KINETICS OF REACTIONS OF LABILE METAL IONS WITH BIDENTATE AND TRIDENTATE LIGANDS

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Abstract—The temperature-jump technique has been applied to the study of the complexation reactions of nickel(II) and cobalt(II) with the ligands α -alanine, β -alanine, iminodiacetic acid, aspartic acid and iminodipropionic acid and of copper(II) with the latter three ligands. These results, when considered with those in the literature for copper(II) and the alaninates, lead us to conclude that the Sterically Controlled Mechanism which has been shown to apply to the chelate formation of bidentate ligands forming six-membered rings, applies to tridentate ligands as well. The effect is pronounced when the ligand forms chelate rings all of which are greater than five-membered.

INTRODUCTION

RECENT studies have demonstrated that, for complexation reactions involving labile metal ions, ring closure can under certain conditions become rate determining. The first examples of this Sterically Controlled Substitution involved ligands which form six-membered chelate rings, β -alanine[1] and β -aminobutyric acid[2]. Other systems for which ring closure has been shown to be rate determining include malonic acid[3] which also forms a six-membered ring, carnosine [4] which forms a seven-membered chelate ring and ethylenediamine[5] which forms a five-membered chelate ring but only for the reaction

$$Ni(en)_2(H_2O)_2 + en \rightleftharpoons Ni(en)_3.$$

In all of these cases, the attacking ligand is a bidentate. In the present study, we are reporting on the complexation kinetics of a number of potentially tridentate ligands with nickel(II), cobalt(II) and copper(II). In particular, the ligands we have studied are iminodiacetic acid (IDA) which forms two five-membered chelate rings, aspartic acid (ASP) which forms one five-membered and one six-membered chelate ring and iminodipropionic acid (IDP) which forms two six-membered chelate rings when behaving as tridentate ligands.

EXPERIMENTAL

Relaxation studies were carried out using a temperature-jump apparatus which has been described elsewhere[6]. The alanines and aspartic acid were obtained from Nutritional Biochemicals Corp. Iminodiacetic acid was purchased from Eastman Organic Chemicals as was iminodipropionitrile which was the starting material for the iminodipropionic acid ligand. The synthesis[7] resulted in

- 1. K. Kustin, R. F. Pasternack and E. M. Weinstock, J. Am. chem. Soc. 88, 4610 (1966).
- 2. A. Kowalak, K. Kustin, R. F. Pasternack and S. Petrucci, *ibid.* 89, 3126 (1967).
- 3. U. Nickel, H. Hoffmann and W. Jaenicke, Ber. Bunsenges. Physk. Chem. 72, 526 (1968); H. Hoffmann and E. Yeager, Ber. Bunsenges. Physk. Chem. 74, 641 (1970).
- 4. R. F. Pasternack and K. Kustin, J. Am. chem. Soc. 90, 2295 (1968).
- 5. J. P. Jones and D. W. Margerum, J. Am. chem. Soc. 92, 470 (1970).
- 6. R. F. Pasternack, K. Kustin, L. A. Hughes and E. Gibbs, J. Am. chem. Soc. 91, 4401 (1968).
- 7. J. H. Ford, J. Am. chem. Soc. 67, 876 (1945).

the monoammonium salt of the acid which had a melting point of $172-174^{\circ}C$ after recrystallization from methanol.

Anal. Calcd. for C₆H₁₄N₂O₄: C, 40·44; H, 7·92; N, 15·72. Found: C, 40·36; H, 8·03; N, 15·59.

Baker reagent grade nitrate salts of potassium, nickel, cobalt and copper were used. Stock solutions of the transition metal ions were prepared and the concentrations determined via EDTA titrations using murexide as the indicator[8]. The indicators used to follow the course of the reactions were Allied Chemical methyl orange, methyl red and chlorophenol red and Eastman Organic bromothymol blue. The indicator concentration was kept at about 5×10^{-5} M for all solutions.

Solutions were freshly prepared from the solid ligand and stock solutions of transition metal ion and indicator. The ionic strength was raised to 0.1 M with KNO₃. The solutions were degassed and the pH was adjusted by the dropwise addition of dilute NaOH and/or HNO₃ to ± 0.01 pH unit. A constant stream of dry nitrogen was maintained in the cell compartment during the course of the experiments. The final temperature after the "jump" was that shown in Table 1; the temperature at

α-Alanine (25°C) ^a	β-Alanine (25°C) ^a	Iminodiacetic acid (30°C) ^b	Aspartic acid (30°C) ^c	Iminodipropionic acid (30°C) ^b
$K_{\text{H}_{3L}} = \frac{[\text{H}][\text{HL}]}{[\text{H}_2\text{L}]} = 5.30 \times 10^{-3}$	3·02 × 10 ^{−4}	2.88×10⁻³	2·09 × 10 ^{−4}	$7.76 imes 10^{-5}$
$K_{\rm HL} = \frac{[{\rm H}][{\rm L}]}{[{\rm HL}]} = 1.35 \times 10^{-10}$	5.50×10^{-11}	7·59×10 ⁻¹⁰	3·47 × 10 ⁻¹⁰	2·45 × 10 ⁻¹⁰
$K_1^{\text{Co}} = \frac{[\text{CoL}]}{[\text{Co}][\text{L}]} = 1.86 \times 10^4$	1.00×104	8·91×10 ⁶	7 ·94 × 10 ⁵	8·32×10 ⁴
$K_2^{\text{Co}} = \frac{[\text{CoL}_2]}{[\text{CoL}][\text{L}]} = 2.82 \times 10^3$	1·00 × 10 ³	2·19×10 ⁵	1·91 × 104	1.82×10^3
$K_1^{\rm Ni} = \frac{[\rm NiL]}{[\rm Ni][L]} = 9.12 \times 10^5$	4·26 × 10⁴	1.62×10 ⁸	1·32×10 ⁷	1·38×10 ⁶
$K_2^{\text{Ni}} = \frac{[\text{NiL}_2]}{[\text{NiL}][\text{L}]} = 5.02 \times 10^4$	2·51 × 10 ³	$2.24 imes 10^6$	1-86×10 ⁵	5·89 × 10 ³
$K_1^{Cu} = \frac{[CuL]}{[Cu][L]} = 1.23 \times 10^8$	1.82×10 ⁷	3.55×10 ¹⁰	3·72 × 10 ⁸	2·29 × 10 ⁹
$K_2^{Cu} = \frac{[CuL_2]}{[CuL][L]} = 4.57 \times 10^6$	4·27 × 10 ⁵	4·47 × 10 ⁵	6·03 × 10 ⁶	4·79 × 10 ³
$K_{\mathrm{HI}n_{i}} = \frac{[\mathrm{H}^{+}][\mathrm{I}n_{i}]^{\mathrm{d}}}{[\mathrm{HI}n_{i}]}$				
HIn _i = Methyl Orange Methyl Red Chlorphenol Red	$K_{1n_i} = 3.47$ 1.00 1.00	$\times 10^{-4}$ $\times 10^{-5}$ $\times 10^{-6}$		
Bromothymol Blue	7.94	× 10 ⁻⁸ .		

Table 1. Equilibrium constants at $\mu = 0.1 M$

Table references:

^aSee Reference [1] and W. B. Makinen, A. F. Pearlmutter and J. E. Stuehr, J. Am. chem. Soc. 91, 4083 (1969) for primary references.

^bS. Chaberek, Jr. and A. E. Martell, J. Am. chem. Soc. 74, 5052 (1952).

°S. Chaberek, Jr. and A. E. Martell, J. Am. chem. Soc. 74, 6021 (1952).

^dI. M. Kolthoff, J. phys. Chem. 34, 1466 (1930).

8. G. Schwarzenbach, Complexometric Titrations. Interscience, New York (1957).

which the thermodynamic data were obtained. The experimental conditions employed as well as the observed relaxation times are shown in Tables 2-6. Each relaxation time represents an average of at least three photographic determinations. The relative error for these measurements is $\pm 10\%$. Test solutions of either metal ion or ligand in the absence of the other showed no discernible relaxation

······································	25%			
$[M] \times 10^3$	25°	-0 -1	$M \text{ KNU}_3$	- (
			Tobs, (Insec)	$\tau_{calc.}$ (msec)
(a) Nickel(II)	•			
5.74	6.51	7.03	38	45
5.74	6.51	6.82	36	47
5.74	6.51	7.36	39	38
2.87	4.77	7.01	72	65
2.87	5·79	6.81	63	62
2.87	4.77	6 ·8 7	64	70
8.62	3.92	6.73	82	70
8.62	3.92	7.04	82	75
2 ·8 7	12.1	6.81	34	38
2.87	12.1	6.99	36	35
8.62	1.62	6.71	200	180
8.62	1.62	7.09	160	190
11.5	1.10	6.71	220	250
11.5	1·1 0	7.07	240	270
2.30	13-1	6.75	39	39
2.87	9.73	5.99	220	190
2.87	5.77	6.19	210	190
$k_1 = 3$	$1 \times 10^4 M^{-1} \text{ sec}^{-1}$		$k_{2} = 3 \cdot 1 \times 10^{4} M$	$^{-1} \rm sec^{-1}$
$k_{-1} = 3$.	$4 \times 10^{-2} \text{sec}^{-1}$	k	$c_{-2} = 0.62 \text{ sec}^{-1}.$	
(b) Cobek(II)				
(0) Coball(11)	10.1	6 0/	1.0	1.0
5.30	10.1	2.80	1.8	1.8
5.30	10.1	6.32	0.61	0.64
2.20	3.22	2.92	2.5	2.6
2.08	11.0	5.04	2.3	2.1
2.08	11.0	5.84	3.1	2.7
2.00	11.9	0.32	1.0	1.1
10.7	2.19	0.09 2.00	1.8	2.1
10.7	2.19	5.89	2.9	2.8
10.7	2.19	0.32	1.2	1.2
1.61	1.09	0.01	3.2	2.8
1.61	22.0	/100	0.60	0.54
1.01	22.0	0.97	0.65	0.58
2.09	10.0	0.90	U•54	0.45
$k_1 = 1.9$	$9 \times 10^6 M^{-1} \mathrm{sec}^{-1}$		$k_2 = 1.0 \times 10^6 M$	$^{-1}$ sec ⁻¹
$k_{-1} = 100 \text{ sec}^{-1}$		k	$_{-2} = 350 \text{ sec}^{-1}$.	

Table 2	. Relaxation	spectra	of α -alanine	systems
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effects. These "blank" experiments were carried out at concentration levels of the free metal ion and ligand characteristic of solutions containing a mixture of the two. The rate constants obtained in this study are being reported to $\pm 25\%$, except for the copper(II)-iminodipropionic acid and nickel-iminodiacetic acid systems as discussed later. In each case the reverse rate constant reported was calculated from the forward rate constant and the appropriate equilibrium constant (cf. Table 1).

	25°C	0.1	M KNO3	
$[M]_0 \times 10^3$	$[\beta-Ala]_0 \times 10^3$	pH	$ au_{ m obs.}$ (msec)	$\tau_{\rm calc.}({\rm msec})$
(a) Nickel(II)		<u>ana</u>	1 1 10	
11.5	1 0·4	6.78	100	88
11.5	10.4	7·19	48	56
5.74	5.05	6.81	240	270
5.74	5.03	7.17	150	170
5.74	9.92	6.76	190	170
5.74	9-92	7.18	94	100
14.4	9.83	6.75	98	78
14.4	9.83	7.27	45	44
2.87	9.08	6·79	270	280
2.87	9.08	7.05	220	220
4.60	10-0	7.02	240	150
4.60	10.0	6.82	140	190
$k_1 = 5$	$0 \times 10^3 M^{-1} \mathrm{sec}^{-1}$		$k_a = 6.0 \times 10^3 M$	$\int_{-1}^{-1} \sec^{-1}$
$k_{-1} = 0.12 \text{ sec}^{-1}$		k	$_{-2} = 2 \cdot 4 \sec^{-1}$.	
(b) Cobalt(II)				
10.7	10.4	6.89	3.6	3.0
10.7	10.4	7.18	2.3	2.1
13.4	10.0	6.70	3.6	3.2
13.4	1.06	6.84	9.2	8.4
13.4	0.988	7.15	8.4	8.2
5.36	5.05	6 ·77	5.6	7.8
5.36	5.05	7.21	4.5	5.9
2.68	9.08	6.81	7.6	7.4
2.68	9.08	7.25	5.2	6.1
5.36	9.11	6·77	7.2	6.7
5.36	9.11	7.19	4.1	4.1
4.02	10.0	6.83	5.6	7 ⋅0
4.02	10.0	7.24	3.3	4.6
$k_1 = 1$	$3 \times 10^5 M^{-1} \mathrm{sec}^{-1}$		$k_2 = 1 \cdot 2 \times 10^5 M$	⁻¹ sec ⁻¹
$k_{-1} = 13$	sec ⁻¹	k	$_{-2} = 120 \text{ sec}^{-1}$.	

Table 3. Relaxation spectra of β -alanine systems

RESULTS

The reactions we are reporting on are of the form:

$$M_{(aq.)} + L_{(aq.)} \underset{k=1}{\overset{k_1}{\underset{k=1}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_2}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\overset{k_1}{\underset{k=2}{\atopk_1}{\underset{k=2}{\atopk_1}{\underset{k=2}{\atopk_1}{\underset{k=2}{\atopk_1}{\underset{k=2}{\atopk_1}{\atopk_1}{\underset{k=2}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1}{\atopk_1$$

where M refers to Co^{2+} , Ni^{2+} or Cu^{2+} and L represents α -alaninate⁻, β -alaninate⁻, iminodiacetate²⁻, aspartate²⁻ or iminodipropionate²⁻. It did not prove possible to analyze the relaxation data for these systems in the way previously described to determine experimental values for the rate constants involving zwitterion attack

	30°C	0.1	M KNO3	
$[M]_0 \times 10^3$	$[IDA]_0 \times 10^3$	pН	$\tau_{\rm obs.}$ (msec)	$ au_{ m calc.}$ (msec)
(a) Nickel(II)				
10.2	29.8	6.88	280	320
12.3	29.8	7.06	290	270
10.2	34.8	7.06	310	290
10.2	24.8	7.07	290	300
12.3	34.8	7.00	290	300
	$k_2 \sim 2.5$	$5 \times 10^4 M$	⁻¹ sec ⁻¹	
	$k_{-2} \sim 1 >$	< 10 ⁻² sec	~ ¹ ,	
(b) Cobalt(II)				
4.99	10.0	5.53	1.2	1.2
			15	$\tau_{-} = 15$
2.49	5-05	5.61	2.4	1.7
2.49	5.05	5.90	1.3	1.1
2.49	29.8	5.41	1.0	1.2
4.99	20.0	5.37	1.4	1.4
4.99	20.0	6.00	0.27	0.28
4.99	20.0	5.76	0.44	0.48
4.99	29.8	5.64	0.64	0.54
4.99	29.8	5.99	0.33	0.22
4.99	49·7	5.20	2.1	2-4
4.99	49 ·7	5.61	0.72	0.51
9.97	5.03	5.49	1.7	2.0
9.97	5.03	6.05	1.2	1.9
9.97	9.92	5.30	1.2	1.4
15.0	4.99	6.29	0.86	0.75
15.0	4.99	6.66	0.85	0.94
9.97	2.61	6.73	1.3	1.6
9.97	2.61	6.04	1.3	1.2
15.0	10.2	6.25	0.53	0.35
9·97	5.20	6.73	1.0	1.0
9.97	5.20	7.27	0.90	0.78
9.97	5.20	6.23	0.82	0.68
$k_1 = 1$	$1 \times 10^7 M^{-1} \mathrm{sec}^{-1}$		$k_2 = 2 \cdot 4 \times 10^6 \text{A}$	$I^{-1} \sec^{-1}$
$k_{-1} = 1$	-2 sec ⁻¹	1	$k_{-2} = 11 \text{ sec}^{-1}$.	

Table 4. Relaxation spectra of iminodiacetic acid systems

[6, 9] except for the cobalt(II)-iminodipropionate system. In this one case, the relaxation times showed virtually no dependence on k_2 and it could be shown directly that the rate constant for zwitterion attack is zero within experimental error. For each of the other systems, although there is considerable variation in pH, the rate constants show no pH dependence. This is completely consistent with results obtained for other systems in which it could be shown that the zwitterion is an extremely unreactive form for complexation [6, 9, 10].

9. R. F. Pasternack, E. Gibbs and J. C. Cassatt, J. Phys. Chem. 73, 3814 (1969).

10. J. C. Cassatt and R. G. Wilkins, J. Am. chem. Soc. 90, 6045 (1968).

	30°C	0.1	M KNO3	
$[M]_0 \times 10^3$	[ASP] ₀ ×10 ³	pН	$\tau_{\rm obs.}$ (msec)	$ au_{ m calc.}$ (msec)
a) Nickel(II)				
10.8	15.0	7.27	15	13
10.8	15.2	7.23	15	13
13.5	16.5	7.00	26	22
13.5	16.5	7.41	20	20
10.8	15.3	7.06	24	19
10.8	15.3	7.41	20	16
8.12	13.3	7.05	15	15
13.5	11.3	7.06	37	30
10.8	18-8	7.00	15	13
10.8	26.4	7·00	5.4	7·8
$k_1 = 2$	5 × 105 M ⁻¹ sec ⁻¹		$k_{\rm c} = 3.6 \times 10^4 M$	f ⁻¹ sec ⁻¹
$k_1 = 2^{1}$ $k_2 = 1$	9 × 10 ⁻² epo-1	1	$n_2 = 5.0 \land 10^{-10}$	
$n_{-1} - 1^{-1}$	2010 300		-2 = 0.17300	
b) Cobalt(II)				
8.59	9.44	5.83	2.2	2.2
10·7	12.8	6.20	0.67	0.62
12.4	9.76	6.02	0.95	0.89
2.68	8.98	6.16	1.8	2.4
1.07	9.95	6.15	5.0	4.1
2.68	8.83	7.22	0.48	0.63
5.36	4.59	7.11	0.50	0.46
2.15	5.01	6.86	0.79	0.82
2.15	8.30	7.16	0.53	0.71
2.15	2.19	7.09	1.0	1.1
1.61	1.42	7.08	1.5	1.7
k = A	$2 \times 106 M^{-1} coc^{-1}$		$k = 2.0 \times 10^6 k$	1 -1 sec -1
$k_1 = 4$	$4 \mathrm{sec}^{-1}$	1	$\kappa_2 = 2.0 \times 10^{-1}$	300
$n_{-1} - J^{-1}$	- 300	Ŷ		
c) Copper(II)				
2.80	7.51	4.00	6.8	8 ∙1
2.80	7.51	3.84	9.4	9.4
7.28	6.26	3.48	13	10
16.8	8.44	3.22	11	10
1 3 ·9	5.78	3.24	8.5	11
13.9	5.78	3.54	7.1	6.1
11-1	4.00	3.22	12	11
11.1	4.00	3.52	9.0	8.2
11-1	2.04	3.24	12	11
11-1	3.06	3.55	12	8.2
11-1	2.04	3.56	11	9.3
8.33	2.22	3.50	11	11
16·7	1.12	3-54	8.6	10
16.7	1.12	3.79	6.4	5.6
8.33	2.22	3.82	8.5	5.8
L A.	9 × 109 M-1 epc-1		$k_{\rm c} = 5.4 \times 10^8 {\rm A}$	(-1 sec-1
$k_1 = 4.9 \times 10^8 M^{-1} \text{ sec}^{-1}$				

Table 5. Relaxation spectra of aspartic acid systems

Kinetics with bidentate and tridentate ligands

	30°C	0.1	M KNO3		
$[M]_0 \times 10^3$	$[IDP]_0 \times 10^3$	pH $\tau_{obs.}$ (msec)		$ au_{ m calc.}$ (msec)	
(a) Cobalt(II)					
9.97	5.02	6.34	12	9.1	
9.97	4.98	5.91	46	47	
2.49	4.94	6.03	88	95	
2.49	9.96	6.58	19	18	
2.49	9.96	6.15	62	65	
4.98	9.96	5.94	64	73	
4.98	9.96	6.32	20	21	
4.98	4.96	5.87	72	91	
4.98	4.96	6.32	24	22	
4.98	4.96	6.59	9.6	9.1	
9.97	9.92	6.34	17	10	
9.97	9.92	5.99	43	35	
9.97	19.8	6.33	15	12	
	$k_1 = 2 \cdot 7$	$V \times 10^5 M^{-1}$	$^{-1} sec^{-1}$		
	$k_{-1} = 3 \cdot 2$	$2 \operatorname{sec}^{-1}$.			
(b) Copper(II)					
10.4	5.03	4.50	43	65	
10.4	9.90	4.58	58	60	
10.4	9.90	5.38	68	60	
15.5	9.97	5.01	22	18	
15.5	14.9	4.57	70	59	
15.5	19.9	4.61	90	60	
15.5	19.9	4.97	42	57	
12.4	11.9	4.60	66	60	
12.4	11.9	5.68	48	61	
$k_1 \sim 2$	$2 \times 10^8 M^{-1} \mathrm{sec}^{-1}$		$k_2 \sim 8 \times 10^5 M^{-1}$	⁻¹ sec ⁻¹	
$k_{-1} \sim 0$	0.1 sec^{-1}	k	$c_{-2} \sim 200 \text{ sec}^{-1}$.		

Table 6. Relaxation spectra of iminodipropionic acid systems

Relaxation times were calculated, using trial values of the rate constants, from the expression

$$(\tau_{+,-})^{-1} = \frac{1}{2} [(a_{11} + a_{22}) \pm ((a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21}))^{1/2}]$$
(2)

where

$$a_{11} = k_1 \left(\frac{[\mathbf{M}]}{1+\alpha} + [\mathbf{L}] + 1/K_1 \right)$$

$$a_{12} = k_1 \left(\frac{1}{K_1} - \frac{[\mathbf{M}]}{1+\alpha} \right)$$

$$a_{21} = k_2 \left([\mathbf{L}] - \frac{[\mathbf{ML}]}{1+\alpha} \right)$$

$$a_{22} = k_2 \left(\frac{[\mathbf{ML}]}{1+\alpha} + [\mathbf{L}] + 1/K_2 \right)$$
(3)

and

$$\alpha = \frac{K_{\text{H}_{2}\text{L}}[\text{H}] + \beta[\text{H}][\text{H}_{L}] + [\text{H}]^{2} + \beta K_{\text{H}_{2}\text{L}}[\text{OH}] + \beta[\text{H}][\text{OH}]}{K_{\text{H}_{L}}K_{\text{H}_{2}\text{L}} + 4\beta K_{\text{H}_{L}}[\text{H}_{L}] + \beta K_{\text{H}_{2}\text{L}}[\text{L}] + \beta K_{\text{H}_{2}\text{L}}[\text{OH}]/[\text{H}]} \beta = \frac{K_{\text{H}_{2}\text{L}}[\text{H}_{L}] + \beta K_{\text{H}_{2}\text{L}}[\text{L}] + \beta K_{\text{H}_{2}\text{L}}[\text{OH}]/[\text{H}]}{K_{\text{H}_{1}n} + [\text{H}] + [\text{I}_{n}]} .$$
(4)

These calculated relaxation times are shown in Tables 2–6 for comparison with the experimental values.

Relaxation effects were obtained for all the metal-ligand systems attempted except for copper-IDA and nickel-IDP. Apparently, for these systems either an 8°C temperature jump does not sufficiently perturb the equilibrium so as to lead to a relaxation process and/or the relaxation times are outside the range of the temperature-jump technique. For the nickel-IDA and copper-IDP systems, effects could be obtained over a relatively narrow concentration and pH range and the fit between calculated and experimental relaxation times was not as satisfactory as for other systems. Therefore, for these cases we are reporting rate constants to $\pm 50\%$ only and have shown these values as estimates. The kinetic results are summarized in Table 7.

DISCUSSION

The complexation studies reported on here have been carried out in a pH region considerably below the pK of the respective ligands. There are both advantages and disadvantages to working in a relatively low pH region. This low

Ligand	Co	Co ²⁺		Ni ²⁺		Cu ²⁺	
	k_1	k_2	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₁	<i>k</i> 2	
Glycinate ⁻	2×10^{6a}	2×10 ^{6a}	4 × 10 ^{4a}	6×10^{4a}	4×10 ^{9b}	$4 imes 10^{8\mathrm{b}}$	
α -Alaninate ⁻	$2 imes 10^6$	1×10^{6}	3×10 ⁴	3 × 10 ⁴	$1 imes 10^{9c}$	2×10^{8c}	
	$(6 \times 10^5)^{d}$	$(8 \times 10^5)^{d}$	$(2 \times 10^4)^{d}$	$(4 \times 10^4)^d$			
β-Alaninate [−]	1×10^{5}	1×10^{5}	5×10^{3}	6×10^{3}	$2 imes 10^{ m sc}$	$8 imes 10^{60}$	
	$(8 \times 10^4)^{d}$	$(9 \times 10^4)^{d}$	$(1 \times 10^4)^{d}$	$(7 \times 10^3)^d$			
IDA ²⁻	1×10^{7}	2×10^{6}	5×10^{4e}	$\sim 2 \times 10^4$			
			9×10^{4f}	$1 imes 10^{4g}$			
ASP ²⁻	4×10^{6}	2×10^{6}	2×10^{5}	4×10^4	5×10^{9}	5×10^{8}	
IDP ²⁻	3 × 10 ⁵				$\sim 2 \times 10^8$	$\sim 8 imes 10^5$	

Table 7. Forward rate constants $(M^{-1} \sec^{-1})$ for complexation*

*Rate constants for glycinate⁻, α -alaninate⁻ and β -alaninate⁻ are reported at 25°C while those for IDA²⁻, ASP²⁻ and IDP²⁻ are reported at 30°C.

Table references:

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¹J. C. Cassatt, Doctoral Dissertation, State University of New York at Buffalo, 1969. This study was carried out at 25°C.

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pH technique (1) permits the investigation of the complexation reactions of copper(II) via temperature-jump, (2) allows for experiments in which $[M^{2+}]_{total} > [Ligand]_{total}$ from which independent determinations of k_1 and k_{-1} can be made and (3) makes it unnecessary to consider hydrolyzed metal species of the type MOH⁺. Perhaps the most serious disadvantage of this technique is that the analysis of relaxation data becomes extremely dependent upon the thermo-dynamic data for the system. The cobalt-alanine and nickel-alanine systems had been studied earlier but in a higher pH range[1]. Because of the advantages and disadvantages outlined above it seemed worthwhile to reconsider these systems at a lower pH and to compare the two sets of results.

As may be seen from an examination of Table 7, the rate constants obtained for the alanine systems at the low pH conditions used here (pH $5\cdot8-7\cdot3$) agree, for the most part, to well within a factor of two with those obtained earlier in a higher pH region. Therefore, the arguments presented in the earlier work[1] are equally applicable here. That is, the complexation rate constants for cobalt(II), nickel(II) and copper(II)[11] show a dependence on the ring size of the attacking ligand. This has led to the proposal of the so-called Sterically Controlled Substitution mechanism[1, 2].

For glycine and α -alanine, the rate constants k_1 and k_2 are, for each metal, in quite good agreement, within a factor of two in most cases. However, the values of k_1 and k_2 decrease by a factor of five or greater when the chelate ring size passes from five members to six. As has been discussed earlier, we believe that the underlying cause for the slowness of these reactions is the difficulty in forming a six-membered chelate ring as compared to the more frequently encountered five-membered chelate ring.

The results for the potentially tridentate ligands, which are the new systems we are reporting on here, also show some evidence of sterically controlled substitution. When behaving as a tridentate ligand, iminodiacetic acid (IDA) forms two five-membered rings; aspartic acid (ASP), one five-membered and one six-membered ring; and iminodipropionic acid (IDP), two six-membered rings. The results for cobalt(II) and nickel(II) indicate that sterically controlled substitution is considerably less important for a tridentate ligand forming a fiveand a six-membered ring than for ligands forming only six-membered rings be they bidentate or tridentate. The most complete set of results is for cobalt(II) and it may be seen from Table 7 that the k_1 for ASP²⁻ is not markedly different from the value obtained for IDA²⁻ although Co(ASP) involves a six-membered as well as a five-membered chelate ring. Only for IDP²⁻ in which the thermodynamic evidence points to the formation of two six-membered chelate rings is there a dramatic decrease in rate constant, k_1 . The results for nickel(II) also lead to similar conclusions where data are available. The values for k_1 for the nickel(II)iminodiacetic acid system, obtained through use of the stopped-flow technique, are comparable or even a bit smaller than the value we obtain for k_1 for the nickel(II)-aspartic acid system. Furthermore, the k_2 values obtained by Coombs and Margerum and by us for IDA^{2-} are in good agreement with the k_2 value for ASP²⁻. For bidentate ligands, the SCS mechanism is manifested in small

^{11.} W. B. Makinen, A. F. Pearlmutter and J. E. Stuehr, J. Am. chem. Soc. 91, 4083 (1969).

values for k_2 as well as k_1 . Therefore, the results indicate that sterically controlled substitution does not lead to a significant lowering of rate constants when the ligand forms one or more chelate rings unless all of them are greater than five-membered.

The results for copper are consistent with this conclusion. It might be noted from Table 1 that the complexes of this ligand do not obey the Irving-Williams order correlating ring size and stability[12]. Chaberek and Martell noted and accounted for this unusual behavior in terms of the structure of aspartic acid and by assuming a coordination number of four for copper[13]. If aspartic acid is behaving as a tridentate ligand, it can satisfy three of the square planar copper binding sites only with the introduction of considerable strain in the chelate rings. It is also possible that the Cu(ASP) complex involves bidentate chelation only. Unfortunately, we were unable to obtain a value of k_1 for copper with iminodiacetic acid for comparison. However, the value of k_1 for copper with aspartic acid bears about the same relationship to k_1 with the α -amino acids as do the values for nickel and cobalt. Therefore, on the basis of this indirect evidence, we conclude that if there is additional strain in the chelate rings introduced with the formation of Cu(ASP), it does not show up in the forward rate constant to any appreciable extent. Furthermore, it can be stated with some certainty that if ASP^{2-} is acting as a bidentate, the ring size is five-membered whereas IDP^{2-} chelate rings are always six-membered. Therefore, the decrease in rate constants going from ASP²⁻ to IDP²⁻ can be correlated with an increase in the number of six-membered chelate rings formed.

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