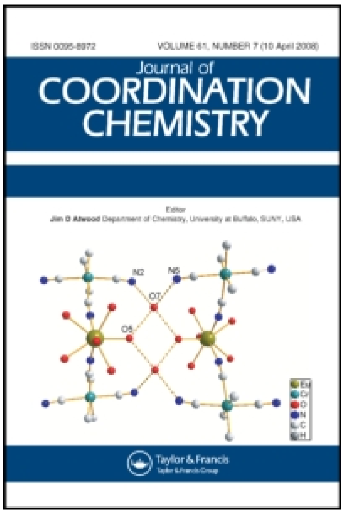


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PYRIDINE DERIVATIVES AS COMPLEXING AGENTS XII. Thermodynamics of Complex Formation with 2-Pyridylmethyl-iminodiacetic Acid and its 6-Methyl Substituted Derivative

G. Anderegg[a]
[a] Laboratorium für Anorganische Chemie, Zürich, Switzerland

To cite this Article Anderegg, G.(1981) 'PYRIDINE DERIVATIVES AS COMPLEXING AGENTS XII. Thermodynamics of Complex Formation with 2-Pyridylmethyl-iminodiacetic Acid and its 6-Methyl Substituted Derivative', Journal of Coordination Chemistry, 11: 3, 171 — 175

To link to this Article: DOI: 10.1080/00958978108079065

URL: http://dx.doi.org/10.1080/00958978108079065

J. Coord. Chem., 1981, Vol. 11, pp. 171–175
0095-8972/81/1103-0171 $06.50/0

PYRIDINE DERIVATIVES AS COMPLEXING AGENTS XII. Thermodynamics of Complex Formation with 2-Pyridylmethyl-iminodiacetic Acid and its 6-Methyl Substituted Derivative

G. ANDEREGG

Laboratorium für Anorganische Chemie, ETH, CH-8092 Zürich, Switzerland

(*Received April 10, 1981*)

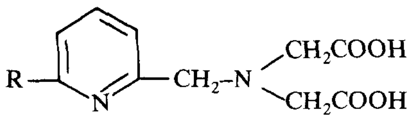
The equilibrium constants and the involved thermodynamic data for the formation of the complexes between two pyridyl-methyl-iminodiacetic acids and the following cations: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and Ag^{+} have been obtained by potentiometric and direct calorimetric measurements. The data are discussed in relation with the results for other similar ligands.

INTRODUCTION

In connection with our investigations of complex formation with ligands containing pyridyl residues,[1] we report here the results with two acids:

(i) N-(2-pyridylmethyl)-iminodiacetic acid (A) and
(ii) N-(6-methyl-2-pyridylmethyl)-iminodiacetic acid (B).

Abbreviations for the unprotonated ligand L^{2-}:



$R = H : A$ PMIM

$R = CH_3 : B$ MMIM

and the following metal ions: Ag^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}. We have obtained the stability constants by potentiometric measurements and the corresponding thermodynamic functions ΔH and ΔS for the formation of the complexes by direct calorimetric measurements.

Some stability constants, especially for the acid A have been published by other authors.[2–4] Their data are not always in good agreements with ours, for reasons which are discussed below.

EXPERIMENTAL

The Equilibria

The two acids have four basic groups and therefore, besides the unprotonated species L^{2-}, the following protonated species can be formed: HL^{-}, H_2L, H_3L^{+} and H_4L^{2+}. The solution of the neutral acids H_2L show for the proton number $\bar{p}$[5] values which do not exceed two and therefore (as further discussed later) the following three equilibria need to be considered:

$$H_3L^{+} \rightleftharpoons H_2L + H^{+} \qquad \text{I}$$

$$H_2L \rightleftharpoons HL^{-} + H^{+} \qquad \text{II}$$

$$HL^{-} \rightleftharpoons L + H^{+} \qquad \text{III}$$

The three pK values of the acids were obtained (see Table I) from the results of alkalimetric titrations of the neutral acids. For solutions having the same quantity of ligand H_2L and of added strong base, the addition of a solution of metal ion causes a pH decrease, which depends on the magnitude of the stability constants of the formed complexes. From such measurements, it was possible for the weaker 1 : 1 complexes and for most 1 : 2 complexes, to obtain the equilibrium constants $K_1 = [ML]/([M][L])$ and $K_2 = [ML_2]/([ML][L])$ reported in Table I (pH method[6] abbreviated as pH). If the complex is already formed in the solution to be titrated with strong base, this method will not give results having the required accuracy. In these cases one or more of the following methods have been used:

i) exchange equilibria of type IV between the complex ML and a second ligand such as a protonated amine (for example, H_3tren^{3+7}) or of type V involving the mercury complex HgL and a second metal ion,[8] provided the pH of the solution allows an exact evaluation of the

$$ML + H_3tren^{3+} \rightleftharpoons Mtren^{2+} + L^{2-} + 3H^+ \quad IV$$

$$HgL + M^{2+} \rightleftharpoons ML + Hg(OH)_2 + 2H^+ \quad V$$

concentrations of the equilibrated species;

ii) metal electrode measurements have been used to obtain directly the stability constants of the divalent cations of these metals (Hg[9], Cu[10]) and indirectly the stability constants of the other cations using the equilibrium constant for the exchange VI.

$$ML + M^{*2+} \rightleftharpoons M^*L + M^{2+} \quad VI$$

The number of experimental points for each cation-ligand system was between 30 and 50. An exception is represented by silver(I), for which more than 200 points for each ligand were obtained. The calculations of the constants were carried out as described elsewhere.[11] In all cases appropriate programs[6] on a CDC 6500-6400 computer were used. The errors given in the Table were obtained taking into account the systematic error of the glass electrode. In the calculation of the pK values of the acids the standard deviation of the normalized function to be minimized was strongly reduced by considering the equilibria I, II and III instead of only II and III because the pK values of H_3L^+ and H_2L are quite near each other (see Table I); although the proton number is always lower than 2.

Calibrations of the electrodes (H, Hg, Cu) were carried out using the concentration scale in the chosen standard state, i.e. I = 0.1 with $NaNO_3$ as inert salt.

Calorimetric Measurements

The measurements were carried out using an LKB 8700/2 titration calorimeter. Solutions containing strong acid or the metal ion were titrated with a 0.05 M solution of the ligand. The heat changes corrected for the heat of dilution were calculated. The composition of the solutions before and after the reaction were obtained[12] by use of the program KALOR which also calculates the enthalpy values.

Preparation of the Ligands

The two acids investigated were prepared in a similar way to that reported in the literature.[2,3,4] Analysis of the acids:

2-aminomethylpyridine-N,N'-diacetic acid
$C_{10}H_{12}O_4N_2 \cdot 0.4H_2O$

	C	H	N	O
Calcd.	C 51.90	H 5.57	N 12.10	O 30.40
Found	C 51.90	H 5.74	N 12.34	O 30.46

6-methyl-2-aminomethylpyridine-N,N'-diacetic acid
$C_{11}H_{14}O_4N_2$

	C	H	N	O
Calcd.	C 55.40	H 6.00	N 11.80	O 26.85
Found	C 55.38	H 5.97	N 11.86	O 27.12

The metal nitrates (Merck or Riedel-de-Haen, p.a.) were used for preparation of the solutions.

RESULTS AND DISCUSSION

The Stability Constants

The stability constants given in Table I are valid for an ionic strength 0.1 ($NaNO_3$) and 20°C. Comparison to the data of Irving and Da Silva[2] (I = 0.1 (KNO_3) and 20°C) for log K_1 with PMIM indicates good agreement for Mg^{2+} (difference in log K_1: 0.08), Ca^{2+} (0.01), Sr^{2+} (0.05), Ba^{2+} (0), Mn^{2+} (0.13) and Fe^{2+} (0.06) but the difference increases considerably as the value of K_1 increases especially for Co^{2+} (0.44), Zn^{2+} (0.22), Cd^{2+} (0.65) and Pb^{2+} (0.29). This is due to the inappropriate use of the direct pH method by these authors, since in the latter cases the complex is largely formed in the solutions to be investigated by alkalimetric titrations. The measured data hence largely refer to the neutralisation of the (eventual) excess of protonated ligand and to the free hydrogen ions already in the solution. For similar reasons the values for Cu^{2+} (log K_1 = 10.75), for Ni^{2+} (11.22) and for Co^{2+} (10.39) obtained by Souchay, Israily and Gouzerh[3] cannot be considered reliable. They give for the complex formation function $f(\bar{n}, pL)$ of Cu^{2+}, Ni^{2+} and Co^{2+} curves which are coincident for $\bar{n} \leq 0.8$, indicating the inadequacy of these data to obtain K_1. Further, these authors[3] have only considered the formation of H_2L and not of H_3L^+ in acidic solutions. Indeed, using the data for the alkalimetric titration of A given in their paper, it is possible to show a remarkable decrease of the standard deviation of the proton number $\bar{p}$, by considering also the presence of H_3L^+. In this case the following results are obtained: pK of H_2L = 2.768 and pK of H_3L^+ = 2.569. In the list of stability constants of PMIM reported by Irving and Da Silva[2] there is given a log K_1 value for Na^+ of 0.85 – a value which we were not able to reproduce. From our measurements at I = 0.1 (KNO_3), calibrating the cell with the same inert salt composition as that used for the complex

TABLE I
Logarithm of the stability constants of the complexes of the ligands A and B at 20°C and I = 0.1 (NaO_3).

	PMIM : pK values of H_3L^+ : 2.70; 2.70; 8.22				MMIM : pK values of H_3L^+ : 2.60; 3.45; 8.39			
	log K_1 (±0.05)	log K_2 (±0.1)	log β_2	Method	log K_1 (±0.05)	log K_2 (±0.1^2)	log β_2	Method
Mg^{2+}	3.98			pH	3.0			pH
Ca^{2+}	4.91			pH	3.55			pH
Sr^{2+}	3.70			pH	n.i.			
Ba^{2+}	3.40			pH	2.55			pH
Mn^{2+}	7.10	3.50	10.60	pH	6.60	3.5		pH
Fe^{2+}	9.00			pH	8.55			pH
Co^{2+}	10.60	2.90	13.50	Hg, pH, $Hg(OH)_2$	9.80			Hg
Ni^{2+}	12.65	3.70	16.35	Cu, pH	11.45			
Cu^{2+}	14.20[a]	<3		Cu, tren	12.70			Cu, tren
Zn^{2+}	10.65			tren, pH, Hg, $Hg(OH)_2$	9.80			tren
Cd^{2+}	10.00	5.25	15.25	Cu, pH, Hg, $Hg(OH)_2$	8.75	5.10	13.85	Hg, pH
Hg^{2+}	14.90	9.20	24.10	Hg	14.90	9.10	24.00	Hg
Pb^{2+}	10.60			Cu, tren, pH, Hg, $Hg(OH)_2$	10.15			Hg, tren, pH

[a] pK of CuI: ~9.0

formation we obtained log $K_1 \leqslant 0$. Probably the value of 0.85 in the above work might be explained as arising from differences in the junction potential between the calibrating and measuring solutions. Our values for log K_2 with Mn^{2+}, Co^{2+} and Cd^{2+} are in agreement with those of Irving and Da Silva.

We have investigated carefully the formation of the silver complexes because of the possible formation of dimeric and protonated species, as found previously with diamines such as ethylenediamine[12,14,15], 2-(aminomethyl)-pyridine and 6-methyl-2-(methylaminomethyl)-pyridine.[16] It was found that four different species are formed; MHL, ML^-, $M_2L_2^{2-}$ and M_2L (Table II). This takes place even in solution containing a molar ratio $[ML]_t : [L]_t$ of 1 : 2; i.e. no tendency to form 1 : 2 complexes was observed. The stability of $M_2L_2^{2-}$ in comparison to that of ML^-, represented by the dimerisation constant $K_D = [M_2L_2]/[ML]^2$ is less pronounced than for the two aromatic diamines mentioned above but greater with respect to ethylenediamine.

In comparison with the tridentate iminodiacetate[17] the investigated tetradentate ligands form complexes with a given cation which are in general more stable: K_1 is greater by a factor between 10 to $10^{4.5}$. Because of the lower number of available coordination sites in ML, the value of K_2 is in general lower. On comparison with the two corresponding aromatic amines,[18] the presence of the two acetate residues causes an increase in the stability constant K_1 by a factor of approximately 10^5 for all divalent 3d cations as well as for Hg^{2+} and Cd^{2+}. In both series of ligands the introduction of the methyl group causes a remarkable drop by a factor of 10 to 100 in K_1 with exception of the largest ions Mn^{2+}, Pb^{2+} and Hg^{2+} for which destabilisation is less and becomes sometimes negligible.

The Thermodynamic Data (Table III)

The enthalpy and the entropy of protonation of L^{2-} for both ligands are of the expected magnitude, on comparison with the corresponding values for iminodiacetate[19] $\Delta H = -8.15$ kcal mol^{-1} and $\Delta S = 15.4$ cal mol^{-1} K^{-1}) and for methyliminodiacetate[20] ($\Delta H = -4.73$ kcal mol^{-1} and $\Delta S = 28.4$ cal mol^{-1} K^{-1}). On consideration to the respective pK values for HL^-, it seems appropriate to assume, that in these monoprotonated species, the proton is bound to the aliphatic

TABLE II
Logarithm of the stability constants for the silver(I) complexes at 25°C and I = 0.1 (KNO_3).

PMIM : pK values of H_3L^+ : 2.70; 2.70; 8.20				MMIM : pK values of H_3L^+ : 2.62; 3.45; 8.29			
log $\beta_{1,1,1}$	log $\beta_{1,0,1}$	log $\beta_{2,0,2}$	log $\beta_{2,0,1}$	log $\beta_{1,1,1}$	log $\beta_{1,0,1}$	log $\beta_{2,0,2}$	log $\beta_{2,0,1}$
9.73(10)	5.64(10)	14.83(10)	7.15(50)	10.25(10)	6.10(20)	15.85(10)	–

[a] Three times the standard deviation of the last digit is given in parentheses.

TABLE III
Thermodynamic data for complex formation at 20°C and I = 0.1 ($NaNO_3$).

	PMIM		MMIM	
	ΔH[kcal/mol][a]	ΔS[cal/(mol · K)][b]	ΔH[kcal/mol][a]	ΔS[cal/(mol · K)][b]
Protonation of the ligand:				
$H^+ + L^{2-} \rightarrow HL^-$	−3.7	24.9	−3.76	25.6
$H^+ + HL^- \rightarrow H_2L$	−0.2	12.9	−1.1	12.0
Complex formation:				
$Mg^{2+} + L^{2-} \rightarrow MgL$	3.8	31.1	4.8	31.4
$Ca^{2+} + L^{2-} \rightarrow CaL$	−1.5	17.3		
$Sr^{2+} + L^{2-} \rightarrow SrL$	−1.0	13.5		
$Ba^{2+} + L^{2-} \rightarrow BaL$	−1.7	9.7		
$Mn^{2+} + L^{2-} \rightarrow MnL$	−0.4	31.1		
$Co^{2+} + L^{2+} \rightarrow CoL$	−3.5	36.5	−2.2	37.3
$Ni^{2+} + L^{2-} \rightarrow NiL$	−6.7	35.0	−4.65	36.8
$NiL + L^{2-} \rightarrow NiL_2^{2-}$	−4.1	2.9		
$Cu^{2+} + L^{2-} \rightarrow CuL$	−6.8	41.8	−3.8	45.1
$Zn^{2+} + L^{2-} \rightarrow ZnL$	−3.2	37.8	−2.2	37.3
$Cd^{2+} + L^{2-} \rightarrow CdL$	−6.6	23.2	−2.0	33.2
$CdL + L^{2-} \rightarrow CdL_2^{2-}$	−5.8	4.2	−8.2	−4.6
$Pb^{2+} + L^{2-} \rightarrow PbL$	−5.6	29.4	−4.4	31.4
$Hg^{2+} + L^{2-} \rightarrow HgL$	−11.95	27.4	−11.64	28.4
$HgL + L^{2-} \rightarrow HgL_2^{2-}$	−11.6	2.5	−11.85	1.2
$2Ag^+ + 2L^{2-} \rightarrow Ag_2L_2^{2-}$	−21.5	−1.7	−22.0	−2.1

[a] ±0.1
[b] ±0.3

amino group in each case, as was postulated by Irving and Da Silva.[2] As already discussed by these authors the situation is quite different for the second protonation step, because the other available positions, namely the carboxylate groups and the pyridine group may have similar protonation constants. However this argument was not considered by them in the calculation of the proton ligand equilibria in acidic solutions.

In Figures 1 and 2 are given the ΔH and ΔS values for the formation of the 1 : 1 complexes between several 3d divalent cations with the two ligands investigated as well as with nitrilotriacetate[21] (NTA) and methyliminodiacetate[20] (MIM). For both ΔH and ΔS, the general trend is, for each ligand, very similar. For the considered ligands with a charge of −2, PMIM gives the more negative ΔH values because of the increased number of donors. The differences in ΔH represent mainly the enthalpic gains due to the formation of the bond involving the pyridine nitrogen atom, corrected for the dehydration terms of the ligand and the metal ion. Considering the corresponding ΔS values, the larger values for the formation of the complexes of MMIM and PMIM probably are mainly due to the loss of more H_2O molecules than occurs for the complexes with MIM. This is in agreement with the above interpretation of the ΔH values. Among the

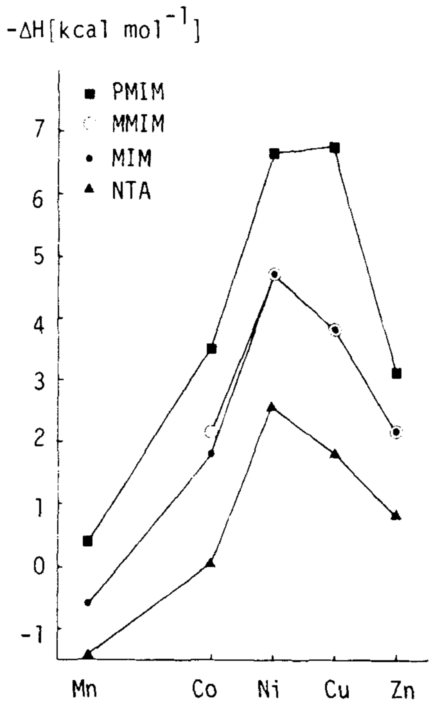


FIGURE 1 The enthalpies of complex formation of 3d divalent cations with some iminodiacetate ligands.

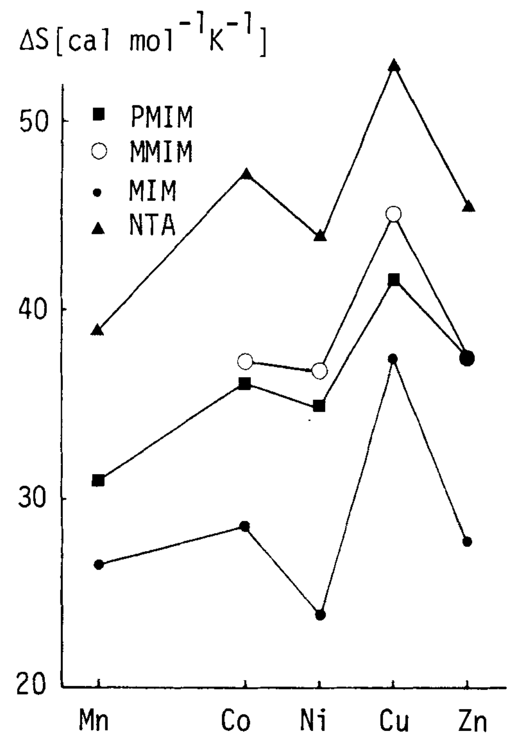


FIGURE 2 The entropies of complex formation of 3d divalent cations with some iminodiacetate ligands.

ligands considered, because of its higher negative charge, NTA should immobilize more water molecules[22,23] and these should be held quite strongly. Therefore on complex formation a larger number of water molecules would be endothermically released thus giving larger ΔS values and more positive ΔH values. For the 6-methyl substituted MMIM the values of ΔH are less positive than those for PMIM and very similar to those for MIM: the effect of the methyl group can best be explained by the presence of some steric strain in the complex as already observed for other analogous systems.[1] From the data for Cd^{2+}, an interesting feature is observed for the formation of Cd(MMIM): ΔH is 4.6 kcal mol^{-1} lower and ΔS by 10 cal mol^{-1} K^{-1} larger in comparison to the values for the PMIM complex of the same cation. This may be explained by an endothermic release of one H_2O more in the formation of the former respect to the latter complex. This difference is mainly compensated in the second step of complex formation; indeed, for the overall reaction VI, the

$$Cd^{2+} + 2L^{2-} \longrightarrow CdL_2^{2-} \qquad \text{VI}$$

following data are obtained: PMIM : $\Delta H = -12.4$ kcal mol^{-1}, $\Delta S = 27.4$ cal mol^{-1} K^{-1}; MMIM : $\Delta H = -10.2$ kcal mol^{-1} and $\Delta S = 28.6$ cal mol^{-1} K^{-1}.

The author is grateful to J. Gerber, O. Q. Fröhlich, S. Frankel and B. Rüttimann for the potentiometric and calorimetric measurements.

REFERENCES AND NOTES

1. G. Anderegg, E. Hubmann, N. G. Podder and F. Wenk, *Helv. Chim. Acta*, **60**, 123 (1977).
2. H. Irving and J. J. R. F. Da Silva, *J. Chem. Soc.*, **1963**, 945.
3. P. Souchay, N. Israily and L. P. Gouzerh, *Bull. Soc. Chim. France*, **12**, 3917 (1966).
4. L. Thompson, *Inorg. Chem.*, **3**, 1015 (1964).
5. $\bar{p}$ (proton number) = average number of protons bound per ligand ion L^{2-}.
6. G. Anderegg, *Helv. Chim. Acta*, **44**, 1673 (1961).
7. H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1544 (1949). G. Anderegg, P. Nägeli, F. Müller and G. Schwarzenbach, *Helv. Chim. Acta*, **42**, 627 (1959).
8. G. Anderegg, G. Schwarzenbach, M. Padmoyo and Ö. F. Borg, *Helv. Chim. Acta*, **41**, 988 (1958). G. Anderegg, *Helv. Chim. Acta*, **44**, 2397 (1963).
9. G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **40**, 1773 (1957).
10. G. Anderegg, *Helv. Chim. Acta*, **41**, 414 (1960).
11. H. Stünzi and G. Anderegg, *Helv. Chim. Acta*, **59**, 1621 (1976).
12. G. Anderegg, *Helv. Chim. Acta*, **45**, 901 (1962).
13. G. Schwarzenbach, B. Maissen and H. Ackermann, *Helv. Chim. Acta*, **35**, 2333 (1952).
14. G. Schwarzenbach, H. Ackermann, B. Maissen and G. Anderegg, *Helv. Chim. Acta*, **35**, 2337 (1952).
15. H. Othaki and Y. Ito, *J. Coord. Chem.*, **3**, 131 (1973).
16. A. M. Gouminne and L. Eckhart, *J. inorg. nucl. Chem.*, **36**, 357 (1974).
17. G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).
18. G. Anderegg, *Helv. Chim. Acta*, **54**, 309 (1971).
19. G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).
20. G. Anderegg, *Helv. Chim. Acta*, **48**, 1718 (1965).
21. G. Anderegg, *Experientia, Suppl. IX*, 75 (1964).
22. R. W. Gurney, *Ionic Processes in Solutions*, London 1953.
23. G. Anderegg, *Helv. Chim. Acta*, **51**, 1856 (1968).