

Table III. Comparison of the Constants for the Two Complexes

	$K_2 = (C/T)_{eq}$	$K_1^{-1} = (T^+/C^+)_{eq}$	$K_1^{-1}/K_2$	$k_{b1}/k_{f2}$	$k_{f1}/k_{b2}$
Mo	150	$10^4$	66	1750	26
W	130	$1.6 \times 10^3$	12	175	14

$K_2$ ,  $k_{b1}$ , and  $k_{b2}$ , that the ratio  $y$  in the region around  $E^{\circ}_2$  remains practically the same as for an EC (irreversible) system (Figure 8, supplemental).

The variations of  $\log k_{f2}$  with  $T^{-1}$  are shown in Figure 9 (supplemental). The activation energies are respectively 67 and 72 kJ for the Mo and W complexes; extrapolation gives the value of  $k_{f2}$  at 60 °C, and the value of  $k_{b2}$  is deduced from  $K_2$  (Figure 1); see Table I.

### Discussion and Conclusion

All the experiments reported above were repeated with THF and  $\text{Me}_2\text{SO}$  as solvents; the same quantitative results were obtained. Also, we introduced the ligand DPE into the solution at diverse concentrations, but this did not affect the constants. The cis-trans reaction is thus a process purely internal to the molecule. This conclusion was already reached by Bond et al.,<sup>4</sup> who determined  $K_{f2}$  and  $k_{f1}$  in different solvents. The values they measured are comparable with ours, although the activation energies are somewhat different.

Our theory allows more complete information to be obtained about the complexes. The behaviors of the Mo and W complexes are analogous, although quantitative differences exist. First, if we compare  $K_1^{-1}$  to  $K_2$  (Table III), we see that for both complexes the equilibrium is much more in favor of the stable form ( $T^+$ ) in the couple  $C^+/T^+$  than in favor of the stable form C in the couple C/T. However, from the ratio of  $K_1^{-1}$  to  $K_2$ , it appears that the difference in stability is much larger in the case of the Mo complex (ratio 66 instead of 12).

On the other hand, for comparing the mobility of the reaction  $T^+/C^+$  to that of the reaction T/C, we can compare  $k_{b1}$  to  $k_{f2}$  and  $k_{f1}$  to  $k_{b2}$ , respectively. The ratios obtained are always larger than 1 (they vary from 14 to 1750; Table III), which shows that the reaction  $T^+ \rightleftharpoons C^+$  is faster in both directions than the reaction  $T \rightleftharpoons C$  for both complexes. If now we compare the two complexes, we see that the difference in mobility of the two reactions is larger in the case of Mo than of W; the rate toward the more stable form  $T^+$  is 10 times larger than that toward the stable form C ( $k_{b1}/k_{f2}(\text{Mo}) = 10k_{b1}/k_{f2}(\text{W})$ ), whereas the rate in the reverse direction is about twice as fast in the case of Mo than in the case of W ( $k_{f1}/k_{b2}(\text{Mo}) \approx 2k_{f1}/k_{b2}(\text{W})$ ).

**Acknowledgment.** We express our thanks to Professor A. Dormond for his help in the preparation of the complexes.

**Supplementary Material Available:** Figures 2, 5, 8, and 9, showing a voltammogram of the W cation ( $T^+$  form), theoretical variations of the ratio  $y$  for the  $T^+/T$  couple in the square scheme for the W complex, and variations of  $\log k_{b1}$  and  $\log k_{f2}$  with  $T^{-1}$  for both complexes (4 pages). Ordering information is given on any current masthead page.

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### Solvent Effects on Axial Ligation of Isomeric (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) Cations with Mononegative Ligands

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The complex ion (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II),  $\text{Cu}(\text{Me}_6[14]4,11\text{-diene-N}_4)^{2+}$ , can exist in two diastereoisomeric forms,  $\text{Cu}(N\text{-rac-Me}_6[14]4,11\text{-diene-N}_4)^{2+}$  and  $\text{Cu}(N\text{-meso-Me}_6[14]4,11\text{-diene-N}_4)^{2+}$ , depending on the configurations of the two asymmetric nitrogen centers (see Figure 1). The crystal structures of these isomers have been determined by three-dimensional X-ray methods.<sup>1,2</sup> Previously, we have reported the equilibrium constants for the reactions of these isomeric copper(II) complexes with several mononegative bases in aqueous solution represented by eq 1.<sup>3</sup> Here L is the macrocyclic ligand  $N\text{-rac-Me}_6[14]4,11\text{-diene-N}_4$  or  $N\text{-meso-Me}_6[14]4,11\text{-diene-N}_4$ . In order to study solvent effects on these ligation constants, the equilibria of these reactions in dimethylformamide (DMF), dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ), and methanol (MeOH) were studied by spectrophotometric methods.

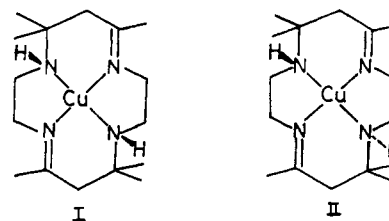


Figure 1. Structures of  $\text{Cu}(N\text{-rac-Me}_6[14]4,11\text{-diene-N}_4)^{2+}$  (I) and  $\text{Cu}(N\text{-meso-Me}_6[14]4,11\text{-diene-N}_4)^{2+}$  (II).

$\text{CuL}^{2+} + \text{X}^- \rightleftharpoons \text{CuLX}^+$  (1)

diene- $\text{N}_4$  or  $N\text{-meso-Me}_6[14]4,11\text{-diene-N}_4$ . In order to study solvent effects on these ligation constants, the equilibria of these reactions in dimethylformamide (DMF), dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ), and methanol (MeOH) were studied by spectrophotometric methods.

### Experimental Section

**Reagents.** The macrocyclic complexes  $\text{Cu}(N\text{-rac-Me}_6[14]4,11\text{-diene-N}_4)(\text{ClO}_4)_2$  and  $\text{Cu}(N\text{-meso-Me}_6[14]4,11\text{-diene-N}_4)(\text{ClO}_4)_2$  were the same as those reported earlier.<sup>1-3</sup> The organic solvents, DMF,  $\text{Me}_2\text{SO}$ , and MeOH, used in this work were of spectroscopic grade. All other chemicals used were of GR grade from Merck.

Dimethylformamide was vacuum-distilled from phosphorus pentoxide. Dimethyl sulfoxide was dried over molecular sieves for 24 h and then refluxed over calcium hydride for 16 h; it was then carefully distilled under reduced pressure. Methanol was dried by fractional distillation, followed by treatment with Drierite for a period of several days.<sup>4,5</sup>

Analysis of water in solvents was carried out by using an automatic Karl Fischer titrator. The water content of all purified solvents was found to be less than 100 ppm.

**Instrumentation.** A Cary 17 spectrophotometer and a Perkin-Elmer Lambda-5 UV/vis spectrophotometer with a thermostated cell compartment were used to record absorption spectra. The temperature was maintained within  $\pm 0.1$  °C. Equilibrium constants were obtained by a linear least-squares fit of the data using a CDC Cyber-172 computer.<sup>6,7</sup>

### Results

Addition of the solution of mononegative ligand,  $\text{X}^-$ , to a solution of copper(II) tetraaza macrocyclic complex results in the replacement of coordinated solvent by  $\text{X}^-$ . The apparent molar absorptivities were obtained by using eq 2, where  $A$  is the ab-

$$\epsilon_{app} = A/lC_T \quad (2)$$

sorbance of the solution,  $l$  is the length of the cell, and  $C_T$  is the total concentration of the copper(II) complexes,  $[\text{CuL}^{2+}] + [\text{CuLX}^+]$ . The values of apparent molar absorptivities for these systems as a function of  $[\text{X}^-]_T$  are deposited as supplementary material (Tables A-C).

The apparent molar absorptivities have a linear dependence on  $(\epsilon_{app} - \epsilon_{\text{CuL}})/[\text{X}^-]$  in accordance with eq 3, where  $\epsilon_{\text{CuL}}$  and  $\epsilon_{\text{CuLX}}$

$$\epsilon_{app} = (-1/K_X)(\epsilon_{app} - \epsilon_{\text{CuL}})/[\text{X}^-] + \epsilon_{\text{CuLX}} \quad (3)$$

are the molar absorptivities of  $\text{CuL}^{2+}$  and  $\text{CuLX}^+$ , respectively. The value of  $[\text{X}^-]$  was calculated by an iterative procedure in which an estimated value of  $K_X$  was used to calculate the value

(1) Lu, T.-H.; Lee, T.-J.; Liang, B.-F.; Chung, C.-S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2333-2336.

(2) Lee, T.-J.; Lu, T.-H.; Chung, C.-S.; Lee, T.-Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 70-72.

(3) Wu, S.-Y.; Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 2548-2550.

(4) Chen, C.-S.; Wang, S.-J.; Wu, S.-C. *Inorg. Chem.* **1984**, *23*, 3901-3903.

(5) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall: New York, 1970; p 119.

(6) Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 639-644.

(7) Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 4162-4166.

**Table I.** Equilibrium Constants ( $M^{-1}$ ) for  $CuL^{2+} + X^- \rightleftharpoons CuLX^+$  at  $25.0 \pm 0.1$  °C<sup>a</sup>

X <sup>-</sup>	H <sub>2</sub> O (81.7) <sup>b</sup>	Me <sub>2</sub> SO (45.0)	DMF (36.7)	MeOH (32.6)
Cu( <i>N-rac</i> -Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>				
Cl <sup>-</sup>	1.1	$4.46 \times 10^2$	$2.15 \times 10^3$	$8.10 \times 10^3$
Br <sup>-</sup>	2.0	$2.33 \times 10^2$	$1.07 \times 10^3$	$4.95 \times 10^3$
I <sup>-</sup>	6.5	$1.56 \times 10^2$	$4.53 \times 10^2$	$1.10 \times 10^3$
N <sub>3</sub> <sup>-</sup>	7.8	$8.98 \times 10^2$	$2.97 \times 10^3$	$9.80 \times 10^3$
Cu( <i>N-meso</i> -Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>				
Cl <sup>-</sup>	1.0	$4.04 \times 10^2$	$2.70 \times 10^3$	$1.04 \times 10^4$
Br <sup>-</sup>	1.8	$2.44 \times 10^2$	$1.27 \times 10^3$	$4.23 \times 10^3$
I <sup>-</sup>	6.2	$1.65 \times 10^2$	$5.83 \times 10^2$	$1.07 \times 10^3$
N <sub>3</sub> <sup>-</sup>	7.5	$8.10 \times 10^2$	$3.66 \times 10^3$	$9.91 \times 10^3$

<sup>a</sup> Dielectric constants of solvents are given in parentheses. <sup>b</sup>  $\mu = 0.10$  M (NaX + NaNO<sub>3</sub>); see ref 3.

**Table II.** Values of  $s_X$  and  $b_X$  for  $CuL^{2+} + X^- \rightleftharpoons CuLX^+$  in Various Solvents at  $25.0 \pm 0.1$  °C

X <sup>-</sup>	Cu( <i>N-rac</i> -Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>		Cu( <i>N-meso</i> -Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>	
	$s_X$	$b_X$	$s_X$	$b_X$
Cl <sup>-</sup>	9.62	44.1	10.00	44.2
Br <sup>-</sup>	8.26	36.8	8.35	36.9
N <sub>3</sub> <sup>-</sup>	7.65	36.3	7.79	36.4
I <sup>-</sup>	5.48	26.9	5.63	27.0

of [X<sup>-</sup>] and then this was used to obtain a new value of  $K_X$  until the least-squares deviation in the plot of  $\epsilon_{app}$  vs.  $-(\epsilon_{app} - \epsilon_{CuL})/[X^-]$  reached a minimum value.<sup>8</sup> The equilibrium constants in DMF, Me<sub>2</sub>SO, and MeOH determined in this work are compiled in Table I, along with those in aqueous solution reported in an earlier study for comparison.<sup>3</sup>

### Discussion

The results listed in Table I indicate that the equilibrium constants for these reactions increase with change in solvent in the order  $K_{H_2O} \ll K_{Me_2SO} < K_{DMF} < K_{MeOH}$ . In general, the value of the ion association constant for a given equilibrium is strongly influenced by the dielectric constant,  $D$ , of the medium. As expected from the electrostatic theory, the force acting between  $CuL^{2+}$  and  $X^-$  increases with decreasing dielectric constant of the solvent. Plots of  $\ln K_X$  for these reactions against  $\ln(1/D)$  for the solvents give straight lines as shown in Figure 2 and Figure A (supplementary material). Thus, we can express  $\ln K_X$  in terms of  $\ln(1/D)$  (eq 4) where  $s_X$  and  $b_X$  are the slope and the intercept,

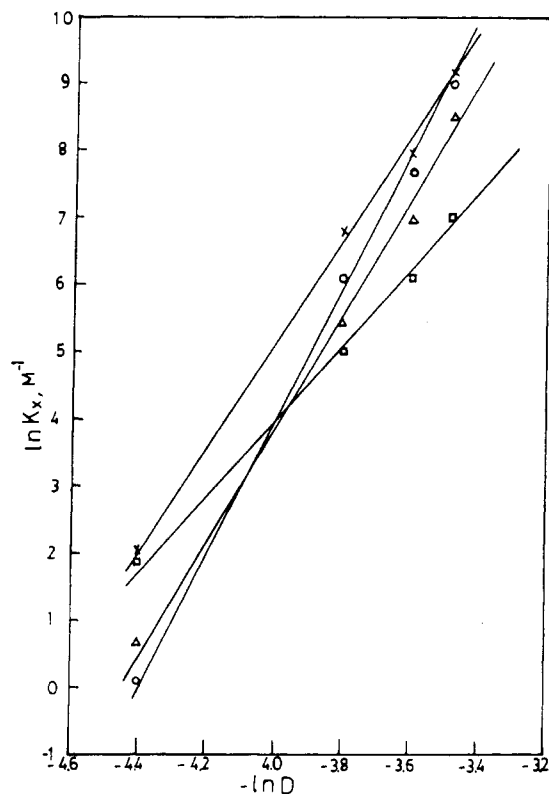
$$\ln K_X = s_X[\ln(1/D)] + b_X \quad (4)$$

respectively, of each of these straight lines (Table II). As expected from Coulomb's law, the slope of each of these straight lines decreases with increasing size of the anion.

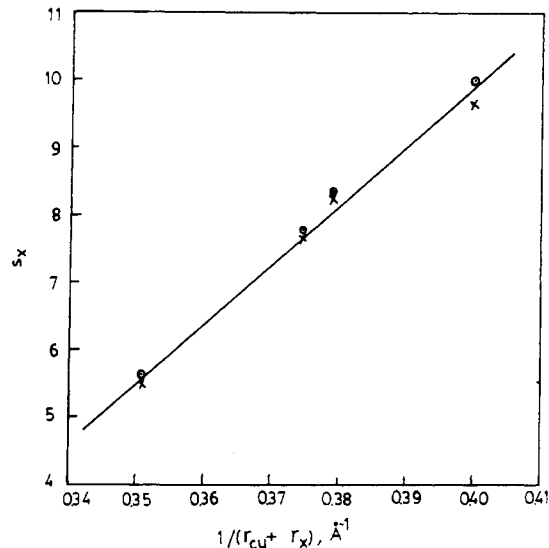
For each of these complexes, a plot of the slope against  $(r_{Cu} + r_X)^{-1}$ , where  $r_{Cu}$  is the radius of  $Cu^{2+}$  and  $r_X$  is the thermochemical radius of the mononegative ligand,<sup>9,10</sup> gives a straight line, as shown in Figure 3. Thus,  $\ln K_X$  and the radius of the mononegative ligand  $r_X$  can be related by eq 5.

$$\ln K_X = [87.6/(r_{Cu} + r_X) - 25.0][\ln(1/D)] + b_X \quad (5)$$

For each of these copper(II) macrocyclic complexes, the complexation tendency for the mononegative ligand increases in the order  $I^- < Br^- < Cl^- < N_3^-$  in Me<sub>2</sub>SO, DMF, and MeOH, whereas in H<sub>2</sub>O it varies as  $Cl^- < Br^- < I^- < N_3^-$ . The values of the relative free energies of solvation (solv) for these anionic ligands in organic and aqueous solvents,  $(\Delta G_{org}^\circ - \Delta G_{H_2O}^\circ)_{solv}$ ,<sup>11-13</sup> and the relative



**Figure 2.** Correlation of the equilibrium constants for  $Cu(N-rac-Me_6[14]4,11-dieneN_4)^{2+} + X^- \rightleftharpoons Cu(N-rac-Me_6[14]4,11-dieneN_4)X^+$  at  $25.0 \pm 0.1$  °C with the dielectric constants of the solvents: O, Cl<sup>-</sup>; Δ, Br<sup>-</sup>; □, I<sup>-</sup>; ×, N<sub>3</sub><sup>-</sup>.



**Figure 3.**  $s_X$  vs.  $(r_{Cu} + r_X)^{-1}$  plot in various solvents at  $25.0 \pm 0.1$  °C: O, Cu(*N-rac*-Me<sub>6</sub>[14]4,11-dieneN<sub>4</sub>)<sup>2+</sup>; ×, Cu(*N-meso*-Me<sub>6</sub>[14]4,11-dieneN<sub>4</sub>)<sup>2+</sup>.

free energies of axial ligation (lig) (eq 1) of these copper(II) complexes in these solvents,  $(\Delta G_{org}^\circ - \Delta G_{H_2O}^\circ)_{lig}$ , are given in Table III. The linear relationships between these quantities are shown in Figure 4 and Figure B (supplementary material). Similar linear relationships have been found for the reactions of red (*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II), Cu(tet a)(red)<sup>2+</sup>, and red (*C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II), Cu(tet b)(red)<sup>2+</sup>, with these anions.<sup>12</sup> These linear correlations indicate that the equilibrium constants depend strongly

(8) Liang, B.-F.; Margerum, D. W.; Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 2001-2007.

(9) Jenkis, H. D. B.; Thakur, K. P. *J. Chem. Educ.* **1979**, *56*, 576-577.

(10) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1982; p 78.

(11) Gutmann, V. *Fortschr. Chem. Forsch.* **1972**, *27*, 77.

(12) Liang, B.-F.; Tsay, Y.-K.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1983**, 995-997.

(13) Hunt, J. P. *Metal Ions in Aqueous Solutions*; Benjamin: New York, 1963; pp 14-17.

**Table III.** Values (kJ/mol) of  $(\Delta G^{\circ}_{\text{org}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}^a$  and  $(\Delta G^{\circ}_{\text{org}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$  for  $\text{Cu}(\text{Me}_6[14]4,11\text{-dieneN}_4)^{2+}$  Isomers with Various Anions at  $25.0 \pm 0.1$  °C

X <sup>-</sup>	$(\Delta G^{\circ}_{\text{Me}_2\text{SO}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}$	$(\Delta G^{\circ}_{\text{Me}_2\text{SO}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$	
		<i>N-rac</i> -[CuL] <sup>2+</sup>	<i>N-meso</i> -[CuL] <sup>2+</sup>
Cl <sup>-</sup>	46.0	-14.89	-14.88
Br <sup>-</sup>	32.6	-11.79	-12.17
I <sup>-</sup>	15.9	-7.88	-8.13
N <sub>3</sub> <sup>-</sup>	30.5	-11.76	-11.61

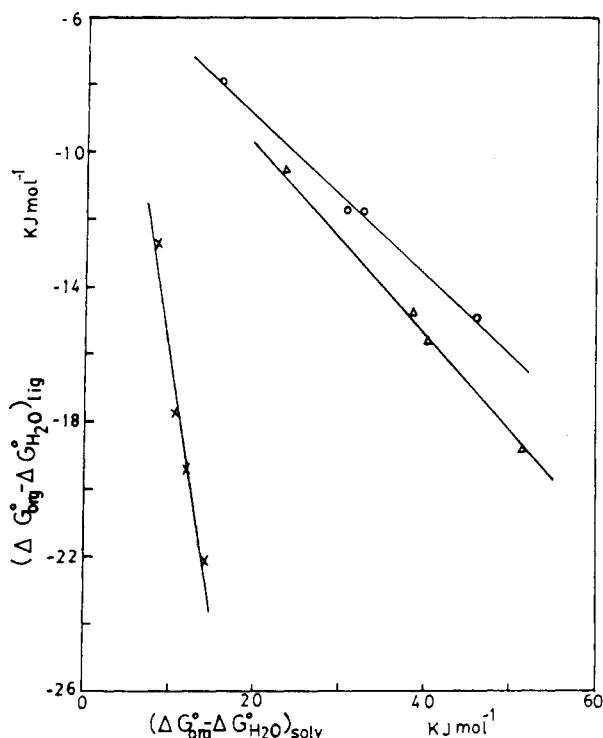
  

X <sup>-</sup>	$(\Delta G^{\circ}_{\text{DMF}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}$	$(\Delta G^{\circ}_{\text{DMF}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$	
		<i>N-rac</i> -[CuL] <sup>2+</sup>	<i>N-meso</i> -[CuL] <sup>2+</sup>
Cl <sup>-</sup>	51.5	-18.78	-19.59
Br <sup>-</sup>	40.2	-15.57	-16.26
I <sup>-</sup>	23.4	-10.52	-11.26
N <sub>3</sub> <sup>-</sup>	38.5	-14.73	-15.34

X <sup>-</sup>	$(\Delta G^{\circ}_{\text{MeOH}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}$	$(\Delta G^{\circ}_{\text{MeOH}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$	
		<i>N-rac</i> -[CuL] <sup>2+</sup>	<i>N-meso</i> -[CuL] <sup>2+</sup>
Cl <sup>-</sup>	14.2	-22.07	-22.93
Br <sup>-</sup>	12.1	-19.37	-19.24
I <sup>-</sup>	8.4	-12.72	-12.77
N <sub>3</sub> <sup>-</sup>	10.5	-17.69	-17.81

<sup>a</sup>See ref 11.



**Figure 4.** Plot of  $(\Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$  against  $(\Delta G^{\circ}_{\text{org}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}$  at  $25.0 \pm 0.1$  °C for  $\text{Cu}(\text{N-rac-Me}_6[14]4,11\text{-dieneN}_4)^{2+}$ :  $\Delta$ , DMF;  $\circ$ ,  $\text{Me}_2\text{SO}$ ;  $\times$ , MeOH.

on the extent of solvation of the monodentate ligands and the complexation in this study is mainly electrostatic.

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**Registry No.**  $[\text{Cu}(\text{N-rac-1,7-CT})]^{2+}$ , 48186-23-8;  $[\text{Cu}(\text{N-meso-1,7-CT})]^{2+}$ , 48186-22-7; Cl<sup>-</sup>, 16887-00-6; Br<sup>-</sup>, 24959-67-9; I<sup>-</sup>, 20461-54-5; N<sub>3</sub><sup>-</sup>, 14343-69-2; DMF, 68-12-2; Me<sub>2</sub>SO, 67-68-5; MeOH, 67-56-1.

**Supplementary Material Available:** Tables A-C, showing the values of apparent molar absorptivities for  $\text{Cu}(\text{N-rac-Me}_6[14]4,11\text{-dieneN}_4)^{2+}\text{-X}^-$  and  $\text{Cu}(\text{N-meso-Me}_6[14]4,11\text{-dieneN}_4)^{2+}\text{-X}^-$  systems as a function of [X<sup>-</sup>] in DMF, Me<sub>2</sub>SO, and MeOH, respectively, and Figures A and B, plots of  $\ln K_{\text{X}}$  vs.  $\ln (1/D)$  and  $(\Delta G^{\circ}_{\text{org}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{lig}}$  vs.  $(\Delta G^{\circ}_{\text{org}} - \Delta G^{\circ}_{\text{H}_2\text{O}})_{\text{soliv}}$  (5 pages). Ordering information is given on any current masthead page.

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### Sequential Biphotonic Processes: Photochemical Reactivity of Phthalocyanine Radicals

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Phthalocyanine radicals have been generated by chemical and photochemical means, and it is possible to consider them as common intermediates in redox reactions of metallophthalocyanines.<sup>1,2</sup> From a structural standpoint, these species, related to porphyrin radicals, are very likely species with an unpaired electron in a ligand-centered molecular orbital.<sup>3</sup> Previous work on the photochemistry of Rh(III) phthalocyanine cation radicals has shown that these species undergo different photochemical transformations for excitations in the UV and vis bands, respectively.<sup>1</sup> The UV excitation results in the reduction of the radical and oxidation of the solvent, a photoprocess associated with the abstraction of hydrogen from the solvent by  $n\pi^*$  ligand-centered excited states. Moreover, photodecomposition of the radical is induced by irradiation at wavelengths longer than 500 nm. Such UV and vis photoreactivities can be related to the population of different photoreactive states, i.e.  $\pi\pi^*$ ,  $n\pi^*$  ligand-centered states and charge-transfer states. Insofar as the position of the charge-transfer states (relative to ligand-centered states) depends on the metal center, the photochemical properties exhibited by a series of phthalocyanine radicals differing in the metal center can be used as a probe of the charge-transfer-state participation in the photodecomposition of the radicals. In this regard, the photochemistries of Rh(III), Al(III), and Zn(II) phthalocyanine cation radicals have been investigated in this work.

### Experimental Section

**Photochemical Procedures.** A flash photolysis apparatus, based on the synchronous triggering of two flash-lamp-pumped dye lasers, was used for the time resolution of optical events in sequential biphotonic photolyses (Figure 1). For these experiments we used a side-on excitation, i.e. with the monitoring light beam crossing the laser beams at a right angle. The overlap of the beams was regularly verified by either burning Polaroid film or maximizing the concentration of excited state produced by the excitation of various metallophthalocyanines. A fraction of the laser light was aimed at photodiodes in order to obtain reports concerning the intensity of the pulses and their relative delay. The time-resolved change in optical density induced by the sequential excitation was obtained as an average of 5-10 experiments, whereas the 100 data points of each experiment were obtained by subtracting two traces, corresponding each of them to the excitation of the photolyte with one of the two lasers from the trace recorded in the sequential excitation with both lasers. In this manner, the time-resolved net change in optical density corresponds to processes induced by the biphotonic irradiation. Namely, any contribution from monophotonic irradiations ( $\lambda_1$  or  $\lambda_2$  in Figure 1) has been removed from the one induced by the sequential irradiation ( $\lambda_1 + \lambda_2$  in Figure 1). Other experimental conditions used in connection with the sequential biphotonic excitation of phthalocyanines have been described elsewhere.<sup>4-6</sup>

**Materials.** Literature reports were followed for the preparation and purification of  $[\text{Co}(\text{bpy})_3](\text{ClO}_4)_3$  (bpy = bipyridine).<sup>7</sup> The pure Rh(III) phthalocyanines were available from a previous work.<sup>5,6</sup> Eastman chloro(phthalocyaninato)aluminum(III), Al(pc)Cl, and zinc phthalocyanine, Zn(pc), were recrystallized three times from suitable solvents. Other materials were reagent grade and used without further purification.

- Ferraudi, G.; Oishi, S.; Muralidharan, S. *J. Phys. Chem.* **1984**, *88*, 5261 and references therein.
- Ferraudi, G.; Geiger, D. K.; Madden, K.; Granifo, J.; Rillema, D. P. *J. Phys. Chem.* **1985**, *89*, 3890.
- Barley, M.; Becker, J. Y.; Domazetis, G.; Dolphin, D.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1981**, 982.
- Muralidharan, S.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 4877.
- Ferraudi, G. *J. Phys. Chem.* **1984**, *88*, 3938.
- Muralidharan, S.; Ferraudi, G.; Schmatz, K. *Inorg. Chem.* **1982**, *21*, 2961.
- Maki, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2275.