involving two oxidation states higher than those considered above was inspected. On the other hand, also the data reported in Table I for the nonreversible processes $Ni^I \rightleftharpoons Ni^{II} + e^-$ appear in agreement with our reasoning, provided all these investigated processes exhibit comparable irreversibility degrees.

Registry No. $Ni(ClO_4)_2$, 13637-71-3; PPh_3, 603-35-0; $PEtPh_2$, 607-01-2; PEt_2Ph, 1605-53-4; PEt_3, 554-70-1; dppe, 1663-45-2; $P(c\text{-}Hx)_3$, 2622-14-2; $P(OEt)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; $P(O\text{-}o\text{-}tol)_3$, 2622-08-4.

Contribution from the Institute of Inorganic Chemistry,
University of Basel, CH-4056 Basel, Switzerland

Enhanced Stability of Ternary Complexes in Solution[1,2] through the Participation of Heteroaromatic N Bases. Comparison of the Coordination Tendency of Pyridine, Imidazole, Ammonia, Acetate, and Hydrogen Phosphate toward Metal Ion Nitrilotriacetate Complexes

DEBABRATA BANERJEA,[3] THOMAS A. KADEN, and HELMUT SIGEL*

Received February 9, 1981

So that our understanding of the selectivity observed in biological systems could be mimicked and improved, mixed-ligand complexes of the type M(Nta)(A), where $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}, or Zn^{2+}, Nta^{3-} = nitrilotriacetate, and A = pyridine, imidazole, NH_3, CH_3COO^-, or HPO_4^{2-}, have been studied by potentiometric pH titrations ($I = 0.1$, $NaNO_3$; 25 °C); the mentioned monodentate ligands are the simplest models for the corresponding ligating groups often occurring in nature. The change observed in stability by mixed-ligand complex formation is quantified by $\Delta \log K_M = \log K^{M(Nta)}_{M(Nta)(A)} - \log K^M_{M(A)}$, which corresponds to the equilibrium $M(Nta)^- + M(A^n)^{2+n} \rightleftharpoons M(Nta)(A)^{n-1} + M^{2+}$. For A = pyridine and $M^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}, or Zn^{2+} $\Delta \log K_M$ = 0.04, 0.31, 0.54, and 0.22, respectively; with A = imidazole the values are 0.02, 0.02, 0.25, and 0.16, respectively. Hence, for these systems *positive* $\Delta \log K_M$ values are observed in contrast to common experience and the statistical expectation. However, for the ternary systems with A = NH_3, CH_3COO^-, or HPO_4^{2-}, $\Delta \log K_M$ is *negative*. Both the discrimination and the enhanced stabilities in the formation of the ternary complexes depend on the participation of a heteroaromatic N base such as pyridine or imidazole. The cooperative effect between the imidazole and the O donors is suggested as being one of the sources used by nature to achieve selectivity; indeed this combination of ligating groups is observed in many metalloenzymes.

The phosphate, carboxylate, amino, and imidazole groups are important metal ion binding sites in biological systems.[4] Among these groups the imidazole residue is especially versatile,[4-6] and due to its relatively low basicity ($pK_a \approx 7$), it is far more accessible for many metal ions than the amino group ($pK_a \approx 9.5$), for which the competition with the proton is much larger in the physiological pH region.[4]

For the imidazole group, it was in addition suggested,[7] on the basis mainly of results obtained with 2,2′-bipyridyl, histamine, and other heteroaromatic N bases, that mixed-ligand complexes formed by a metal ion of the second half of the 3d series, the imidazole residue, and O donors should be especially stable. As this behavior imparts also discriminating properties between different ligands, the formation of mixed-ligand complexes may be one of the tools of nature to achieve selectivity. Although this view had been questioned,[8] it was reaffirmed,[9] and its importance for biological systems again emphasized.

As the increased stability of such mixed-ligand complexes depends on the π-accepting properties of the heteroaromatic N base,[10] the "pyridine" nitrogens occurring in pyrimidines and purines[11,12] may as potent metal ion binding sites impart similar qualities.

The simplest ligands which may allow further elucidation of the properties of the mentioned natural binding sites are the corresponding monodentate ligands hydrogen phosphate, acetate, ammonia, imidazole, and pyridine. We have therefore measured the stability of the ternary complexes formed by Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}, the tetradentate nitrilotriacetate (Nta^{3-}), and the listed monodentate ligands.

The stability of these mixed-ligand complexes may be quantified[7,13] by determining the position of equilibrium 1.

$$M(Nta)^- + M(A^n)^{2+n} \rightleftharpoons M(Nta)(A)^{n-1} + M^{2+} \quad (1)$$

---

[1] This is part 37 of the series "Ternary Complexes in Solution".[2]

[2] Part 36: Sigel, H.; Prijs, B.; Martin, R. B. *Inorg. Chim. Acta*, in press. For part 35 see ref 38a.

[3] Done during a leave of absence from the Department of Chemistry of the University of Calcutta to the University of Basel.

[4] Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201-208.

[5] Freeman, H. C. In "Inorganic Biochemistry"; Eichorn, G. L., Ed.; Elsevier: Amsterdam, London, and New York, 1973; Vol. 1, Chapter 4.

[6] Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471-517.

[7] (a) Sigel, H. *Chimia* **1967**, *21*, 489-500. (b) Sigel, H. *Met. Ions Biol. Syst.* **1973**, *2*, 63-125. (c) Sigel, H. *Angew. Chem.* **1975**, *87*, 391-400; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394-402. (d) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489-4496. (e) Sigel, H. "Plenary Lecture"; Conference Volume of the XXth International Conference on Coordination Chemistry; Banerjea, D., Ed.; published by I.U.P.A.C. through Pergamon Press, Oxford, 1980.

[8] Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527-1531.

[9] Sigel, H. *Inorg. Chem.* **1980**, *19*, 1411-1413.

[10] (a) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945-947. (b) Huber, P. R.; Sigel, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27*, 1319-1323. (c) Walker, F. A.; Sigel, H.; McCormick, D. B. *Inorg. Chem.* **1972**, *11*, 2756-2763. (d) Fischer, B. E.; Sigel, H. *Ibid.* **1979**, *18*, 425-428.

[11] Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 57-124.

[12] Scheller, K. H.; Hofstetter, F.; Mitchell, P. R.; Prijs, B.; Sigel, H. *J. Am. Chem. Soc.* **1981**, *103*, 247.

0020-1669/81/1320-2586$01.25/0

The values for the corresponding equilibrium constant (eq 2)

$$10^{\Delta \log K_{\mathrm{M}}} = [\mathrm{M(Nta)(A)}][\mathrm{M}]/[\mathrm{M(Nta)}][\mathrm{M(A)}] \quad (2)$$

follow[7c] from relation 3. According to the rule $K_1 > K_2$,[14-16]

$$\begin{aligned}\Delta \log K_{\mathrm{M}} &= \log K^{\mathrm{M(Nta)}}{}_{\mathrm{M(Nta)(A)}} - \log K^{\mathrm{M}}{}_{\mathrm{M(A)}} \\ &= \log K^{\mathrm{M(A)}}{}_{\mathrm{M(A)(Nta)}} - \log K^{\mathrm{M}}{}_{\mathrm{M(Nta)}} \quad (3)\end{aligned}$$

which generally holds for binary complexes, one expects by analogy that equilibrium 1 is on its left side; i.e., for $\Delta \log K_{\mathrm{M}}$, *negative* values are expected. This reasoning is also in accordance with statistical considerations:[7c] at a regular octahedral (oh) coordination sphere of a metal ion six equivalent positions are available for the entering monodentate ligand, while only two remain if four are occupied by Nta^{3-}; as the probability of dissociation is the same for the binary and ternary complexes, i.e., 1, the statistical value for $\Delta \log K_{\mathrm{st/oh}}$ is log (2/6) = –0.5. For the square-planar (sp) (or distorted octahedral (do))[7c] coordination sphere of Cu^{2+}, the value is log (1/4) (or log (1/6)); i.e., $\Delta \log K_{\mathrm{st/sp(do)}} = -0.6$ (–0.8).

It is now shown that *negative* values for $\Delta \log K_{\mathrm{M}}$ are obtained for the ternary complexes with hydrogen phosphate, acetate, and ammonia, as is expected from the reasonings given in the preceding paragraph; however, *positive* values are measured for the mixed-ligand complexes with imidazole and pyridine.

Experimental Section

Materials. The nitrate salts of the metal ions, the disodium salt of edta, nitric acid, NaOH (Titrisol), pyridine (py), imidazole (Im), $\mathrm{NH_4NO_3}$, $\mathrm{CH_3COONa{\cdot}3H_2O}$, and $\mathrm{NaH_2PO_4{\cdot}H_2O}$ (all these reagents were of pA grade) were from Merck AG, Darmstadt, Federal Republic of Germany. Nitrilotriacetic acid (complexon I) was obtained from Siegfried AG, Zofingen, Switerland.

The titer of the NaOH used for the titrations was determined with potassium hydrogen phthalate (Merck AG); the exact concentrations of the stock solutions of the ligands were measured by titrations with NaOH. The concentrations of the metal ion stock solutions were determined with edta.

The buffers (pH 4.64, 7.00, and 9.00) used for calibrating the potentiometers were from Metrohm AG, Herisau, Switzerland. The direct pH meter readings were used in the calculations.

Potentiometric Measurements. The titrations were carried out with a Metrohm potentiograph E336 and a Metrohm macro EA 121 glass electrode. The acidity constants $K^{\mathrm{H}}{}_{\mathrm{H(A)}}$ of $\mathrm{H(py)^+}$, $\mathrm{H(Im)^+}$ and $\mathrm{CH_3COOH}$ were determined by titrating 50 mL of aqueous 0.0017 M $\mathrm{HNO_3}$ and $\mathrm{NaNO_3}$ (I = 0.1; 25 °C) in the presence and absence of 0.0014 M pyridine, imidazole, or acetate under $\mathrm{N_2}$ with 1 mL of 0.1 M NaOH. The acidity constants of $\mathrm{NH_4^+}$ and $\mathrm{H_2PO_4^-}$ were determined in exactly the same way, but the aqueous $\mathrm{HNO_3}$ was only 0.0003 M. $K^{\mathrm{H}}{}_{\mathrm{H(A)}}$ was calculated within the range between 3% and 97% neutralization, where possible.

The conditions for the determination of the stability constants $K^{\mathrm{M}}{}_{\mathrm{M(A)}}$ of the binary complexes (I = 0.1; 25 °C) were the same as for the acidity constants, but (a part of) $\mathrm{NaNO_3}$ was replaced by $\mathrm{M(NO_3)_2}$ with ratios of $\mathrm{M^{2+}}$:A between 12:1 and 24:1, with $\mathrm{Cu^{2+}}$ also ratios as low as 7:1 have been used. Under these conditions practically only the 1:1 complexes form, i.e., the concentration of the species $\mathrm{M(A)}_m$ with $m \geq 2$, can be neglected. Hence, the stability constants $K^{\mathrm{M}}{}_{\mathrm{M(A)}}$ were computed by taking into account the species $\mathrm{H^+}$, H(A), A, $\mathrm{M^{2+}}$, and M(A).[17] Data were usually collected from 10% complex formation to the beginning of hydrolysis of $\mathrm{M(aq)^{2+}}$, which was evident from the titrations without A.

Correspondingly, the stability constants $K^{\mathrm{M(Nta)}}{}_{\mathrm{M(Nta)(A)}}$ of the ternary complexes were determined from solutions with $[\mathrm{A}]_{\mathrm{tot}}$ = 0.0014 M, containing a 7- to 24-fold excess of $\mathrm{M^{2+}}$ and $\mathrm{Nta^{3-}}$. As the stability of the binary $\mathrm{M(Nta)^-}$ complexes is high,[14,15] complete complex formation can be assumed. This assumption was checked for each metal ion by separate titrations, which were also used to detect the pH where hydroxo complexes begin to form. Data were collected only in this pH range where $\mathrm{M(Nta)^-}$ complex formation is practically complete and where no hydrolysis occurs. Hence, the stability constants $K^{\mathrm{M(Nta)}}{}_{\mathrm{M(Nta)(A)}}$ were calculated by considering the species $\mathrm{H^+}$, H(A), A, $\mathrm{M(Nta)^-}$, and M(Nta)(A).

All the equilibrium constants listed were calculated from at least three independent titration curves.

Results and Discussion

From potentiometric pH titrations, the stability constants of the ternary metal ion complexes containing $\mathrm{Nta^{3-}}$ and $\mathrm{HPO_4^{2-}}$, $\mathrm{CH_3COO^-}$, $\mathrm{NH_3}$, imidazole, or pyridine (eq 4) were

$$\mathrm{M(Nta)^-} + \mathrm{A}^n \rightleftharpoons \mathrm{M(Nta)(A)}^{n-1}$$

$$K^{\mathrm{M(Nta)}}{}_{\mathrm{M(Nta)(A)}} = [\mathrm{M(Nta)(A)}]/([\mathrm{M(Nta)}][\mathrm{A}]) \quad (4)$$

calculated. Similarly, the constants of the binary complexes (eq 5) were also determined or taken from the literature.[14-16,18]

$$\mathrm{M^{2+}} + \mathrm{A}^n \rightleftharpoons \mathrm{M(A)}^{2+n}$$

$$K^{\mathrm{M}}{}_{\mathrm{M(A)}} = [\mathrm{M(A)}]/([\mathrm{M}][\mathrm{A}]) \quad (5)$$

With the constants of eq 4 and 5, the position of equilibrium 1 may now be quantified; i.e., $\Delta \log K_{\mathrm{M}}$ may be calculated with eq 3.

The obtained results are listed in Table I. The constants of the binary pyridine and acetate complexes agree well with the data given in the literature.[14-16a,c] The agreement between the constants of the ternary complexes determined by us with those which have been determined earlier is also excellent (see Table I; values in parentheses), with the exception of some few values.[23-25]

Stability of Complexes. The most interesting results of Table I are certainly the *positive* values for $\Delta \log K_{\mathrm{M}}$ of the ternary complexes formed with pyridine or imidazole. For all these mixed-ligand complex systems, equilibrium 1 is on its right side, indicating that pyridine or imidazole coordinate better to $\mathrm{M(Nta)^-}$ than to $\mathrm{M(aq)^{2+}}$. From eq 3 it is in addition evident that this result also means that the coordination tendency of $\mathrm{Nta^{3-}}$ is more pronounced toward $\mathrm{M(py)^{2+}}$ or $\mathrm{M(Im)^{2+}}$ than toward $\mathrm{M(aq)^{2+}}$. That the stability is somewhat more strongly enhanced in the ternary complexes containing pyridine, compared to those with imidazole, is in agreement with the better π-accepting properties of the pyridyl group.[10,26]

---

(13) Martin, R. B.; Prados, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1665–1670.

(14) Sillén, L. G.; Martell, A. E. "Stability Constants of Metal-Ion Complexes" (a) *Spec. Publ.-Chem. Soc.* **1964**, *No. 17*; (b) *Spec. Publ.-Chem. Soc., Suppl. 1* **1971**, *No. 25*.

(15) Perrin, D. D. "Stability Constants of Metal-Ion Complexes", Part B, "Organic Ligands"; IUPAC Chemical Data Series No. 22; Pergamon Press: Oxford, 1979.

(16) (a) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York and London, 1975; "Amines", Vol. 2. (b) *Ibid.*, 1976; "Inorganic Complexes", Vol. 4. (c) Martell, A. E.; Smith, R. M. *Ibid.*, 1977; "Other Organic Ligands", Vol. 3.

(17) Griesser, R.; Sigel, H. *Inorg. Chem.* **1970**, *9*, 1238–1243.

(18) Sigel, H.; Becker, K.; McCormick, D. B. *Biochim. Biophys. Acta* **1967**, *148*, 655–664.

(19) Israeli, J.; Saulnier, H. *Inorg. Chim. Acta* **1968**, *2*, 482–484.

(20) Jackobs, N. E.; Margerum, D. W. *Inorg. Chem.* **1967**, *6*, 2038–2043.

(21) Fridman, A. Ya.; Dyatlova, N. M.; Fridman, Ya. D. *Zh. Neorg. Khim.* **1969**, *14*, 3304–3308.

(22) Fridman, A. Ya.; Dyatlova, N. M.; Lastovskii, R. P. *Zh. Neorg. Khim.* **1970**, *15*, 701–706.

(23) $\log K^{\mathrm{Ni(Nta)}}{}_{\mathrm{Ni(Nta)(py)}} = 1.21$ and $\log K^{\mathrm{Zn(Nta)}}{}_{\mathrm{Zn(Nta)(py)}} = 0.76$ (I = 1.5; 25 °C) may be calculated from the constants given in ref 15, which were collected from ref 21 ($\mathrm{Ni^{2+}}$) and 22 ($\mathrm{Zn^{2+}}$). These values differ from ours by about 1 and 0.5 log units, respectively.

(24) The following value differs from ours by about 1.2 log units: $\log K^{\mathrm{Cu(Nta)}}{}_{\mathrm{Cu(Nta)(NH_3)}} = 2.55$ (I = 0.1, $\mathrm{NaNO_3}$; 25 °C). Still, E. *Anal. Chim. Acta* **1979**, *107*, 105–112.

(25) $\mathrm{Log}\ K^{\mathrm{Zn(Nta)}}{}_{\mathrm{Zn(Nta)(HPO_4)}} = \log \beta^{\mathrm{Zn}}{}_{\mathrm{Zn(Nta)(HPO_4)}} - \log K^{\mathrm{Zn}}{}_{\mathrm{Zn(Nta)}} = 21.50 - 10.31 = 11.2$ (I = 0.1, $\mathrm{NaClO_4}$; 25 °C; Ramamoorthy, S.; Manning, P. G. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1671–1674); this value is clearly off by at least 10 log units.

Table I. Comparison of the Stability Constants of Several Ternary M(nitrilotriacetate) (A) Complexes with the Corresponding Data of the Binary M(A) Complexes[a-f]

ligand (A)	M^{2+}	log $K^{M(Nta)}_{M(Nta)(A)}$	log $K^{M}_{M(A)}$	Δ log K_M
pyridine[b]	Co^{2+}	1.29 ± 0.02	1.25 ± 0.02	0.04
	Ni^{2+}	2.18 ± 0.01	1.87 ± 0.01	0.31
	Cu^{2+}	3.03 ± 0.02	2.49 ± 0.02	0.54
	Zn^{2+}	1.22 ± 0.03	1.00 ± 0.03	0.22
imidazole[c]	Co^{2+}	2.41 ± 0.01 (2.35 ± 0.03)[g]	2.39 ± 0.04 (5)[h,i]	0.02
	Ni^{2+}	3.02 ± 0.01 (3.01 ± 0.05)[g]	3.00 ± 0.03 (5)[h,i]	0.02
	Cu^{2+}	4.47 ± 0.01 (4.35 ± 0.03)[g]	4.22 ± 0.03 (7)[h,i]	0.25
	Zn^{2+}	2.73 ± 0.02 (2.73 ± 0.03)[g]	2.57 ± 0.02 (6)[h,i]	0.16
NH_3 (cf. *d*)	Co^{2+}	1.82 ± 0.03	2.08 ± 0.03 (6)[i,m]	−0.26
	Ni^{2+}	2.54 ± 0.02 (2.54 ± 0.04)[k] (2.50)[l]	2.74 ± 0.06 (9)[i,m]	−0.20
	Cu^{2+}	3.79 ± 0.08	4.18 ± 0.03 (17)[i,m]	−0.39
	Zn^{2+}	~2.3[j] (2.33)[l]	2.41 ± 0.09 (3)[i,m]	~−0.1
CH_3COO^- (cf. *e*)	Co^{2+}	⩽0.3[n]	0.60 ± 0.05	⩽−0.3
	Ni^{2+}	0.37 ± 0.18	0.68 ± 0.06	−0.3
	Cu^{2+}	0.32 ± 0.09	1.81 ± 0.02	−1.5
	Zn^{2+}	⩽0.3[n]	0.86 ± 0.06	⩽−0.6
HPO_4^{2-} (cf. *f*)	Co^{2+}	⩽0.4	2.18 ± 0.05[o]	⩽−1.8
	Ni^{2+}	⩽0.4	2.08 ± 0.05[o]	⩽−1.7
	Cu^{2+}	0.61 ± 0.14	3.2[o]	−2.6
	Zn^{2+}	0.6 ± 0.2	2.4[o]	−1.8

[a] $I = 0.1$ ($NaNO_3$) and 25 °C if nothing else is mentioned. The errors given are three times the standard error of the mean value or the sum of the probable systematic errors, whichever is larger. [b] $pK^{H}_{H(py)} = 5.26 \pm 0.01$. [c] $pK^{H}_{H(Im)} = 7.04 \pm 0.01$. [d] $pK^{H}_{H(NH_3)} = 9.36 \pm 0.01$. [e] $pK^{H}_{CH_3COOH} = 4.54 \pm 0.01$. [f] $pK^{H}_{H_2PO_4} = 6.73 \pm 0.01$ for $I = 0.1$ ($NaNO_3$) and 25 °C. At the same temperature but different ionic strength, $pK^{H}_{H_2PO_4} = 6.63 \pm 0.01$ for $I = 0.2$ ($NaNO_3$) and 6.79 ± 0.01 for $I = 0.1$ (KNO_3); this indicates that HPO_4^{2-} forms complexes with the alkali ions, especially with Na^+. [g] $I = 0.1$ ($NaClO_4$) and 25 °C.[19] [h] Average of the constants listed in ref 14, 15 and 16a for $I = 0.1$–0.2 and 25 °C. [i] The range of error given is the standard error of the mean value resulting from averaging the values of the literature; the number in parentheses gives the number of available constants. [j] Estimate; the experiments were hampered by hydroxo complex formation. [k] $I = 0.5$ ($NaClO_4$) and 25 °C; determined by spectrophotometry.[20] [l] $I = 1.5$ and 25 °C; calculated from the constants listed in ref 15 which were collected from ref 21 (Ni^{2+}) and 22 (Zn^{2+}). [m] Average of the constants listed in ref 14 and 16b for $I = 0$–2 and 20–30 °C; a view on the constants given in the literature shows that the influence of ionic strength and temperature is small. [n] This upper limit corresponds to a depression of the buffer region (ΔpH) of 0.03 log units. [o] $I = 0.1$ ($NaClO_4$) and 25 °C.[18]

Table II. Comparison of the Coordination Tendency of Ammonia, Imidazole, or Pyridine toward $M(Nta)^-$ and $M(A)^{2+}$ According to Equation 10[a]

	Δ log K^*_M		
ternary complex	A = NH_3	A = imidazole	A = pyridine
$Co(Nta)(A)^-$	0.23 (1.59 ± 0.05/6)[b]	0.45 (1.96 ± 0.02/3)[c]	0.74 (0.55 ± 0.04/7)[c]
$Ni(Nta)(A)^-$	0.39 (2.15 ± 0.04/9)[b]	0.52 (2.50 ± 0.06/4)[c]	1.09 (1.09 ± 0.07/7)[c]
$Cu(Nta)(A)^-$	0.27 (3.52 ± 0.03/15)[b]	0.97 (3.50 ± 0.02/7)[c]	1.15 (1.88 ± 0.02/5)[c]
$Zn(Nta)(A)^-$	~−0.1 (2.22 ± 0.09/3)[b]	0.38 (2.35 ± 0.02/4)[c]	0.82 (0.40 ± 0.09/5)[c]

[a] These values for Δ log K^*_M were calculated with eq 10 by using the log $K^{M(Nta)}_{M(Nta)(A)}$ values of Table I and those given in parentheses. These constants in parentheses are the average of the values given in the literature for log $K^{M(A)}_{M(A)_2}$. The range of error corresponds to the standard error of the mean value; the last number gives the available constants. [b] Average of the constants listed in ref 14 and 16b for $I = 0$–2 and 20–30 °C (cf. footnote *m* of Table I). [c] Average of the constants listed in ref 14, 15, and 16a for $I = 0.1$–0.2 (imidazole) or 0.1–0.5 (pyridine) and 25 °C.

Ammonia forms mixed-ligand complexes for which the values of Δ log K_M are *negative*; this was also observed earlier for aliphatic amines.[7] These amines, like ammonia, have no π-accepting properties, and therefore, no enhanced stabilities and no discriminating effects (vide infra) are observed in mixed-ligand systems containing these N ligands. It should be stressed that the results of Table I *cannot* be explained by steric effects. For example, the steric restrictions within the coordination sphere of Cu^{2+} are rather somewhat smaller for NH_3 than for imidazole, as is evident from a comparison of the differences between the successive stability constants of the corresponding binary complexes (for NH_3 see ref 16b; for imidazole see ref 8; compare also the corresponding data of Tables I and II).

As one would expect, the Δ log K_M values for the ternary systems with acetate are more negative than those with NH_3, because the electrostatic interaction between the negatively charged ions CH_3COO^- and $M(Nta)^-$ is certainly less favorable than between CH_3COO^- and $M(aq)^{2+}$. The same consideration explains also the even more negative Δ log K_M values found for the complexes with the dinegative HPO_4^{2-}. Hence, the decreasing values of Δ log K_M (Table I) within the series py > Im > NH_3 > CH_3COO^- > HPO_4^{2-} may be rationalized.

Of course, there are also other ways these results may be viewed. For example, for CH_3COO^- and HPO_4^{2-}, equilibrium 1 corresponds to equilibrium 6 if we restrict ourselves to *octahedral* coordination spheres and if we represent the N and O donor atoms of the ligands by N and O, respectively. Hence, for O donor ligands there is no net change in the coordination spheres on each side of equilibrium 6; this is different for ammonia, imidazole, and pyridine where one obtains on the same basis equilibrium 7. For a comparison where the number of N and O donors in the coordination spheres of the

$$M(N)(O)_5 + M(O)_6 \rightleftharpoons M(N)(O)_5 + M(O)_6 \quad (6)$$

$$M(N)(O)_5 + M(N)(O)_5 \rightleftharpoons M(N)_2(O)_4 + M(O)_6 \quad (7)$$

---

(26) That Zn^{2+} (a) and other metal ions (b) with a d^{10}-electron configuration may act as π-electron donors is known, e.g.: (a) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *9*, 1-4. (b) Hancock, R. D.; Finkelstein, N. P. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 477-484.

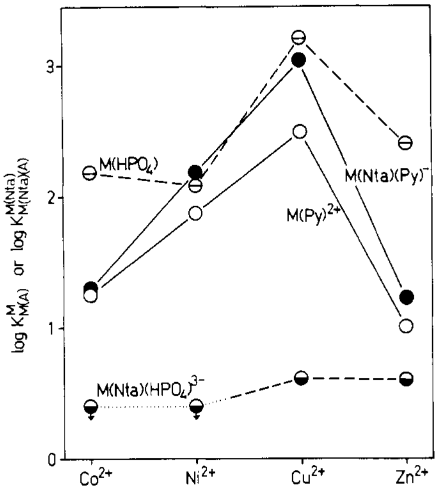


Figure 1. Plots of the stability constants log $K^{M}{}_{M(A)}$ and log $K^{M(Nta)}{}_{M(Nta)(A)}$ (Table I) for the binary $M(py)^{2+}$ (○) or $M(HPO_4)$ (⊖) and the ternary $M(Nta)(py)^-$ (●) or $M(Nta)(HPO_4)^{3-}$ (◒) complexes according to the Irving–Williams series.

metal ions remains unchanged one has to consider equilibrium 8, which corresponds to equilibrium 9. The equilibrium

$$M(N)(O)_5 + M(N)_2(O)_4 \rightleftharpoons M(N)_2(O)_4 + M(N)(O)_5 \quad (8)$$

$$M(Nta)^- + M(A)_2^{2+} \rightleftharpoons M(Nta)(A)^- + M(A)^{2+} \quad (9)$$

constant for this reaction may be calculated from equation 10,

$$\Delta \log K^*_M = \log K^{M(Nta)}{}_{M(Nta)(A)} - \log K^{M(A)}{}_{M(A)_2} \quad (10)$$

and the statistically expected value is log $K^*_{st/oh}$ = log [(2/1)/(5/2)] = −0.1. The values for Δ log K^*_M are listed in Table II. The data for the NH_3 systems are only slightly larger than statistically expected,[27] while the values for the imidazole and pyridine systems are clearly enhanced. Hence, this reasoning also confirms the preceding conclusions about the stability of the ternary $M(Nta)(A)^-$ complexes which increases within the series A = NH_3 < imidazole < pyridine.

Discriminating Properties. There is one further aspect to be noted. For example, the coordination tendency of NH_3 and imidazole toward Cu^{2+} is identical within experimental error (see Table I), while the coordination tendency of the same ligands toward $Cu(Nta)^-$ differs by 0.7 log units, i.e., by a factor of about 5. Hence, discriminating properties are observed; in other words, *selectivity* occurs in mixed-ligand complex formation.

Similarly, the coordination tendency of pyridine toward Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+} is 0.2–1.4 log units *lower* than the one of HPO_4^{2-} toward the same metal ions, while the coordination tendency of pyridine toward $M(Nta)^-$ is 0.6–2.4 log units *larger* than the one of HPO_4^{2-}. These alterations in the coordinating properties of pyridine and HPO_4^{2-} become even more clear from Figure 1 where log $K^{M}{}_{M(A)}$ and log $K^{M(Nta)}{}_{M(Nta)(A)}$ are plotted according to the Irving–Williams series[28,29] for the mentioned systems. It is evident that the insertion of a second ligand into a complex system may very drastically alter the coordinating properties of the ligand already present.

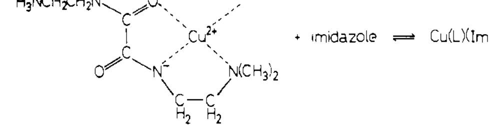
Table III. Comparison of the Coordination Tendency of Pyridine (py) and the Dianion of *p*-Hydroxybenzenesulfonate (pps^{2-}) toward Tridentately Coordinated Cu^{2+} (25 °C)

	pyridine		*p*-hydroxybenzene-sulfonate: log $K^{Cu(L)}{}_{Cu(L)(pps)}$ [b,d]
Cu(L)[a]	log $K^{Cu(L)}{}_{Cu(L)(py)}$ [b]	Δ log K_{Cu} [c]	
$Cu(dien)^{2+}$	1.77 ± 0.09	−0.72	1.72 ± 0.27
$Cu(dpa)^{2+}$	1.76 ± 0.09	−0.73	2.37 ± 0.09
$Cu(terpy)^{2+}$	1.81 ± 0.06	−0.68	2.71 ± 0.12
Cu(ida)	2.65 ± 0.02	0.16	
Cu(pdc)	2.97 ± 0.02	0.48	

[a] L = diethylenetriamine (dien), dipicolylamine (dpa), 2,2′,2″-terpyridine (terpy), iminodiacetate (ida^{2-}), pyridine-2,6-dicarboxylate (pdc^{2-}). [b] I = 0.1, KNO_3; these constants are from the work of Yamauchi, Benno, and Nakahara.[30] [c] Calculated with log $K^{Cu}{}_{Cu(py)}$ = 2.49 ± 0.02 of Table I; I = 0.1, $NaNO_3$. [d] See ref 31.

General Conclusions. That the discussed results are of general validity may be further substantiated by the data given in Table III. The coordination tendency of pyridine toward $Cu(dien)^{2+}$, $Cu(dpa)^{2+}$ and $Cu(2,2',2''\text{-terpy})^{2+}$ is, within experimental error, the same: Δ log $K_{Cu} \simeq -0.7$. However, as soon as Cu^{2+} is coordinated by iminodiacetate or pyridine-2,6-dicarboxylate, the tendency to bind pyridine increases substantially and *positive* Δ log K_{Cu} values are observed. Similarly, the coordination of the O ligand *p*-hydroxybenzenesulfonate[30] toward $Cu(2,2',2''\text{-terpy})^{2+}$ is by a factor of 10 larger than toward $Cu(dien)^{2+}$;[31,32] the value for the reaction with $Cu(dpa)^{2+}$ is, as expected, intermediate, because here the tridentate N ligand has only two heteroaromatic N donors. Both series of data, those for the pyridine and the *p*-hydroxybenzenesulfonate complexes, confirm the possibility that the coordination tendency may be promoted by using certain ligand combinations and that in this way also selectivity may be obtained: in the present cases with factors of about 10, the discrimination is quite pronounced.

The following two examples, which agree also with the described ones, are of special interest with regard to biological systems. (i) In equilibrium 11, imidazole coordinates rather



(11)

strongly to a Cu^{2+} complex with an ionized amide group;[33] the value of Δ log K_{Cu} is clearly positive:

$$\begin{aligned}\Delta \log K_{Cu} &= \log K^{Cu(L)}{}_{Cu(L)(Im)} - \log K^{Cu}{}_{Cu(Im)} \\ &= 4.6 \text{ (ref 33)} - 4.22 \text{ (Table I)} = +0.4\end{aligned}$$

(ii) Adenosine forms through coordination with the heteroaromatic N-7 a complex with nickel (hydrogen triphosphate)$^{2-}$ which is 11 times more stable than the one with $Ni(aq)^{2+}$.[11,34] It is to be expected that this increased coordination tendency

---

(27) The somewhat increased stability of the ternary complexes with NH_3 is to a significant part attributable to the relatively low stability of the binary $M(NH_3)_2^{2+}$ complexes. This means, the statistical value for log K_2 − log K_1 = log [(5/2)/(6/1)] = −0.38 is in general larger than the values observed for the differences log $K^{M(NH_3)}{}_{M(NH_3)_2}$ − log $K^{M}{}_{M(NH_3)}$ (cf. the data given in Tables I and II).

(28) Irving, H.; Williams, R. J. P. *Nature (London)* **1948**, *162*, 746–747; *J. Chem. Soc.* **1953**, 3192–3210.

(29) The relative equality of the stability of binary M^{2+}/phosphate complexes has been noted and discussed before.[4]

(30) Yamauchi, O.; Benno, H.; Nakahara, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3458–3462.

(31) Values of Δ log K_{Cu} can in this case not be calculated as the stability constant log $K^{Cu}{}_{Cu(pps)}$ is not known.

(32) The coordination tendency of *n*-butylamine seems also more pronounced toward $Cu(2,2',2''\text{-terpy})^{2+}$ than toward $Cu(dien)^{2+}$;[30] in this case, however, more research is necessary before conclusions may be drawn, especially the stability of the binary $Cu(n\text{-}BuNH_2)^{2+}$ complex should first be determined.

(33) Zuberbühler, A.; Kaden, Th. *Chimia* **1969**, *23*, 418–420.

(34) Mariam, Y. H.; Martin, R. B. *Inorg. Chim. Acta* **1979**, *35*, 23–28.

may also be observed for other 3d metal ions.

In conclusion, in all the described examples, a monodentate ligand coordinates to a metal ion which has already a rather saturated coordination sphere. This situation resembles quite well the conditions present in many metalloenzymes, where only some few coordination positions remain accessible for the substrate. For example, in carbonic anhydrase[35,36] and in carboxypeptidase,[36,37] $\mathrm{Zn^{2+}}$ is coordinated to three imidazole residues, and to one carboxylate and two imidazole groups, respectively; the fourth position at $\mathrm{Zn^{2+}}$ is in both enzymes occupied by a water molecule which may be replaced by the substrate.[36,37] It is striking indeed that imidazole is often observed[7d] in the coordination sphere of metal ions bound to proteins. On the basis of our results, one is tempted to suggest that this is a way to achieve selectivity toward the substrate, which is one of the prime goals in enzymic systems. Aside from the use of certain combinations of ligating atoms, the degree of selectivity in nature may be further promoted by making use also of direct *intra*molecular ligand–ligand interactions which are possible within mixed-ligand complexes.[7e,38] These interactions may be of, e.g., ionic or hydrophobic nature; in any case selectivity will be improved.[39]

Acknowledgment. The potentiometric titrations were carried out with the skillful technical assistance of Ms. Rita Baumbusch and Ms. Madeleine Imhof. The computer was made available by the Rechenzentrum der Universität Basel (Univac 1100/81). These supports and research grants from the Swiss National Science Foundation are gratefully acknowledged.

---

(35) Waara, I.; Lövgren, S.; Liljas, A.; Kannan, K. K.; Bergstén, P.-C. *Adv. Exp. Med. Biol.* **1972**, *28*, 169–187. Kannan, K. K.; Notstrand, B.; Fridborg, K.; Lövgren, S.; Ohlsson, A.; Petef, M. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 51–55.

(36) Chlebowski, J. F.; Coleman, J. E. *Met. Ions Biol. Syst.* **1976**, *6*, 1–140.

(37) Quiocho, F. A.; Lipscomb, W. N. *Adv. Protein Chem.* **1971**, *25*, 1–78. Lipscomb, W. N. *Chem. Soc. Rev.* **1972**, *1*, 319–336.

(38) (a) Fischer, B. E.; Sigel, H. *J. Am. Chem. Soc.* **1980**, *102*, 2998–3008. (b) Sigel, H. "Session Lecture"; Conference Volume of the Vth International Symposium on Solute-Solute-Solvent Interactions (June 1980, Florence); Bertini, I., Lunazzi, L., Dei, A., Eds.; Plenum Publishing Company: New York and London. (c) Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* **1979**, *62*, 1723–1735. (d) Sigel, H.; Naumann, C. F. *J. Am. Chem. Soc.* **1976**, *98*, 730–739.

(39) The kinetics of the $\mathrm{Ni(Nta)^-/Im}$ system have been studied: Banerjea, D.; Kaden, T. A.; Sigel, H. *Inorg. Chim. Acta*, in press.

Contribution from the Department of Chemistry,
Atlanta University, Atlanta, Georgia 30314

Photodecomposition of *cis*-Azidoamminebis(2,4-pentanedionato)cobalt(III). The Photoactive State

JAMES L. REED

Received April 15, 1980

The photodecomposition of *cis*-$\mathrm{Co(acac)_2N_3NH_3}$ (acac = 2,4-pentanedionate) occurs with the formation of $\mathrm{Co(acac)_2}$ and azide radicals. This reaction has been effected with the use of exciting radiations throughout the 250–580-nm region, and in the 250–470-nm region the quantum efficiency for this reaction is surprisingly wavelength independent. Examination of the optical spectra of $\mathrm{Co(acac)_2N_3NH_3}$ and $\mathrm{Co(acac)_3}$ and the respective optical electronegativities of the azide and 2,4-pentanedionate ligands suggests that photooxidation of the 2,4-pentanedionato group should be favored over that of the azido group. Yet photooxidation of the azido group is the only observed reaction. This observation, the relative constancy of the quantum efficiency, and the energy of the threshold for the onset of redox photodecomposition ($(21.3–17.2) \times 10^3$ cm^{-1}) suggest that the photoactive state is a triplet charge-transfer state involving the azido group. The photoreaction has an apparent activation energy of 11.7 kcal/mol, and solvent assistance in the loss of the azide radical is implicated.

Introduction

In a recent communication from these laboratories, the photodecomposition of *cis*-azidoamminebis(2,4-pentanedionato)cobalt(III) ($\mathrm{Co(acac)_2N_3NH_3}$) by 350-nm radiation was examined in some detail.[1] Although the photochemistry of metal azido complexes has received considerable attention in recent years,[1-11] the reasons for their diverse photochemistry are not yet understood. Metal azides undergo one or more of three reported modes of photodecomposition. These are substitution of the azido group, oxidation of the azido group, or formation of coordinated nitrene. The 350-nm irradiation of this complex, which corresponds to one or more charge-transfer excitations,[1,12] yields azide radicals and $\mathrm{Co(acac)_2}$, and only one mode of photodecomposition is observed. The simplicity of the photochemistry is somewhat surprising considering the number of modes of photodecomposition which have been observed for other complexes containing the ligands comprising this complex.[13-19] Thus it provides an excellent test for the various models which have been proposed for metal azide photochemistry and charge-transfer photochemistry in general.[5,7,8]

Although one mode of photodecomposition seems to be favored over numerous others, the quantum efficiency for this

---

(1) J. L. Reed, *Inorg. Chem.*, **17**, 1725 (1978).

(2) J. L. Reed, F. Wang, and F. Basolo, *J. Am. Chem. Soc.*, **94**, 1773 (1972).

(3) H. D. Gafney, J. L. Reed, and F. Basolo, *J. Am. Chem. Soc.*, **95**, 7998 (1973).

(4) J. L. Reed, H. D. Gafney, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 1363 (1974).

(5) W. Beck and K. Schorpp, *Angew. Chem., Int. Ed. Engl.*, **9**, 753 (1970).

(6) G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).

(7) J. I. Zink, *Inorg. Chem.*, **14**, 446 (1975).

(8) T. Inoue, J. F. Endicott, and G. Ferraudi, *Inorg. Chem.*, **15**, 3098 (1976).

(9) M. Katz and H. D. Gafney, *Inorg. Chem.*, **17**, 93 (1978).

(10) V. M. Miskowski, G. L. Nobinger, and G. S. Hammond, *Inorg. Chem.*, **15**, 2904 (1976).

(11) R. M. Dahlgren and J. I. Zink, *Inorg. Chem.*, **18**, 597 (1979).

(12) L. J. Boucher and D. R. Herrington, *Inorg. Chem.*, **11**, 1772 (1972).

(13) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(14) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1962).

(15) N. Filipescu and H. Way, *Inorg. Chem.*, **8**, 1863 (1969).

(16) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Am. Chem. Soc.*, **97**, 219 (1975).

(17) J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.*, **87**, 3348 (1965).

(18) R. A. Pribush, C. K. Poon, C. M. Bower, and A. W. Adamson, *J. Am. Chem. Soc.*, **87**, 3349 (1965).

(19) A. Vogler and A. W. Adamson, *J. Am. Chem. Soc.*, **90**, 5943 (1968).

0020-1669/81/1320-2590$01.25/0