

## Thermodynamic and Spectroscopic Properties of Mixed-ligand Complexes of Copper(II) with Pyridine, 2,2'-Bipyridyl, and 2,2':6',2''-Terpyridyl in Aqueous Solution

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Thermodynamic and e.s.r. studies in aqueous solution have been carried out on the following systems: Cu–bipy–py, Cu–terpy–py, and Cu–terpy–bipy, where bipy, terpy, and py are 2,2'-bipyridyl, 2,2':6',2''-terpyridyl, and pyridine respectively. Two ternary species  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  were found in the first system, while only one species is present in the second and the third systems. The experimental data clearly indicate tetragonally distorted octahedral geometries except in  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$ , for which five-co-ordination involving a square-pyramidal stereochemistry is proposed. The use of the stabilization parameters,  $\Delta \log K$  and  $\log K_m$ , in comparison with a combined thermodynamic and spectroscopic approach, is also critically discussed.

Among mixed-ligand complexes containing transition-metal ions, those with copper(II) are surely the most studied.<sup>1-3</sup> On the basis of previous studies on ternary complexes containing 2,2'-bipyridyl (bipy) and other aromatic or heteroaromatic N bases,<sup>4-11</sup> an increased stability has been ascertained in aqueous solution for certain ligand combinations. In particular, this extra stability occurs when the metal ion is co-ordinated to heteroaromatic N and O donor ligands<sup>2</sup> and was attributed in large measure to the  $\pi$ -accepting properties of the ligand. Recent studies<sup>10,12-15</sup> on the stability of copper(II) mixed-ligand complexes with bi- or tri-dentate N bases having  $\pi$ -accepting properties and bi- or tri-dentate dicarboxylate ligands have had a significant effect on the previous generalization about the origin of the stabilization effect, restricting it to the case of ternary complexes in which the metal ion is four-co-ordinated.

We have now determined the thermodynamic and spectroscopic (e.s.r. and electronic) parameters, in aqueous solution, of ternary complexes of copper(II) with bipy or 2,2':6',2''-terpyridyl (terpy) and pyridine (py). Because of the different numbers of N donor atoms involved, it was possible to evaluate the effects of ligand denticity and geometric characteristics on the co-ordination properties of copper(II). The thermodynamic and spectroscopic data obtained have been compared with those of the corresponding parent complexes previously determined,<sup>16-19</sup> in order to highlight the differ-

ences between the binary and ternary complexes with the same set of donor atoms.

### Experimental

**Chemicals.**—2,2'-Bipyridyl (C. Erba RPE) and 2,2':6',2''-terpyridyl (Fluka) were recrystallized from water–ethanol mixtures, while pyridine (Fluka) was used as received. The purity of these compounds was checked by determining the values of their protonation constants; the values found agreed with those previously determined.<sup>16,17,20</sup>

All solutions were prepared with twice-distilled water and their ionic strength was kept at 0.1 mol dm<sup>-3</sup> by use of potassium nitrate. The standardization of solutions was carried out as previously described.<sup>21</sup>

**E.m.f. Measurements.**—Potentiometric measurements were performed by means of an Orion 801 A meter equipped with EIL glass and Ingold saturated calomel electrodes. This apparatus was connected to an AMEL timer-printer (model 882) which controlled the addition of the titrant delivered from an AMEL digital dispenser (model 232). Table I shows the experimental details of potentiometric titrations; other details can be found in previous papers.<sup>8,12</sup> Some data from earlier work were also used, namely the stability constants of simple complexes<sup>16,17,20</sup> as well as the formation constant of  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$ .<sup>22</sup>

Table I. Experimental details of potentiometric measurements at 25 °C and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ )

Titration vessel <sup>a</sup>				Titrant	No. of titrations
$C_{\text{Cu}}$	$C_{\text{bipy}}$	$C_{\text{terpy}}$	$C_{\text{py}}$		
1.5	2.1	1.5	—	0.1 mol dm <sup>-3</sup> KOH	3
0.91	3.0	0.92	—		3 pH = 2.4–4.5 <sup>b</sup>
2.0	4.1	2.0	—		3
2.0	2.0	—	5.9	0.25 mol dm <sup>-3</sup> KOH	3
3.0	3.0	—	8.8		2
1.5	1.5	—	7.8		2 pH = 2.5–5.5
4.5	4.4	—	23.4		2
4.6	4.5	—	48.0		3

<sup>a</sup> Concentrations in mmol dm<sup>-3</sup>. <sup>b</sup> The initial pH was adjusted by adding  $\text{HNO}_3$ .

**Calorimetric Measurements.**—An LKB precision calorimeter (model 8700) and a 100-cm<sup>3</sup> titration vessel (model 8726—1) were employed for the calorimetric measurements. The reproducibility of the system and other details of the calorimetric titrations have already been reported.<sup>16</sup> Experimental conditions are reported in Table 2. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values of the simple complexes were taken from the literature.<sup>16,17,23</sup>

**Spectroscopic Measurements.**—Electronic absorption spectra of aqueous solutions were recorded at room temperature with an Optica CF 4 NI double-beam spectrophotometer in 1-cm quartz cells. In order to obtain the spectral patterns of individual species, spectra with different ratios of metal to ligand were run. The concentration of each species was calculated on the basis of its formation constant by using the EQUIL program.<sup>24</sup> Particular attention had to be paid to the Cu-bipy-py system in order to determine experimental conditions under which the species  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  were present. This was not necessary in the Cu-terpy-py and Cu-terpy-bipy systems which both gave a single species, namely  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$  respectively.

First-derivative X-band e.s.r. spectra were recorded by means of a Bruker ER 200 D instrument equipped with a standard low-temperature control unit. All measurements were carried out at 120 K, using quartz sample tubes. The solutions were prepared from those employed in the optical study by adding methanol [methanol-water (1:3)] to the aqueous solution in order to increase resolution. Only one

set of lines characteristic of copper(II) mononuclear species was observed in each case. Field calibration was checked by using diphenylpicrylhydrazyl (dpph) as a *g* marker.

The perpendicular parts of the spectra were analysed by means of a simulation program based on formulae derived from second-order perturbation theory,<sup>18,25</sup> while the parallel parts were clear enough to yield reasonable values of  $g_{\parallel}$  and  $A_{\parallel}$ .

Spin-Hamiltonian parameters for these systems are reported in Table 3 together with the values of  $\nu_{\text{max}}$  and  $\epsilon_{\text{max}}$  taken from the optical study. Also shown are some spin-Hamiltonian parameters of simple complexes useful to the comparison with systems having the same set of N donor atoms.

**Calculations.**—The checks of the purity of the ligands and the  $E^\circ$  determinations were carried out by using the ACBA program.<sup>26</sup> The formation constants were computed by the programs SCOGSB<sup>27,28</sup> and MINQUAD,<sup>29,30</sup> and the DOEC program<sup>31</sup> was used to evaluate the formation enthalpies. Calculations were first performed separately on each potentiometric and calorimetric titration and later simultaneously on all titrations of each system. The errors listed in Table 4 represent three times the standard deviation. Throughout this paper 1 cal = 4.148 J.

## Results and Discussion

Copper(II) ions with terpy and bipy give rise to the species  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$ , while with bipy and py both  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  are formed. One species only was found in the system Cu-terpy-py, namely  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$ .<sup>22</sup> Due to the high ratio of py:  $[\text{Cu}(\text{bipy})]^{2+}$ , the possibility of the formation of  $[\text{Cu}(\text{bipy})(\text{py})_3]^{2+}$  was also considered. Statistical parameters<sup>32,33</sup> of the 1:1:1 Cu: bipy: py species have been improved by taking into account the formation of the 1:1:2 species ( $\sigma = 1.6 \times 10^{-4}$ ,  $R = 1.1\%$  in the first model and  $\sigma = 3.6 \times 10^{-5}$  and  $R = 0.25\%$  in the second model). Introduction of the 1:1:3 species did not result in any noteworthy improvement of the statistical parameters. Hence, the formation of the species  $[\text{Cu}(\text{bipy})(\text{py})_3]^{2+}$  was excluded. Moreover, because  $[\text{Cu}^{2+}]: [\text{bipy}] = 1$ , species containing two molecules of bipy were not taken into consideration. The formation of hydrolytic species could be excluded at the pH range explored.

Thermodynamic data for the formation of these mixed-ligand complexes are reported in Table 4. Large negative  $\Delta H^\circ$  values with  $\Delta S^\circ$  values close to zero were found except for the  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$  complex. The enthalpy changes

**Table 2.** Experimental details of calorimetric measurements at 25 °C and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ )

Titration vessel <sup>a</sup>			Titrant <sup>a</sup>	No. of titrations	pH <sup>b</sup>
$c_{\text{Cu}}$	$c_{\text{terpy}}$	$c_{\text{bipy}}$			
2.0	2.0	—	bipy 20.0	4	5.2–7.4
1.5	1.5	—	bipy 20.0	3	
5.0	—	5.0	py 954.0	5	5.0–6.6
4.5	—	4.5	py 900.0	4	
2.0	2.0	—	py 954.0	4	5.3–7.3
1.5	1.5	—	py 954.0	4	

<sup>a</sup> Concentrations in  $\text{mmol dm}^{-3}$ . <sup>b</sup> Adjusted by adding  $\text{HNO}_3$ .

**Table 3.** E.s.r. and electronic visible spectral data for copper(II) mixed-ligand complexes. Values in parentheses are the presumed errors in the last decimal figure

Complex	No. of N atoms	<i>g</i>	$10^4 A / \text{cm}^{-1}$	$g_{\parallel}$	$10^4 A_{\parallel} / \text{cm}^{-1}$	$10^4 A_{\perp} / \text{cm}^{-1}$	$10^4 A_{\perp}^N / \text{cm}^{-1}$	$10^{-3} \nu_{\text{max}} / \text{cm}^{-1}$	Ref.
$[\text{Cu}(\text{bipy})]^{2+}$	2	2.308	166	2.068	7	14	10	—	36
$[\text{Cu}(\text{bipy})(\text{py})]^{2+}$	3	2.268(2)	174(2)	2.052(5)	12(3)	15(2)	10(2)	15.4(78)	This work
$[\text{Cu}(\text{terpy})]^{2+}$	3	2.270	175	2.064	15	14	10	14.7(80)	18
$[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$	4	2.239(1)	181(2)	2.036(5)	16(3)	16(2)	11(2)	15.6(82)	This work
$[\text{Cu}(\text{terpy})(\text{py})]^{2+}$	4	2.228(2)	173(2)	2.039(5)	18(3)	14(2)	10(2)	16.0(97)	This work
$[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$	5	2.242(4)	161(3)	2.053(5)	14(3)	14(2)	10(2)	15.5(81)	This work
$[\text{Cu}(\text{bipy})_3]^{2+}$	6	2.266	161	2.070	13	16	10	—	36

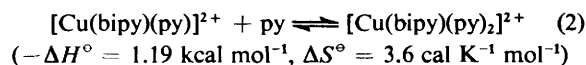
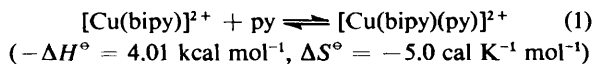
\* Values of  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  are given in parentheses.

Table 4. Thermodynamic values for copper(II) mixed-ligand complexes at 25 °C and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ )

Reaction	$-\Delta G^\circ/\text{kcal mol}^{-1}$	$-\Delta H^\circ/\text{kcal mol}^{-1}$	$\Delta S^\circ/\text{cal K}^{-1} \text{ mol}^{-1}$
$\text{Cu}^{2+} + \text{terpy} + \text{py} \rightleftharpoons [\text{Cu}(\text{terpy})(\text{py})]^{2+}$	19.20 <sup>a</sup>	$19.05 \pm 0.46$	$0.5 \pm 1.5$
$\text{Cu}^{2+} + \text{bipy} + \text{py} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{py})]^{2+}$	$13.57 \pm 0.11$	$14.67 \pm 0.20$	$-3.7 \pm 0.8$
$\text{Cu}^{2+} + \text{bipy} + 2 \text{py} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$	$15.82 \pm 0.15$	$15.85 \pm 0.28$	$-0.1 \pm 0.9$
$\text{Cu}^{2+} + \text{terpy} + \text{bipy} \rightleftharpoons [\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$	$23.87 \pm 0.23$	$18.72 \pm 0.36$	$17.3 \pm 1.5$
$\text{Cu}^{2+} + \text{terpy} \rightleftharpoons [\text{Cu}(\text{terpy})]^{2+}$ <sup>b</sup>	16.75	14.03	9.1
$\text{Cu}^{2+} + 2 \text{bipy} \rightleftharpoons [\text{Cu}(\text{bipy})_2]^{2+}$ <sup>c</sup>	18.62	16.74	6.3

<sup>a</sup> Ref. 22, <sup>b</sup> Ref. 17, <sup>c</sup> Ref. 16.

are as expected in the case of interaction of copper(II) with nitrogen-donor atoms. Thus, the  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  complexes show enthalpy changes similar to those accompanying the formation of  $[\text{Cu}(\text{terpy})]^{2+}$  and  $[\text{Cu}(\text{bipy})]^{2+}$ . The more positive entropy changes can be ascribed to the formation of two chelate rings in the simple complexes compared with a single ring in both mixed-ligand species. Considering the thermodynamic results corresponding to equilibria (1) and (2), one can see that the formation of



$[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  is more enthalpically favoured than  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$ . This can only be explained by invoking a weaker interaction with solvent molecules of the metal ion bound to four nitrogen atoms. The positive  $\Delta S^\circ$  for the formation of  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  as well as the spectroscopic data for these two complexes (see Table 3) are consistent with this interpretation.

All the e.s.r. spectra show  $g_{\parallel} > g_{\perp} \approx 2.040$  and therefore are characteristic of a  $d_{x^2-y^2}$  or  $d_{xy}$  ground state in octahedral, square-planar, or square-pyramidal geometries.<sup>34,35</sup> Only the spectra of  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  show a quite well resolved ligand hyperfine structure (Figure). This is very important since it allows us to assign the in-plane donor atoms. In the spectrum of  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  [Figure (b)] it appears on the 3/2 and 1/2 lines (even though it is not very clear, more than five components can be observed), whereas in the spectrum of  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  [Figure (c)] only the -3/2 line gives a well resolved superhyperfine structure showing the theoretical pattern of nine lines with approximate intensity ratio 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1. From a comparison of the  $g_{\parallel}$  and  $A_{\parallel}$  values with those of  $[\text{Cu}(\text{bipy})]^{2+}$  it can be concluded that the pyridine molecules substitute the two water molecules in the equatorial plane. In fact there is a marked decrease in  $g_{\parallel}$  and a moderate increase in  $A_{\parallel}$ , suggesting that a progressive increase of the equatorial field is occurring. Moreover, the appearance of superhyperfine structure leads us to think that in-plane chromophores of the type  $\text{CuN}_3\text{O}$  and  $\text{CuN}_4$  can be reasonably assumed for  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  respectively. This conclusion is supported by a comparison between the e.s.r. parameters of  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{terpy})]^{2+}$  which have similar in-plane chromophores,  $\text{CuN}_2\text{N}'\text{O}$  and  $\text{CuN}_3\text{O}$  respectively. Apart from minor differences their parameters are quite similar. The  $A_{\parallel}$  value of  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$ , higher than that of  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$ , can be also ascribed to a weaker interaction with apical solvent molecules.

There has been a great debate in the past about the e.s.r. spectra of *trans*- and *cis*- $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ . Sigel and

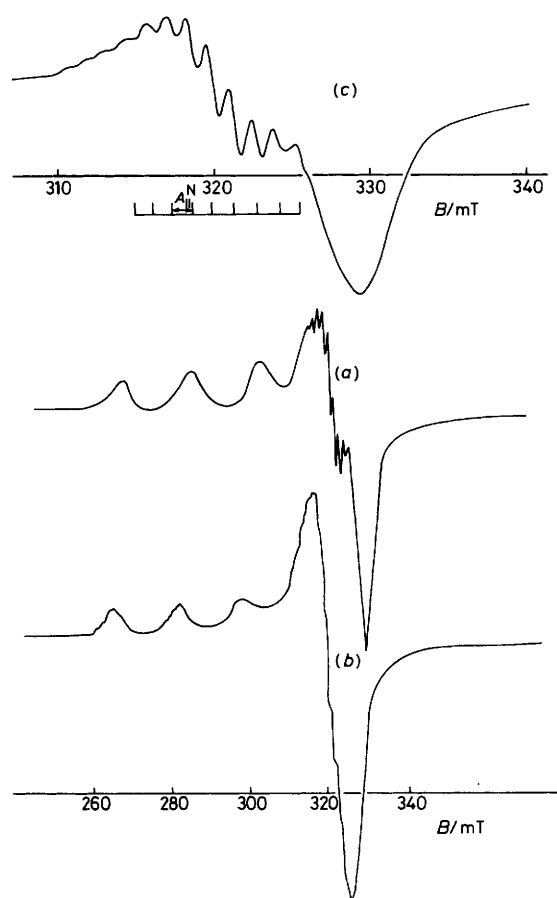


Figure. Frozen-solution e.s.r. spectra of (a)  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  ( $[\text{Cu}^{2+}] = [\text{bipy}] = 3 \times 10^{-3}$ ,  $[\text{py}] = 4.6 \times 10^{-2} \text{ mol dm}^{-3}$ ) and (b)  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  ( $[\text{Cu}^{2+}] = [\text{bipy}] = 3 \times 10^{-3}$ ,  $[\text{py}] = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$ ), in water-methanol at 120 K. The perpendicular part of the  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$  spectrum is also shown enlarged in (c)

Walker<sup>36,37</sup> pointed out that the e.s.r. spectrum of a frozen solution where  $[\text{Cu}] : [\text{bipy}] = 1 : 2$  comprises an overlap of the spectra of  $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{Cu}(\text{bipy})_3]^{2+}$ . They considered the observation of Noack and Gordon<sup>38</sup> on the existence of *cis*- $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$  at low temperature to be erroneous. Marov *et al.*<sup>39</sup> re-examined the problem and postulated the existence of a *cis*- $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$  species with  $g_{\parallel}$  ranging from 2.222 to 2.227 and  $A_{\parallel}$  from 0.0118 to 0.0129  $\text{cm}^{-1}$ . For the corresponding *trans* species they assumed valid some previous values,<sup>38,40</sup> namely  $g_{\parallel} = 2.281-2.285$  and  $A_{\parallel} = 0.0160-0.0165 \text{ cm}^{-1}$ . They did not comment on the differences in the  $g_{\parallel}$  and  $A_{\parallel}$  values of the two species. These different parameters are obviously associated with two

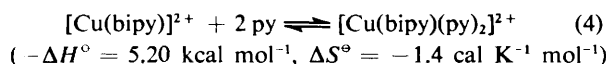
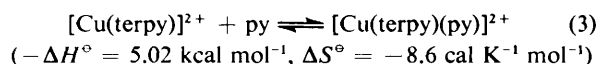
Table 5.  $\Delta \log K$  values for some copper(II) mixed-ligand complexes with N donor ligands

Reaction	$\Delta \log K$	Ref.
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{py})]^{2+} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{py})]^{2+} + \text{Cu}^{2+}$	-0.68	This work
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{py})_2]^{2+} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{py})_2]^{2+} + \text{Cu}^{2+}$	-0.85	This work
$[\text{Cu}(\text{terpy})]^{2+} + [\text{Cu}(\text{py})]^{2+} \rightleftharpoons [\text{Cu}(\text{terpy})(\text{py})]^{2+} + \text{Cu}^{2+}$	-0.72	This work
$[\text{Cu}(\text{terpy})]^{2+} + [\text{Cu}(\text{bipy})]^{2+} \rightleftharpoons [\text{Cu}(\text{terpy})(\text{bipy})]^{2+} + \text{Cu}^{2+}$	-2.89	This work
$[\text{Cu}(\text{pn})]^{2+} + [\text{Cu}(\text{en})]^{2+} \rightleftharpoons [\text{Cu}(\text{pn})(\text{en})]^{2+} + \text{Cu}^{2+}$	-1.39	4
$[\text{Cu}(\text{hist})]^{2+} + [\text{Cu}(\text{en})]^{2+} \rightleftharpoons [\text{Cu}(\text{hist})(\text{en})]^{2+} + \text{Cu}^{2+}$	-1.49	4
$[\text{Cu}(\text{hist})]^{2+} + [\text{Cu}(\text{pd})]^{2+} \rightleftharpoons [\text{Cu}(\text{hist})(\text{pd})]^{2+} + \text{Cu}^{2+}$	-2.23	4
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{en})]^{2+} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{en})]^{2+} + \text{Cu}^{2+}$	-1.29	5
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{pd})]^{2+} \rightleftharpoons [\text{Cu}(\text{bipy})(\text{pd})]^{2+} + \text{Cu}^{2+}$	-2.47	5
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{ida})] \rightleftharpoons [\text{Cu}(\text{bipy})(\text{ida})] + \text{Cu}^{2+}$	-1.90	14
$[\text{Cu}(\text{bipy})]^{2+} + [\text{Cu}(\text{pydca})] \rightleftharpoons [\text{Cu}(\text{bipy})(\text{pydca})] + \text{Cu}^{2+}$	-1.30	14

en = Ethylenediamine; pd = 1,3-diaminopropane; hist = histamine; ida = iminodiacetate; pydca = pyridine-2,6-dicarboxylate.

different stereochemistries. The lower  $A_{\parallel}$  value for the *cis* complex is due to a compression along the *z* axis because of the stronger bonds with two nitrogen-donor atoms. The higher  $A_{\parallel}$  value, which is comparable with that of  $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ ,<sup>36</sup> can be explained by taking into account a  $\text{CuN}_4$  chromophore as well as a tetrahedral distortion, owing to the difficulty of accommodating two bipy molecules in the same plane.<sup>41,42</sup> Obviously in the  $[\text{Cu}(\text{bipy})(\text{py})]^{2+}$  complex the overall situation is different, there being two pyridine molecules and only one bipy molecule. There is no reason why the two nitrogens of the two pyridine molecules could not be coplanar with the two nitrogens of the bipy molecule. In fact the relatively high  $A_{\parallel}$  and the low  $g_{\parallel}$  value probably reflect the occurrence of a  $\text{CuN}_4\text{O}_2$  octahedral complex where the apical water molecules are far away from the metal ion. Hence, in this case the *trans*-diaqua is the only species that can be obtained. Our data are in agreement with previous studies on  $\text{CuN}_4$  chromophores (with N from pyridine or pyridine derivatives) both in solution and in the solid state.<sup>43-46</sup> Furthermore, these data give indirect support to the analysis of Marov *et al.*<sup>39</sup> for distinguishing between the spectra of *cis*- and *trans*- $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ .<sup>38</sup>

Comparing the thermodynamic data for the equilibria (3) and (4), where the final species involve the same number of N



donor atoms, one can see that both complexes are equally enthalpically favoured, while their  $\Delta S^\circ$  values are different. This trend can be attributed to the limited accessibility of the fourth binding site after co-ordination of a planar terpy molecule to copper. Analogous considerations apply to the differences observed in the  $\Delta S^\circ$  values between the  $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$  systems (Table 4). In the case of  $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$  the *cis*-diaqua-configuration removes possible steric crowding between the two chelate rings of the di-imine. This is not the case for  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$  in which the terpy chelate rings are fused giving rise to strain. The greater equatorial field due to the three nitrogen atoms of terpy explains the more exothermic  $\Delta H^\circ$  value.

The e.s.r. data for  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$  are approximately similar to those of  $[\text{Cu}(\text{bipy})(\text{py})_2]^{2+}$ , slight differences in the

$g_{\parallel}$  and  $A_{\parallel}$  values being ascribed to a stronger and, simultaneously, less symmetric field present in the former.

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values of  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$  show that the formation of this complex is more entropically and less enthalpically favoured than that of  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$ . On the basis of thermodynamic data, this can only be attributed to the formation of a new chelate ring around the copper(II) ion, *i.e.* that of bipy ligand, already co-ordinated to terpy. No conclusion can be drawn about the stereochemistry adopted by the copper ion in this complex. Hence, the spectroscopic data are crucial. Comparing the magnetic parameters of  $[\text{Cu}(\text{terpy})(\text{py})]^{2+}$  and  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$ , the  $g_{\parallel}$  and  $A_{\parallel}$  values are higher and lower respectively for the latter. These shifts can only be explained by taking into account a strong apical interaction of the second bipy nitrogen with the metal ion, in other words a square-pyramidal geometry with a shorter apical Cu-N bond distance. This is supported by the shift observed in the optical spectral maximum.

## Conclusions

The combination of thermodynamics and spectroscopy employed brings to light the co-ordination plasticity of copper(II) in these mixed-ligand complexes. It is precisely because of this plasticity that great care is needed in the use of  $\Delta \log K$  (see Appendix) values.<sup>47</sup> In some cases the differences found in  $\Delta \log K$  values (Table 5) seem to correlate fairly well with the electronic and geometric characteristics of the mixed-ligand complexes, and also at first sight to be in agreement with previous results. In fact, the  $\Delta \log K$  values are negative for all the ternary complexes, as found for other mixed amine complexes.<sup>48,49</sup> The more negative value in the case of  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$ , similar to those found for ternary complexes containing heteroaromatic N base and O donor ligands, is consistent with the number of donor atoms being higher than four.<sup>10,12</sup> However, this behaviour is 'strange', because, among the complexes reported here,  $[\text{Cu}(\text{terpy})(\text{bipy})]^{2+}$  is the only one showing entropy and enthalpy stabilization. This fact does not seem to influence the  $\Delta \log K$  value. Therefore, care should be employed in the interpretation of this parameter, particularly when it is used to compare the degree of stabilization of ternary complexes with their bonding details.<sup>50,51</sup>

In the series of mixed-ligand complexes reported here, two interesting points emerge.

(1)  $\Delta \log K$  values seem to be influenced by the stability constants of simple complexes. They become more negative

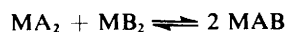
as the difference between the stability constants of the simple parent complexes decreases.

(2) The comparison of  $\Delta \log K$  values on the basis of the statistical approach, within a series of ternary complexes in which the metal ion has different co-ordination numbers and geometries, may give incorrect results, due to different 'cratic' contributions.

Finally,  $\Delta \log K$  quantifies the position of the equilibrium  $MA + MB \rightleftharpoons MAB + M$  but one should be careful in using this parameter to draw conclusions on the inorganic features of transition-metal complexes. We think the knowledge gained in the way we have outlined and the comparison of thermodynamic functions accompanying mixed-ligand complex formation will surely be more useful.

### Appendix

The tendency towards mixed-ligand complex formation is usually expressed in two different ways.<sup>1</sup> In the first approach the stability of a ternary species with different ligands is compared with the stability of the parent 1:2 complexes. The mixed-ligand complex formation is then represented by equations (A1) and (A2). From statistical considerations



$$K_m = [MAB]^2/[MA_2][MB_2] \quad (A1)$$

$$\log K_m = 2 \log \beta_{MAB}^M - (\log \beta_{MA_2}^M + \log \beta_{MB_2}^M) \quad (A2)$$

$K_m = 0.60$ . Differences from this value are currently discussed in terms of enhanced or reduced stability of the mixed-ligand complex. However, this has been severely criticized in at least two papers<sup>47,48</sup> and is now rarely employed.

The second approach relates the stability of the mixed-ligand complex to the simple 1:1 complexes according to equations (A3) and (A4). Since the ligand A (or B) co-



$$\Delta \log K = \log \beta_{MAB}^M - (\log K_{MA}^M + \log K_{MB}^M) \quad (A4)$$

ordinates more easily to the metal ion than to the simple complex MB (or MA),  $\Delta \log K$  should be negative. Usually this is the case in simple binary complexes in which  $\log K_1$  is larger than  $\log K_2$ . On the contrary, in the case of mixed-ligand complexes  $\Delta \log K$  is positive for certain combinations of bidentate ligands.<sup>1</sup> This parameter has been considered to be a better measure of the intrinsic tendency towards mixed-ligand complex formation than  $\log K_m$ . Also in this case a statistical approach has been proposed.<sup>1</sup>

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