

### 17. *Stability Constants of Copper(II)-2,2'-Bipyridyl Complexes.*

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The values of the successive formation constants of copper(II)-2,2'-bipyridyl chelate compounds in alcohol-water mixtures have been determined potentiometrically by using a competitive technique with  $\text{Ag}^+$  as competitive cation. The enthalpy and entropy contributions to the free energy of formation of the complexes have been determined.

The numerical values of some of the stability constants have been verified by spectrophotometric measurements.

THE present paper reports experimental data for the stability constants of copper(II)-2,2'-bipyridyl compounds as a part of a general study.<sup>1</sup>

Other workers<sup>2</sup> have shown that the reaction between  $\text{Cu}^{2+}$  ions and 2,2'-bipyridyl (bip) leads to mononuclear complexes with a maximum of three ligand molecules. Onstott and Laitinen<sup>3</sup> first determined the overall formation constant of the compound with maximum co-ordination, and Wagner-Jauregg *et al.*<sup>4</sup> reported that the  $[\text{Cu}(\text{bip})]^{2+}$  ion is a strong catalyst for the hydrolysis of the di-isopropyl fluorophosphate. Later the equilibria in solutions of copper(II)-bipyridyl in the ratio 1:1, with various amounts of added

<sup>1</sup> Cf. Cabani and Scrocco, *Ann. Chim. (Italy)*, 1958, **48**, 85, 99; *J. Inorg. Nuclear Chem.*, 1958, **8**, 332

<sup>2</sup> Jaeger and Van Dijk, *Z. anorg. Chem.*, 1936, **227**, 273; *Proc. Acad. Sci. Amsterdam*, 1934, **37**, 395, 618; Pflaum and Brandt, *J. Amer. Chem. Soc.*, 1954, **76**, 6215.

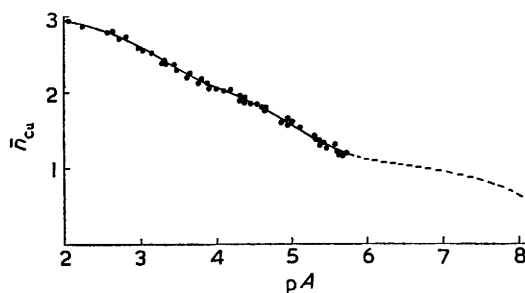
<sup>3</sup> Onstott and Laitinen, *J. Amer. Chem. Soc.*, 1950, **72**, 4724.

<sup>4</sup> Wagner-Jauregg, Hackley, jun., Lies, Owens, and Proper, *J. Amer. Chem. Soc.*, 1955, **77**, 922.

hydroxyl ion, were investigated by Fowkes, Ronay, and Ryland<sup>5</sup> who found that, in such conditions, the  $[\text{Cu}(\text{bip})]^{2+}$  species undergoes hydrolysis with formation of a dimer  $[\text{Cu}(\text{bip})(\text{OH})]_2^{2+}$  and an uncharged species  $\text{Cu}(\text{bip})(\text{OH})_2$ . This hydrolysis has been also studied by Gustafson and Martell<sup>6</sup> who give the hydrolysis constants of the hydroxo-complexes and the stability constant of the original species  $[\text{Cu}(\text{bip})]^{2+}$ . The complete curve of formation of the copper(II)-bipyridyl compounds has been reported by Irving<sup>7</sup> on the basis of partition data.

From these results it appears that in aqueous solution of  $\text{pH} < 6$  copper(II)-bipyridyl compounds containing one, two, or three ligand molecules per  $\text{Cu}^{2+}$  ion may exist, depending on the ligand-metal concentration ratio. The overall stability constant of  $[\text{Cu}(\text{bip})_3]^{2+}$  species, obtained by Onstott and Laitinen from polarographic measurements, is  $\log \beta_3 = 17.85$  (in aqueous solution with ionic strength  $\mu$  0.1 at  $25^\circ$ ); and the  $\log k_1$  (the stability constant of the 1:1 complex) is reported to be 6.33 (in aqueous solution with 0.1M-potassium nitrate at  $25^\circ$ ) by Gustafson and Martell.<sup>6</sup> From the formation curve reported by Irving, use of the points at half- $\bar{n}$  values leads to the following values of  $\log k_i$  (consecutive

FIG. 1. Formation curve of copper(II)-2,2'-bipyridyl complexes in alcohol-water (41.5% w/w EtOH) at  $20^\circ$ . The curve is obtained from stability constants:  $\log k_1$  8.20;  $\log \beta_2$  13.34;  $\log \beta_3$  16.52.



formation constants):  $\log k_1 \approx 8.20$ ;  $\log k_2 \approx 5.45$ ;  $\log k_3 \approx 3.25$  (the temperature and ionic strength are not recorded).

To obtain complete thermodynamic data for the various steps we have investigated the formation equilibria of the uni-, bis-, and tris-bipyridyl compounds in aqueous-alcoholic media. Both pAg-metric and spectrophotometric techniques have been employed because the former does not allow, in the present instance, the study of the first step. In fact, as may be seen in Fig. 1, experimental data begin at  $\bar{n} \approx 1.2$  and  $\text{pA} \approx 5.7$ . The e.m.f. corresponding to such a value of  $\text{pA}$  is only 0.36 mv, so that data obtained at higher values of  $\text{pA}$  are not reliable.

The pAg-metric technique has been described by us earlier.<sup>1</sup> In this paper we describe in detail the elaboration of the spectrophotometric data. We refer to the curves describing the variation of the mean molar extinction coefficients as functions of the ligand: metal ratio ( $R$ ) at several wavelengths. In some spectral ranges such curves have the typical shape shown in Fig. 2 ( $\lambda = 900 \text{ m}\mu$ ). This curve shows that, for  $R = 1$ , the bisbipyridyl complex is present only in small concentration, in agreement with the large separation factor between the stability constants of uni- and bis-bipyridyl compounds.

From the formation curve obtained potentiometrically  $k_2$  and  $k_3$  values can be accurately determined; so the numerical value of  $\log k_1$  could be evaluated by trial and error, and the test for its correctness was its ability to reproduce the corresponding experimental data for all values of ligand: metal ratio at all the wavelengths used. This method gives also an independent check of  $\log k_2$  and  $\log k_3$  values obtained from potentiometric results.

Suppose that  $k_2$  and  $k_3$  are known and let us arbitrarily choose a tentative value for

<sup>5</sup> Fowkes, Ronay, and Ryland, *J. Phys. Chem.*, 1958, **62**, 798, 867.

<sup>6</sup> Gustafson and Martell, *J. Amer. Chem. Soc.*, 1959, **80**, 526.

<sup>7</sup> Irving, Internat. Conference on Co-ordination Chemistry, *Chem. Soc. Special Publ. No. 13*, 1959, p. 16.

$k_1$ : it is easy from these values to compute the molar fractions  $x_n$  of the  $N$  species present in the solution namely,  $\text{Cu}^{2+}$ ,  $[\text{Cu}(\text{bip})]^{2+}$ ,  $[\text{Cu}(\text{bip})_2]^{2+}$ , and  $[\text{Cu}(\text{dip})_3]^{2+}$ . (For instance the final accepted values of the three constants give, in our case, the distribution of the various species shown in Fig. 3.)

Let  $\varepsilon_n$  be the molar extinction coefficient of the  $n$ -th species and  $E$  the extinction coefficient of the solution; if we assume that the absorptions are additive we may write

$$E = \sum_{n=0}^N x_n \varepsilon_n, \quad (1)$$

where

$$\sum_{n=0}^N x_n = 1,$$

the formation function being

$$\bar{n} = \sum_{n=0}^N n x_n. \quad (2)$$

The contribution of the  $\text{MA}_r$  and  $\text{MA}_{r+1}$  species may be formally separated in equations (1) and (2) by writing

$$\begin{aligned} E'_{r,r+1} &= \frac{E - \left( \sum_{n=0}^{r-1} x_n \varepsilon_n + \sum_{n=r+2}^N x_n \varepsilon_n \right)}{x_r + x_{r+1}} \\ &= \frac{x_r \varepsilon_r + x_{r+1} \varepsilon_{r+1}}{x_r + x_{r+1}} = x'_r \varepsilon_r + x'_{r+1} \varepsilon_{r+1}; \end{aligned} \quad (3)$$

and

$$\begin{aligned} \bar{n}' &= \frac{\bar{n} - \left( \sum_{n=0}^{r-1} n x_n + \sum_{n=r+2}^N n x_n \right)}{x_r + x_{r+1}} \\ &= \frac{r x_r + (r+1) x_{r+1}}{x_r + x_{r+1}} = r x'_r + (r+1) x'_{r+1}. \end{aligned} \quad (3')$$

Since

$$x'_r + x'_{r+1} = 1, \quad (4)$$

it follows that

$$E'_{r,r+1} = \varepsilon_r + (\varepsilon_{r+1} - \varepsilon_r)(\bar{n}' - r), \quad (5)$$

and thus the system has been formally reduced to a binary one containing only two species,  $\text{MA}_r$  and  $\text{MA}_{r+1}$ , of molar fractions  $x'$  and  $x'_{r+1}$ . Concordant values for  $\varepsilon_r$  and  $\varepsilon_{r+1}$  will be obtained for the various pairs  $\text{MA}_r$ - $\text{MA}_{r+1}$  by extrapolating linearly to  $\bar{n}' = r$  and  $\bar{n}' = r+1$  according to equation (5), only if the  $x_i$  (*i.e.*,  $\beta_i$ ) values are correct.

In practice, the molar extinction coefficients of the copper(II)-bipyridyl complexes have been obtained by drawing a first straight line through the experimental points between  $\bar{n} = 0$  and  $\bar{n} = 0.8$  {in this range only  $\text{Cu}^{2+}$  and  $[\text{Cu}(\text{bip})]^{2+}$  species are present and therefore  $\bar{n} = \bar{n}'$ }. This line gives  $\varepsilon_1$  values as the  $E$  value at  $\bar{n} = 1$ . When the extinction coefficient  $\varepsilon_1$  of the unbipyridyl complex is known it is possible to draw a second line between  $\bar{n}' = 2$  and  $\bar{n}' = 3$  which leads to the values for  $\varepsilon_2$  and  $\varepsilon_3$ , the extinction coefficients of  $[\text{Cu}(\text{bip})_2]^{2+}$  and  $[\text{Cu}(\text{bip})_3]^{2+}$ , respectively. Then we may use the  $\varepsilon_3$  value to draw a third line between  $\bar{n}' = 1$  and  $\bar{n}' = 2$  from which we obtain again values of  $\varepsilon_1$  and  $\varepsilon_2$ . At all the 20 wavelengths examined, agreement between the two  $\varepsilon_1$  values obtained from the first and the second line, and the two  $\varepsilon_2$  values obtained from the second and the third line, was within 2%. The same agreement was achieved between  $\varepsilon_0$  values obtained, respectively, from solutions containing only  $\text{Cu}^{2+}$  ions and from the line drawn between  $0 < \bar{n}' < 1$ .

Fig. 4 shows the straight lines drawn from the spectra at 900 m $\mu$ . The full circles are

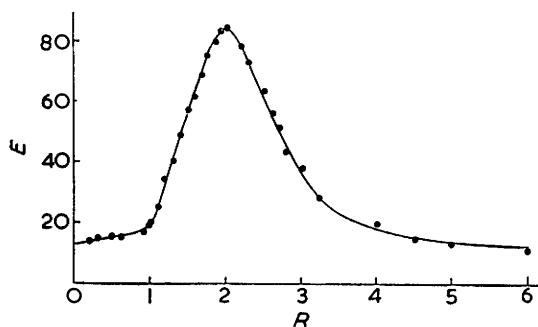


FIG. 2.

FIG. 2. Plot of molar extinction coefficients of copper(II)-bipyridyl system in aqueous alcohol against ligand : metal ratio  $R$  (EtOH 41.5% w/w; 20°;  $[Cu^{2+}] 5 \times 10^{-3}M$ ) at 900  $m\mu$ . The curve was calculated by using the values of the stability constants at 20° and the extinction coefficients 13.1, 17.2, 99.2, and 8.6 for  $Cu^{2+}$ ,  $[Cu(bip)]^{2+}$ ,  $[Cu(bip)_2]^{2+}$ , and  $[Cu(bip)_3]^{2+}$  complexes, respectively.

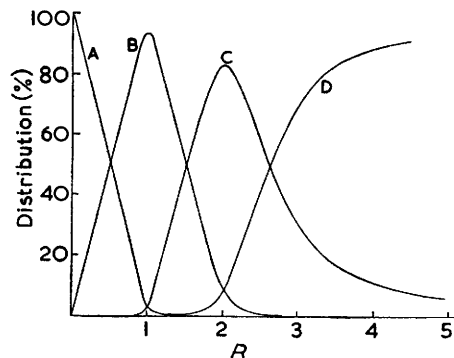


FIG. 3.

FIG. 3. Distribution (%) of species present in aqueous-alcoholic solutions of cupric ions and 2,2'-bipyridyl as a function of the ligand : metal ratio  $R$ . EtOH 41.5% w/w; 20°;  $[Cu^{2+}] 5 \times 10^{-3}M$ .

A,  $Cu^{2+}$ . B,  $[Cu(bip)]^{2+}$ . C,  $[Cu(bip)_2]^{2+}$ . D,  $[Cu(bip)_3]^{2+}$ .

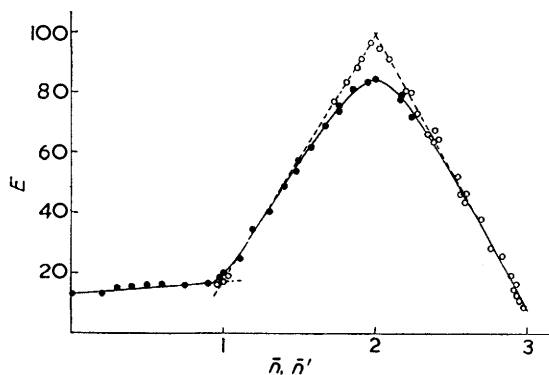


FIG. 4. Plot of the molar extinction coefficients ( $E$ ) of solutions containing  $Cu^{2+}$  ions and 2,2'-bipyridyl, against  $\bar{n}$ . Full circles denote experimental values; open circles denote calculated extinction coefficients of hypothetical solutions containing only two species  $[Cu(bip)_r]^{2+}$  and  $[Cu(bip)_{r+1}]^{2+}$ .

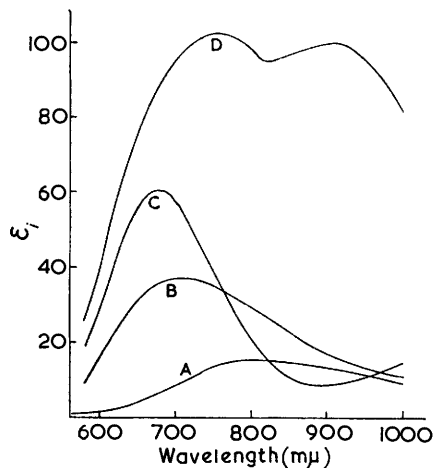


FIG. 5. Molar extinction coefficients ( $\epsilon_i$ ) of single species existing in solutions of  $Cu^{2+}$  ions and 2,2'-bipyridyl. A,  $Cu^{2+}$ . B,  $[Cu(bip)]^{2+}$ . C,  $[Cu(bip)_3]^{2+}$ . D,  $[Cu(bip)_2]^{2+}$ .

experimental data ( $E$  values) plotted against  $n$ , and open circles are calculated  $E'$  values against  $\bar{n}'$ .  $n$  values were obtained from potentiometric data and from the assumed value of  $k_1$ , while  $\bar{n}'$  values were calculated from equation (4). In Fig. 5 the curves  $\varepsilon_i = f(\lambda)$ , obtained from  $\varepsilon_i$  values calculated as previously described, are recorded. We have compared several experimental spectra at various ligand:metal ratios (with fixed total concentrations of metal ion) with the data calculated from the  $x_i$  and  $\varepsilon_i$  values of Figs. 3 and 5. The agreement between calculated and experimental result is within the limits of experimental reproducibility ( $\Delta E \approx \pm 2\%$ ) for all the conditions used in this work. We believe this to be a fairly good test for the stability constants obtained from potentiometric measurements and for the assumed value of  $k_1$ ; the latter is reasonably close to the value that may be deduced from the formation curve reported by Irving,<sup>7</sup> but does not agree with Gustafson and Martell's value.<sup>6</sup>

TABLE 1.

Formation constants of copper(II)-2,2'-bipyridyl chelate compounds in aqueous-alcoholic solution (ethanol 41.5% by wt.).

Temp.	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_2$	$\log \beta_3$
12°	(8.44)	5.38	3.38	13.82	17.20
20	(8.20)	5.14	3.18	13.34	16.52
25	(8.06)	5.04	3.13	13.10	16.23
30	(7.92)	4.89	3.00	12.81	15.81
36	(7.78)	4.77	2.91	12.55	15.46
40	(7.68)	4.70	2.88	12.38	15.26

$k_i$ 's are the values of the single-step constants;  $\beta_i$  indicates the values of the overall constants.  $\log k_1$  in parentheses have not been obtained experimentally, but have been assumed as explained in the text. The mean deviations are for  $\log k_1$  at 20°  $\pm 0.2$ , for  $\log k_2 \pm 0.04$ , and for  $\log k_3 \pm 0.06$  at all temperatures.

TABLE 2.

Formation constants of copper(II)-2,2'-bipyridyl chelate compounds in ethanol-water at 25°. <sup>a</sup>

Alcohol (wt. %)	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_2$	$\log \beta_3$	Method	Ref.
0	(8.47)	5.58	3.51	14.05	17.56	pAg <sup>b</sup>	<sup>d</sup>
	—	5.52	3.40	—	—	pH <sup>c</sup>	<sup>d</sup>
	6.33	—	—	—	—	pH	6
	8.20	5.45	3.25	13.65	16.90	Partition	7
	—	—	—	—	17.85	Polarographic	3
20	(8.30)	5.35	3.34	13.65	16.99	pAg <sup>c</sup>	<sup>d</sup>
30	(8.20)	5.25	3.28	13.45	16.73	pAg <sup>c</sup>	<sup>d</sup>
41.5	(8.06)	5.04	3.13	13.10	16.23	pAg	<sup>d</sup>

<sup>a</sup> The values corresponding to pAg-metric measurements were obtained by assuming the following values of the stability constants for Ag(I)-2,2'-bipyridyl compounds: EtOH 20% w/w,  $\log \beta_1$  3.71,  $\log \beta_2$  7.08; EtOH 30%,  $\log \beta_1$  3.74,  $\log \beta_2$  7.18; EtOH 41.5%,  $\log \beta_1$  3.70,  $\log \beta_2$  7.22. The results for 41.5% by weight of alcohol were reported earlier.<sup>1</sup> The error in  $\log \beta_1$  is  $\pm 0.05 \log k$  unit and in  $\log \beta_2$  is  $\pm 0.03$ . Because of the low solubility of Ag(I)-2,2'-bipyridyl complexes in mixtures with a low content of alcohol, these measurements were carried out with rather low concentrations of Ag<sup>+</sup> ion. Extrapolation to zero ethanol content gives  $\log \beta_1 = 3.72$  and  $\log \beta_2 = 7.02$ .

<sup>b</sup> Values in this line were obtained by extrapolating the results for alcohol-water mixtures. About  $\log k_1$  see the text. <sup>c</sup>  $\pm 0.05 \log k$  unit. <sup>d</sup> Present work.

In Table 1  $\log k_2$  and  $\log k_3$  obtained at several temperatures are reported. Formation curves used in calculating these results were tested by assuming  $\log k_1$  values calculated on the hypothesis that the entropy change in the first step is zero. This hypothesis has little or no influence on the calculated formation curve in the range  $1.3 < \bar{n} < 3$ , since the first two constants are very far apart.  $\log k_2$  and  $\log k_3$  values almost coincide with the pA values at  $\bar{n} = 1.5$  and  $\bar{n} = 2.5$ , respectively. (The differences between the final and the initial values of  $\log k_2$  and  $\log k_3$ , in the iteration process, carried out as described

by Carlson *et al.*,<sup>8</sup> were, respectively,  $-0.007$  and  $+0.014$  unit of  $\log k$ .) At each temperature the agreement between experimental data and formation curves calculated by using  $\beta_i$  values from Table 1 is similar to that shown in Fig. 1.

In Table 2 the results for decreasing concentrations of ethanol are reported. It has been assumed that the change of  $\log k_1$  with the concentration of ethanol is of the same order of magnitude as the change of  $\log k_2$ . The stability constants extrapolated to zero concentration of ethanol give a formation curve in reasonable agreement with the part of the curve obtained from direct pH measurements.

Table 3 lists the thermodynamic constants calculated from the equation,  $\log k_i = f(1/T)$ . Here the errors have been evaluated by methods described earlier.<sup>1</sup>

The large difference found between  $\log k_1$  and  $\log k_2$  is, perhaps, due to the rather unusual steric conformation of the bisbipyridyl complex. In fact Jørgensen<sup>9</sup> deduced

TABLE 3.

Values of the thermodynamic functions for the formation of copper(II)-2,2'-bipyridyl complexes in aqueous alcohol (41.5% by wt. of alcohol).

Reaction	$-\Delta F^\circ$ (cal./mole)	$-\Delta H^\circ$ (cal./mole)	$\Delta S^\circ$ (e.u.)
$\text{Cu}^{2+} + \text{bip} = \text{Cu}(\text{bip})^{2+}$ .....	$11,000 \pm 270^a$	—	—
$\text{Cu}(\text{bip})^{2+} + \text{bip} = \text{Cu}(\text{bip})_2^{2+}$ .....	$6876 \pm 55$	$9962 \pm 332$	$-10.3 \pm 1.3$
$\text{Cu}(\text{bip})_2^{2+} + \text{bip} = \text{Cu}(\text{bip})_3^{2+}$ .....	$4270 \pm 82$	$7392 \pm 500$	$-10.5 \pm 1.9$

<sup>a</sup> At 20°; others at 25°.

from spectrophotometric data that the  $[\text{Cu}(\text{bip})_2(\text{H}_2\text{O})_2]^{2+}$  ion is present almost exclusively in the *cis*-configuration, and this has been confirmed by proton-spin relaxation measurements.<sup>10</sup>

Since there are often large discrepancies between thermodynamic results obtained from the relation  $\log k_i = f(1/T)$  and from direct calorimetric measurements, and also in order to cover the lack of data about enthalpy changes in the formation of the unibipyridyl complex, it would be useful to test the results reported in the present paper by calorimetric methods.

*Experimental.*—The apparatus and techniques used in the pAg- and pH-metric measurements were as described previously.<sup>1</sup>

Absorption spectra were measured with a model 3000 "Spectracord" double-beam spectrophotometer and were reproducible within 2–3%.

Copper nitrate concentrations in pAg- and pH-metric measurements ranged from  $5 \times 10^{-4}$  to  $10^{-2}\text{M}$ ; silver nitrate concentrations varied between  $10^{-3}$  and  $5 \times 10^{-3}\text{M}$  in pAg-metric experiments; the nitric acid concentration was always  $10^{-3}\text{M}$  in pH-metric experiences.

Merck's "extra pure" copper nitrate was used for the stock solution, to which a small quantity of nitric acid was added to prevent hydrolysis. The concentration of the solution was determined by electrodeposition.

Silver nitrate, potassium nitrate, and 2,2'-bipyridyl were Merck products. The purity of the bipyridyl was verified by its m. p.; when necessary the compound was purified by precipitation from a concentrated solution in ethanol by water.

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<sup>8</sup> Carlson, Reynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

<sup>9</sup> Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

<sup>10</sup> Morgan, Murphy, and Cox, *J. Amer. Chem. Soc.*, 1959, **81**, 5043.