

Factors Influencing the Formation of Mixed Ligand Complexes of Nickel(II) and Zinc(II)

IMRE SÓVÁGÓ and ARTHUR GERGELY*

Institute of Inorganic and Analytical Chemistry, Lajos Kossuth University, Debrecen, Hungary, H-4010

Received March 23, 1979

The stability constants of some different diamine–diamine and diamine–glycine nickel(II) and zinc(II) mixed ligand complexes have been determined pH-metrically. The formation enthalpies of the nickel(II) complexes were measured calorimetrically. It was found that the higher the difference between the log K_1/K_2 values of the parent complexes, the higher the stability of the mixed complexes. Thermodynamic and spectral parameters of the nickel(II) complexes revealed that mixed ligand complex formation will be unfavourable if five-membered and six-membered chelate rings are simultaneously involved in the coordination sphere.

Introduction

During the past two decades, the various mixed ligand complexes have been dealt with in ever increasing detail. The results achieved to date and the factors determining the stability have been discussed in a number of reviews [1–4].

In connection with the copper(II) mixed ligand complexes of diamines and aminoacids, it was pointed out earlier [5] that a stability higher than the statistical case is often a consequence of the different equilibrium relations of the parent complexes. Namely, mixed ligand complexes containing aliphatic diamines or aminoacids tend to be the more stable, the greater the difference between the values of log K_1/K_2 for the parent complexes. At the same time, on the basis of the thermodynamic parameters of aminoacid–aminoacid [6] and particularly histamine–aminoacid [7] mixed ligand complexes containing copper(II), nickel(II) or zinc(II), we concluded that the factors influencing the stability are sometimes manifested in a manner differing from metal ion to metal ion. Accordingly, it is considered to be of interest that the earlier copper(II) investigations [5] relating to the roles of the steric effects and the value of log K_1/K_2 should be extended to other central metal ions.

Hence, the aim of the present work is the equilibrium and thermodynamic study of diamine–diamine and diamine–glycine (gly) mixed ligand complexes formed with nickel(II) and zinc(II). The diamines examined were ethylenediamine (en), 1,3-diaminopropane (pn), N,N'-dimethylethylenediamine (sdmen) and N,N-dimethylethylenediamine (admen).

Experimental

Chemicals Used and Experimental Conditions

The glycine used was a Reanal product of the highest analytical purity, while the diamines were Fluka products of *puriss.* quality. The glycine was purified by double recrystallization from an ethanol–water mixture, and the diamines by vacuum distillation. Both the pH-metric and the calorimetric examinations were made at an ionic strength of 0.2 M KCl at 25 °C. Determination of the concentrations of the stock solutions and the pH-metric [8] and calorimetric [9] measurements were performed as described previously.

Calculations

The species formed in the systems in question can be described by the following general equilibrium equation:



The corresponding stability constants are:

$$\beta_{pqr} = \frac{[M_p A_q B_r]}{[M]^p [A]^q [B]^r} \quad (2)$$

As regards the mixed ligand complexes, calculations were also made of the enthalpy changes and of the constants defined by the equations below.

The stabilization constant $\Delta \log \beta_{111}$ is the difference between the measured value and that calculated on the basis of statistical considerations:

$$\Delta \log \beta_{111} = \log \beta_{111} - \frac{1}{2} (\log \beta_{120} + \log \beta_{102} + \log 4) \quad (3)$$

*Author to whom correspondence should be addressed.

TABLE I. Thermodynamic Data on Nickel(II) Parent Complexes of Aliphatic Diamines and Glycine, $t = 25\text{ }^\circ\text{C}$; $I = 0.2\text{ M}$ KCl.

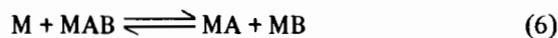
Ligand	$\log\beta_{110}$	$\log\beta_{120}$	$\log\beta_{130}$	$\log K_1/K_2$	$-\Delta H_{110}$ kJ mol $^{-1}$	$-\Delta H_{120}$
en	7.36	13.52	17.78	1.20	39	76
pn	6.31	10.62	13.40	2.00	36	67
admen	5.76	9.61	11.27	1.91	29	52
sdmen	6.76	10.76	13.09	2.76	34	57
gly	5.65	10.40	13.78	0.90	19	39

The mixing constant K_M can be given as follows:



$$K_M = \frac{[MAB]^2}{[MA_2][MB_2]} \quad (5)$$

The $\Delta\log K$ value (which corresponds to the value of $\log K_1/K_2$ relating to the parent complexes), expressing the relation of the stepwise stability constants, may be calculated from the following equations:



$$K = \frac{[MA][MB]}{[M][MAB]} \quad (7)$$

The relevant stability constants and enthalpies were calculated from the pH-metric and calorimetric titration curves [10].

Results and Discussion

Although reliable constants for the nickel(II) and zinc(II) parent complexes of the diamines are available in the literature [11–13], evaluation of the mixed ligand equilibrium systems with higher accuracy necessitated the redetermination of these data at an ionic strength of 0.2 M KCl. Since the protonation constants and proton dissociation heats of the ligands were determined earlier [5], in the present work we report only the values obtained for the parent complexes. Tables I and II list the data relating to the complexes of nickel(II) and zinc(II), respectively.

TABLE II. Equilibrium Data on Zinc(II) Parent Complexes of Aliphatic Diamines and Glycine. $t = 25\text{ }^\circ\text{C}$; $I = 0.2\text{ M}$ KCl.

Ligand	$\log\beta_{110}$	$\log\beta_{120}$	$\log K_1/K_2$
en	5.78	10.73	0.83
admen	4.47	7.90	1.04
sdmen	5.04	8.74	1.34
gly	4.84	9.02	0.66

The errors in the stability constants in Tables I and II are within ± 0.02 – 0.04 log unit, while those in the enthalpy changes do not exceed values of ± 0.5 – 1.0 kJ mol $^{-1}$. The pH-metric measurements were in general carried out at several different metal ion–ligand ratios, while the calorimetric examinations were in all cases performed at a ratio of 1:2. Thus, with regard to the larger possibility of error in the calorimetric measurements, the ΔH_{130} values were not determined. The stability constant $\log\beta_{130}$ and the ΔH values were not determined in the case of the zinc(II) complexes, because of the disturbing effect of hydrolysis. The data in Tables I and II indicate that, as observed for the copper(II) complexes, for steric reasons the substituent on the N atom decreases the stability of the complexes, as manifested by an increase in the value of $\log K_1/K_2$.

The mixed ligand complexes were studied at a metal ion–ligand A–ligand B ratio of 1:1:1, under which conditions formation of the species MA_2B and MAB_2 can be neglected. The corresponding data of the nickel(II) and zinc(II) mixed ligand complexes of type MAB are given in Tables III and IV, respectively.

TABLE III. Equilibrium Data on Nickel(II) Mixed Ligand Complexes. $t = 25\text{ }^\circ\text{C}$; $I = 0.2\text{ M}$ KCl.

Ligands	$\log\beta_{111}$	$\Delta\log\beta_{111}$	$\Delta\log K$
en–gly	12.47	0.21	0.54
admen–gly	11.02	0.71	0.39
sdmen–gly	11.94	1.06	0.47
pn–gly	11.60	0.79	0.36
admen–en	12.24	0.37	0.88
sdmen–en	12.97	0.53	1.15
pn–en	12.45	0.08	1.22
admen–pn	10.22	–0.20	1.85
sdmen–pn	11.35	0.36	1.72

It emerges from the data in Tables III and IV that the previous finding [5] tends to hold for the nickel(II) and zinc(II) mixed ligand complexes also. That is, the stability of the mixed ligand complexes is the higher, the larger the difference between the $\log K_1/K_2$ values of the parent complexes. It may further be established from Table III that the mixed ligand

TABLE IV. Equilibrium Data on Zinc(II) Mixed Ligand Complexes. $t = 25^\circ\text{C}$; $I = 0.2\text{ M KCl}$.

Ligands	$\log\beta_{111}$	$\Delta\log\beta_{111}$	$\Delta\log K$
en-gly	10.53	0.35	0.09
admen-gly	9.34	0.58	-0.03
sdmen-gly	9.80	0.62	0.08
admen-en	9.68	0.06	0.57
sdmen-en	10.23	0.19	0.59

complexes containing 1,3-diaminopropane are somewhat less stable than expected. This difference shows up to a greater extent in the calorimetric and spectral data in Table V.

Table V suggests that the formation via reaction (4) of the mixed ligand complexes containing glycine is determined by both enthalpy and entropy changes. This is in agreement with the effect of the change in charge and also with the fact that in the mixed ligand complexes no steric hindrance occurs that might result in distortion of the bonds. Accordingly, the formation of mixed ligand complexes containing ethylenediamine is reflected only in the enthalpy change, in agreement with the earlier results for the copper(II) complexes [5]. At the same time, in the systems containing 1,3-diaminopropane reaction (4) is rather endothermic and the absorption band measurable in the near infrared appears at a somewhat lower energy value than expected. In these complexes, therefore, the ligand field strengths are smaller, as manifested in the decreases in the equilibrium and thermodynamic data. Thus, whereas the complexes containing both five- and six-membered chelate rings are very stable for copper(II) [14], these results indicate that the situation is the reverse in the case of nickel(II), mixed ligand complex formation being inhibited by an increase in the asymmetry of the ligand field.

In the case of zinc(II) as central metal ion, the systems containing 1,3-diaminopropane could not be

examined, because of the readily occurring hydrolysis. Hence, the effect of the size of the chelate ring on the stability cannot be interpreted for zinc(II). As regards this metal ion, however, the difference between the values of $\log K_1/K_2$ is a factor promoting mixed ligand formation.

The effect of $\log K_1/K_2$ appears particularly striking if the data relating to the copper(II), the nickel(II) and the zinc(II) complexes are evaluated jointly. Fig. 1 shows the $\log K_M$ values for these systems as a function of the difference between the values of $\log K_1/K_2$.

It may be seen from Fig. 1 that, apart from few exceptions, the value of $\log K_M$ generally increases with increasing $\delta\log K_1/K_2$. This may be explained by assuming that the increased value of $\log K_1/K_2$ in the parent complexes is predominantly a consequence of steric reasons. However, the steric hindrance is not exhibited in the mixed ligand complexes if ligand B is small in size, *i.e.* the value of $\log K_1/K_2$ is also small for the complexes formed with this ligand. This means that the mixed ligand complex formation occurs in accordance with the stability conditions of the parent complex of ligand B, which displays the lower value of $\log K_1/K_2$. That is, if $(\log K_1/K_2)^A > (\log K_1/K_2)^B$, ligand B will bind with the same probabilities to MA and MB, whereas the coordination of ligand A is favoured only to MB.

It may further be established from Fig. 1 that more significant differences from the value determined by $\delta\log K_1/K_2$ arise only for the various mixed ligand complexes of 1,3-diaminopropane (Fig. 1, point 17) and histamine (Fig. 1, points 26, 27, 31 and 34). These differences, however, point to the effects resulting from the size of the chelate ring and from the specific natures of the donor atoms. Participation of the imidazole N atom of the histamine in the coordination in the case of copper(II) makes the coordination of ligands with O donor atoms especially favoured. It is further obvious that the simultaneous coordination of aliphatic and aromatic N donor atoms in the case of nickel(II) is less favoured [3].

TABLE V. Thermodynamic and Spectral Parameters on Nickel(II) Mixed Ligand Complexes. $t = 25^\circ\text{C}$; $I = 0.2\text{ M KCl}$.

Ligands	$-\Delta H_{111}$ kJ/mol	$-\Delta H_M$	ΔS_{111} J mol^{-1}	ΔS_M	10 Dq measured 10^3 cm^{-1}	δ^a
en-gly	58	1	44	15	10.35	0.00
admen-gly	49	6	49	19	10.10	0.20
sdmen-gly	53	11	52	17	10.35	0.20
pn-gly	57	6	34	21	10.10	-0.15
admen-en	70	12	1	-13	10.40	0.05
sdmen-en	72	12	8	-7	10.60	0.05
pn-en	70	-4	6	27	10.65	-0.15
admen-pn	59	-3	1	12	10.05	-0.25

^a $\delta = 10\text{ Dq measured} - \frac{1}{2}(10\text{ Dq(MA}_2) + 10\text{ Dq(MB}_2))$.

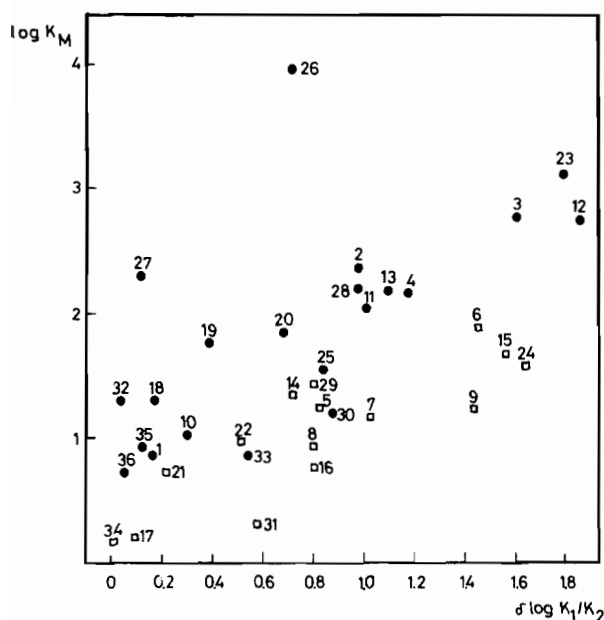


Fig. 1. $\log K_M$ values for copper(II), nickel(II) and zinc(II) mixed ligand complexes as a function of the difference of the $\log K_1/K_2$ values for the parent complexes. Notations: ● with charge change, □ without charge change. Cu(II) complexes: see ref. [5]. Complexes of histamine (hm) and histidine (his): see ref. [7].

- | | |
|-----------------------|-----------------------|
| 1. Cu(II)-en-gly; | 2. Cu(II)-admen-gly; |
| 3. Cu(II)-sdmen-gly; | 4. Cu(II)-pn-gly; |
| 5. Cu(II)-admen-en; | 6. Cu(II)-sdmen-en; |
| 7. Cu(II)-pn-en | 8. Cu(II)-sdmen-pn; |
| 9. Cu(II)-sdmen-pn; | 10. Ni(II)-en-gly; |
| 11. Ni(II)-admen-gly; | 12. Ni(II)-sdmen-gly; |
| 13. Ni(II)-pn-gly; | 14. Ni(II)-admen-en; |
| 15. Ni(II)-sdmen-en; | 16. Ni(II)-pn-en; |
| 17. Ni(II)-admen-pn; | 18. Zn(II)-en-gly; |
| 19. Zn(II)-admen-gly; | 20. Zn(II)-sdmen-gly; |
| 21. Zn(II)-admen-en; | 22. Zn(II)-sdmen-en; |
| 23. Cu(II)-hm-gly; | 24. Cu(II)-hm-en; |
| 25. Cu(II)-hm-His; | 26. Cu(II)-hm-tiron; |
| 27. Cu(II)-His-tiron; | 28. Cu(II)-His-gly; |
| 29. Cu(II)-His-en; | 30. Cu(II)-hm-gly; |
| 31. Ni(II)-hm-en; | 32. Ni(II)-hm-His; |
| 33. Ni(II)-His-en; | 34. Zn(II)-hm-en; |
| 35. Zn(II)-His-gly; | 36. Zn(II)-His-en. |

From the above consideration it is obvious that $\Delta \log K$ is the most appropriate for characterizing the extra-stabilization of the mixed ligand complexes [15]. According to the foregoing, a high stabilization constant or $\log K_M$ value may result from the difference in the stability conditions of the parent complex. However, taking the statistical factor also into consideration, the $\Delta \log K$ has a value close to the $\log K_1/K_2$ of the parent complex of smaller value. On the other hand, if the $\Delta \log K$ value also decreases or increases appreciably, this is a consequence of other special effects characteristic of the type of ligands.

References

- 1 Y. Marcus, I. Eliezer, *Coord. Chem. Rev.*, **4**, 273 (1969).
- 2 'Metal Ions in Biological Systems', Vol. 2. Mixed Ligand Complexes, Ed. H. Sigel, Marcel Dekker, New York, 1973.
- 3 Ya. D. Fridman, 'Formation of Mixed Ligand Complexes in Solutions', *Proceedings of the 3rd Symposium on Coord. Chem.*, Vol. 2, p. 77, Akadémiai Kiadó, Bp., 1971.
- 4 R. B. Martin, R. Prados, *J. Inorg. Nucl. Chem.*, **36**, 1665 (1974).
- 5 I. Sóvágó, A. Gergely, *Inorg. Chim. Acta*, **20**, 27 (1976).
- 6 A. Gergely, I. Sóvágó, I. Nagypál, R. Király, *Inorg. Chim. Acta*, **6**, 435 (1972).
- 7 I. Sóvágó, T. Kiss, A. Gergely, *J. Chem. Soc. Dalton Trans.*, 964 (1978).
- 8 I. Nagypál, A. Gergely, E. Farkas, *J. Inorg. Nucl. Chem.*, **36**, 699 (1974).
- 9 A. Gergely, I. Sóvágó, *Inorg. Chim. Acta*, **20**, 19 (1976).
- 10 I. Nagypál, *Acta Chim. Acad. Sci. Hung.*, **82**, 29 (1974).
- 11 L. G. Sillen, A. E. Martell, 'Stability Constants of Metal Ion Complexes', Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971.
- 12 J. J. Christensen, D. J. Eatough, R. M. Izatt, 'Handbook of Metal Ligand Heats', Marcel Dekker, New York, 1975.
- 13 P. Paoletti, L. Fabrizzi, R. Barbucci, *Inorg. Chim. Acta Reviews*, **7**, 43 (1973).
- 14 H. Sigel, R. Caraco, B. Prijs, *Inorg. Chem.*, **13**, 462 (1974).
- 15 H. Sigel, *Angew. Chem. Intern. Edit.*, **14**, 394 (1975).