Stability Constants for Complex Formation between Cobalt(II), Nickel(II), and Copper(II) and 2,3-Diaminopropionic Acid, 2,4-Diaminobutyric Acid, Ornithine, Lysine, and Arginine †

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The formation constants of the complexes formed between H^+, Co^{2+}, Ni^{2+}, and Cu^{2+} and DL-2,3-diaminopropionic acid, L-2,4-diaminobutyric acid, L-ornithine, L-lysine, and L-arginine have been measured potentiometrically at 25 °C and $I = 0.10$ mol dm^{-3} (K[NO$_3$]). At intermediate pH values the equilibria have been shown to include a complicated range of protonated complexes with ligands behaving as either bi- or tri-dentate ligands depending on the pH and separation of the nitrogen donor atoms. Probable structures for the various complexes are discussed.

MANY amino-acids are potentially tridentate ligands. When the third donor site (*i.e.* the non-glycine-like site) is an oxygen atom the tendency to form tridentate chelates is limited, but when this third site is a nitrogen atom marked tridentate behaviour is frequently found particularly when the additional chelate ring is five or six membered, *e.g.* with histidine (His).[1,2] Nitrogen donor atoms are generally able to co-ordinate with hydrogen ions at intermediate pH values (*i.e.* those found in biological systems). Hence there is often significant competition between hydrogen and metal ions for co-ordination to this third donor site with the result that a number of equilibria are present simultaneously, producing an array of variously protonated complexes. Metal complexes of His have been studied by a number of workers,[1,2] but there has been no systematic study of the effects of ring size on tridentate behaviour.

We report the results of a detailed study of the complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} with some potentially tridentate amino-acids with nitrogen as the third donor site. We have restricted our study to pH values below 10, and below 7.5 with Cu^{2+}, since, above these regions, hydroxo-complexes become important. Complexes formed with Zn^{2+} are not included because hydroxo-complex formation was important by pH 7 and treatment of the experimental data produced major problems in species selection.

The ligands studied were of general formula $NH_2\cdot[CH_2]_n\cdot CH(NH_2)CO_2H$ (HL), where $n = 1$ (DL-2,3-diaminopropionic acid, dpa), $n = 2$ (L- or DL-2,4-diaminobutyric acid, dba), $n = 3$ (L-ornithine, Orn), and $n = 4$ (L-lysine, Lys). In addition L-arginine, $NH{:}C(NH_2)NH[CH_2]_3CH(NH_2)CO_2H$, Arg, was also studied since it occurs naturally in proteins and is similar to Lys. It will be noticed that all the ligands studied are of the L configuration with the exception of DL-dpa which was not obtainable in an optically pure form. However, careful comparison of titration curves for L- and DL-dba in the presence of metal ions suggests that stereoselectivity is negligible with dba. It was therefore assumed that it would also be unimportant with dpa, making direct comparisons among the complexes studied realistic.

The only previous systematic study of the metal complexes of these ligands was carried out by Albert,[3]

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† No reprints available.

[1] D. R. Williams, *J.C.S. Dalton*, 1972, 790.

[2] T. P. Kruck and B. Sarkar, *Canad. J. Chem.*, 1973, **51**, 3549, 3563.

[3] A. Albert, *Biochem. J.*, 1952, **50**, 690.

TABLE 1

Formation constants for the complexes of α, ω-diaminocarboxylic acids at 25 °C and $I = 0.10$ mol dm^{-3} (K[NO$_3$]). Values of log β_{xyz} are for the complex species [$M_xL_yH_z$]. Standard deviations (σ values) are given in parentheses

		dpa	dba	Orn	Lys	Arg
log β_{011}		9.393(2)	10.200(2)	10.521(1)	10.669(1)	12.07(2)
		9.51 ^{a}	10.44 ^{b}	10.73 ^{c}	10.72 ^{b}	11.5 ^{c}
log $K_{012}{}^{011}$		6.662(3)	8.154(2)	8.752(1)	9.139(1)	9.02(2)
		6.79 ^{a}	8.24 ^{b}	8.98 ^{c}	9.18 ^{b}	9.36 ^{c}
log $K_{013}{}^{012}$		1.31(1)	1.45(1)	1.75(1)	2.20(1)	1.96(1)
		1.30 ^{a}	1.85 ^{b}		2.18 ^{b}	
log β_{xyz}						
Cu^{2+}	111	15.551(2)	17.137(1)	17.812(1)	18.29(2)	19.625(4)
		15.82 ^{a}	17.59 ^{a}	18.60 ^{c}		19.4 ^{c}
	122	30 060(4)	33.194(2)	34.448(1)	35.45(2)	38.147(5)
			33.88 ^{a}	35.51 ^{c}	35.14 ^{b}	37.5 ^{c}
	121	25.343(3)	26.928(4)		25.52(2)	
		25.25 ^{a}	27.66 ^{a}			
	110	10.514(6)	10.500(2)			
		11.46 ^{a}	10.4 ^{a}	11.3 ^{c}		11.9 ^{c}
	120	19.831(4)	19.02(1)		15.05(2)	
		19.95 ^{a}	19.48 ^{a}			
Ni^{2+}	111	13.428(6)	14.738(2)	15.255(8)	15.600(8)	17.06(1)
				15.45 ^{c}		16.7 ^{c}
	122	36.30(2)		29.78(1)	30.49(1)	33.15(1)
				30.52 ^{c}		32.5 ^{c}
	133			43.29(4)	44.05(2)	48.38(2)
	132			34.09(7)	34.26(3)	37.62(2)
	131			24.53(9)		
	121	21.062(9)	22.837(6)	21.46(1)	20.43(5)	
	110	8.159(3)	8.909(1)	7.113(9)	5.75(7)	
	120	15.156(3)	15.965(1)	12.03(1)	10.34(1)	
	130			14.36(4)		
Co^{2+}	111	12.30(2)	13.60(1)	14.168(5)	14.505(4)	15.925(8)
	122			27.776(8)	28.406(8)	31.05(2)
	133				41.45(5)	45.53(9)
	132				31.6(1)?	
	121	17.96(8)	19.92(1)	18.65(1)	18.50(4)	
	110	6.28(1)	6.748(4)	5.01(1)		
	120	11.36(1)	11.996(8)	8.49(1)	8.46(2)	

^{a} Ref. 4. ^{b} Ref. 3. ^{c} Ref. 7.

but he was able to consider the bis complex, [ML$_2$], only. Since in many cases this is only a minor component of the equilibrium mixture at all but very high pH values, the results are very misleading. However, his titration data for dpa and dba in the presence of Cu^{2+} have since been treated so as to consider a wider range of species using the SCOGS computer program.[4] Other work in the field has been limited to some u.v.–visible and c.d. spectral studies in an attempt to identify the bonding centres in the complexes,[5,6] and a potentiometric study of some of the complexes of Orn and Lys.[7] The general conclusion has been that complexes of Orn, Lys, and Arg with Cu^{2+} are generally glycine-like, bonding through the carboxyl and α-amino-groups only. With Ni^{2+} (and possibly Co^{2+}) the bonding was thought to be glycine-like at low pH, but possibly tridentate at high pH, although the chelate rings formed by the two nitrogen donors would be abnormally large. Complexes of dpa and dba with Cu^{2+} can be either glycine-like or, at high pH, can involve diamine-like bonding through the two nitrogen atoms. With Co^{2+} and Ni^{2+}, tridentate behaviour is to be expected at high pH with five- or six-membered chelate rings.

From a detailed study of the various protonated complexes of the ligands with Cu^{2+}, Ni^{2+}, and Co^{2+}, and comparison with formation constants of the complexes of related ligands, we have been able to postulate the bonding centres used, as a function of pH, and to discuss the probable structures of the complexes.

EXPERIMENTAL

The amino-acids were obtained from Sigma Chemical Co. (SIGMA grade).

Complex-formation constants were calculated from potentiometric titration curves obtained as described previously.[8] The glass electrode was calibrated in terms of hydrogen-ion concentrations and titrations were carried out at 25 °C with an ionic background of 0.10 mol dm^{-3} K[NO$_3$]. Calculations were made with the aid of the MINIQUAD computer program.[9] A number of metal to ligand ratios were used and various models were fitted to the data. The model selected was that which gave the best statistical fit, consistent with chemical logic, to the range of titration data without giving any systematic drifts in the magnitudes of

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[9] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

the residuals, Δc_M [*i.e.* c_M (calc.) $-$ c_M(obs.)], Δc_L, or Δc_H for the mass-balance equations in total metal (c_M), ligand (c_L), and hydrogen (c_H). At high pH hydroxo-complexes were often present. Since these data could not be fitted satisfactorily to any simple model, points above the onset of a systematic drift in residuals were omitted.

RESULTS AND DISCUSSION

Calculated hydrogen-ion and metal complex-formation constants are given in Table 1 together with literature values for comparison. The constants quoted are generally overall formation constants, $\beta_{xyz} = [M_xL_yH_z]/[M]^x[L]^y[H]^z$. Stepwise constants for reactions such as $[M_xL_yH_z] + H \longrightarrow [M_xL_yH_{z+1}]$ are expressed as $K_{xy(z+1)}{}^{xyz} = [M_xL_yH_{z+1}]/[M_xL_yH_z][H]$. For example, $K_{013}{}^{012} = [H_3L]/[H_2L][H]$. The neutral ligand is referred to as HL. Where values for a particular species are not included in Table 1 it means that the species was apparently absent or contributed an insignificant amount to the equilibrium (and hence had an insignificant effect on the statistical fit of the data). Table 2 records some derived constants, based on those reported in Table 1, which assist discussion of the modes of bonding.

TABLE 2

Some derived equilibrium constants

	dpa	dba	Orn	Lys	Arg
Cu^{2+}					
log $K_{121}{}^{111}$	9.79	9.79		7.23	
log $K_{111}{}^{011}/K_{122}{}^{111}$	1.04	1.08	1.13	1.12	1.10
log $K_{110}/K_{120}{}^{110}$	1.19	1.97			
Ni^{2+}					
log $K_{121}{}^{111}$	7.63	8.09	6.20	4.83	
ΔpK	4.12	4.37	2.38	0.82	
$\Delta pK'$			1.32	0.87	1.31
Co^{2+}					
log $K_{121}{}^{111}$	5.66	6.32	4.49	4.00	
ΔpK	3.37	3.34	1.36		

ΔpK = log $K_{\omega\text{-NH}_2}$ $-$ log $K_{111}{}^{110}$, $\Delta pK'$ = log $K_{\omega\text{-NH}_2}$ $-$ log $K_{133}{}^{132}$.

The hydrogen-ion complex-formation constants shown in Table 1 represent a protonation sequence which is assumed to be the same for all the ligands, namely ω-NH$_2$ > α-NH$_2$ > CO$_2^-$. There is a gradual increase in the basicity of the ω-amino-nitrogen as the chain length is increased, moving the ω-NH$_3^+$ group further from the carboxyl group. Similarly the basicity of the α-amino-group increases as its separation from the ω-NH$_3^+$ group increases, so that they approach comparable values for the apparent 'macro' constants in Lys. The basicities of the nitrogen atoms in dpa differ markedly due to their close proximity and the resulting hydrogen bonding in the monoprotonated species (*cf.* diaminoethane).

Arginine contains a very basic terminal nitrogen atom as a result of resonance stabilization of the protonated guanidine group. Hence the lower precision in the calculated value for β_{HL}. Protonation of the carboxyl groups is difficult as a result of coulombic repulsion of the two NH$_3^+$ groups in the diprotonated ligand, $[H_2L]^+$.

Complexes with Cu^{2+}.—These are the only metal complexes which have been studied in any detail. Hay *et al.*[4] concluded that the complex $[Cu(HL)_2]^{2+}$ (122 species) was negligible in the dpa system and that $[CuL]^+$ was unimportant in the dba system. Only titrations having a ligand to metal ratio of 2 : 1 were made. The present work substantiates this latter fact in titrations in mixtures of ratio dba : Cu^{2+} = 3 : 1, but when a ratio of 1.5 : 1 was employed the species $[Cu(dba)]^+$ reached a maximum concentration of *ca.* 30% total Cu^{2+} and computation from titration data for both 3 : 1 and 1.5 : 1 ratios revealed that the species $[Cu(HL)_2]^{2+}$ is significant in each titration. The value for log β_{110} for the dpa system obtained in the present study is very different to that reported previously.[4]

The full reaction sequence of Cu^{2+} with Orn could not be observed because of precipitation at *ca.* pH 6 for ligand : metal ratios up to 5 : 1. As a result of the high basicity of the ω-NH$_2$ group of Arg and, to a smaller extent, of Lys, fully deprotonated complexes could not be detected with certainty in the pH range employed.

The mode of bonding in the $[Cu(HL)]^{2+}$ complexes of Orn, Lys, and Arg is almost certainly glycine-like with the proton residing on the ω-amino-nitrogen atom. The same is probably true for the complex with dba, but there is the possibility of ω-NH$_2$–carbonyl chelate formation with dpa contributing towards the overall formation constant measured. Equilibrium constants for reaction (1) may be compared to those for the analogous reaction, (2), with glycine (Gly), and result

$$Cu^{2+} + [H_2L]^+ \overset{K_c}{\rightleftharpoons} [Cu(HL)]^{2+} + H^+ \qquad (1)$$

$$Cu^{2+} + HL \rightleftharpoons [CuL]^+ + H^+ \qquad (2)$$

in the following values for log K_c: -0.50 (dpa); -1.22 (dba); -1.46 (Orn); -1.51 (Lys); -1.47 (Arg); and -1.24 (Gly). These results suggest that there is a difference in bonding in the dpa complex.

The magnitudes of the values of log β_{110} for the complexes with dpa and dba suggest that the bonding is diamine-like with, probably, some participation from the carboxyl oxygen atom. Comparison of the values shown in Table 3 shows that, even though the value for log β_{H_2L} for diaminoethane is over 1.0 log unit larger than for dpa, the values of log β_{ML} for the complexes of the two ligands are comparable. The same trend is also found on comparing complexes of 1,3-diaminopropane with those of dba. It is reasonable to suppose that this enhancement in stability of the metal complexes is the result of weak apical bonding by the carboxyl oxygen atom. This enhancement is greater with dba than dpa. This result is to be expected for tridentate *facial* bonding

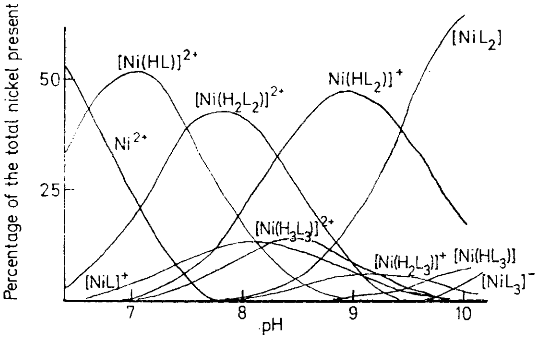
TABLE 3

Some comparable complex-formation constants

		Diamino-ethane	dpa	1,3-Diamino-propane	dba
	log β_{012}	17.15	16.06	19.70	18.35
Cu^{2+}	log β_{110}	10.52	10.51	9.77	10.50
Ni^{2+}	log β_{110}	7.4	8.1	6.3	8.9
Ni^{2+}	log $K_{120}{}^{110}$	6.1	7.0	4.3	7.0

to Cu^{2+} since there is less strain in the complex when a five- and a six-membered chelate ring is formed rather than two five-membered rings.

The values of log $K_{121}{}^{111}$ given in Table 2 are the same for dpa and dba and are of the order expected for tridentate bonding of L^- in the complex $[Cu(HL)L]^+$. In Lys, on the other hand, the $[Cu(HL)L]^+$ complex is presumed to contain two glycine-like ligands with only one ω-NH_2 group protonated. It is doubtful whether the unprotonated terminal NH_2 group participates in the bonding since this would require the formation of an eight-membered chelate ring. Evidence supporting this may be inferred from the hydrogen-ion dissociation constant (pK value) of the $[Cu(HL)_2]^{2+}$ complex which is *ca.* 10.0, only 0.6 log unit smaller than the pK value for unbound Lys. The pK of the $[Cu(HL)L]^+$ complex of Lys is 10.5 which suggests that both lysinate anions bond in a glycine-like manner in the complex $[CuL_2]$. The ratio of the stepwise constants for formation of $[CuL_2]$ for dpa (log value = 1.19) suggests that both ligands have some tridentate character. The ratio for dba, however, is much larger (log value = 1.97) suggesting marked steric hindrance, or a different manner of bonding, in this complex. Since log $K_{120}{}^{110}$ is larger for Cu^{2+} with dba than with 1,3-diaminopropane, there is probably still some tridentate behaviour in the former complex. It is possible, therefore, that the bis complex of dba relieves steric interference by having three nitrogen and one oxygen donor in the equational plane with the fourth nitrogen atom in an apical position.



Species distribution for the nickel(II)–ornithine system (concentration ratio 1 : 5)

Complexes with Ni^{2+}.—These are more complicated than those with Cu^{2+} as a result of the higher stable co-ordination number of Ni^{2+}. Tris complexes are common and, under certain circumstances, all complex species $[NiL_yH_z]$ (x and y = 1—3) are significant species. The Figure shows a typical species distribution graph for a 1 : 5 mixture of Ni^{2+} and Orn. Experimental conditions were selected to favour the formation of as wide a range of complex species as possible. Preliminary computer output suggested where titration curves should be extended, or conditions modified, to gain further information on particular complexes and hence yield the wide coverage recorded in Table 1.

Some general observations on the behaviour of the various systems are as follows. (*a*) For the dpa system (M : L = 1 : 1.25) the $[Ni(HL)]^{2+}$ complex reaches a maximum concentration of 25% total metal at pH 5.2, $[Ni(HL)]^{2+}$ reaches 6% at pH 5.5, and $[NiL]^+$ reaches a maximum of 40% at pH 5.8. (*b*) For the dba system, $[Ni(HL)]^{2+}$ reaches 20% total metal at pH 6.0, there is insufficient $[Ni(HL)_2]^{2+}$ formed to give a reliable formation constant, and $[NiL]^+$ reaches a peak of 60% at pH 6.7. (*c*) With Orn, $[Ni(HL)]^{2+}$ has a maximum of 50% total metal at pH 7.0, $[Ni(HL)_2]^{2+}$ a maximum of 30% at pH 8.0, and $[NiL]^+$ of 25% at pH 8.5. (*d*) With Lys a sharp end-point is reached before appreciable formation of deprotonated complexes occurs; $[Ni(HL)]^{2+}$ has a maximum concentration of 55% at pH 7.6, $[Ni(HL)_2]^{2+}$ of 70% at pH 8.7, and $[Ni(HL)_3]^{2+}$ of 20% at pH 9.3. The fully deprotonated complexes $[NiL]^+$ and $[NiL_2]$ only become important above pH 9.5. (*e*) With Arg the only complex to form in appreciable concentrations in addition to the $[Ni(HL)_x]^{2+}$ species is $[Ni(HL)_2L]^+$ (the 132 species) which reaches 25% of the total metal in a solution of Ni : L ratio 1 : 4 at pH 10.4.

These observations correlate well with the values for ΔpK (*i.e.* log $K_{\omega\text{-}NH_2}$ − log $k_{111}{}^{110}$), the decrease in basicity of the ω-amino-group on complex formation (Table 2). The order of decreasing ΔpK is dba > dpa > Orn > Lys. Thus the hydrogen ion is lost from the $[Ni(HL)]^{2+}$ complex of dba with the greatest ease which accounts for the fact that $[Ni(HL)]^{2+}$ loses a proton to form $[NiL]^+$ before appreciable formation of $[Ni(HL)]^{2+}$ can occur. The slightly smaller value for ΔpK for Ni^{2+} with dba allows the formation of a few percent of the $[Ni(HL)_2]^{2+}$ complex prior to deprotonation. The much smaller value for the Orn system allows the formation of both the $[Ni(HL)_2]^{2+}$ and $[Ni(HL)_3]^{2+}$ complexes before deprotonation. With Lys the situation is reversed; ΔpK is so small that by the time the pH has risen sufficient for proton removal there is very little $[Ni(HL)]^{2+}$ in solution, the bis and tris complexes predominating. Hence the main complexes containing the lysinate anion are $[Ni(HL)L]^+$ and $[NiL_2]$.

In the monoprotonated complexes the ligands are probably bound in a glycine-like manner (*cf.* Cu^{2+}) with the ω-nitrogen atom protonated. Once this amino-group is deprotonated a rearrangement of donor centres can take place. The $[NiL]^+$ complexes of dpa and dba can be conveniently considered together. A comparison with the formation constants for diaminoethane and 1,3-diaminopropane complexes (given in Table 3) shows that both dpa and dba are bonding in a tridentate manner in both $[NiL]^+$ and $[NiL_2]$ complexes. The value of log β_{110} for the complex with dba is greater than that with dpa while the reverse is true when comparing diaminoethane with 1,3-diaminopropane. This illustrates that, although individual five-membered rings are more stable than six-membered rings, when a ligand is bonding facially in a tridentate manner the two five-membered rings are less stable than a five- and a six-membered ring. It is clear from the values of log

K_{120}^{110} that both ligands in the bis complexes of dpa and dba are bound in a tridentate manner.

The mode of bonding of the deprotonated forms of Orn, Lys, and Arg is less clearly identified. The removal of a proton from one of the bound ligands in $[Ni(HL)_3]^{2+}$ ought to increase the stability of the tris complex by lowering the electrostatic repulsion between Ni^{2+} and the co-ordinating ligands. Viewed another way, the basicity of the ω-NH_2 groups should be lowered by the positively charged complex. $\Delta pK'$ (log $k_{\omega\text{-NH}_2}$ − K_{133}^{132}) for the tris (Lys) complex is 0.87 which appears to be a reasonable lowering of the basicity assuming only electrostatic forces are operative. That is, the ω-NH_2 group does not co-ordinate with the Ni^{2+} on deprotonation. However, for the Orn and Arg complexes, $\Delta pK'$ is 1.32 and 1.31 respectively, which is an increase in stability of *ca.* 0.5 log unit over what would be expected on the basis of electrostatic effects operating. It is therefore reasonable to suggest that both these ligands change their bonding characteristics when the $[Ni(HL)_3]^{2+}$ complex is monodeprotonated. Since only two co-ordination sites are available to each ligand in the tris complexes, the deprotonated ligand must bond in a diamine-like manner with the carboxy group non-co-ordinating.

For Lys, ΔpK is approximately equal to $\Delta pK'$ which suggests that in the $[NiL]^+$ complex the bonding is glycine-like with little or no participation in the bonding by the ω-NH_2 group. However, ΔpK for the Orn system is 2.38, over 1.5 log units higher than for the Lys system. This is conclusive evidence that ornithinate bonds to Ni^{II} as a tridentate ligand. Similarly, the magnitude of log K_{121}^{111} suggests that in the complex $[Ni(HL)L]^+$, the ornithinate anion is tridentate and the monoprotonated Orn, glycine-like. The value of log K_{120} for the Orn system is substantially higher than that for the reaction of a simple amino-acid with Ni^{2+}, yet the ratio log K_{110} : log K_{120} is higher than expected. It is reasonable to suppose therefore that in the $[NiL_2]$ complex one ornithinate anion is bound in a tridentate manner and the other is bound as a diamine, or both ligands are tridentate with a high degree of steric hindrance present in the complex.

It is noteworthy that log K_{110} and log K_{120} for the Lys system are rather larger than values relating to the stability of nickel(II) complexes of simple amino-acids. This could imply weak apical bonding by the ω-NH_2 groups. With Cu^{2+}, the tendency for tridentate bonding is very small with Orn and absent with Lys, but with Ni^{2+} it appears to be considerable with Orn and slight with Lys. This is a reflection of the size of the metal ion and the tendency for Ni^{2+} to be bound octahedrally.

Complexes with Co^{2+}.—The systems dpa and dba were extremely susceptible to oxidation, particularly at higher pH values. This in itself is indicative of the ligands bonding through both nitrogen atoms, giving rise to strong ligand-field splittings. The titrations of these two systems were made under rigorously oxygen-free conditions. The results given in Table 1 show trends similar to those observed among the complexes with Ni^{2+}. Thus the $[Co(HL)]^{2+}$ complexes of dpa and dba are insignificant in the titrations studied due to the relatively high values of ΔpK for the systems. Both $[Co(HL)_2]^{2+}$ and $[CoL]^+$ appear in significant concentrations in the Orn titrations but for the Lys system ΔpK is so small, in fact immeasurable, that the complex $[CoL]^+$ does not form in significant concentrations.

Glycine-like bonding is suggested for the monoprotonated forms of the ligands. The ΔpK values for the dpa and dba systems indicate that the ω-NH_2 groups participate in the bonding, the log K_{110} values suggesting tridentate bonding. Values for log K_{110} are greatest for the dba system. This confirms the observations made with Cu^{2+} and Ni^{2+} that tridentate chelation is less strained with five- and six-membered rings than with two five-membered rings. The value of ΔpK for Orn suggests tridentate chelation in the $[CoL]^+$ complex. This is substantiated by comparing the value of log K_{110} for this system with the value for the tryptophan (Trp) system (4.33). Thus, although the tendency towards tridentate chelation, forming a seven-membered diamine ring, is not as pronounced with Co^{2+} as with Ni^{2+}, it is still significant. Values for log K_{121}^{111} for the 2,3 dpa, dba, and Orn systems show that L^- bonds to $[Co(HL)]^{2+}$ in the same manner as it bonds to Co^{2+}; log K_{120}^{110} for the Orn system implies simple glycine-like co-ordination for the second ornithinate anion.

[5/1034 *Received, 2nd June,* 1975]