496. *Factors Influencing the Rates of Dissociation of Metal Complexes. Part V.*[1] *The Effect of Increased Chelation on the Dissociation of Nickel*(II)–*Polyamine Complexes.*

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The step-wise nature of the dissociation of nickel(II)-polyamine complexes has been examined by the stopped-flow method. The kinetic parameters have been determined for the dissociation of the nickel(II) complexes of 1,2,3-triaminopropane, 2,2'-diaminodiethylamine, 2,2'-diaminodipropylamine, tri-(2-aminoethyl)amine, *NN'*-di-(2-aminoethyl)ethylenediamine and *NNN'N'*-tetra-(2-aminoethyl)ethylenediamine. Thus, the effect of number of rings, ring-size, ligand-branching, and strain factors can be assessed.

THE complexes of nickel(II) with unidentate and bidentate amines have been investigated previously,[2,3] and a basis has thus been laid for an examination of the complexes of polyamines which may contain three, four, or even six donor atoms within the molecule. We chose to study the step-sequence in the process of chelation by examining the dissociation, rather than the formation, of the complex since this is the simpler to investigate. There is a limiting rate for dissociation in acid media which relates unequivocally to the metal–nitrogen bond cleavage. On the other hand, more than one species may be involved in the formation process, which will be strongly pH-dependent and will involve successive second-order reactions, with attendant interpretative difficulties.

The mononickel chelates of the following polyamines were investigated: 1,2,3-triaminopropane (ptn) (cf. I), 2,2'-diaminodiethylamine (dien) (cf. II), 2,2'-diaminodipropylamine (dapa) (cf. III), tri-(2-aminoethyl)amine (tren) (cf. IV), *NN'*-di-(2-aminoethyl)-ethylenediamine (trien) (cf. V), and *NNN'N'*-tetra-(2-aminoethyl)ethylenediamine (penten) (cf. VII). It was then possible to assess the effect of the number of rings (two, I—III; three, IV, V; five, penten), ring-size (five- or six-membered, II and III), branching within the ligand (*e.g.*, compare I and II), and strain of terminal-NH_2 attachments (*e.g.*, compare I and penten) on the dissociation of the nickel complex. The thermodynamics of metal-complex formation with these amines has been thoroughly studied.[4] Protonated species (in which a non-co-ordinated nitrogen in the complex is protonated) have in certain cases been detected and their stabilities measured. This characterisation

[1] Part IV, Wilkins, *J.*, 1962, 4475.
[2] Melson and Wilkins, *J.*, 1962, 4208.
[3] Ahmed and Wilkins, *J.*, 1959, 3700; 1960, 2895, 2901.
[4] Prue and Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, (*a*) 995 (ptn), (*b*) 985 (dien); (*c*) Hares, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1956, **78**, 1816 (dapa); (*d*) Schwarzenbach and Prue, *Helv. Chim. Acta*, 1950, **33**, 963 (tren); (*e*) Schwarzenbach, *ibid.*, p. 974 (trien); (*f*) Schwarzenbach and Moser, *ibid.*, 1953, **36**, 581 (penten).

is valuable since these species will occur as kinetic intermediates in the acid decomposition of the complex.

Preliminary experiments [5] showed that the rates would need to be measured by fast-reaction techniques, and the stopped-flow method was employed, utilising the spectral differences in solution of the completely chelated, the partially chelated, and the unchelated nickel(II) ion and also the pH-changes accompanying the reaction, *e.g.*, (I) ⟶ (IA) ⟶ (IB). It was thus hoped to elucidate in detail the manner in which polyamines unravel from the metal during the decomposition of the complex.

EXPERIMENTAL

Materials.—Dien, dapa, and trien were commercial materials; N-propylethylenediamine, tren, and penten were prepared as described in the literature.[6] [14C]Penten was prepared from [14C]ethylene by way of [14C]ethylenediamine.[7,8] All amines were dried over sodium wire and redistilled *in vacuo* before use. The salt ptn,3HCl,H$_2$O was a gift from Professor G. Schwarzenbach, to whom we are very grateful. It was recrystallised several times from aqueous alcohol before use. Preliminary studies on the kinetics of dissociation of [Ni(trien)]$^{2+}$, prepared from the redistilled amine, showed that it contained a slower-reacting impurity (almost certainly the tren analogue). The amine was therefore further purified as the dinitrate, trien,2HNO$_3$.[9] This effect then disappeared [cf. ref. 4 (*e*)]. Tren was used both as the free amine and as the salt tren,4HCl,H$_2$O, with similar results. Aqueous solutions of amines were estimated with standard acid or prepared from the salts and standard alkali. Chloride was replaced by nitrate ion by using silver nitrate. " AnalaR " reagents were used throughout, metal solutions being estimated complexometrically with EDTA.[10]

Kinetic Experiments.—The addition of aqueous amine to nickel nitrate gave clear solutions except with penten, which gave a bluish precipitate. This, however, dissolved after several hours at room temperature or after about 30 min. on a steam-bath. The solution was then, significantly, lilac. An excess of nickel ion ensured that the monocomplex was the only complex species present in important amounts. A nitrate anionic medium was used throughout and, unless otherwise indicated, the ionic strength was 1·0M. Temperatures were accurate to ±0·2°. Each stage of the endothermic decomposition of the complex was accompanied by some 0·1—0·2° decrease in temperature. The spectral properties of the monoprotonated complex [M(HA)]$^{3+}$ were known where A = ptn, trien, tren, and penten and these were used to measure the [MA]$^{2+}$ ⟶ [M(HA)]$^{3+}$ change spectrophotometrically with the stopped-flow apparatus described previously.[2] The last stage of the decomposition to nickel ions could be measured in all cases directly without knowledge of the spectra of intermediates. The initial stage in the decomposition of [Ni(dien)]$^{2+}$ * and of [Ni(dapa)]$^{2+}$ was measured by the indicator method. The reduction in acidity which occurred to a predictable degree as each nickel-nitrogen bond was ruptured, could be followed by using *p*-nitroaniline as indicator.[2] When both the indicator and the direct spectral method could be employed, the agreement was good. Information on the number of kinetically distinct stages in the decomposition of [Ni(trien)]$^{2+}$, [Ni(tren)]$^{2+}$, and [Ni(penten)]$^{2+}$ was obtained by studying spectral changes at a number of wavelengths. All kinetic work was restricted to the 375—675 mμ region. The results are recorded in Table 1, where rate-constants were always the mean of two or three individual runs.

Exchange Experiments.—[63]*Nickel exchange.* An excess of nickel ion and ligand was adjusted to the required temperature and pH, and exchange was initiated by addition of [63]Ni^{2+} ion. The mono-complex was precipitated with freshly prepared Reinecke's salt, which induced little zero-time exchange. Complete exchange was caused when thiocyanate or antimonyl tartrate was used as the separating agent. For ~0·1M-solutions of complex and nickel ion, exchange

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* In general, co-ordinated water will be omitted from such formulæ.

[5] Hogg, Melson, and Wilkins in " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 391.

[6] (*a*) King and Macmillan, *J. Amer. Chem. Soc.*, 1946, **68**, 1774; (*b*) Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 444; (*c*) Gauss, Moser, and Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2359.

[7] Popplewell and Wilkins, *J.*, 1955, 2521.

[8] Melson, Ph.D. Thesis, Sheffield, 1962.

[9] Jonassen, LeBlanc, Meibohm, and Rogan, *J. Amer. Chem. Soc.*, 1950, **72**, 2430.

[10] Schwarzenbach, " Complexometric Titrations," transl. by Irving, Methuen, London, 1957.

TABLE 1.

Dissociation of nickel(II)–polyamine complexes in nitric acid.

$[Ni(ptn)]^{2+} \longrightarrow [Ni(Hptn)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
3.0°	0.10	0.05	0.50	575	6.1
	0.10	0.05	0.50	575	5.9
15.2	0.10	0.05	0.50	575	20
	0.10	0.05	0.50	575	21
	0.10	0.05	0.25 †	575	20
25.0	0.10	0.05	0.50	575	63
	0.10	0.05	0.50	575	69

$[Ni(Hptn)]^{3+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
3.0	0.10	0.05	0.50	575	0.039
	0.10	0.05	0.50	575	0.038 ‡
15.2	0.10	0.05	0.50	620	0.15
	0.10	0.05	0.25	575	0.15
25.0	0.10	0.05	0.50	625	0.35
	0.10	0.05	0.50	575	0.33
	0.10	0.05	0.50	575	0.34

$[Ni(dien)]^{2+} \longrightarrow [Ni(Hdien)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.2	0.20	0.10	0.20	448 §	1.9
18.0	0.20	0.10	0.20	448 §	7.7
	0.20	0.10	0.20	448 §	7.5

$[Ni(Hdien)]^{3+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
15.6	0.10	0.05	0.50	600	1.1
	0.10	0.05	0.50	600	1.1
25.0	0.10	0.05	0.50	650	2.7
	0.10	0.05	0.50	625	2.9
	0.10	0.05	0.50	600	3.0
	0.10	0.05	0.50	410	3.3
	0.10	0.05	0.20	448§	2.8
34.0	0.10	0.05	0.50	600	6.3
	0.10	0.05	0.50	600	6.5

$[Ni(trien)]^{2+} \longrightarrow [Ni(Htrien)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
15.0	0.10	0.05	0.50	450	6.5
25.0	0.10	0.05	0.50	450	16
	0.20	0.05	0.50	450	16
	0.10	0.05	0.20	450	15
	0.10	0.05	0.20	450 §	16
35.0	0.10	0.05	0.50	450	35
	0.10	0.05	0.50	450	36

$[Ni(Htrien)]^{3+} \longrightarrow [Ni(H_2trien)]^{4+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
15.0	0.10	0.05	0.50	420	1.4
25.0	0.20	0.10	0.50	420	4.0
	0.20	0.10	0.50	425	4.0
35.0	0.10	0.05	0.50	420	9.5

$[Ni(H_2trien)]^{4+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
15.0	0.10	0.05	0.50	650	0.85
25.0	0.10	0.05	0.50	650	2.2
	0.10	0.05	0.20	650	2.1
	0.20	0.05	0.50	650	2.4
	0.10	0.05	0.20	450 §	2.3
35.0	0.10	0.05	0.50	650	5.1

$[Ni(N\text{-}pren)]^{2+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.8	0.033	0.016	0.50	600	0.043
	0.10	0.05	0.50	570	0.041
6.8	0.033	0.016	pH = 4.0¶	600	0.064
16.6	0.10	0.05	0.50	600	0.14
	0.10	0.05	0.50	570	0.15
25.0	0.10	0.05	0.50	600	0.32
33.7	0.10	0.05	0.50	600	0.77

$[Ni(dapa)]^{2+} \longrightarrow [Ni(Hdapa)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.6°	0.10	0.05	0.20	450 §	1.3
15.5	0.10	0.05	0.20	450 §	4.0
	0.10	0.05	0.20	450 §	3.9
25.0	0.10	0.05	0.20	450 §	11
	0.10	0.05	0.20	450 §	9

$[Ni(Hdapa)]^{3+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.6	0.15	0.05	0.15	620	0.22
	0.10	0.05	0.20	450 §	0.23
15.0	0.05	0.025	0.50	650	0.74
	0.05	0.025	0.50	620	0.74
	0.15	0.05	0.15	620	0.69
	0.10	0.05	0.20	450 §	0.67
	0.10	0.05	0.20	450 §	0.67
25.0	0.10	0.05	0.20	650	1.6
	0.05	0.025	0.50	650	1.7
	0.05	0.025	0.20	620	1.7
	0.10	0.05	0.20	450 §	1.5
34.9	0.05	0.025	0.50	620	4.3
	0.05	0.025	0.50	580	4.7
	0.05	0.025	0.50	580	4.4
	0.10	0.05	0.20	450 §	4.2

$[Ni(tren)]^{2+} \longrightarrow [Ni(Htren)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
4.0	0.10	0.05	0.50	550	12
	0.10	0.05	0.50	550	12
5.0	0.10	0.05	0.20	550	13
	0.10	0.05	0.20	450 §	~13
15.0	0.10	0.05	0.50	550	31
	0.10	0.05	0.50	550	30
25.0	0.15	0.05	0.50	550	60
	0.10	0.05	0.50	550	66
	0.10	0.05	0.50	550	63

$[Ni(Htren)]^{3+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
15.0	0.10	0.05	0.50	550	0.079
	0.10	0.05	0.50	600	0.083
25.0	0.10	0.05	0.50	650	0.22
	0.15	0.05	0.50	600	0.23
	0.10	0.05	0.50	550	0.22
	0.10	0.05	0.50	420	0.21
35.0	0.10	0.05	0.50	550	0.57
	0.10	0.05	0.20	450 §	0.60

$[Ni(penten)]^{2+} \longrightarrow [Ni(Hpenten)]^{3+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.9	0.05	0.055	0.50	540	~70
10.0	0.05	0.055	0.50	540	~140

$[Ni(Hpenten)]^{3+} \longrightarrow [Ni(H_2penten)]^{4+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
5.9	0.05	0.055	0.50	585	9.8
	0.05	0.055	0.50	540	9.3
	0.05	0.055	0.50	540	8.6
10.0	0.05	0.055	0.50	585	13
15.0	0.05	0.055	0.50	540	23
	0.05	0.055	0.50	540	22
25.0	0.05	0.055	0.50	540	49
	0.05	0.055	0.50	540	53

$[Ni(H_2penten)]^{4+} \longrightarrow [Ni(H_3penten)]^{5+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
25.0	0.05	0.055	0.50	420	~3

$[Ni(H_3penten)]^{5+} \longrightarrow [Ni(H_4penten)]^{6+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
25.0	0.05	0.055	0.50	630	~0.43
	0.05	0.055	0.50	675	~0.41

$Ni(H_4penten)^{6+} \longrightarrow Ni^{2+}$

Temp.	[Ni]total (M)	[Amine]total (M)	[HNO₃]* (M)	Wave-length (mμ)	k (sec.⁻¹)
25.0	0.05	0.055	0.50	630	~0.035

* Acidity at commencement of experiment.   † Also 0.25M-NaNO₃.   ‡ Conventional spectrophotometric method.³   § Indicator method.   ¶ 0.2M-Potassium hydrogen phthalate.

half-lives observed at 0° at pH 7 were [Ni(dien)]²⁺ 8·8 hr., [Ni(trien)]²⁺ 6·4 hr., and [Ni(tren)]²⁺ ~18 days. The value for [Ni(en)]²⁺ was 14 min. (ref. 3).

[¹⁴C]*Penten exchange.* The solution containing metal ion (0·027M) and an excess of penten (0·045M) was equilibrated, and a small amount of [¹⁴C]penten in aqueous solution added to initiate exchange. The complex was precipitated rapidly on addition of perchlorate (nickel

TABLE 2.

Exchange of bivalent metal–penten complexes with [¹⁴C]penten in nitrate medium at 0·5°.

Metal	pH	Ligand co-ordination	Ionic strength (M)	$t_{\frac{1}{2}}$ (exch) (min.)
Manganese	7·0	6?	0·3	Complete within 1 min.
Cobalt	7·0	5 + 6	0·3	15
	10·2	6	0·3	11
Nickel	6·8 *	5 + 6	1·0	8·5
	10·2 *	6	1·0	8·5
	6·8 †	5 + 6	1·0	50
Copper	7·0	5?	0·3	5·7
	9·3	5?	0·3	~0·3
Zinc	7·0	5?	0·3	3·7
	8·2	5?	0·2	~0·5
	10·0	5?	0·2	Complete within 1 min.
Cadmium	7·0	5 + 6	0·3	~1
	10·2	6	·0·3	~0·5
Mercury	7·0	5?	0·3	~0·3

* At 45·0°.   † At 25·0°, [Ni] = 0·10M, [penten]$_{total}$ = 0·16M.

with iodide on scratching). The precipitate was washed with a small amount of ice-cold water, alcohol, and ether, and air-dried.

All radioassays were in a Harwell type gas-flow proportional counter. The exchange half-time was estimated from the usual semi-logarithmic plot which was linear with small zero-time exchange. The experiments with the cobalt(II) complex were performed in a nitrogen atmosphere to avoid rapid aerial oxidation. The results are collected in Table 2.
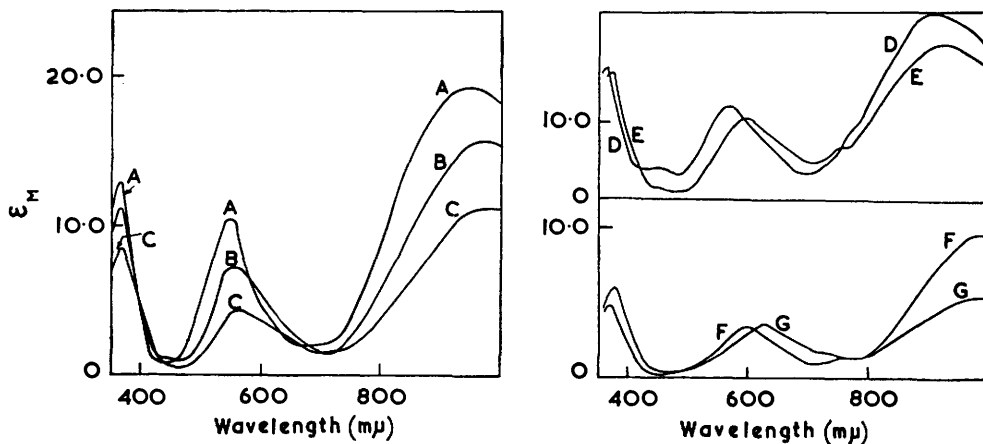

FIG. 1. Absorption spectra of nickel–polyamine complexes: A, [Ni(penten)]²⁺. B, [Ni(Hpenten)]³⁺. C, [Ni(H₂penten)]⁴⁺. D, [Ni(trien)]²⁺. E, [Ni(Htrien)]³⁺. F, [Ni(ptn)]²⁺. G, [Ni(Hptn)]³⁺.

Spectra.—These were recorded between 350 and 1000 mμ on a Unicam S.P. 600 spectrophotometer at room temperature. The spectra of protonated species were obtained from measurements for mixtures of known composition, calculated from stability data that relate, however, to somewhat different medium conditions. Alternatively, one or two equivalents of acid could be added to the completely chelated species and the spectra quickly measured

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on a Unicam S.P. 700 recording spectrophotometer. The extinction coefficients for intermediates estimated from the kinetic studies agreed well with those estimated from the static measurements. Some spectra are shown in Fig. 1, and results are recorded in Table 3. For

TABLE 3.

Spectral characteristics of nickel–polyamine complexes.

[Complex]	$\lambda_{max.}$ (mμ)	ε_M	[Complex]	$\lambda_{max.}$ (mμ)	ε_M	[Complex]	$\lambda_{max.}$ (mμ)	ε_M
[Ni(penten)]$^{2+}$ ...	362	12·8	[Ni(trien)]$^{2+}$	360	10·9	[Ni(Hptn)]$^{3+}$	375	5·8
	546	10·4		565	6·1		625	3·7
	825 *	12·0		775	5·0		730	1·9
	952	19·2		920	12·4		980	5·3
[Ni(Hpenten)]$^{3+}$	365	11·4	[Ni(Htrien)]$^{3+}$ ...	370	8·3	[Ni(en)]$^{2+}$	372	7·8
	562	7·3		590	5·3		630	4·9
	820	7·3		740	3·3		730	2·1
	980	15·6		920	10·2		980	6·0
[Ni(H$_2$penten)]$^{4+}$	366	8·2	[Ni(dien)]$^{2+}$	360	8·0	[Ni(*N*-pren)]$^{2+}$ ...	385	6·0
	565	4·3		595	5·0		640	4·3
	790	4·1		740	2·7		740	2·3
	980	10·4		950	9·0		980	5·5
[Ni(tren)]$^{2+}$	365	10·5	[Ni(dapa)]$^{2+}$	375	8·9	[Ni(H$_2$O)$_6$]$^{2+}$	395	5·0
	565	7·8		625	5·5		650	1·8
	775 *	5·0		735	2·4		720	2·1
	940	14·1		975	3·7		>1000	
[Ni(Htren)]$^{3+}$ †...	370	7·4	[Ni(ptn)]$^{2+}$	365	4·7			
	580	4·9		595	3·4			
	770	3·0		760	1·6			
	970	9·9		990	9·8			

* Shoulder, here and elsewhere.   † Approx. values only.

three other complexes, the ratio of ε_M at the maxima at 600—640 mμ to that at 950—980 mμ was determined as follows: [Ni(*rac*-bn)]$^{2+}$ 0·7, [Ni(1,3-pn)]$^{2+}$ 1·7, and [Ni(histamine)]$^{2+}$ 1·5, where bn and 1,3-pn are 2,3-diaminobutane and 1,3-diaminopropane.

RESULTS AND DISCUSSION

The rates of dissociation of the complexes in neutral solution (as shown by metal or penten exchange) are slow and even for the " labile " metals, easily measurable. However, the interpretation of these rates in terms of elementary formation and dissociation steps is impossible. It is thus more profitable to examine the decomposition in an excess of acid, and since there is little dependence of rate on acidity once this is greater than 0·05M, it is evident that nickel–nitrogen bond rupture is being measured, *i.e.*, the proton acts as an effective scavenger for the released amine group, without aiding bond-rupture.[3]
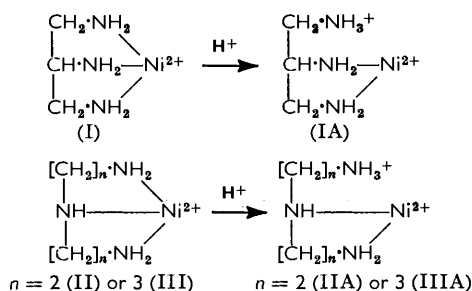
Complexes Containing One Terdentate Ligand.—The triamine ptn can chelate in one manner only, to form a 1,2,3-substituted complex * in which all three donor nitrogen atoms are *cis* to one another. Since [Ni(Hptn)]$^{3+}$ (IA) has been identified and its stability assessed,[4] the spectrum can be easily determined (see Fig. 1). The dien and the dapa complex, on the other hand, are less straightforward. These might be 1,2,3 or 1,2,6 stereochemically oriented, although for dien at least there is some evidence for the latter.[11] In addition, protonated species are of little importance,[4] so that their spectra cannot be determined.

The reaction (I) ⟶ (IA) can be measured directly at 575 mμ even although the optical density change is small (Fig. 1). Fortunately, subsequent decomposition (IA) ⟶ (IB) is very much slower. However, the behaviour of dien and dapa complexes is more complicated. If the usual first-order plot is made from the optical density–time figures obtained at 550 mμ, a marked curvature is obtained. This is the clue that two stages of comparable rate are involved. Examination of results obtained at other wavelengths confirms this, but since we can only guess the spectrum of [Ni(Hdien)]$^{3+}$ and [Ni(Hdapa)]$^{3+}$,

* 1—6 represent the six octahedral positions around nickel, 1,6, 2,4, and 3,5 being *trans* to one another.

[11] Crayton and Mattern, *J. Inorg. Nuclear Chem.*, 1960, **13**, 248.

Stage One:

$$\begin{array}{ccc}
\text{CH}_2\cdot\text{NH}_2 & & \text{CH}_2\cdot\text{NH}_3{}^+ \\
| & \searrow & | \\
\text{CH}\cdot\text{NH}_2\!\!-\!\!\text{Ni}^{2+} & \xrightarrow{\text{H}^+} & \text{CH}\cdot\text{NH}_2\!\!-\!\!\text{Ni}^{2+} \\
| & \nearrow & | \\
\text{CH}_2\cdot\text{NH}_2 & & \text{CH}_2\cdot\text{NH}_2 \\
\text{(I)} & & \text{(IA)}
\end{array}$$

$$\begin{array}{ccc}
[\text{CH}_2]_n\cdot\text{NH}_2 & & [\text{CH}_2]_n\cdot\text{NH}_3{}^+ \\
| & \searrow & | \\
\text{NH}\!\!-\!\!\!-\!\!\!-\!\!\text{Ni}^{2+} & \xrightarrow{\text{H}^+} & \text{NH}\!\!-\!\!\!-\!\!\!-\!\!\text{Ni}^{2+} \\
| & \nearrow & | \\
[\text{CH}_2]_n\cdot\text{NH}_2 & & [\text{CH}_2]_n\cdot\text{NH}_2
\end{array}$$

$$n = 2\ \text{(II) or 3 (III)} \qquad n = 2\ \text{(IIA) or 3 (IIIA)}$$

direct spectral observations are of limited value for estimating the rate of the first stage. The acidity decrease accompanying reactions (II) $\longrightarrow$ (IIA) and (III) $\longrightarrow$ (IIIA) has been used, by examining the early part of the decomposition for the first stage (and late times for the second). Models indicate that it would be more difficult to remove the central NH_2 or NH than the terminal NH_2 groups in this first stage. In addition, with complex (II) or (III) an eight- or ten-membered ring results on " central " cleavage and this would be expected to decompose much more rapidly than is in fact observed. It is more difficult to decide on this basis for complex (I) since the difference would be only between a five- and a six-membered ring, and indeed Spiro and Ballhausen [12] suggest that $[\text{Ni(Hptn)}]^{3+}$ involves middle-nitrogen protonation. We do not believe that in fact this is the case, for the following reason. The value of $\varepsilon_{\text{max.}}$ (600—640 mμ)/$\varepsilon_{\text{max.}}$ (950—980 mμ) for a series of complexes containing one six-membered ring is 1·5—1·7, whereas 0·7—0·8 is the corresponding value for a five-membered ring. The value of less than unity for the ratio for $[\text{Ni(Hptn)}]^{3+}$ observed for both equilibrium and kinetic conditions suggests that

TABLE 4.
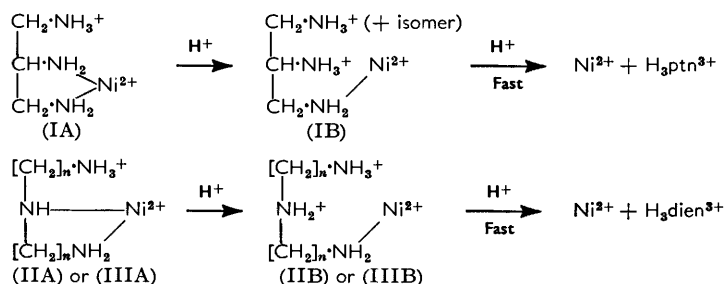
Kinetic data for Ni–N bond rupture in amine complexes at 25°.

Ligand	Stage 1			Stage 2			Stage 3		
	k (sec.$^{-1}$)	E (kcal. mole^{-1})	log A	k (sec.$^{-1}$)	E (kcal. mole^{-1})	log A	k (sec.$^{-1}$)	E (kcal. mole^{-1})	log A
NH_3 *	5·8	14·3	11·2	—	—	—	—	—	—
en †	0·15	20·5	14·3	—	—	—	—	—	—
N-pren	0·32	17·7	12·5	—	—	—	—	—	—
ptn	63	17·8	14·9	0·34	16·1	11·4	—	—	—
dien	14	17·9	14·3	2·8	16·2	12·4	—	—	—
dapa	11	17·8	14·1	1·7	17·1	12·8	—	—	—
tren	66	14·1	12·2	0·22	17·3	11·5	—	—	—
trien	15	14·8	12·1	4·0	16·7	12·9	2·1	16·0	12·1
penten	70 ‡	—	—	49	14·9	12·6	~3	—	—

* From ref. 2.   † From ref. 3.   ‡ At 6°.

it should be formulated as (IA). Results are collected in Table 4 and will be discussed with other kinetic results in the last section below.

Stage Two:

$$\begin{array}{ccccc}
\text{CH}_2\cdot\text{NH}_3{}^+ & & \text{CH}_2\cdot\text{NH}_3{}^+\ (+\ \text{isomer}) & & \\
| & \xrightarrow{\text{H}^+} & | & \xrightarrow[\text{Fast}]{\text{H}^+} & \text{Ni}^{2+} + \text{H}_3\text{ptn}^{3+} \\
\text{CH}\cdot\text{NH}_2 & & \text{CH}\cdot\text{NH}_3{}^+\quad\text{Ni}^{2+} & & \\
| & \searrow\text{Ni}^{2+} & | & \nearrow & \\
\text{CH}_2\cdot\text{NH}_2 & & \text{CH}_2\cdot\text{NH}_2 & & \\
\text{(IA)} & & \text{(IB)} & &
\end{array}$$

$$\begin{array}{ccccc}
[\text{CH}_2]_n\cdot\text{NH}_3{}^+ & & [\text{CH}_2]_n\cdot\text{NH}_3{}^+ & & \\
| & \xrightarrow{\text{H}^+} & | & \xrightarrow[\text{Fast}]{\text{H}^+} & \text{Ni}^{2+} + \text{H}_3\text{dien}^{3+} \\
\text{NH}\!\!-\!\!\!-\!\!\!-\!\!\text{Ni}^{2+} & & \text{NH}_2{}^+\quad\text{Ni}^{2+} & & \\
| & \nearrow & | & \nearrow & \\
[\text{CH}_2]_n\cdot\text{NH}_2 & & [\text{CH}_2]_n\cdot\text{NH}_2 & & \\
\text{(IIA) or (IIIA)} & & \text{(IIB) or (IIIB)} & &
\end{array}$$

[12] Spiro and Ballhausen, *Acta Chem. Scand.*, 1961, **15**, 1707.

Stage 2 is concerned with the decomposition of an unsymmetrical bidentate complex. The first bond-rupture is rate-determining, the subsequent decomposition of the unidentate species being very rapid.[2,3]   The dissociation of a complex containing an unsymmetrical ligand $NHR \cdot CH_2 \cdot CH_2 \cdot NH_2$, will proceed by two *concurrent* first-order reactions (involving Ni–NHR and Ni–NH_2 rupture) and thus remains first-order.[13]   The observed rate constant equals $(k_1 + k_2)$ where $2k_1$ and $2k_2$ represent the rate constants for the complexes containing $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ and $NHR \cdot CH_2 \cdot CH_2 \cdot NHR$.   The results shown in Table 5 verify

TABLE 5.

Dissociation of nickel(II) complexes of diamines ($R \cdot NH \cdot CHR' \cdot CHR'' \cdot NHR'''$) at $0.4°$
in perchloric acid (limiting rate).

R	R'	R''	R'''	$10^3 k$ (sec.$^{-1}$) *	R	R'	R''	R'''	$10^3 k$ (sec.$^{-1}$) *
H	H	H	H	6·6	Et	H	H	Et	10·3
Me	H	H	H	4·5	H	Me	H	H	3·7
Me	H	H	Me	1·8	H	Me	Me	H †	0·7
Et	H	H	H	8·7					

* Taken from ref. 3 and unpublished work with Dr. R. Hogg.   † Racemic isomer.

this relationship, which holds also for *C*-substituted diamines.   Thus, a comparison of the rate for stage two with that for the ethylenediamine complex ($k = 0.15$ sec.$^{-1}$ at $25.0°$) shows that at least 95% of first-bond ruptures involve the secondary amine with (IIA) or (IIIA) and that reaction (IA) ⟶ (IB) proceeds mainly as shown, but that there is an important contribution (20%) from a reaction involving breakage of the other NH_2–Ni bond.

Complexes Containing One Quadridentate Ligand.—Relatively few quadridentate groups are known, since the possibility of such co-ordination requires special geometrical conditions for a reasonably strain-free structure to result.[14]   Two ligands which fulfil these conditions are tren and trien.   Tren behaves as a triacidic base[4] but as a quadridentate ligand.   The structure of [Ni(tren)(NCS)$_2$] shows that the nickel is surrounded by six nitrogen atoms in a slightly distorted octahedron, with the thiocyanate groups in *cis*-positions.[15]   This configuration for the complexed amine must persist in solution since the position of the absorption maxima is the same for the reflection spectrum of the solid thiocyanate and the absorption spectrum of [Ni(tren)(H$_2$O)$_2$]$^{2+}$ in solution.[16]   There is evidence for " unstable hydrogen complexes " [Ni(Htren)]$^{3+}$ and [Ni(H$_2$tren)]$^{4+}$ in solution.[4] The tetra-acidic base trien forms the species [Ni(trien)(H$_2$O)$_2$]$^{2+}$ which may in solution be a *cis–trans*-mixture.[17]   No evidence for higher protonated species than [Ni(Htrien)]$^{3+}$ has been adduced from the studies by Schwarzenbach's school.

There are only two observable stages in the decomposition of the tren complex and these correspond to the formation of the mono- and the di-protonated species, respectively:

$$\text{(IV) [Ni(tren)]}^{2+} \xrightarrow{\text{H}^+} \text{[Ni(Htren)]}^{3+} \text{ (IVA)}$$

$$\text{(IVA) [Ni(Htren)]}^{3+} \xrightarrow{\text{H}^+} \text{[Ni(H}_2\text{tren)]}^{4+} \text{ (IVB)}$$

$$\text{[Ni(H}_2\text{tren)]}^{4+} \xrightarrow[\text{Fast}]{\text{H}^+} \text{Ni}^{2+} + \text{H}_3\text{tren}^{3+}$$
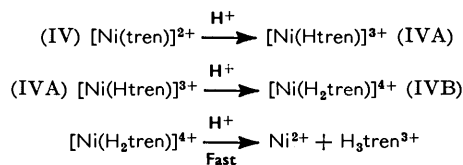
There is no change in optical density at 450 mμ during the complete decomposition of the complex, so that the indicator experiments are simply performed and these show (*a*) that

[13] Frost and Pearson, " Kinetics and Mechanism," Wiley, New York, 1961, p. 160.
[14] Schwarzenbach, in " Advances in Inorganic and Radiochemistry," ed. Eméleus and Sharpe, Academic Press, Inc., New York, Vol. III, 1961, Chapter 6.
[15] Rasmussen, *J. Inorg. Nuclear Chem.*, 1958, **8**, 441; *Acta Chem. Scand.*, 1959, **13**, 2009; Hall and Woulfe, *Proc. Chem. Soc.*, 1958, 346.
[16] Bostrup and Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.
[17] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

there is no very rapid dissociative step (faster than the time-resolution of the apparatus, a few milliseconds), and (*b*) a fast step followed by a slower reaction with half-lives similar to that obtained from the direct spectral change at 550 mμ. There is insufficient difference in ε_M for [Ni(tren)]$^{2+}$ and [Ni(Htren)]$^{3+}$ at 600 or 650 mμ for a quantitative study of the first step, but the result for the second stage is consistent with that at 550 mμ.
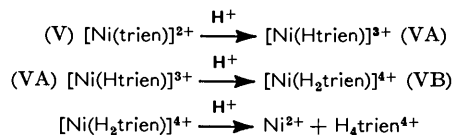
The assignment of these changes to definite molecular processes must be ambiguous. Examination of models shows that the tertiary nitrogen atom cannot be the first group removed. There are two types of primary amine group: (*a*) *cis* to both water molecules completing the octahedron (two possibilities) and (*b*) *cis* only to one water molecule (one possibility). It is not possible to say which type of amine is removed in the first step, but in both cases a substituted diethylenetriamine results, differing only in its stereo-chemical disposition (1,2,3 or 1,2,6, severally), *e.g.*, for type (*a*):
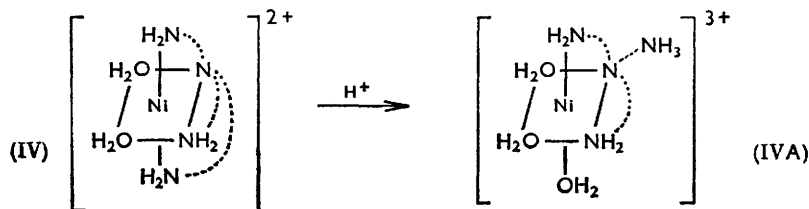
where each broken line represents –CH$_2$·CH$_2$–.

The second stage we would then suppose, from the work with dien, to involve breakage of one of the other co-ordinated primary amine groups. This leaves an *NN*-disubstituted ethylenediamine derivative containing a tertiary nitrogen which would be expected from its high degree of substitution and charge to break rapidly free from the nickel.

The complete dissociation of [Ni(trien)]$^{2+}$ at 450 mμ produces the oscilloscope trace shown in Fig. 2. Three stages are apparent. The optical density at the end of stage one (point B) corresponds with that calculated for [Ni(Htrien)]$^{3+}$, and the indicator method confirms at this point the uptake of only one proton with rates corresponding reasonably well with one another. At this wavelength the extinction coefficients of the mono- and the di-protonated species and of the nickel ion must all be small. Further evidence that three stages are involved is obtained by examining the system at other wavelengths. At 25° the optical density fall at 450 mμ is virtually complete (90%) within 150 msec., at 420 mμ within 450 msec. and at 650 mμ only after about 1 second, so that the relative extinction coefficients are such that one is observing and can thus measure the first, second, and third stages at these wavelengths. The indicator experiments confirm this. The results are only moderately accurate for the second stage:

$$\text{(V) [Ni(trien)]}^{2+} \xrightarrow{\text{H}^+} \text{[Ni(Htrien)]}^{3+} \text{ (VA)}$$

$$\text{(VA) [Ni(Htrien)]}^{3+} \xrightarrow{\text{H}^+} \text{[Ni(H}_2\text{trien)]}^{4+} \text{ (VB)}$$

$$\text{[Ni(H}_2\text{trien)]}^{4+} \xrightarrow{\text{H}^+} \text{Ni}^{2+} + \text{H}_4\text{trien}^{4+}$$

We cannot hope to give stereochemical configuration to these compounds and can only make plausible assignments of molecular configuration. Thus species (VA) involves a terminal *N*-substituted dien:
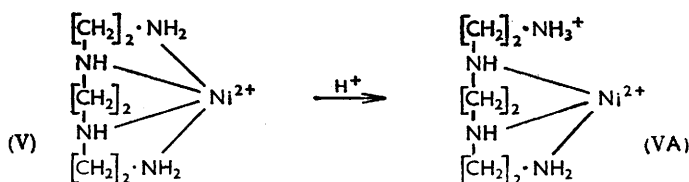
which can then decompose to give either an unsymmetrical (terminal NH–Ni breakage) or a symmetrical (NH_2–Ni breakage) product (VB). We favour the former since the rate of the final stage [decomposition of (VB)] ($2 \cdot 1$ sec.$^{-1}$ at $25°$) is similar to that for [Ni(Hdien)]$^{3+}$ ($2 \cdot 8$ sec.$^{-1}$) and slower than expected for an *NN'*-disubstituted compound.

Penten Complexes.—The amine *NNN'N'*-tetra-(2-aminoethyl)ethylenediamine (penten) was the first sexidentate ligand to be prepared with six nitrogen donor atoms.[6c] It forms a pentaprotonated species H_5penten^{5+}, the sixth nitrogen atom resisting protonation even in quite strong acid solution. Schwarzenbach and Moser [4f] measured the stability constants of the penten complexes with bivalent manganese, iron, cobalt, nickel, copper, zinc, cadmium, and mercury. They suggested that the complexes of copper(II), zinc(II), and
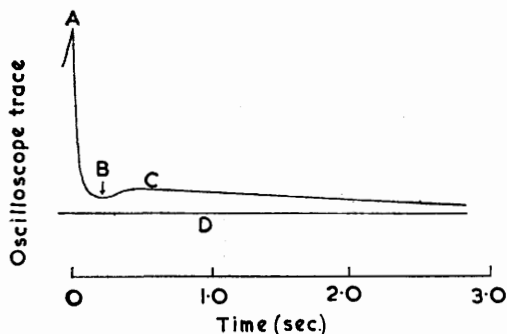
FIG. 2. Oscilloscope trace of dissociation of [Ni(trien)]$^{2+}$ at 450 mμ. The "*y*" ordinate is a measure of increasing optical density of the solution.

A, [Ni(trien)]$^{2+}$.   C, [Ni(H$_2$trien)]$^{4+}$.
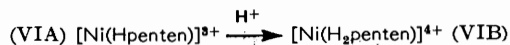B, [Ni(Htrien)]$^{3+}$.   D, Ni$_{aq.}$$^{2+}$.

mercury(II) must contain at least one unco-ordinated amine group but that with iron(II), cobalt(II), nickel(II), and cadmium(II) the amine functioned as a sexidentate ligand. These last complexes still added protons easily to form protonated complexes and in the case of, for example, nickel, both [Ni(Hpenten)]$^{3+}$ and [Ni(H$_2$penten)]$^{4+}$ were detected.

The lability in neutral and alkaline solution of metal–penten complexes is shown by the exchange of ligand between complex and [^{14}C]penten (Table 2). Apart from the nickel d^8-system, they all have similar, fairly fast, exchange rates. An interesting difference in the effect of pH is noted, however. The exchange of complexes which are believed to contain five-co-ordinated penten is markedly base-catalysed (copper and zinc), but the other complexes (cobalt, nickel, and cadmium) show little difference in exchange rate at pH 7 or 10. Exchange with the manganese and the mercury complex is almost complete within the time of separation. Although these exchange experiments are useful in showing the general order of stability of the metal complexes, the rates will be a complicated function of several dissociation and formation rate constants and this approach was abandoned in favour of acid decomposition experiments, where results are less equivocal. Now, however, the rates are rapid so that only the nickel complex can be examined, at present. Also the reaction is more complex, and, although the five possible stages in the decomposition can be separated and approximate reaction times assigned, only the early stages could be examined in any detail.

At 540 and 585 mμ, a rapid loss of optical density corresponds to the formation of [Ni(H$_2$penten)]$^{4+}$. The first stage can be observed and measured only at lower temperatures ($<10°$):
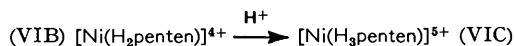
$$\text{(VI) [Ni(penten)]}^{2+} \xrightarrow{\text{H}^+} \text{[Ni(Hpenten)]}^{3+} \text{ (VIA)}$$

but the second is more easily investigated:

$$\text{(VIA) [Ni(Hpenten)]}^{3+} \xrightarrow{\text{H}^+} \text{[Ni(H}_2\text{penten)]}^{4+} \text{ (VIB)}$$
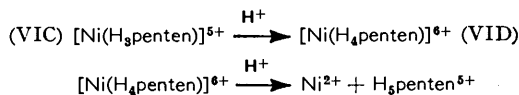
A knowledge of the spectra of the species (Fig. 1) and application of the indicator method are essential here.

The wavelength 420 mμ is an isosbestic point for species (VI), (VIA), and (VIB) and a
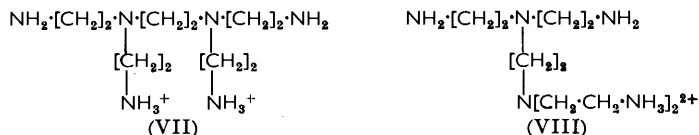
rise of optical density ($t_{\frac{1}{4}}$ ~0·25 sec. at 25°) after an initial " rounding-off " of the trace corresponds to:

$$\text{(VIB) } [\text{Ni}(\text{H}_2\text{penten})]^{4+} \xrightarrow{\ \text{H}^+\ } [\text{Ni}(\text{H}_3\text{penten})]^{5+} \text{ (VIC)}$$

An isosbestic point is observed again at 630 and 675 mμ but from its duration this must be for (VI), (VIA), (VIB), and (VIC) species. The subsequent change consists of two distinct steps at 630 mμ ($t_{\frac{1}{4}}$ ~1·6 and 20 sec. at 25°, but the slower change is not observed at 675 mμ). It is suggested these stages correspond to

$$\text{(VIC) } [\text{Ni}(\text{H}_3\text{penten})]^{5+} \xrightarrow{\ \text{H}^+\ } [\text{Ni}(\text{H}_4\text{penten})]^{6+} \text{ (VID)}$$

$$[\text{Ni}(\text{H}_4\text{penten})]^{6+} \xrightarrow{\ \text{H}^+\ } \text{Ni}^{2+} + \text{H}_5\text{penten}^{5+}$$

It is possible to make only a few worthwhile comments about the mechanism. The initial protonations correspond to removal of NH$_2$ groups. Thus [Ni(H$_2$penten)]$^{4+}$ can contain either a trien (3 stereochemical forms) or tren (1 form) derivative, (VII) or (VIII), respectively:

$$
\begin{array}{cc}
\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{N}\cdot[\text{CH}_2]_2\cdot\text{N}\cdot[\text{CH}_2]_2\cdot\text{NH}_2 & \text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{N}\cdot[\text{CH}_2]_2\cdot\text{NH}_2 \\
\quad\quad\;\; | \quad\quad\;\; | & \quad\quad\;\; | \\
\quad\quad\;\; [\text{CH}_2]_2 \;\; [\text{CH}_2]_2 & \quad\quad\;\; [\text{CH}_2]_2 \\
\quad\quad\;\; | \quad\quad\;\; | & \quad\quad\;\; | \\
\quad\quad\;\; \text{NH}_3^+ \quad \text{NH}_3^+ & \quad\quad\;\; \text{N}[\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_3]_2{}^{2+} \\
\quad\quad\quad\;\; \text{(VII)} & \quad\quad\quad\quad \text{(VIII)}
\end{array}
$$
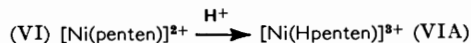
The latter is favoured since addition of sodium perchlorate to [Ni(H$_2$penten)]$^{4+}$ produces no semblance of a peak at 440 mμ, which is obtained for a trien, but not a tren, complex.[16] Further investigations will be necessary to obtain more detailed information about the decomposition.

General Conclusions.—Examination of Table 1 shows that neither an increased [Ni] : [amine] ratio nor different acid concentrations affected the rate, so that we are certain that we are studying the mono-species in the limiting acid region. Often, the detailed mechanism could not be evaluated and, where it arose, the problem whether *cis–trans*-isomers were produced remained unsolved. This did not interfere with the determination of the kinetics. In the main, we are able to answer the questions posed in the introduction. In all cases (except ethylenediamine) the first NH$_2$ group is rapidly removed (Table 4) and where models indicate particular strain (*e.g.*, ptn, tren, and penten) the rate is barely within the time resolution of the flow-method. The second stage is slower than the first by a factor which ranges from 4 to 200. It does not appear to be associated particularly with the energy or the entropy of activation. The last stage of decomposition, when the complex is joined by one nitrogen only is, once again, very fast and, of course, undetected. The energy of activation for the first bond rupture falls neatly into groups. It is highest for the bidentate ethylenediamine complex, containing the most strain-free ring (~21 kcal. mole^{-1}), around 18 kcal. mole^{-1} for complexes with terdentate ligands, and only 15 kcal. mole^{-1} for those with quadri- and quinque-dentate amines, and with ammonia itself. The entropies of activation fall into similar sets, although the striking agreement for the activation parameters within a group must be somewhat fortuitous because of the limited accuracy of the method ($E_{\text{act}} \pm 1$—1·5 kcal. mole^{-1}). The accelerating effect of charge placed near the reacting donor centre is seen by comparing the nickel complex of NH$_2\cdot$CH$_2\cdot$CH$_2\cdot$NH$\cdot$CH$_2\cdot$CH$_2\cdot$CH$_3$ (*N*-pren) with NH$_2\cdot$CH$_2\cdot$CH$_2\cdot$NH$\cdot$CH$_2\cdot$CH$_2\cdot$NH$_3^+$, which is isoelectronic (IIA ⟶ IIB). The small effect of ring size on the decomposition rate is shown from the behaviour of [Ni(dien)]$^{2+}$ and [Ni(dapa)]$^{2+}$, this in spite of the increased thermodynamic stability of the former.[4] The first stage for decomposition of [Ni(trien)]$^{2+}$ ($k_{25} = 15$ sec.$^{-1}$; $E = 14\cdot8$; log $A = 12\cdot1$) is similar in rate to that of [Ni(en)$_2$]$^{2+}$ ($k_{25} = 5\cdot2$ sec.$^{-1}$; $E = 19\cdot8$; log $A = 15\cdot3$). Thus " tying-back " the two en residues by a CH$_2\cdot$CH$_2$ link in trien produces a much decreased energy and entropy

of activation. The thermodynamic stability of the nickel complex of trien is similar to that of the bis(ethylenediamine) complex. It is interesting that this also arises from a balance between a lower heat of formation and a higher entropy change for the quadridentate ligand.[18]

Our initial hopes on the value of the stopped-flow method for studying the reactivity of nickel complexes have been amply justified, but it is, at present, of less value for the more labile complexes, *e.g.*, of manganese(II) and zinc(II). Extension of the method to lower temperatures may overcome this difficulty.

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[18] Sacconi, Paoletti, and Ciampolini, *J.*, 1961, 5115.