866. *Factors Influencing the Rates of Dissociation of Metal Complexes. Part IV.*[1] *A Comparison of Nickel*(II)*– and Copper*(II)*–Diamine Complexes.*

By R. G. Wilkins.

The rates of dissociation, in acid, of copper(II) complexes of ethylenediamine, racemic butane-2,3-diamine, and 2,3-dimethylbutane-2,3-diamine and its tetra-*N*-methyl isomer have been studied by the stopped-flow method. The kinetic parameters are compared with those of the corresponding nickel complexes.

Few kinetic data exist on the reactions of copper(II) complexes in aqueous solution. It is apparent from previous qualitative observations [2] that the rates of acid dissociation of copper complexes of aliphatic diamines may be measurable by flow techniques. Comparison of the results with those for the corresponding nickel complexes [1–3] is then possible. There is no difficulty in measuring the rate of dissociation of the bis- and mono-copper(II) complexes since the spectra of these species differ markedly from one another and they absorb much more strongly than the product, aquated copper(II) ion (see Figure).[4]

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[1] Part III, Ahmed and Wilkins, *J.*, 1960, 2901.

[2] Wilkins, *J.*, 1957, 4521.

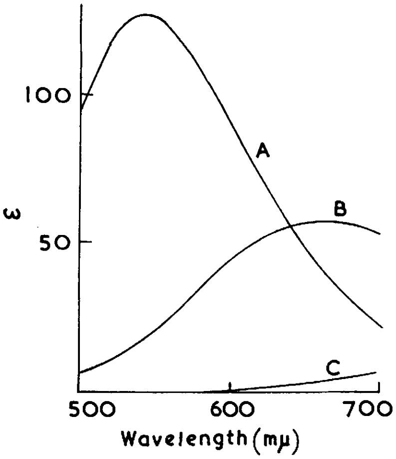
[3] Ahmed and Wilkins, *J.*, 1960, 2895.

[4] Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297; Irving and Griffiths, *J.*, 1954, 213; Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

EXPERIMENTAL

Materials.—The aliphatic diamines were prepared (or purchased) and purified as described previously.[2, 3] *NNN'N'*-Tetramethylethylenediamine (*N*-tetraMeen) dihydrochloride was a gift from Dr. D. L. Leussing, to whom we are very grateful.

Kinetic Experiments.—The dissociation of the bis-species was followed spectrally at 460—500 mμ and of the mono-species at 580—630 mμ. For 5—20mM-solutions of complex, appreciable optical density changes and linear first-order plots (up to five half-lives) were obtained. Except for the experiments with [Ni(*N*-tetraMeen)]$^{2+}$ at lower temperatures, the stopped-flow apparatus was used, with the previously estimated errors.[5] The results are collected in Table 1.



Absorption spectra of copper complexes:
A, [Cu(*C*-tetraMeen)$_2$]$^{2+}$.
B, [Cu(*C*-tetraMeen)]$^{2+}$.
C, Cu$_{aq}^{2+}$.

RESULTS AND DISCUSSION

The rapid interchange of diamine between [Cu(en)$_2$]$^{2+}$ and ethylenediamine is indicated by [^{14}C]ethylenediamine exchange experiments[6] and, more recently, by observations of proton-spin relaxation in solutions of copper(II)–ethylenediamine complexes.[7] These processes may, however, occur through bimolecular exchange. Evidence for the dissociative lability of the two copper–ethylenediamine complexes comes from acid-decomposition experiments at low temperatures in methanol.[8] Our results are in general agreement with these values. The results for the copper(II) and nickel(II) complexes are collected in Table 2. We can be fairly certain that these rates refer to the first copper–nitrogen bond cleavage, subsequent decomposition being rapid. Thus, the pH-dependence of the dissociation of [Cu(*C*-tetraMeen)$_2$]$^{2+}$ resembles closely that for the thoroughly investigated and understood [Ni(en)]$^{2+}$ and [Ni(*C*-tetraMeen)$_2$]$^{2+}$ systems.[9] The rate of dissociation is independent of acidity from pH 7 to 4, then increases, and reaches a limiting value in 0·1—0·5M-nitric acid.

Without exception the copper complex reacts more rapidly than the corresponding nickel compound, and with the racemic butane-2,3-diamine and *C*-tetraMeen compounds (where data are most accurate) this is governed by a 4—5 kcal. mole^{-1} difference in energy of activation. This, more than entropy of activation, is the important parameter which accounts for the difference in reactivity of nickel and copper. This is observed whether

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[5] Melson and Wilkins, *J.*, 1962, 4208.

[6] Popplewell and Wilkins, *J.*, 1955, 4098.

[7] Morgan, Murphy, and Cox, *J. Amer. Chem. Soc.*, 1959, **81**, 5043; Cox and Morgan, *ibid.*, p. 6409.

[8] Bjerrum, Poulsen, and Poulsen, Proceedings of the Symposium on Coordination Chemistry, Danish Chem. Soc., 1954, p. 51.

[9] Ahmed and Wilkins, *J.*, 1959, 3700; Ahmed, Ph.D. Thesis, Sheffield, 1960.

TABLE 1.

Dissociation of copper(II)–diamine complexes in nitric acid.

Dissociating species *	Temp.	$[Cu]_{total}$ (mM)	$[A]_{total}$ (mM)	$[HNO_3]$ (M)	Wavelength (mμ)	*k* (sec.$^{-1}$)
$[Cu(en)_2]^{2+}$	0·8°	5·0	15·0	0·15	520	**43·3**
$[Cu(en)]^{2+}$	0·8	50·0	20·0	0·15	630	**17·3**
	6·4	50·0	20·0	0·15	630	**27·7**
	6·8	50·0	20·0	0·15	630	**22·4**
	15·8	50·0	20·0	0·15	630	**63·0**
	25·0	50·0	20·0	0·15	630	~115
$[Cu(bn)_2]^{2+}$	15·2	5·0	15·0	0·20	500	8·56
		5·0	15·0	0·20	500	7·70
		5·0	15·0	0·20	585 †	8·56
	25·0	5·0	15·0	0·20	500	14·4
		5·0	15·0	0·20	500	15·1
	34·0	5·0	15·0	0·20	500	27·7
		5·0	15·0	0·20	500	27·7
		5·0	15·0	0·50	500	31·5
$[Cu(bn)]^{2+}$	15·2	5·0	15·0	0·20	585 ‡	1·90
		5·0	15·0	0·20	585 ‡	2·13
	25·0	5·0	15·0	0·20	585 ‡	5·06
		25·0	10·0	0·20	585	4·62
	34·0	25·0	10·0	0·20	585	8·88
$[Cu(C\text{-tetraMeen})_2]^{2+}$	0·7	10·4	33·4	pH 6·8	—	0·0029 §
	0·7	10·4	33·4	pH 3·5	—	0·0033 ¶
	0·7	10·4	33·4	0·15	—	0·079 ‖
	16·0	5·0	12·5	0·15	460	0·35
	25·0	5·0	12·5	0·15	460	0·85
		5·0	12·5	0·15	460	0·78
		5·0	12·5	0·15	500	0·76
	32·8	5·0	12·5	0·15	460	1·64
		5·0	12·5	0·15	460	1·62
	39·0	5·0	12·5	0·15	460	2·44
$[Cu(C\text{-tetraMeen})]^{2+}$	16·0	20·0	5·0	0·15	620	0·22
	24·9	20·0	5·0	0·15	620	0·42
	33·4	20·0	5·0	0·15	620	0·76
		20·0	5·0	0·15	580	0·80
	40·4	20·0	5·0	0·05	620	1·04
		20·0	5·0	0·15	620	1·25
		20·0	5·0	0·15	620	1·37
		20·0	5·0	0·50	620	1·49
$[Cu(N\text{-tetraMeen})]^{2+}$	6·5	12·5	6·3	0·5	600	9·69
	25·8	12·5	6·3	0·5	600	40·1
$[Ni(N\text{-tetraMeen})]^{2+}$	1·5 **	100·0	50·0	0·5	620	0·0069
	1·6 **	100·0	50·0	0·5	620	0·0074
	10·3 **	100·0	50·0	0·5	960	0·025
	14·4 **	100·0	50·0	0·5	620	0·029
	20·1	150·0	75·0	0·5	620	0·086
	26·6	100·0	50·0	0·5	620	0·14
	34·3	150·0	75·0	0·25	620	0·41
		150·0	75·0	0·5	620	0·48

* en = $H_2N{\cdot}[CH_2]_2{\cdot}NH_2$; bn = $H_2N{\cdot}[CHMe]_2{\cdot}NH_2$; *C*-tetraMeen = $H_2N{\cdot}[CMe_2]_2{\cdot}NH_2$; *N*-tetraMeen = $Me_2N{\cdot}[CH_2]_2{\cdot}NMe_2$. † From initial portion of curve and known opt. density of mono-species. ‡ Using later portion of run. § Ref. 2. ¶ pH-stat experiment (ref. 9). ‖ Extrapolated value. ** Conventional spectrophotometric study (ref. 9).

TABLE 2.

Kinetic data, $k_d = A \exp(-E/\boldsymbol{R}T)$, for first-order dissociation of nickel(II)– and copper(II)–diamine complexes in nitric acid at 25·0°.

Species ‡	k_d (sec.$^{-1}$)	*E* (kcal. mole^{-1})	log *A* (sec.$^{-1}$)	Species ‡	k_d (sec.$^{-1}$)	*E* (kcal. mole^{-1})	log *A* (sec.$^{-1}$)
$[Ni(en)_2]$	5·21	19·8	15·3	$[Ni(C\text{-tetraMeen})_2]$	0·0033	20·0	12·2
$[Cu(en)_2]$	43·3 *	—	—	$[Cu(C\text{-tetraMeen})_2]$	0·80	15·5	11·3
$[Ni(en)]$	0·15	20·5	14·3	$[Cu(C\text{-tetraMeen})]$ †	0·42	13·7	9·7
$[Cu(en)]$	~115	~13	~12				
				$[Ni(N\text{-tetraMeen})]$	0·14	20·9	14·5
$[Ni(bn)_2]$	0·26	16·1	11·2	$[Cu(N\text{-tetraMeen})]$	38·5	12·0	10·5
$[Cu(bn)_2]$	15·1	11·9	9·9				
$[Ni(bn)]$	0·020	18·4	11·8				
$[Cu(bn)]$	4·56	14·5	11·3				

* At 1·0°. † Data for nickel complex not measurable.[2] ‡ For key see Table 1.

one compares octahedral nickel, $[Ni(rac\text{-}bn)_2(H_2O)_2]^{2+}$,* or "planar" nickel, $[Ni(C\text{-}tetraMeen)_2]^{2+}$ with the corresponding "planar" copper complexes. Since the $[Zn(C\text{-}tetraMeen)_2]^{2+}$–$[^{14}C]$tetraMeen exchange is very fast, the order of rates Zn > Cu > Ni obtains.[10]

The effect of increasing *C*-substitution is to decelerate the rate of dissociation of the complex, but the effect appears less important with copper than with nickel. The dissociative behaviour of $[Ni(en)]^{2+}$ and $[Ni(N\text{-}tetraMeen)]^{2+}$ is almost indistinguishable. This is rather surprising in view of the marked decrease in thermodynamic stability of the complex of the *N*-substituted ligand[11] ($K_1 = 10^{7\cdot6}$ and $10^{4\cdot1}$, respectively), it having been previously established that some relation exists between kinetic and thermodynamic stability of nickel complexes with a variety of aliphatic diamines.[3] The mono-complex invariably reacts more slowly than the corresponding higher species and this resides in a higher energy of activation term, except for the copper–tetraMeen complexes.

The markedly higher dissociative lability and thermodynamic stability of the copper than of the nickel complexes means that the formation rate constants for the copper complexes must be several orders the larger; this has been observed in the formation of the sulphate complexes by using sound-absorption relaxation methods,[12] and it is also in agreement with the much higher water-exchange rate for Cu_{aq}^{2+} than of Ni_{aq}^{2+}, obtained from nuclear magnetic resonance studies.[13]

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* Normally, co-ordinated water has been omitted.

[10] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 203.

[11] Leussing, personal communication.

[12] Eigen in "Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 371.

[13] Connick and Stover, *J. Phys. Chem.*, 1961, **65**, 2075.