Stability and Lability of Dicopper Double-Stranded Helicates in Solution

by **Riccardo F. Carina, Alan F. Williams***, and **Claude Piguet**

Département de Chimie Minérale et Analytique, Université de Genève, 30 quai Ernest-Ansermet, CH-1211 Genève 4

Stability constants have been measured for a series of ligands based on a 2,2′-(pyridine-2,6-diyl)bis[1*H*-benzimidazole] unit which forms dinuclear double-stranded helical complexes with copper(I). Variation of different structural parameters confirms the importance of the coordinate bond, the stacking interactions, and the weakly bridging pyridine units observed by X-ray crystallography. The stabilities of the complexes depend strongly on the solvent, and in MeCN, which is a good solvent for copper(I), the complexes are less stable and assemble in a stepwise manner. The interconversion of the enantiomers may be followed by ^{1}H-NMR and takes place on a millisecond time scale around room temperature. The trends in lability are similar to those found for the stability of the complexes.

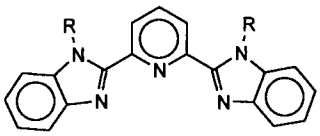
Introduction. – There is currently considerable interest in the use of the coordinate bond to assemble supramolecular structures [1], since, compared to the other forces used to combine the modular units of a supermolecule, the coordinate bond offers a number of advantages: the interaction between a metal ion and a coordination site is frequently stronger than intermolecular forces, and, by virtue of the stereochemical preferences of the metal ion, possesses a directional character which can control the structure of the assembled product. Despite its strength, the coordinate bond is frequently labile, and it is, therefore, possible for rapid rearrangements to occur, and for a system held together by such bonds to reach the free-energy minimum corresponding to strict self-assembly as defined by *Lindsey* [2].

Polynuclear helical complexes, or helicates [3], occupy a privileged position in metallosupramolecular chemistry. A considerable body of research now exists and has established the structural principles of the formation of polynuclear helicates with a wide variety of metals and ligands. With these principles, it should be possible to design new systems which maximize the interactions leading to helication and enhance the stability of the complexes. To do this, we need data on the quantitative importance of effects such as stacking interactions, the strength of the coordinate bond, *etc.* The techniques used to study helicate formation, typically X-ray crystallography, NMR, and mass spectroscopy, are powerful structure-analysis techniques but do not generally yield quantitative data about the stability of the helices. Thermodynamic studies of helicate formation in solution are quite rare and have generally been concerned with the identification of the formation pathways for complexes [4–6] rather than with the relative stability of helicates containing closely related ligands.

Our first objective in this paper is to compare the stabilities of a series of dicopper double helicates containing closely related ligands in order to evaluate the importance of the various factors proposed from X-ray structure analysis to be important for helicate formation. The second aim is to study the dynamics of these systems. Since the coordi-

nate bond is labile, one might imagine that structural rearrangements would be rapid in solution. Helical systems are inherently chiral, and the lability may conveniently be measured by studying the rate of conversion between (*P*)- and (*M*)-helices [7] in solution. This question is particularly interesting since it was recently found that a dinuclear triple helix showed a remarkable stability to inversion [8].

The systems to be studied are based on the dicopper double helix $[Cu_2(\mathbf{1a})_2]^{2+}$ which we reported some years ago [9]. In this complex, each Cu-atom is essentially linearly coordinated by two 1*H*-benzimidazole units, one from each strand. In addition, we observed an interaction with the bridging pyridine units which was assumed to be weak since the Cu–N(pyridine) distance (average 2.5 Å) is much longer than the Cu–N(benzimidazole) (average 1.915 Å). Finally, an intramolecular stacking interaction between 1*H*-benzimidazole units of different strands was observed. To evaluate the importance of these three effects, the ligand system was modified. Ligand **2a** gave a



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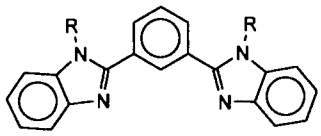
b R = dmb



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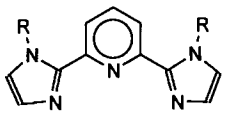
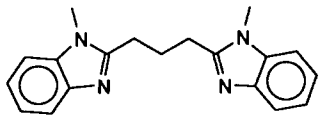
b R = dmb



3a R = Me
b R = dmb



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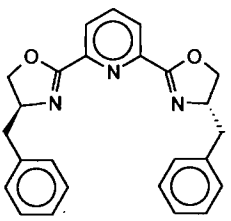

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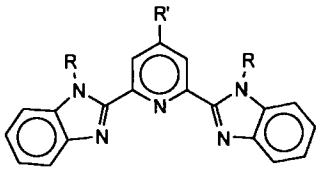
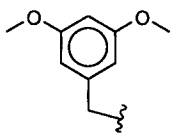


6 R = dmb, R' = Ph
7 R = dmb, R' = *p*-$O_2NC_6H_4$
8 R = dmb, R' = *p*-$Et_2NC_6H_4$
9 R = dmb, R' = MeO

dmb =



centrosymmetric 'side-by-side' complex $[Cu_2(\mathbf{2a})_2]^{2+}$ implying that the bridging pyridine is essential for helication [10]. Ligand **3a** was used to investigate the importance of the stacking interaction, since models showed that replacement of 1*H*-benzimidazole by 1*H*-imidazole would not give an intramolecular stacking interaction. The crystal structure showed $[Cu_2(\mathbf{3a})_2]^{2+}$ to have a double-helical structure, with intermolecular stacking between 1*H*-imidazole units [11]. Ligand **4** formed a mononuclear complex $[Cu(\mathbf{4})(MeCN)]^+$ establishing that the ligand must be sufficiently rigid to prevent it from acting as a bidentate ligand for one metal [12]. Finally, we have shown very recently that introduction of chirality, in the form of a dihydrooxazole unit as in **5**, leads to stereospecific formation of helices of one chirality [13].

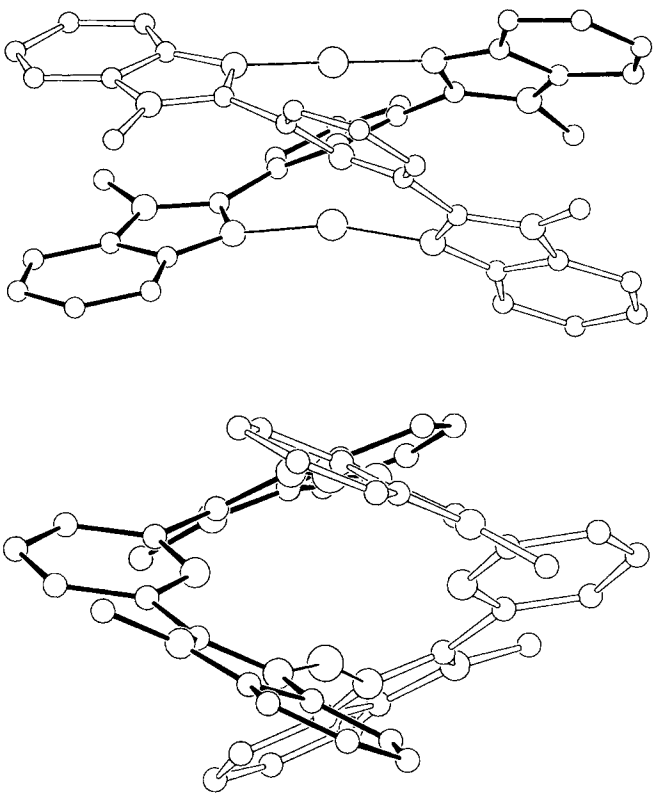


Fig. 1. *Structure of* $[Cu_2(\mathbf{1a})_2]^{2+}$ [9]

In this paper, we report and discuss the relative stabilities and labilities of the dinuclear complexes of ligands **1**–**3**, together with the ligands **6**–**9** which were synthesized [14] to modify the donor strength of the pyridine. We replaced the methyl substituent of the 1*H*-benzimidazole by the 3,5-dimethoxybenzyl (dmb) substituent. This greatly increases the solubility of the ligand and makes titration of the ligand by metal feasible, and also offers the advantage that in a chiral complex, the methylene protons

are diastereotopic, [10] and inversion of the helix may be followed by NMR line broadening. A preliminary account of some of this work has appeared [15].

Results. – *Measurement of Stability Constants.* Stability constants were measured either by spectrophotometric titration or by potentiometric titration. Comparison of the two methods for $[Cu_2(\mathbf{1b})_2]^{2+}$ in MeCN gave the same values within experimental error. The results are summarized in *Table 1*.

Table 1. *Stability Constants* (log β) *in Dimethylformamide* (DMF) *or MeCN + 10% DMF at 295 K*

	log β	
	DMF	MeCN + 10% DMF
$[Cu_2(\mathbf{1b})_2]^{2+}$	14.5(3)[a])	8.72(3)[a]) 8.59(1)[b])
$[Cu(\mathbf{2b})_2]^{+}$	n.o.	5.4(1)[b])
$[Cu_2(\mathbf{2b})_2]^{2+}$		7.7(2)[b])
$[Cu_2(\mathbf{3b})_2]^{2+}$	12.8(4)[a])	10.0(2)[b])
$[Cu_2(\mathbf{6})_2]^{2+}$	15.0(3)[a])	
$[Cu_2(\mathbf{7})_2]^{2+}$	14.5(15)[a])	
$[Cu_3(\mathbf{7})_2]^{3+}$	18(2)[a])	
$[Cu_2(\mathbf{8})_2]^{2+}$	16.0(3)[a])	

[a]) Determined by UV/VIS titration. [b]) Determined by potentiometry; n.o. not observed.

In all cases, the fitting of the data was much better for a 2:2 complex $[Cu_2L_2]$ than for a model supposing a 1:1 complex, in agreement with electron spray ionisation (ES) MS results [16]. In DMF, $[Cu_2L_2]$ was the only complex observed by spectroscopic titration, with the exception of ligand **7** where the data suggested subsequent formation of a complex $[Cu_3(\mathbf{7})_2]^{3+}$. For this reason, the error of the stability constants for $[Cu_2(\mathbf{7})_2]^{2+}$ is rather large. The results in DMF show the ligands **1b** and **6**–**8** to have rather similar stability constants although $[Cu_2(\mathbf{8})_2]^{2+}$ is slightly more stable. The kinetic results discussed below confirm this, implying that the electron-donating *p*-$Et_2NC_6H_4$ substituent stabilizes the complex, either by increasing the donor strength of the bridging pyridine, or, less probably, by increasing the stacking interactions. The 1*H*-imidazole ligand **3b** forms a significantly less stable complex, suggesting that the stacking interactions contribute *ca.* 9 kJ/mol to the stability of the complex.

The complex $[Cu_2(\mathbf{2b})_2]^{2+}$ was too sensitive to oxidation for a reliable stability constant to be measured in DMF solution, and so the stability was studied in MeCN. As expected, $[Cu_2(\mathbf{2b})_2]^{2+}$ is less stable than $[Cu_2(\mathbf{1b})_2]^{2+}$ in the same solvent although the difference of 1 log unit is quite small. Given that MeCN is an excellent solvent for Cu^{I}, the stability constants of all complexes studied were much lower than in DMF, although, surprisingly, the decrease was much less for $[Cu_2(\mathbf{3b})_2]^{2+}$ than $[Cu_2(\mathbf{1b})_2]^{2+}$, the former actually being more stable in MeCN than the latter.

A study of the temperature dependence of the stability constant of $[Cu_2(\mathbf{1b})_2]^{2+}$ in MeCN gave values of $\Delta H^\circ = -35(1)$ kJ/mol and $\Delta S^\circ = +45(4)$ J/mol/K. The very

favourable entropy term presumably arises from the liberation of solvent molecules (*Eqn. 1*).

$$2\,[Cu(MeCN)_4]^+ + 2\,\mathbf{1b} \rightarrow [Cu_2(\mathbf{1b})_2]^{2+} + 8\,MeCN \quad (1)$$

Although **1b** appeared to form only the 2:2 complex, the potentiometric titration of **2b** showed clearly the formation of $[Cu(\mathbf{2b})_2]^+$ in an initial step, and this was confirmed by a ^{1}H-NMR titration showing two end points at metal/ligand ratios of 0.5 and 1. Spectroscopic titration of **3b** suggested the formation of traces of $[Cu(\mathbf{3b})_2]^+$, but this was not observed in the potentiometric titration or the ^{1}H-NMR titration at room temperature. At −35°, however, a ^{1}H-NMR titration showed clearly the initial formation of $[Cu(\mathbf{3b})_2]^+$, suggesting the two-step reaction of *Eqns. 2* and *3*. The second step (*Eqn. 3*) is strongly favoured by entropy, but may be enthalpically disfavoured by electrostatic repulsions, so that the formation of the dinuclear species may be disfavoured at lower temperature when entropy effects are weaker.

$$2\,L + [Cu(MeCN)_4]^+ \rightarrow [CuL_2]^+ + 4\,MeCN \quad (2)$$

$$[CuL_2]^+ + [Cu(MeCN)_4]^+ \rightarrow [Cu_2L_2]^{2+} + 4\,MeCN \quad (3)$$

Dynamic Studies. – We have shown previously [10] that the methylene protons of the 3,5-dimethoxybenzyl substituent of the ligand are a useful source of configurational information in solution, giving an *AB* signal in a low-symmetry environment. It was also observed [9] that the ^{1}H-NMR spectrum of $[Cu_2(\mathbf{1a})_2]^{2+}$ is strongly temperature-dependent in MeCN, a clearly resolved spectrum being obtained only at low temperature. We have, therefore, studied the temperature dependence of the methylene protons of the complexes of the dmb-substituted ligands. *Fig. 2* shows how the methylene signal varies as a function of temperature for $[Cu_2(\mathbf{1b})_2]^{2+}$ in DMF. At low temperature, the methylene protons give an *AB* signal which collapses on heating to an A_2 signal. The spectra were analysed by fitting to a theoretical lineshape using the programme DNMR5 [17], and the resulting kinetic parameters are summarized in *Table 2*.

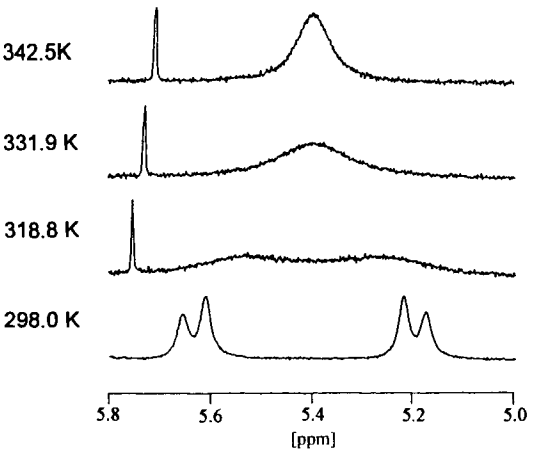


Fig. 2. *^{1}H-NMR Spectrum in (D_7)DMF of the methylene region of $[Cu_2(\mathbf{1b})_2]^{2+}$ as a function of temperature showing the change from an* AB *to an* A_2 *spin system*

Table 2. *Kinetic Parameters for Isomerization of the Double-Helical Complexes*

	Solvent	T_c [K]	$\Delta G^{\ddagger}_{298}$ [kJ/mol]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/mol/K]
$[Cu_2(\mathbf{1b})_2]^{2+}$	(D_7)DMF	322	64.9(4)	82(5)	59(15)
	$(D_3)MeNO_2$		77.1(8)	99(10)	73(20)
	(D_3)MeCN		57.3(4)	61(5)	12(17)
$[Cu_2(\mathbf{3b})_2]^{2+}$	(D_7)DMF	274	50.6(4)	116(4)	218(16)
	$(D_3)MeNO_2$		56.3(8)	94(8)	127(12)
$[Cu_2(\mathbf{6})_2]^{2+}$	(D_7)DMF	343	68.2(4)	65(4)	−10(12)
$[Cu_2(\mathbf{7})_2]^{2+}$	(D_7)DMF	327	66.7(3)	86(5)	63(15)
$[Cu_2(\mathbf{8})_2]^{2+}$	(D_7)DMF	359	73.4(7)	78(5)	16(14)
$[Cu_2(\mathbf{9})_2]^{2+}$	(D_7)DMF	327	66.1(4)	79(4)	46(14)

The helical systems show coalescence temperatures in the range 0–90° in DMF. There is a good correlation of $\Delta G^{\ddagger}_{298}$ with the measured stability constants, the complex $[Cu_2(\mathbf{3b})_2]^{2+}$, where the stacking interaction is absent, being more labile, while the complex $[Cu_2(\mathbf{8})_2]^{2+}$, where the donor power of the bridge is increased, is significantly less labile (see *Fig. 3*). The observed rates are strongly dependent on solvent, coordinating solvents (DMF, MeCN) giving much faster kinetics than weakly solvating solvents such as nitromethane. This suggests solvent participation in the transition state and excludes the possibility that the isomerization takes place *via* an intramolecular twist about the Cu–Cu axis, passing through an intermediate isostructural with $[Cu_2(\mathbf{2b})_2]^{2+}$. Molecular models show that this transformation is possible and involves only torsion about Cu–N(benzimidazole) and benzimidazole–pyridine bonds, but requires the breaking of the bridging Cu–N(pyridine) bonds. Experiments on the isomerization of $[Cu_2(\mathbf{1b})_2]^{2+}$ in the presence of free **1b** showed that, at temperatures where the dmb methylene protons of the complex gave only an A_2 signal, the methylene protons of the free ligand gave a clearly separate signal, suggesting that the isomerization does not pass through a completely dissociated state. However, the correlation between $\Delta G^{\ddagger}_{298}$ for isomerization and the stability constant suggests a dissociative process of isomerization, possibly through an intermediate such as $[CuL_2]^+$ formed by the reverse of the reaction of *Eqn. 3*.

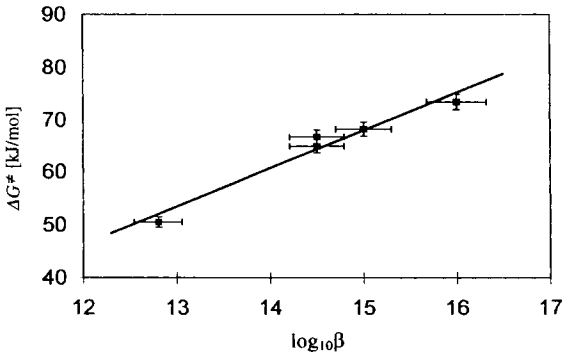


Fig. 3. *Correlation of* $\Delta G^{\ddagger}_{298}$ [kJ/mol] *for inversion and* $\log_{10}\beta$ *for different helicates in DMF*

Although the derived activation parameters are not very accurate because of the limited temperature range available, they show surprisingly large values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the complex $[Cu_2(\mathbf{3b})_2]^{2+}$ compared to $[Cu_2(\mathbf{1b})_2]^{2+}$. If the only difference between the two complexes is the presence in $[Cu_2(\mathbf{1b})_2]^{2+}$ of a stacking interaction which is absent in $[Cu_2(\mathbf{3b})_2]^{2+}$, we would have anticipated a larger $\Delta H^{\neq}$ for the complex of **1b**. We return to this apparent anomaly below.

At all temperatures studied, $[Cu_2(\mathbf{2b})_2]^{2+}$ gave only an A_2 signal for the methylene protons, even though their environment in the solid-state structure is chiral, and would be expected to give an *AB* signal. The side-by-side complex $[Cu_2(\mathbf{2b})_2]^{2+}$ is thus significantly more labile than the other, helical, systems.

Discussion. – The results presented here in general confirm the importance of the structural effects inferred from the X-ray crystal structures. Removal of the stacking interaction (**3b** *vs.* **1b**) or enhancing the donor power of the pyridine (**8** *vs.* **1b**) has the expected effect both on the thermodynamic stability and on the kinetic lability of the complexes. The lability of these complexes is shown by the fact that they undergo rapid isomerization on the millisecond timescale even under conditions allowing essentially complete complexation. Even so, the helical species such as $[Cu_2(\mathbf{1b})_2]^{2+}$ appear to be less labile than the side-by-side complex $[Cu_2(\mathbf{2b})_2]^{2+}$ where no *AB* signal was observed even at low temperatures. This may be regarded as another example of helical inertness observed in other systems [8], and arises from the fact that it is necessary to break several bonds to disrupt the structure of the helix, whereas only one Cu–N bond need be broken to allow free rotation of ligands and metal in $[Cu_2(\mathbf{2b})_2]^{2+}$.

The effect of solvent has hitherto been little discussed in helicate self-assembly reactions, but the results here show how greatly the solvent can influence the self-assembly both in terms of stability and lability. The structural information in the ligands (disposition of binding sites) and the metal ion (configurational preferences) expresses itself by the favourable free-energy change leading to the self-assembled product. A strongly coordinating solvent such as MeCN decreases the free-energy change on complexation, and the potential-energy well corresponding to the self-assembled product is less deep. The result is the observation of other species during the titration and a greater lability of the final product.

The behaviour of $[Cu_2(\mathbf{3b})_2]^{2+}$ shows a certain number of unusual features. Although the stability constant in DMF is less than that for $[Cu_2(\mathbf{1b})_2]^{2+}$ and the kinetics of racemization are faster, it is surprisingly stable in MeCN, and the kinetic data suggest a much higher enthalpy of activation than for $[Cu_2(\mathbf{1b})_2]^{2+}$ in DMF. Examination of the crystal structures shows that the average distances for the copper–imidazole or copper–benzimidazole bonds are different, 1.87(2) Å for **3a** and 1.915(16) Å for **1a**. This, coupled with the greater basicity of 1*H*-imidazole than 1*H*-benzimidazole, suggests that the Cu–N bond in complexes of ligand **3** may be significantly stronger than in complexes of **1** and would indeed explain the lower sensitivity to solvent and the greater activation enthalpy. It is possible that the stacking interaction present in $[Cu_2(\mathbf{1b})_2]^{2+}$ may in fact prevent the Cu–N(benzimidazole) bond attaining its optimum length.

Conclusion. – The study of the closely related complexes presented here has allowed us to investigate the relative importance of the different structural factors inferred from

X-ray crystallography. In general, the conclusions of X-ray crystallography, namely the importance of the coordinate bond, the bridging pyridine moiety, and the stacking interactions, have been confirmed by the measurement of stability and lability of complexes. However, the quantitative results allow a more detailed comparison and have also clearly established the importance of the solvent in the stability and lability of these self-assembled species. The rather unusual results for the complexes of **3**, where the stacking interactions have been eliminated, but the Cu–N bond strengthened, suggest that there may be considerable interplay between the different structural factors.

Experimental Part

1. *General.* Solvents and starting materials were purchased from *Fluka AG*, Buchs, Switzerland, and used without further purification unless otherwise stated. UV/VS: *Perkin-Elmer-Lambda-5* and *Perkin-Elmer-Lambda-2* spectrophotometers; in soln. at 20° using quartz cells of 1-, 0.1-, or 0.01-cm path length. ^{1}H-NMR Spectra: *Varian-XL-200* and *Bruker-AMX-400* spectrometers; chemical shifts δ in ppm rel. to $SiMe_4$; J in Hz. MS: in m/z (rel. %); *VG-7000E* and *Finnigan-4000* instruments for EI; FAB-MS (positive mode from nitrobenzyl-alcohol matrix) were recorded at the Laboratory of Mass Spectroscopy of the University of Fribourg, Switzerland. Elemental analyses were performed by Dr. *H. Eder* of the Microchemical Laboratory of the University of Geneva. Copper contents were determined by atomic absorption (*Pye Unicam SP9*) after acidic oxidative mineralization of the complex.

2. *Titrations.* Spectrophotometric titrations were performed with a *Perkin-Elmer-Lambda-5* spectrophometer connected to a personal computer. In a typical experiment, 15 ml of ligand ($4.2 \cdot 10^{-3}$ M in DMF) were titrated with a $2 \cdot 10^{-2}$ M Cu^I salt soln. in MeCN. After each addition of 0.1 ml, the absorbances at different wavelengths were recorded and transferred to the computer. Ten different wavelengths were used for each titration, and the data were treated as described previously [5]. In all cases, convergence was obtained, with a root-mean-squared difference between observed and calculated absorbances of 0.005 absorbance units or less.

Potentiometric titrations were performed under an inert atmosphere at controlled temperature using a two-electrode system consisting of a copper electrode and a non-aq. Ag/AgCl reference electrode $(Bu_4N)PF_6$ (to maintain ionic strength at 0.1M) served as inert electrolyte, and solvents were distilled from CaH_2. Before each experiment, the system was calibrated by successive additions of a Cu^I soln. ($2 \cdot 10^{-2}$ M + $8 \cdot 10^{-2}$ M $(Bu_4N)PF_6$) to a soln. of $(Bu_4N)PF_6$ (0.1M). In a typical experiment, 15 ml of Cu^I ($5 \cdot 10^{-3}$ M in MeCN) were titrated with a $1.7 \cdot 10^{-2}$ M ligand soln. in MeCN to which 10% DMF had been added to solubilize the ligand. After each addition of 0.1 ml, the Cu/Cu^I potential was recorded with a *Metrohm Digital-Ph-Meter E500* and transferred to the computer. The analysis of the data ($\Delta E_{measured}$/ml added) was performed with SUPERQUAD [18]. In all cases, convergence was obtained.

^{1}H-NMR Titrations were performed at controlled temperature. In a typical experiment, 0.7 ml of ligand ($4.2 \cdot 10^{-3}$ M) was titrated with a 0.15M Cu^I salt soln. After each addition of a 20 µl aliquot, the NMR spectrum was recorded. NMR Kinetic measurements: In a typical experiment, a soln. of PF_6^- complex (10^{-2} M, a concentration where decomplexation was less than 1.5%) was used. The NMR spectra between 6.5 and 4.5 ppm at different temp. covering the range between fast and slow exchange were recorded on a *Bruker AMX 400* spectrometer. For each system, at least 7 spectra were recorded. For each spectrum, a simulation and fitting of the signal width was performed with the program DNMR5 [17], allowing the determination of the rate constant. An *Eyring* plot gave the activation parameters.

3. *Ligands.* 2,2′-(Pyridine-2,6-diyl)bis[1-methyl-1*H*-benzimidazole] (**1a**) 2,2′-(pyridine-2,6-diyl)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole] (**1b**) [9][10], 2,2′-(1,3-phenylene)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole] (**2b**) [10], 2,6-di(1*H*-imidazole-2-yl)pyridine (**3a**) [11], 2,2′-(4-phenylpyridine-2,6-diyl)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole] (**6**), 2,2′-[4-(4-nitrophenyl)pyridine-2,6-diyl]bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole] (**7**), and 2,2′-{4-[4-(dimethylamino)phenyl]pyridine-2,6-diyl}bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole] (**8**) [14] were obtained according to the literature.

*2,6-Bis[1-(3,5-dimethoxybenzyl)-1*H*-imidazol-2-yl]pyridine* (**3b**) was prepared from **3a** as described for **1b**. Yield 80%. ^{1}H-NMR (200 MHz, $CDCl_3$, 20°): 3.62 (*s*, 4 MeO); 5.40 (*s*, 2 CH_2); 6.02 (*d*, ^4J = 2, 4 arom. H); 6.27 (*t*, ^4J = 2, 2 arom. H); 6.91 (*d*, ^3J = 1.2, 2 H (im)); 7.16 (*d*, ^3J = 1.2, 2 H (im)); 7.88 (*t*, ^3J = 7.5, 1 H (py)); 8.13 (*d*, ^3J = 7.5, 2 H (py)). EI-MS (70 eV): 511 (100, M^+), 360 (100, $[M - C_9H_{11}O_2]^+$). Anal. calc. for $C_{29}H_{29}N_5O_4$ (511): C 68.10, H 5.68, N 13.70; found: C 67.77, H 5.76, N 13.44.

*2,2'-(4-Methoxypyridine-2,6-diyl)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole]* (**9**). Chelidamic acid (= 1,4-dihydro-4-oxopyridine-2,6-dicarboxylic acid; 6.02 g, 30 mmol) and benzene-1,2-diamine were mixed in concentrated H_3PO_4 (60 ml) and stirred for 4 h at 200°. After cooling, the soln. was poured into H_2O (1.5 ml) and neutralized with 5M NaOH. The white solid was filtered, washed with H_2O, and recrystallized from MeOH; 2.45 g (25%) of 2,2'-(4-hydroxypyridine-2,6-diyl)bis[1*H*-benzimidazole]. ^{1}H-NMR (200 MHz, (D_6)DMSO, 20°): 7.28 (*m*, 4 H (bim)); 7.69 (*s*, 2 H (py)); 7.73 (*m*, 4 H (bim)); 11.41 (*s*, OH); 12.9 (*s*, 2 NH). EI-MS (70 eV): 327 (100, M^+).

A mixture of 2,2'-(4-hydroxypyridine-2,6-diyl)bis[1*H*-benzimidazole] (100 mg, 0.3 mmol) and 60% NaH in mineral oil (12 mg, 0.33 mmol) in dry DMF (30 ml) was stirred at r.t. for 1 h. MeI (21 µl, 0.33 mmol) was then added, and after stirring overnight, NaH was added again (24 mg, 0.66 mmol), followed by 3,5-dimethoxybenzyl bromide [10] (153 mg, 0.66 mmol). The soln. was stirred overnight, then poured into H_2O (100 ml), and neutralized with dil. HCl soln. The solid was filtered and purified by column chromatography (Al_2O_3, CH_2Cl_2): 105 mg (55%) of **9**. ^{1}H-NMR (200 MHz, $CDCl_3$, 20°): 3.53 (*s*, 4 MeO); 4.03 (*s*, 1 MeO); 5.55 (*s*, 2 CH_2); 5.97 (*d*, ^4J = 2.3, 4 arom. H); 6.28 (*t*, ^4J = 2.3, 2 arom. H); 7.3 (*m*, 6 H (bim)); 7.85 (*m*, 2 H (bim)); 7.92 (*s*, 2 H (py)). EI-MS (70 eV): 641 (100, M^+).

4. *Complexes.* All manipulations were performed under N_2 with *Schlenk* techniques. $[Cu_2(\mathbf{1b})_2](ClO_4)_2$ and $[Cu_2(\mathbf{2b})_2](ClO_4)_2$ were obtained according to the literature [10].

*Bis{µ-{2,6-bis[1-(3,5-dimethoxybenzyl)-1*H*-imidazol-2-yl]pyridine}}dicopper(I) Perchlorate* ($[Cu_2(\mathbf{3b})_2](ClO_4)_2$): Ligand **3b** (50 mg, 0.098 mmol) in MeCN (5 ml) was added to a soln. of $[Cu(MeCN)_4]ClO_4$ [19] (32 mg, 0.098 mmol) in MeCN (5 ml). The resulting red soln. was evaporated, the residue dissolved in MeCN (3 ml), and Et_2O slowly diffused into the soln. The formed thin orange needles were dried: 67 mg (95%) of $[Cu_2(\mathbf{3b})_2](ClO_4)_2$. ^{1}H-NMR (200 MHz, (D_6)acetone, 25°): 3.78 (*s*, 8 MeO); 5.71 (*s*, 4 CH_2); 6.43 (*d*, ^4J = 2.2, 8 arom. H); 6.55 (*t*, ^4J = 2.2, 4 arom. H); 6.81 (*d*, ^3J = 1.5, 4 H (im)); 7.40 (*d*, ^3J = 1.5, 4 H (im)); 8.12 (*d*, ^3J = 7, 4 H (py)); 8.32 (*t*, ^3J = 7, 2 H (py)). FAB-MS (9.2 kV): 1247 (10, $[Cu_2L_2(ClO_4)]^+$), 576 (100, $[CuL]^+$). Anal. calc. for $C_{58}H_{58}Cl_2Cu_2N_{10}O_{16} \cdot 0.5\,H_2O$ (1358.2): C 51.24, H 4.34, Cu 9.35, N 10.31; found: C 50.78, H 4.24, Cu 9.30, N 10.25.

*Bis{µ-{2,2'-(4-phenylpyridine-2,6-diyl)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole]}}dicopper(I) Perchlorate* ($[Cu_2(\mathbf{6})_2](ClO_4)_2$). As described for $[Cu_2(\mathbf{3b})_2](ClO_4)_2$. Yield 80%. ^{1}H-NMR (200 MHz, (D_3)nitromethane, 25°): 3.75 (*s*, 8 MeO); 5.20 (*d*, ^2J = 17.9, 4 H, $C_6H_3CH_2$); 5.46 (*d*, ^2J = 17.8, 4 H, $C_6H_3CH_2$); 6.36 (*d*, ^4J = 2, 8 arom. H); 6.58 (*t*, ^4J = 2, 4 arom. H); 7.30–45 (*m*, 12 H (bim, Ph)); 7.45–70 (*m*, 14 H (bim, Ph)); 8.11 (*s*, 4 H (py)). FAB-MS (9.2 kV): 1601 (6.5, $[Cu_2L_2(ClO_4)]^+$), 750.2 (100, $[CuL]^+$). Anal. calc. for $C_{86}H_{74}Cl_2Cu_2\ N_{10}O_{16} \cdot 2\,H_2O$ (1737.6): C 59.45, H 4.52, Cu 7.31, N 8.06; found: C 59.70, H 4.59, Cu 7.26, N 8.00.

*Bis{µ-{2,2'-[4-(4-nitrophenyl)pyridine-2,6-diyl]bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole]}}dicopper(I) Perchlorate* ($[Cu_2(\mathbf{7})_2](ClO_4)_2$). As described for $[Cu_2(\mathbf{3b})_2](ClO_4)_2$. Yield 85%. ^{1}H-NMR (200 MHz, (D_3)nitromethane, 25°): 3.74 (*s*, 8 MeO); 5.18 (*d*, ^2J = 18.2, 4 H, $C_6H_3CH_2$); 5.45 (*d*, ^2J = 18.2, 4 H, $C_6H_3CH_2$); 6.35 (*d*, ^4J = 2, 8 arom. H); 6.59 (*t*, ^4J = 2, 4 arom. H); 7.30 (*m*, 8 H (bim)); 7.50 (*m*, 8 H (bim)); 7.60 (*d*, ^3J = 7, 4 H, C_6H_4); 8.15 (*s*, 4 H (py)); 8.32 (*d*, ^3J = 7, 4 H, C_6H_4). FAB:MS (9.2 kV): 1691 (35, $[Cu_2L_2(ClO_4)]^+$), 895.8 (55, $[CuL(ClO_4)]^+$), 792.2 (100, $[CuL]^+$). Anal. calc. for $C_{86}H_{72}Cl_2Cu_2\ N_{12}O_{20} \cdot 1.5\,H_2O$ (1818.6): C 56.80, H 4.16, Cu 6.99, N 9.24; found: C 56.90, H 4.19, Cu 6.81, N 9.19.

*Bis{µ-{2,2'-{4-[4-(dimethylamino)phenyl]pyridine-2,6-diyl}bis[1-(3,5-dimethylbenzyl)-1*H*-benzimidazole]}}dicopper(I) Perchlorate* ($[Cu_2(\mathbf{8})_2](ClO_4)_2$). As described for $[Cu_2(\mathbf{3b})_2](ClO_4)_2$. Yield 95%. ^{1}H-NMR (200 MHz, (D_3)nitromethane, 25°): 1.18 (*t*, ^3J = 7, 4 *Me*CH_2); 3.45 (*q*, ^3J = 7, 4 MeCH_2); 3.69 (*s*, 8 MeO); 5.07 (*d*, ^2J = 17.7, 4 H, $C_6H_3CH_2$); 5.33 (*d*, ^2J = 17.7, 4 H, $C_6H_3CH_2$); 6.30 (*d*, ^4J = 2, 8 arom. H); 6.54 (*t*, ^4J (H,H) = 2, 4 arom. H); 6.66 (*d*, ^3J = 8.15, 4 H, C_6H_4); 7.08 (*d*, ^3J = 8.15, 4 H, C_6H_4); 7.25 (*m*, 8 H (bim)); 7.44 (*m*, 8 H (bim)); 7.84 (*s*, 4 H (py)). FAB-MS (9.2 kV): 1744.4 (45, $[Cu_2L_2(ClO_4)]^+$), 921.9 (45, $[CuL(ClO_4)]^+$), 821.3 (100, $[CuL]^+$). Anal. calc. for $C_{94}H_{92}Cl_2Cu_2\ N_{12}O_{16} \cdot 2\,H_2O$ (1879.9): C 60.06, H 5.15, Cu 6.76, 8.94; found: C 59.98, H 5.05, Cu 6.59, N 8.88.

*Bis{µ-{2,2'-(4-methoxypyridine-2,6-diyl)bis[1-(3,5-dimethoxybenzyl)-1*H*-benzimidazole]}}dicopper(I) Perchlorate* ($[Cu_2(\mathbf{9})_2](ClO_4)_2$). As described for $[Cu_2(\mathbf{3b})_2](ClO_4)_2$. Yield 80%. ^{1}H-NMR (400 MHz, (D_7)DMF, 25°): 3.79 (*s*, 4 $(MeO)_2C_6H_3$); 3.86 (*s*, 2 *Me*Opy); 5.28 (*d*, ^2J = 18, 4 H, $C_6H_3CH_2$); 5.68 (*d*, ^2J = 18, 4 H, $C_6H_3CH_2$); 6.35 (*d*, ^4J = 2, 8 arom. H); 6.61 (*t*, ^4J = 2, 4 arom. H); 7.34 (*s*, 4 H, (py)); 7.47 (*m*, 12 H (bim)); 7.53 (*m*, 4 H (bim)).

Complexes $[Cu_2(L)_2](PF_6)_2$. The PF_6 complexes were obtained by the same method used for the perchlorate complexes; they showed identical NMR spectra. For safety reasons, they were used instead of perchlorate salts for the kinetic measurements.

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