36. Metal Complexes with Macrocyclic Ligands

Part XXXV[1])

Stabilities of Some Bivalent Metal-Ion Complexes with 1,4,7-Triazacyclononane-1-acetic Acid

by Hui-Zhi Cai and Thomas A. Kaden*

Institute of Inorganic Chemistry, Spitalstr. 51, CH–4056 Basel

(4.XII.92)

The stability constants of the Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} complexes with 1,4,7-triazacylononane-1-acetic acid (noma) were determined at 25° and 0.5M (KNO_3) by potentiometric titrations. The species [ML] and [ML(OH)] were found in all cases except for Ni^{2+}, whereas [ML_2] was only detected for Cd^{2+}. For the complexes [ML], the order of stability is $Mn^{2+} < Cd^{2+} < Pb^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$, which is consistent with the *Irving-Williams* series.

Introduction. – Functionalization of azamacrocycles through side chains with ligating groups leads to new compounds which possess interesting properties with respect to their complexation with metal ions [2]. Several studies on tetrasubstituted tetraazamacrocycles have appeared [3], but much less is known on the complexation of mono-*N*-substituted derivatives. The preparation of such compounds is relatively easy, when a carboxylic group as for 1,4,7-triazacyclononane-1-acetic acid (noma) is introduced in the side chain [4]. noma has an additional ligating group compared to the parent compound 1,4,7-tri-azacyclononane ([9]aneN$_3$), for which the stability of the complexes with some bivalent metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+}) was investigated [5–7]. For [9]aneN$_3$, the permutation of the *Irving-Williams* order [8] for the Cu^{2+}- and Ni^{2+} complexes was found [6].

There is only one study on the stability constants and on the structure of the Cu^{2+} complexes with noma [9]. Thereby the species [CuL], [CuL(OH)], [CuL$_2$], and
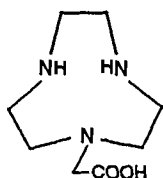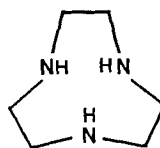
noma   [9]aneN$_3$

---

[1])   Part XXXIV: [1].

[(CuL)$_2$(OH)] were found, and [(CuL)(ClO$_4$)] and [(CuL)$_2$(OH)(ClO$_4$)] were characterized by X-ray structure analysis. It was, therefore, interesting to pursue the study of the complexes of noma with other bivalent metal ions.
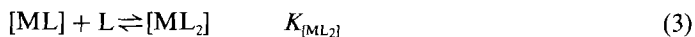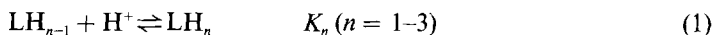
Experimental. – The ligand 1,4,7-triazacyclononane-1-acetic acid (noma) was synthesized as described in [4]. All other reagents, being of anal. grade (*Merck*), were used without further purification. The potentiometric titrations were performed at 25° and $I = 0.5$M (KNO$_3$) with 0.4M NaOH. The titrations of the Pb^{2+}, Cd^{2+}, Zn^{2+}, and Mn^{2+} complexes were run under N$_2$ on an automatic microprocessor-controlled potentiometric titrator, as reported in [10]. The equilibration of the Ni^{2+} complexes, being too slow for the automatic titrator, was measured using a batch technique, in which premixed solns. of Ni^{2+} and ligand at different pH values were kept in a thermostated water bath for 2 d, until constant pH values were reached. The pH electrode was calibrated with two buffer solns. of pH 4 and of pH 7 and checked daily. The concentrations of noma and of the metal ions are listed in *Table 1*.

Table 1. *Concentrations of Metal Ions (C_M) and noma (C_L) for the Potentiometric pH Titrations*

M^{2+}	$C_L \cdot 10^3$ [M]	$C_M \cdot 10^3$ [M]	C_M/C_L [%]
Mn^{2+}	3.99	3.55	96
	3.99	1.77	44
	1.95	1.42	73
Cd^{2+}	3.87	3.69	95
	3.48	1.41	41
	1.93	1.77	92
Pb^{2+}	3.89	3.55	91
	3.89	2.13	55
	1.95	1.42	73
Zn^{2+}	3.95	3.54	90
	4.00	2.83	71
	3.86	1.77	46
	2.00	1.77	89
Ni^{2+}	1.94	1.75	90
	1.93	0.98	51
	1.88	1.69	90
no M^{2+}	3.92		
	3.93		

Results and Discussion. – The protonation constants of the ligand and the stability constants of the complexes were evaluated by fitting a set of two-to-four titration curves with the program TITFIT [10] [11]. A typical example showing the quality of the fit is given in *Fig. 1*.

The definitions of the protonation and stability constants of the species used are given in *Eqns. 1–4* (charges omitted).

$$\text{LH}_{n-1} + \text{H}^+ \rightleftharpoons \text{LH}_n \qquad K_n \ (n = 1\text{–}3) \tag{1}$$

$$\text{M} + \text{L} \rightleftharpoons \text{ML} \qquad K_{[\text{ML}]} \tag{2}$$

$$[\text{ML}] + \text{L} \rightleftharpoons [\text{ML}_2] \qquad K_{[\text{ML}_2]} \tag{3}$$

$$[\text{ML(OH)}] + \text{H}^+ \rightleftharpoons [\text{ML}] \qquad K_{[\text{ML(OH)}]} \tag{4}$$
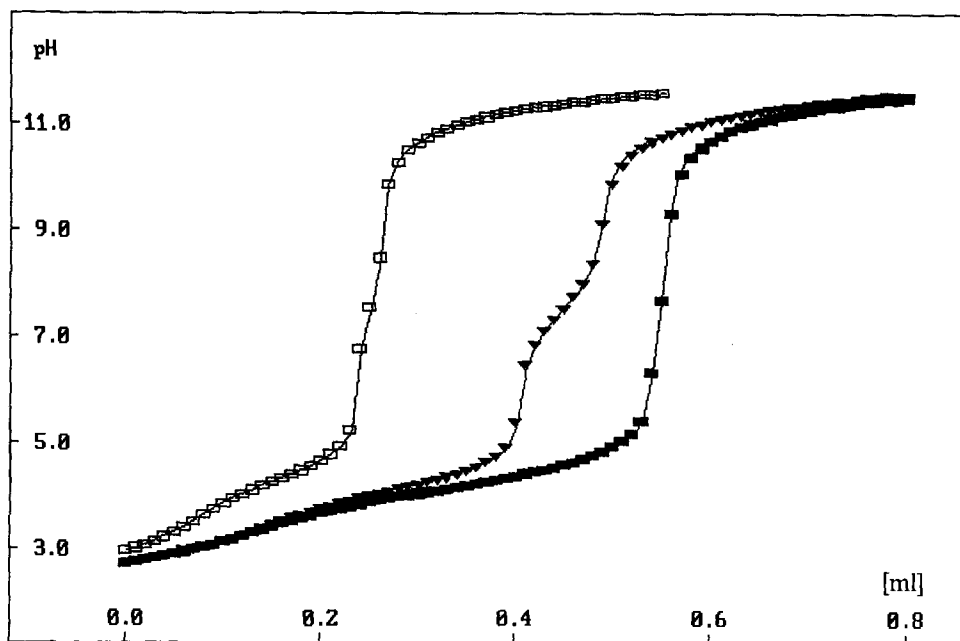
Fig. 1. *Potentiometric titration curves of the Pb^{2+} complexes with noma* (■: $C_L = 3.89 \cdot 10^{-3}$ M, $C_M = 3.55 \cdot 10^{-3}$ M; ▼: $C_L = 3.89 \cdot 10^{-3}$ M, $C_M = 2.13 \cdot 10^{-3}$ M; □: $C_L = 1.95 \cdot 10^{-3}$ M, $C_M = 1.42 \cdot 10^{-3}$ M). Curves calculated with the model [PbL], [PbL(OH)].

The protonation constants obtained in this work (*Table 2*) are in good agreement with those reported in [9].

Table 2. *Protonation and Stability Constants of the Complexes with noma at 25° and* I = 0.5 M *(KNO₃)*

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_{[ML]}$	$\log K_{[ML2]}$	$\log K_{[MLOH]}$	$\sigma_{ml} \cdot 10^3$
noma	11.44(1)	7.46(2)	2.81(3)				1.4
noma [9]	11.47	7.45	2.82				
Mn^{2+}				8.53(1)		11.02(1)	2.2
Cd^{2+}				11.67(1)	4.96(2)	11.01(1)	1.5
Pb^{2+}				13.11(1)		12.34(1)	1.6
Zn^{2+}				14.24(1)		10.59(1)	2.0
Ni^{2+}				17.85(3)			2.3
Cu^{2+} [9]				18.99(1)	5.79(1)	9.39(1)[a]	

[a]) In addition to [MLOH], the dimeric species [M₂L₂OH] was also found for Cu^{2+} [9].

In the metal-ligand titrations, [ML] is usually the dominant species over a wide pH range, although, at high pH, [ML(OH)] is also present in most cases. Only for Ni^{2+}, it was difficult to ascertain, which other species besides [NiL] is present at pH > 10, because only few experimental points were available, as limited by the batch technique.

The magnitude of σ_{ml} indicates that only the model with the species [ML] and [ML(OH)] fits the experimental data best for Mn^{2+} and Zn^{2+}. Test with other models gave no improvement of the fit.

[ML$_2$] was only found for Cd^{2+}. The model with additional species such as [CdL$_2$H] slightly improved the fit ($\sigma_{ml} = 1.3 \cdot 10^{-3}$) over the model with the species [CdL], [CdL$_2$], and [CdL(OH)] ($\sigma_{ml} = 1.5 \cdot 10^{-3}$). However, since [CdL$_2$H] is only formed to less than 5% and the F-test [12] indicates no significant improvement of the fit, we consider the simpler model as the best one.

The interpretation of the equilibria for Pb^{2+} is somewhat ambiguous. The model with only one species [PbL] gave a poor fit of the experimental data, as shown in *Table 3*. A reasonable fit, however, could be achieved when a second species was added.

Table 3. *Results of the Calculations with Different Models for Pb^{2+}*

[PbL]	[PbLOH]	[PbL$_2$]	[Pb$_2$L$_2$OH]	$\sigma_{ml} \cdot 10^3$
×				3.2
×	×			1.5
×			×	1.7
×		×		2.8
×	×	×		1.4
×	×		×	1.4
×	×	×	×	1.2

The model with [PbL] and [PbL(OH)] fits the pH titrations best among those with only two species. The addition of a third or even a fourth complex to the model slightly decreased the standard deviation, but again the F-test shows no significance and the species are formed to less than 5%. Thus, the model with [PbL] and [PbL(OH)] is to be preferred over the other ones.

The species distribution (*Fig. 2*) shows that [PbL(OH)] starts to be formed at relatively high pH value and exists up to only 15% under the experimental conditions.

Table 2 reveals that for the complexes [ML] the order of stability is $Mn^{2+} < Cd^{2+} < Pb^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$, which is consistent with the *Irving-Williams* series $Mn^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$ [8].

It is interesting to compare the stability constants of noma with those of the open-chain analogues sdtma and udtma and of the parent ligand [9]aneN$_3$ (*Table 4*). The stability constants of [ML] for Zn^{2+} and Cu^{2+} are about one order of magnitude larger for noma than for the open-chain ligands sdtma and udtma, while that for Ni^{2+} is about three orders of magnitude larger. The small macrocyclic effect observed for [CuL] with noma

Table 4. *Stability Constants of the Complexes with sdtma [13], udtma [13], and [9]aneN$_3$ [14] at 25° and I = 0.1 M*

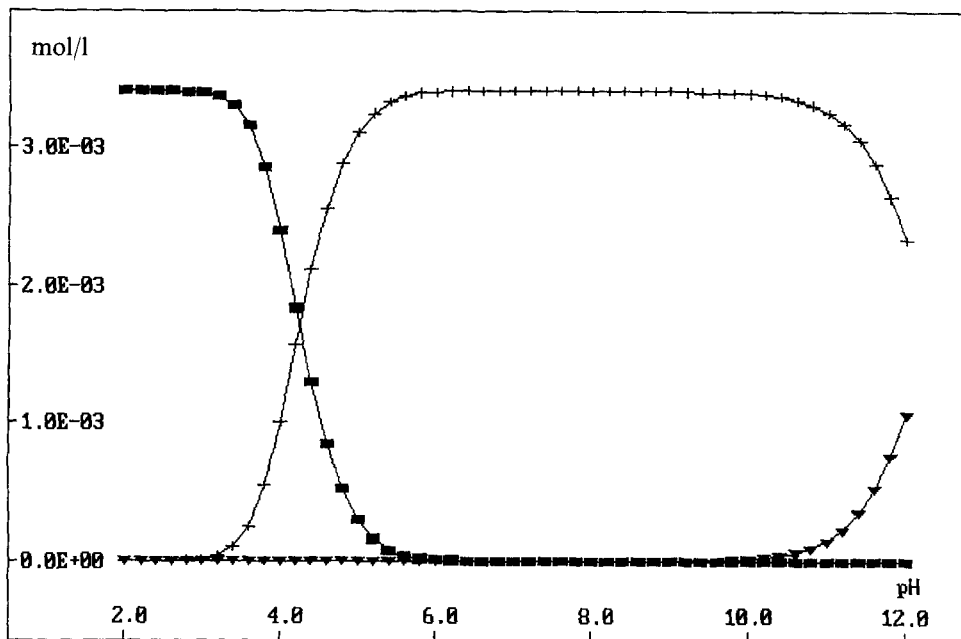|		Mn^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}
sdtma	$\log K_{[ML]}$				13.13	14.37	18.07
udtma	$\log K_{[ML]}$				12.94	14.40	17.29
[9]aneN$_3$	$\log K_{[ML]}$	5.8	9.5	10.3	11.3	12.4	15.4
	$\log K_{[ML2]}$	3.6	8.4	5.1	9.2	6.8	12.01

Fig. 2. *Species distribution of the Pb²⁺ complexes with noma* ($C_L = 3.89 \cdot 10^{-3}$ M, $C_M = 3.55 \cdot 10^{-3}$ M).
■: Pb²⁺; +: [PbL]; ▼: [PbL(OH)].

was interpreted as a consequence of the very favorable facial coordination of the three N-atoms of the ligand [9]. noma, which has one pendant arm, probably meets the geometrical requirement of M^{2+} (M^{2+} = Mn²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Ni²⁺) better than the open-chain ligands sdtma and udtma.
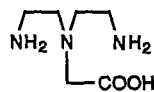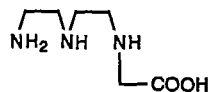
sdtma   udtma

In the case of [9]aneN₃, the permutation of the *Irving-Williams* order for the stability of [CuL] and [NiL] and no macrocyclic effect for [CuL] was found [6]. This is interpreted by the fact that [9]aneN₃ is sterically constrained to facial coordination, while meridional coordination is preferred by Cu²⁺. This results in a destabilization of [CuL] with respect to [NiL].

Two conclusions can be drawn from the comparison of the results shown in *Table 2* and *4*. First, in the present work [ML] and [ML(OH)] were generally found, whereas [ML₂] was only detected for Cd²⁺. In contrast, for [9]aneN₃ the complexes [ML₂] are present in all cases and [ML(OH)] was only observed for Cu²⁺ [6]. Secondly, the introduction of an additional ligating group into [9]aneN₃, leads to an increase in the stability for

[ML] and a decrease in the stability for [ML$_2$]. This can be understood by the fact that the carboxylate group of the side chain can form an additional bond in [ML], but hinders the formation of [ML$_2$] by steric constraints.

REFERENCES

[1] A. Schiegg, A. Riesen, Th. A. Kaden, *Helv. Chim. Acta* **1991**, *74*, 1689.
[2] Th. A. Kaden, *Topics Curr. Chem.* **1984**, *121*, 157.
[3] A. Stetter, W. Frank, *Angew. Chim.* **1976**, *88*, 780; S. Buoen, J. Dale, P. Groth, P. Krane, *J. Chem. Soc., Chem. Commun.* **1977**, 1172; H. Häfliger, Th. A. Kaden, *Helv. Chim. Acta* **1979**, *62*, 683; K. P. Wainwright, *J. Chem. Soc., Dalton Trans.* **1980**, 2117; A. Stetter, W. Frank, R. Mertens, *Tetrahedron* **1981**, *37*, 767; I. Murase, M. Mikuriya, H. Sonoda, S. Kida, *J. Chem. Soc., Chem. Commun.* **1984**, 692; A. Riesen, M. Zehnder, Th. A. Kaden, *Helv. Chim. Acta.* **1986**, *69*, 2067; I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda, S. Kida, *J. Chem. Soc., Dalton Trans.* **1986**, 953; A. Riesen, M. Zehnder, Th. A. Kaden, *Acta Crystallogr., Sect. C* **1988**, *44*, 1740.
[4] M. Studer, Th. A. Kaden, *Helv. Chim. Acta* **1986**, *68*, 2081.
[5] M. Kodama, E. Kimura, *J. Chem. Soc., Dalton Trans.* **1978**, 1081.
[6] R. Yang, L. J. Zompa, *Inorg. Chem.* **1976**, *15*, 1499.
[7] L. J. Zompa, *Inorg. Chem.* **1978**, *17*, 2531.
[8] H. Irving, R. J. P. Williams, *J. Chem. Soc.* **1953**, 3192.
[9] M. Studer, A. Riesen, Th. A. Kaden, *Helv. Chim. Acta* **1989**, *72*, 307.
[10] H. Gampp, M. Maeder, A. D. Zuberbühler, Th. A. Kaden, *Talanta* **1980**, *27*, 513.
[11] A. D. Zuberbühler, Th. A. Kaden, *Talanta* **1982**, *29*, 201.
[12] Ph. R. Bevington, 'Data Reduction and Error Analysis for the Physical Sciences', McGraw-Hill, New York, 1969.
[13] G. McLendon, D. T. MacMillan, M. Hariharan, A. E. Martell, *Inorg. Chem.* **1975**, *14*, 2322.
[14] M. R. Squillante, Ph. D. Thesis 1980, Tufts University, MA, mentioned in Ph. Chaudhuri, K. Wieghardt, *Prog. Inorg. Chem.* **1987**, *35*, 329.