·*n*NH<sub>3</sub> [*n* = 2, or 6] is not well known<sup>7</sup>. Goodgame and co-workers<sup>8</sup> reported [Cu(imidazole)<sub>4</sub>I<sub>2</sub>] and its structure has been determined by X-ray diffraction. Bose *et al.*<sup>9</sup> have described a similar complex with benzimidazole having the composition [Cu(bzd)<sub>4</sub>I<sub>2</sub>].

The green amorphous complex having the composition [Cu( $\gamma$ -pic)<sub>3</sub>I<sub>2</sub>·H<sub>2</sub>O] reported in the present investigation is soluble in acetone, in which medium it is a nonelectrolyte,  $\Lambda_m$  being 16.4 mhos. It is paramagnetic in the solid form, indicating the presence of one unpaired electron ( $\mu = 1.84$  B.M.) and hence the copper atom is in the divalent state. Infra-red spectra show the presence of a broad band at 3500 cm<sup>-1</sup> indicating the presence of co-ordinated water molecule. Some ligand absorption bands are shifted indicating the bonding of the ligand ( $\gamma$ -picoline) to the metal. Absorption spectrum of a chloroform solution in the visible range showed a broad absorption band at 14800 cm<sup>-1</sup> region. Hence a tetragonally distorted octahedral

configuration with weakly bonded iodide ions along the tetragonal axis, as in the corresponding imidazole<sup>8</sup> and benzimidazole<sup>9</sup> complexes, is suggested for the present compound. This is yet another example of a cupric ion stabilised in presence of an iodide ion by complexing.

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### COMPLEXES OF 5, 5'-THIODISALICYLIC ACID WITH SOME *d*<sup>10</sup>-TRANSITION METAL IONS

THIS communication describes the isolation and characterisation of complexes of Ag (I), Hg (II), Th (IV) and UO<sub>2</sub> (VI) with 5, 5'-thiodisalicylic acid, an industrially<sup>1-4</sup> important compound. Mode of co-ordination of the ligand has been deduced from the infrared spectroscopic data. Earlier references cited in the literature on complexation reactions of 5, 5'-thiodisalicylic acid (abbreviated hereafter as TDSA) with some transition metal ions relate to the studies in solution<sup>5-6</sup>.

For preparing the complexes, an alcoholic solution of TDSA (0.1 M, 100 ml) was added in each case to aqueous solution of the metal ion (0.1 M, 25 ml) concerned and the mixture was refluxed for about an hour. The precipitated complex was filtered, washed with water, alcohol and acetone and dried in an electric oven at 80° C. The analysis gave the formulae, shown in Table I, for the compounds thus obtained.

The complexes did not dissolve either in water or in common organic solvents suggesting their polymeric nature. No cryoscopic or conductometric measurements could, therefore, be made.

Magnetic measurements on solid complexes were made by Guoy's method using mercury