910. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part V.* The Rates of Dissociation of Nickel*(II) *and Copper*(II) *Complexes of Carbon-substituted Ethylenediamines.*

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The rates of dissociation in aqueous acid of nickel(II) and copper(II) complexes of substituted amines, $H_2N\cdot CRR'\cdot CR''R'''\cdot NH_2$, decrease as alkyl substitution increases. Although these rates are fairly fast even for complexes of 2 : 3-diamino-2 : 3-dimethylbutane (tetraMeen) ($R = R' = R'' = R''' =$ Me) they are slower at pH 6·8—7·0 and have been measured from $^{63}Ni^{2+}$ and [^{14}C]-2 : 3-diamino-2 : 3-dimethylbutane exchange studies. The first-order dissociation rate constant for [Ni tetraMeen$_2$]$^{2+}$ is $2{\cdot}5 \times 10^{11} \exp(-21{,}000/\boldsymbol{R}T)$ and for [Cu tetraMeen$_2$]$^{2+}$ is $1{\cdot}3 \times 10^{11} \exp(-17{,}100/\boldsymbol{R}T)$, both in units of sec.$^{-1}$. This shows that the increased rate for the latter is almost entirely due to a lower activation energy. On the other hand, it appears from this and the work of others that the slower rate of dissociation of [Ni tetraMeen$_2$]$^{2+}$ than of [Ni en$_2$]$^{2+}$ residues largely in a decreased *PZ* factor. The nickel and copper complexes of 2 : 3-diamino-2 : 3-dimethylpentane ($R = R' = R'' =$ Me; $R''' =$ Et) and 3 : 4-diamino-3 : 4-dimethylhexane ($R = R'' =$ Me; $R' = R''' =$ Et) show even further decreased rates of dissociation.

TETRAMETHYLETHYLENEDIAMINE (2 : 3-diamino-2 : 3-dimethylbutane) † forms a complex with nickel ion which is of interest from stereochemical, thermodynamic, and kinetic viewpoints.[1] Unlike the parent ethylenediamine, which forms the three species [Ni en]$^{2+}$, ‡ [Ni en$_2$]$^{2+}$, and [Ni en$_3$]$^{2+}$, the tetramethyl-compound forms only the yellow diamagnetic [Ni tetraMeen$_2$]$^{2+}$ ion in which the two chelating amines are arranged in a planar disposition about the central nickel atom. Mixtures of Ni_{aq}^{2+} and [Ni tetraMeen$_2$]$^{2+}$ do not interact spectrophotometrically, indicating, almost certainly, the absence in that mixture of any appreciable amount of [Ni tetraMeen]$^{2+}$, while [Ni tetraMeen$_2$]$^{2+}$ does not react even with liquid 2 : 3-diamino-2 : 3-dimethylbutane to form any higher complex. Examination of the molecular model of the bisamine species shows a high steric hindrance to reaction at the fifth and the sixth position and it is unlikely that water co-ordinates even in aqueous solution since in this the yellow colour and diamagnetism [2] persist. The yellow complex does not dissociate " immediately " when placed in excess of acid [1] and this relative " inertness " to substitution is unusual behaviour for a nickel complex with an aliphatic amine. The nickel–ethylenediamine complexes dissociate completely in aqueous acid at 0° within 30 sec.[3] and in order to measure dissociation (and formation) rates involving these complexes, it is necessary to use methanol solution at low temperatures.[4] Since the rates of dissociation of metal–amine complexes are often acid catalysed,[3] it was thought worth while to study the exchange of $^{63}Ni^{2+}$ with [Ni tetraMeen$_2$]$^{2+}$ in neutral solution. Since the monoamine compound is unstable, the study will involve only two exchange species without the attendant difficulties encountered, *e.g.*, in the exchange [5] of [Ni phen$_2$]$^{2+}$ and [Ni phen]$^{2+}$ with $^{63}Ni^{2+}$.

The substitution of four methyl groups having such a pronounced retardation of dissociation rate, it was decided to study the effect of increased *C*-alkyl substitution of

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* Part IV, preceding paper.

† A list of the amine abbreviations used in formulæ of complexes is contained in Table 1.

‡ In this and all subsequent discussion co-ordinated water will be ignored.

[1] Basolo, Yun Ti Chen, and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

[2] Lewis and Wilkins, unpublished work.

[3] Part I, Popplewell, and Wilkins, *J.*, 1955, 4098.

[4] Bjerrum, Poulsen, and Poulsen, " Proceedings of the Symposium on Coordination Chemistry," Danish Chemical Society, 1954, p. 51.

[5] Part IV, Wilkins and Williams, preceding paper.

aliphatic diamines on the dissociation rates of their nickel and copper complexes. The discernible acid dissociation of [Cu tetraMeen$_2$]$^{2+}$ in aqueous acid at 0° caused us to study the exchange of [^{14}C]-2 : 3-diamino-2 : 3-dimethylbutane with [Cu tetraMeen$_2$]$^{2+}$ and with [Ni tetraMeen$_2$]$^{2+}$ in neutral and alkaline solution.

EXPERIMENTAL

Preparation of Amines and Complexes.—2 : 3-Diamino-2 : 3-dimethylbutane,[6, 7] 2 : 3-diamino-2 : 3-dimethylpentane,[8] and 3 : 4-diamino-3 : 4-dimethylhexane [8] were prepared by published methods. Nickel complexes were prepared by treating nickel chloride or nitrate (1 mol.) with the amine dihydrochloride or dinitrate (2·2 mols.) in concentrated aqueous solution at neutral pH. The spectrum of bis(tetraMeen)nickel(II) nitrate in aqueous solution corresponded closely to that reported,[1] with $\varepsilon_{\text{max.}} = 63{\cdot}5$ at 4300 Å (Found: C, 34·2; H, 8·0; N, 20·1. Calc. for $C_{12}H_{32}O_6N_6Ni$: C, 34·7; H, 7·8; N, 20·2%). *Bis-*(3 : 4-*diamino-*3 : 4-*dimethylhexane*)*nickel*(II) *chloride* was quite soluble in alcohol, in contrast to the other nickel–amine complexes examined (Found: C, 45·7; H, 9·9; Cl, 16·7. $C_{16}H_{40}N_4Cl_2Ni$ requires C, 45·9; H, 9·7; Cl, 16·9%). *Bis-*(2 : 3-*diamino-*2 : 3-*dimethylpentane*)*nickel*(II) *chloride* (Found: Cl, 17·9. $C_{14}H_{36}N_4Cl_2Ni$ requires Cl, 18·2%). Attempts to prepare 3 : 4-diethyl-3 : 4-dinitrohexane from 2-bromo-2-nitrobutane and 3-nitropentane [9] in alkali solution yielded an oil which did not solidify or yield the desired amine on reduction. The only solid copper complex isolated was red *bis-*(2 : 3-*diamino-*2 : 3-*dimethylbutane*)*copper*(II) *perchlorate* (Found: C, 29·5; H, 6·5. $C_{12}H_{32}N_4O_8Cl_2Cu$ requires C, 29·1; H, 6·5%) which was precipitated during the exchange studies. When heated to 110°, the substance did not acquire the more usual blue-violet colour of bisaminecopper(II) complexes.[10]

Radioactive Nickel.—This was obtained from The Radiochemical Centre, Amersham, as an aqueous nickel nitrate solution (60 c.c.) containing nickel (3·2 g.) of total activity 250 μc. It contained 12·5 μc of ^{60}Co as radiochemical impurity. In the last stages of the investigation nickel of higher specific activity was used.[5] The purification [11] and radiochemical characterisation [5] have been described previously.

Preparation of Radioactive 2 : 3-*Diamino-*2 : 3-*dimethylbutane.*—Attempts were made to prepare [^{14}C]-2 : 3-diamino-2 : 3-dimethylbutane by irradiating pure unlabelled dioxalate [6] for 2 weeks, with 5×10^{11} neutrons/cm.^{2}/sec. flux at Harwell, having in mind the work of, *e.g.*, Schrodt and Libby.[12] The irradiation product was dissolved in warm 1N-hydrochloric acid (with some effervescence from carbonate produced), nickel chloride solution added, and the pH adjusted to about 7. The yellow solution containing the nickel complex was filtered from a slight gelatinous precipitate and the complex iodide precipitated with concentrated potassium iodide solution. The iodide was converted into the nitrate,[1] which was reconverted into iodide and the cycle repeated until the [Ni tetraMeen$_2$]I$_2$ had approximately constant activity. The activity of early samples (4000 counts per min.; end-window G.M. tube) was reduced to a steady value of about 100 per min. after eight cycles; unfortunately, such activities were too low for accurate exchange work. Direct synthesis of the labelled diamine in reasonable yields was possible from [1 : 3-^{14}C$_2$]acetoxime: [1 : 3-^{14}C$_2$]Acetone (0·1 mc; 2·2 mg.; supplied by The Radiochemical Centre, Amersham) was diluted with inactive acetone (3·5 g.) and mixed with hydroxylamine sulphate (5·0 g.) and sodium carbonate (3·2 g.) in water (40 c.c.). After about 24 hr., [1 : 3-^{14}C$_2$]acetoxime was extracted with ether, and removal of the ether left white crystals (4·0 g.; m. p. 57°).

2-*Bromo-*2-*nitro*[1 : 3-^{14}C$_2$]*propane.* This was prepared from [^{14}C]acetoxime (3·9 g.) by Iffland and Yen's method.[9] The residue (3·3 g.) from the final ligroin treatment was used in the next stage without further purification.

[2-^{14}C]2 : 3-*Dimethyl-*2 : 3-*dinitro*[1-^{14}C]*butane.* Crude 2-bromo-2-nitro[1 : 3-^{14}C$_2$]propane (2·3 g.) in alcohol (10 c.c.) was refluxed with 2-nitropropane (1·3 g.) in aqueous sodium hydroxide

[6] Sayre, *J. Amer. Chem. Soc.*, 1955, **77**, 6689.
[7] Bewad, *Ber.*, 1906, **39**, 1231.
[8] Seigle and Hass, *J. Org. Chem.*, 1940, **5**, 100.
[9] Iffland and Yen, *J. Amer. Chem. Soc.*, 1954, **76**, 4083.
[10] Bailar, jun., "The Chemistry of Coordination Compounds," Chapman and Hall Ltd., London, 1956, p. 66.
[11] Singer and Kurbatov, *J. Amer. Chem. Soc.*, 1954, **76**, 4738.
[12] Schrodt and Libby, *ibid.*, 1956, **78**, 1267.

(0·6 g.; 2·0 c.c.).[8] An almost white solid was finally obtained (2·0 g.; Found: C, 40·6; H, 6·9. Calc. for $C_6H_{12}O_4N_2$: C, 40·9; H, 6·9%).

2 : 3-*Diamino*[2-^{14}C]-2 : 3-*dimethyl*[1-^{14}C]*butane*. Catalytic reduction of the dinitro-compound gave only poor yields, and reduction with tin and hydrochloric acid was most effective.[13] The dinitro-compound (2·0 g.) was heated at 65° with stirring with fine-mesh tin (8·0 g.) and concentrated hydrochloric acid (25 c.c.). When all the dinitro-compound had reacted the clear solution was vigorously refluxed for about 10 min., cooled, made alkaline, and steam-distilled. One or two pellets of sodium hydroxide were added to the distillate and this was steam-distilled again. The identity of the amine solution obtained was confirmed by treatment of a small portion with a slight excess of nickel nitrate solution at a pH ~7 and spectrophotometric examination of the yellow solution; acidimetric titration gave its concentration. The total amine obtained (0·88 g.) represented an overall yield (based on diluted acetone) of 20%. Since dilution of ^{14}C with ordinary carbon occurred at a mid-stage of the synthesis it was considered not worth while to carry out a determination of the radiochemical yield. By obvious methods a small amount of nickel nitrate complex containing [^{14}C]diaminodimethylbutane was prepared as well as a sample of its dihydrochloride (Found: C, 38·2; H, 9·9; N, 15·2; Cl, 37·3. Calc. for $C_6H_{18}N_2Cl_2$: C, 38·1; H, 9·6; N, 14·8; Cl, 37·5%).

Acid Dissociation Experiments.—The rates of acid dissociation of all the copper complexes and of the nickel complexes (except those of 2 : 3-diamino-2 : 3-dimethyl-butane and -pentane and 3 : 4-diamino-3 : 4-dimethylhexane) were measured, visually, as described in Part I[3] and only semi-quantitative reliance is placed on them. The disappearance of the lilac-coloured $[CuA_2]^{2+}$ (where A = diamine in this and all subsequent discussion) was followed at 0° by using 10^{-2}M-complex and 10^{-1}M-hydrochloric acid. When a colour change was not " instantaneous," the bright blue $[CuA]^{2+}$ was observed, quite distinct from the colour of the bis-amine. At these concentrations the Cu_{aq}^{2+} ion was almost colourless.

Apart from 1 : 2-diamino-1 : 2-diphenylethane (*m*-stien) and the fully alkylated diamines (which do not form a tris-complex) all lilac $[NiA_3]^{2+}$ ions dissociated " immediately " at 0°. The resultant yellow, orange-yellow, or blue bis-species then dissociated at visible rates. Blue-green mono-$[NiA]^{2+}$ species, which finally dissociated to the very pale green Ni_{aq}^{2+} ion, was detectable only with 1 : 2-diamino-2-methylpropane (*i*-bn) and *meso*-2 : 3-diaminobutane (*m*-bn). With all other bis-nickel complexes, only a gradual lightening in colour was noticed.

TABLE 1. *Approximate dissociation rates of copper and nickel complexes of amines* (A) *of the type* $H_2N{\cdot}CRR'{\cdot}CR''R'''{\cdot}NH_2$ *at* 0°.

					$CuA_2^{2+} \longrightarrow$	CuA^{2+}	$CuA^{2+} \longrightarrow$	Cu^{2+}	$NiA_2^{2+} \longrightarrow$	NiA^{2+}	$NiA^{2+} \longrightarrow$	Ni^{2+}
A	R	R′	R″	R‴	Time (sec.) *	k_2 (sec.$^{-1}$)	Time (sec.)	k_1 (sec.$^{-1}$)	Time (sec.)	k_2 (sec.$^{-1}$)	Time (sec.)	k_1 (sec.$^{-1}$)
en	H	H	H	H	<1	⩾5	< 1	⩾5	30[c]			
pn	Me	H	H	H	<1	⩾5	< 1	⩾5	180[c]			
i-bn	Me	Me	H	H	<1	⩾5	~3	~1·7	~3	1·7	240	0·002
m-bn	Me	H (*meso*)	Me	H	<1	⩾5	~5	~1·0	~3	1·7	600	0·001
rac-bn ...	Me	H (racemic)	Me	H	<1	⩾5	~10	~0·5	1200[c]			
m-stien ...	Ph	H (*meso*)[d]	Ph	H	<1	⩾5	<1	⩾5	<1			
tetraMeen	Me	Me	Me	Me	15	0·33	120	0·04	4·7[a] 8·8[b]	0·147[a] 0·079[b]		
ethyltri-Meen ...	Et	Me	Me	Me	50	0·1	270	0·02	15[a]			
diethyldi-Meen ...	Me	Et	Me	Et	200	0·025	550	0·01	50[a]			

* *I.e.*, time for reaction. [a] Values refer to $t_{\frac{1}{2}}$ in min.; k_2 in min.$^{-1}$ at 24·0°. [b] Values at 18·0°. [c] Figures refer to time of complete dissociation. [d] Measurements carried out in dioxan–water (1 : 1 by vol.).

Acid dissociation rates for the " inert " yellow nickel complexes $[NiA_2]^{2+}$ (A = 2 : 3-diamino-2 : 3-dimethylbutane or -pentane or 3 : 4-diamino-3 : 4-dimethylhexane) were determined by following the optical density at 4350 Å of a solution 0·014M in complex to which 0·14M-hydrochloric acid had been added. A plot of log$[NiA_2^{2+}]$ against time gave a linear curve over

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[13] Basolo, Murmann, and Chen, *J. Amer. Chem. Soc.*, 1953, **75**, 1478

several half-lives, and from this, a value for k_2 was estimated. The acid dissociation rate of the tetramethyl-complex was measured at 24·0° and 18·0°, allowing an approximate estimate of the energy of activation. No increased rate of dissociation was observed when the acid concentration was raised from 0·14 to 0·45M. I am grateful to Dr. D. T. Elmore for measuring the dissociation rate at pH 5·4—5·5. The rate of consumption of acid (to maintain the constant pH) was measured automatically, and periodically small portions were withdraw for measurement of optical density at 4350 Å. Both methods gave similar values for the concentration of [Ni tetraMeen$_2$]$^{2+}$ remaining at various times. The initial changes were used since formation rates were important at this pH; the value obtained was $8{\cdot}1 \times 10^{-3}$ min.$^{-1}$ at 25°. The results of the acid dissociation experiments are recorded in Table 1, and include some previous observations.[14]

Exchange Experiments.—The results are shown in Tables 2 and 3. Ni$_{aq}$$^{2+}$ was precipitated by the anion component of several buffers and even in the case of ammonium acetate buffer, there was a marked enhancement of rate (Run 4). Somewhat surprisingly there was an approximately 10% decrease in rate of dissociation when the ionic strength was increased from 0·08 to 0·50M (Runs 3, 5, 12, and 13). All experiments were therefore in media of ionic strength made up to 0·5M by addition of sodium nitrate, and the pH adjusted to 6·9 ± 0·1 by addition of acid or base as required. Detection of the effect of replacement of sodium nitrate by sodium perchlorate was prevented by precipitation of complex perchlorate. Use of [Ni tetraMeen$_2$]Cl$_2$ (rather than nitrate) had no effect on the exchange rates. With early runs (1—9) ^{63}Ni$_{aq}$$^{2+}$ was mixed with [Ni tetraMeen$_2$]$^{2+}$ since little further nickel dilution of the original radioactive nickel was possible in view of its low specific activity and the insensitive end-window counting then available. With later runs (9—14), when sensitive gas-flow 2π-counting was possible, a suitable mixture of nickel nitrate, amine dinitrate, and sodium nitrate was adjusted to pH 6·8—7·0 with dilute sodium hydroxide solution and left for some hours. Exchange was initiated by adding either ^{63}Ni^{2+} or [^{63}Ni tetraMeen$_2$]$^{2+}$ obtained from the original radioactive nickel. For amine exchanges, of course, [^{14}C]ligand or [Ni [^{14}C]tetra-Meen$_2$]$^{2+}$ was added. At the pH of exchange the predominant species is the bis-complex, negligible dissociation occurring with both the Ni(II) and Cu(II) complex, as was shown by simple calculation from the known stability constants of these ions [1] and confirmed by spectral examination of two of the exchange mixtures (Runs 3 and 23). The spectra were similar to the known spectra of the bis-species, $\varepsilon_{max.}$ = 63·6 at 4320 Å (63·8 at 4340 Å [1]) for nickel and $\varepsilon_{max.}$ = 114 at 5450 Å (120 at 5470 Å [15]) for copper. No appreciable hydrolysis of nickel ion occurs below pH 8.[16]

Separation, Counting, and Calculation of Results.—Separation of nickel complex as [Ni tetraMeen$_2$]I$_2$ from either nickel ion or amine was easily effected by concentrated potassium iodide solution. In metal-exchange experiments, it was then washed, and converted into nickel dimethylglyoxime, which was washed well with water and acetone. A slurry in acetone of 10 ± 0·2 mg. of the dried material was then evaporated on a large G.E.C. planchet as described previously.[5] This conversion was necessary since the matting of the complex iodide to give a fine, uniform deposit would necessitate much more material than nickel dimethylglyoxime, which can be deposited uniformly even in as small amounts as 2—3 mg. For the ligand exchange, the complex iodide was washed with alcohol and ether, dried for a short while at 110°, and matted on small planchets.[3] Since the iodide was almost insoluble in water, the other exchanging species were recovered from the filtrate after precipitation with the concentrated iodide solution. A ligand solution (at pH ~7) was added to the filtrate when this contained Ni$_{aq}$$^{2+}$ and *vice versa.* In both cases the yellow complex iodide was precipitated, and treatment identical with that described above afforded similar counting materials from both " ends " of a run. This procedure was used for only a few runs, and in these good agreement in results was obtained.

A similar technique was used for the [Cu tetraMeen$_2$]$^{2+}$–[^{14}C]ligand exchanges except that a concentrated sodium perchlorate solution was used to precipitate [Cu tetraMeen$_2$](ClO$_4$)$_2$ and this material, after being washed with water, alcohol, and ether, was used as the sample for radioassay. The effectiveness of the separation was confirmed by our obtaining small exchange values at zero times. The specific activity of both these isotopes was proportional to the count rate since " infinite " or nearly " infinite " thickness of material was used.

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[14] Popplewell and Wilkins, unpublished work.
[15] Jörgensen, *Acta Chem. Scand.*, 1956, **10**, 887.
[16] Gayer and Wootner, *J. Amer. Chem. Soc.*, 1952, **74** 1436.

An examination of exchanges involving the nickel complex in Tables 2 and 3 shows that the exchange process (Rate $= R$, exchange half-life $= t_{\frac{1}{2}}$; A = ligand amine, B = metal, and C = complex) is adequately expressed by the relation $R_{\text{exch.}} = k_{\text{exch.}}[\text{complex}]$, where for the metal exchanges,

$$R_{\text{metal}} = \frac{0{\cdot}693}{t_{\frac{1}{2}(\text{metal})}} \cdot \frac{[\mathrm{C}][\mathrm{B}]}{[\mathrm{C}] + [\mathrm{B}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for the ligand exchanges,

$$R_{\text{ligand}} = \frac{0{\cdot}693}{t_{\frac{1}{2}(\text{ligand})}} \cdot \frac{2[\mathrm{C}][\mathrm{A}]}{2[\mathrm{C}] + [\mathrm{A}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since $R_1 \gg R_2$ for the process pictured below, even under the conditions of ligand exchange,

$$[\text{M ligand}_2]^{2+} \xrightleftharpoons{R_2} [\text{M ligand}]^{2+} + \text{ligand} \quad . \quad . \quad . \quad . \quad . \quad (k_2)$$

$$[\text{M ligand}]^{2+} \xrightleftharpoons{R_1} \mathrm{M}^{2+} + \text{ligand} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (k_1)$$

then it follows that $R_{\text{metal}} = k_2[\mathrm{C}]$ and $R_{\text{ligand}} = 2k_2[\mathrm{C}]$.[17]

TABLE 2. *Exchange of* Ni^{2+} *with* [Ni tetraMeen$_2$]$^{2+}$ *at* pH 6·9 ± 0·1 *and ionic strength* 0·5M.

Run No.	Temp.	[Complex] (mmole l.$^{-1}$)	[Nickel] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ exch. (min.)	10^5R (min.$^{-1}$ mole l.$^{-1}$)	10^3k_2 (min.$^{-1}$)
3 [a]	24·9°	12·3	14·2	42	10·9	8·8
4 [b]	25·2	12·2	14·2	17	26·7	21·9
5	25·1	12·2	14·1	55	8·2	6·8
6	25·2	6·1	14·2	67	4·4	7·2
7	25·0	13·8	5·2	29	9·0	6·6
8	25·0	13·8	15·0	52	9·6	7·0
9	25·1	11·9	13·8	50	8·8	7·4
10	27·6	13·7	40·1	53	13·3	9·7
11 [c]	27·6	13·7	40·1	57	12·4	9·0
12 [a]	32·5	13·7	40·1	27	26·1	19·1
13	32·5	13·7	40·1	32	22·0	16·1
14	37·7	13·7	40·1	18	39·3	28·7

[a] No added sodium nitrate. [b] Ammonium acetate buffer at pH = 7·0. [c] Diffuse light.

TABLE 3. *Exchange of* 2 : 3-*diamino*-2 : 3-*dimethylbutane with* [Ni tetraMeen$_2$]$^{2+}$ (=Ni) *and* [Cu tetraMeen$_2$]$^{2+}$ (=Cu).

Run No.	Temp.	[Ni]	[Cu]	[amine]	$t_{\frac{1}{2}}$ exch. (min.)	10^5R (min.$^{-1}$ mole l.$^{-1}$)	10^3k_2 (min.$^{-1}$)
15	25·0°	11·9	—	3·2	8·0	24·4	10·3
16 [b]	25·0	12·3	—	3·2	10·6	18·8	7·6
17 [b]	24·9	15·0	—	29·6	40	25·8	8·6
18 [b]	25·0	7·7	—	11·3	37	12·2	7·9
19 [a]	24·9	12·4	—	10·6	~0·8	—	—
20 [b]	35·0	12·9	—	14·4	10·8	59·2	23·0
21	0·7	—	10·4	12·6	3·0	181·5	174·4
22	9·9	—	10·4	12·6	1·17	465·5	447·2
23	17·7	—	13·3	15·2	0·43	1544	1164
24 [a]	0·3	—	50·0	50·0	$\leqslant$0·01	—	—

[a] pH = 9·8, otherwise pH = 6·8. [b] Ionic strength = 0·5M.

For the copper complex exchanges, however, it is believed that only the equilibrium analogous to R_2 above is responsible for ligand exchange, and the rate of exchange $R_{\text{ligand}} = k_2[\mathrm{C}]$, since in the acid dissociation experiments (see Table 1) the second dissociation (represented by R_1) is slower than the first and that therefore this condition obtains in neutral solution as well. The exchange of Cu^{2+} with [Cu tetraMeen]$^{2+}$ would resolve this point.

There is a small difference between the values of k_2 estimated from nickel and amine exchanges (mean values $7{\cdot}1 \pm 0{\cdot}4 \times 10^{-3}$ min.$^{-1}$ and $8{\cdot}0 \pm 0{\cdot}5 \times 10^{-3}$ min.$^{-1}$ at 25·0° respectively): it appears to be just outside experimental accuracy, and is too large to be explained by

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[17] Wilkins and Williams, *J. Inorg. and Nuclear Chem.*, in the press.

a possible ^{63}Ni isotope effect, but Runs 16, 17, and 18 indicate that there may be a slight dependence of exchange rate on ligand concentration. The value from Run 16 ($7{\cdot}6 \times 10^{-3}$ min.$^{-1}$) is close to that from Run 6 or 9 and both results agree well with the acid dissociation value at pH 5·5 ($8{\cdot}1 \times 10^{-3}$ min.$^{-1}$). The variation of rate with temperature was similar for both ligand and metal exchange with the nickel complex.

DISCUSSION

Kinetic data pertaining to rates of dissociation of Ni(II)- and Cu(II)-aliphatic amine complexes are summarised in Table 4, and include results for nickel- and copper-ethylenediamine complexes in acid methanol.[4] All results with [Ni tetraMeen$_2$]$^{2+}$ in acid relate to a maximum rate reached by 0·03M-acid and hardly altered in 0·5M-acid. Acid has more effect with copper than with nickel complexes of 2 : 3-diamino-2 : 3-dimethylbutane.[4] The acid dependence suggests that monoprotonated species may be involved in the acid dissociation analogous to the observations of the [Ni phen]$^{2+}$ and [Fe dipy$_3$]$^{2+}$ systems.[18] In fact, the approximate expression at 22·0°:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{NiA_2}] = \frac{0{\cdot}127[\mathrm{H^+}] + 3{\cdot}3 \times 10^{-6}}{[\mathrm{H^+}] + 5{\cdot}95 \times 10^{-4}}[\mathrm{NiA_2}]$$

can be deduced from rate measurements at several pH's. This is the form of pH-rate dependence in which more than one metal complex is involved in dissociation at intermediate pH values. In acid dissociation experiments and in one exchange (Run 4) acetate- (and phthalate-) containing buffers enhanced rates of reaction, but caused no marked spectral change. Rates of dissociation of the 2 : 3-diamino-2 : 3-dimethylbutane complexes of copper and nickel at pH 6·8—7·0 obey the relations $k_2 = 1{\cdot}3 \times 10^{11} \exp(-17{,}100/\boldsymbol{R}T)$ and $k_2 = 2{\cdot}5 \times 10^{11} \exp(-21{,}000/\boldsymbol{R}T)$ sec.$^{-1}$, respectively, so the lower rate of the latter is due almost entirely to a larger activation energy. Provided that the results in methanol can be compared with those in water,[3] the slower dissociation of [Ni tetraMeen$_2$]$^{2+}$ than of [Ni en$_2$]$^{2+}$ resides almost entirely in a decreased *PZ* factor.

TABLE 4. *Kinetic data for the dissociation of* Ni(II)- *and* Cu(II)-*amine complexes at* 0°.

Ion	E_{act} (kcal. mole^{-1})		log *PZ* (sec.$^{-1}$)		log *k* (sec.$^{-1}$)	
	acid	neutral	acid	neutral	acid	neutral
[Ni en$_2$]$^{2+}$	19·9 [b]	—	15·7 [b]	—	−0·2 [b]	—
[Ni tetraMeen$_2$]$^{2+}$	~17·8	21·0	~10·5	11·4	−3·8 [a]	−5·4 [a]
[Cu en$_2$]$^{2+}$	~14·0 [b]	—	—	—	⩾+0·7 [c]	⩾+0·7 [c]
[Cu en]$^{2+}$	17 [b]	—	14 [b]	—	+0·4 [b]	—
[Cu tetraMeen$_2$]$^{2+}$	—	17·1	—	11·1	−0·5	−2·6

[a] Extrapolated value. [b] See ref. 4. [c] See ref. 3.

It is apparent from Table 1 that the rate of dissociation in acid decreases as alkyl *C*-substitution increases. This is not noticed with copper until the dimethyl derivative is examined, and then only at the mono-decomposition stage but the introduction of even the first methyl group with nickel reduces the rate. The introduction of two phenyl groups on the other hand has no noticeable retardation of dissociation rates for the copper and in fact enhances the dissociation rate of the nickel complex. When four methyl groups are added even the dissociation of [CuA$_2$]$^{2+}$ becomes discernible, the rate decreasing on successive replacement of methyl groups by one and then two ethyl groups, so that the decomposition of [Ni diethyldiMeen$_2$]$^{2+}$ in excess of acid is remarkably slow ($t_{\frac{1}{2}}$ ~50 min. at 25°). No attempt was made to separate 3 : 4-diamino-3 : 4-dimethylhexane into the theoretically possible racemic and *meso*-form but the shape of the acid-dissociation curves suggested that probably only one species was undergoing reaction. Likewise, there was no indication of a *cis*- and a *trans*-form of the nickel complex with 2 : 3-diamino-2 : 3-dimethylpentane.

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[18] See, *e.g.*, Krumholz, *J. Phys. Chem.*, 1956, **60**, 87; Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211.

This observed decreased rate, which is particularly noticed at the point of complete alkyl substitution, probably arises from two factors. If it is assumed that the dissociation process involves in fact a bimolecular reaction with water, an increasing steric and hydrophobic effect will accompany increasing *C*-alkyl substitution and appear as a marked decrease in the activation entropy term. A knowledge of the mechanism of ring opening (*i.e.*, which of the two stages is the slower) might help in a more detailed understanding of the *modus operandi* of this effect. Certainly, the decreased rate cannot be correlated with an increased thermodynamic stability of the complex, since Basolo and his co-workers [1] have shown that *C*-substitution of ethylenediamine has only a relatively small and non-systematic effect on the stability of copper and nickel complexes.

The fast exchange of [^{14}C]ligand with [Ni tetraMeen$_2$]$^{2+}$ and with [Cu tetraMeen$_2$]$^{2+}$ (Runs 19 and 24) at pH ~10 indicates that dissociation is markedly base-catalysed although the unlikely possibility exists that a direct S_N2 process involving ligand is involved under these conditions when the concentration of free amine is much higher than at neutral pH.

The kinetic stability of the nickel and copper complexes of 2 : 3-diamino-2 : 3-dimethylbutane and higher homologues suggests that complexes of these ligands with other metals, normally forming " labile " ions, might dissociate at measurable rates. For example, preliminary observations of the Co(II)–2 : 3-diamino-2 : 3-dimethylbutane complex shows that this ion does not " immediately " dissociate in aqueous acid. In addition, because of the enhanced kinetic stability, it may be possible to resolve tetrahedral complexes of mercury(II) and zinc(II) with the diaminopentane or separate the *cis*- and the *trans*-isomer of the palladium(II) complex with the same amine.

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