pendence on the concentrations of reactants, added aquo complexes, and HCN as well as for the sensitivity of the system to light. With only a handful of adjustable parameters, the numerical simulations give results in excellent agreement with experiment.

The elements of this mechanism appear applicable to other oxidations of ferrocyanide, and their extension to such systems is currently under investigation. We also hope in the near future to include the results obtained here in a detailed mechanistic study of the oscillatory $Fe(CN)_6^{4-}$–BrO_3^-–SO_3^{2-} reaction.

Acknowledgment. We thank Kenneth Kustin and Mihaly T. Beck for helpful discussions. This work was supported by the National Science Foundation (Grant No. CHE-8800169) and by a U.S.-Hungarian Cooperative Grant from the NSF (Grant No. INT-8613532) and the Hungarian Academy of Sciences.

Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; BrO_3^-, 15541-45-4.

Contribution from Anorganische Chemie III, Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

Kinetics of the Acid Dissociation of Oligopeptide Complexes of Copper(II) and Nickel(II): General-Acid Catalysis with "Noncoordinating" 2,6-Lutidine Type Buffers

Maria Hauröder, Monika Schütz, Klaus J. Wannowius,* and Horst Elias*

Received May 6, 1988

Stopped-flow spectrophotometry was used to study the general-acid catalytic activity of 2,6-lutidine type buffers in the protonation and acid dissociation of the deprotonated triglycine and tetraglycine copper(II) and nickel(II) complexes $Cu(H_{-2}G_3)^-$, $Cu(H_{-1}G_3)$, $Cu(H_{-2}G_4)^-$, $Cu(H_{-1}G_4)$, and $Ni(H_{-2}G_3)^-$ at 298 K and μ = 0.3 M ($NaClO_4$). The buffers applied possess a very limited coordination power only since they are based on H(LS) (=2,6-lutidine-3-sulfonic acid; pK_a = 4.8), AC (=3-acetyl-2,4,6-collidine; pK_a = 5.9), and a series of other sterically hindered substituted 2,6-lutidines to cover the pH range 7.4–3.1. It was found that, at a given pH, the increase of the experimental rate constant with increasing total buffer concentration, which corresponds to rate constant k_{HB} as a measure for general-acid catalysis of an acid HB, is very small. For H(LS) the rate constant k_{HB} ranges from <0.3 M^{-1} s^{-1} (reaction with $Ni(H_{-2}G_3)^-$) to 5.5 M^{-1} s^{-1} (reaction with $Cu(H_{-1}G_3)$), whereas for protonated AC the range is k_{HB} < 0.3 M^{-1} s^{-1} (reaction with $Cu(H_{-2}G_4)^-$) and k_{HB} = 54.7 M^{-1} s^{-1} (reaction with $Cu(H_{-2}G_3)^-$). Comparing the general-acid catalytic activity of acetic acid with that of H(LS), one finds that H(LS) is less active than acetic acid by a factor of >2000 (reaction with $Ni(H_{-2}G_3)^-$) and approximately 260 (reaction with $Cu(H_{-1}G_3)$ and $Cu(H_{-1}G_4)$). It follows from the results that 2,6-lutidine type buffers are well suited to suppress general-acid catalysis in kinetic studies and that especially the H(LS) buffer with its very reduced activity in general-acid catalysis is an attractive substitute for the standard acetate buffer.

Introduction

The kinetics of the acid-catalyzed protonation and dissociation of deprotonated oligopeptide complexes of copper(II) and nickel(II) have been the subject of numerous studies[1-7] by Margerum and co-workers. It was found that the dissociation according to eq 1 (M = Cu(II), Ni(II); $HL^{\pm}$ = triglycine, tetraglycine; $H_{-x}L$ = x-fold deprotonated peptide) is the overall result of a series of protonation steps, each of which follows rate law 2. The observed first-order rate constant proves the existence of several pathways in the sense that, according to (3), water molecules, protons, and the applied acid HB itself can induce the reaction.[2,4,6] As a matter of fact, the situation can even be more complicated as indicated by eq 4 and eq 5.[7] The contribution of the terms $k_H[H^+]$ and $k_{HB}[HB]$ in eq 3 is referred to as being specific-acid catalysis and general-acid catalysis, respectively.[2,7] It is well-known that the extent of general-acid catalysis caused by an acid HB in reaction 1 depends strongly on the nature of HB. With sterically hindered acids such as HB = $H(MES)^{\pm}$, $H(PIPES)^{\pm}$ there is practically no general-acid catalysis,[7] whereas acetic acid gives rise to a substantial contribution of the term $k_{HB}[HB]$ in eq 3.

$$M(H_{-x}L)^{(x-1)-} + (x+1)H^+ \rightarrow M^{2+} + HL^{\pm} \quad (1)$$

$$\text{rate} = k_{obsd}[M(H_{-x}L)^{(x-1)-}] \quad (2)$$

$$k_{obsd} = k_{H_2O} + k_H[H^+] + k_{HB}[HB] \quad (3)$$

$$k_H = k'_H + k_{H,H}[H^+] \quad (4)$$

$$k_{HB} = k'_{HB} + k_{H,HB}[H^+] \quad (5)$$

We reported earlier[8] that buffers based on sterically hindered derivatives of 2,6-lutidine can be used as practically "noncoordinating" buffers. The present kinetic investigation was undertaken to test the behavior of these buffers as acids HB in the acid-catalyzed dissociation of several triglycine (=$HG_3^{\pm}$) and tetraglycine (=$HG_4^{\pm}$) complexes of copper(II) ($Cu(H_{-2}G_3)^-$, $Cu(H_{-1}G_3)$, $Cu(H_{-2}G_4)^-$, $Cu(H_{-1}G_4)$) and nickel(II) ($Ni(H_{-2}G_3)^-$) according to (1). More specifically, the determination of the catalytic activity of these buffers in general-acid catalysis was the main goal, the comparison of acetic acid (pK_a = 4.64) and sterically hindered 2,6-lutidine-3-sulfonic acid (pK_a = 4.80[8]) being of special interest.

Experimental Section

Complexes. The aqueous solutions of the complexes (ionic strength μ = 0.3 M ($NaClO_4$)) were prepared from $Cu(ClO_4)_2 \cdot 6H_2O$ and $Ni(ClO_4)_2 \cdot 6H_2O$ (Alfa) and a 10% excess of the ligands triglycine and tetraglycine (Sigma), respectively. The pH of the solutions was adjusted with NaOH. Only freshly prepared solutions were used for the kinetic runs.

Buffers. The following abbreviations are assigned to the various buffers: H(LS) = 2,6-lutidine-3-sulfonic acid; AC = 3-acetyl-2,4,6-collidine; H(PS) = pyridine-3-sulfonic acid; py = pyridine; ML = 4-methoxy-2,6-lutidine; lu = 2,6-lutidine; NL = 3-nitro-2,6-lutidine; NC = 3-nitro-2,4,6-collidine; CL = 4-cyano-2,6-lutidine; H(MES) = 2-morpholinoethanesulfonic acid, HOAc = acetic acid.

H(LS) (Merck) and H(MES) (Sigma) were commercially available. The $H(AC)^+$ salts of the acids HBF_4, HNO_3, benzenesulfonic acid, and *p*-toluenesulfonic acid were supplied by Merck, Darmstadt, FRG. The other lutidine type buffers were prepared as described earlier.[8] Their purity was checked by ^1H NMR and microanalysis (C, H, N). The

(1) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 6963.
(2) Billo, E. J.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6811.
(3) Bannister, C. E.; Margerum, D. W.; Raycheba, J. M. T.; Wong, L. F. *Faraday Symp. Chem. Soc.* **1975**, *No. 10*, 78.
(4) Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 3072.
(5) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 837.
(6) Youngblood, M. P.; Chelappa, K. L.; Bannister, C. E.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1742.
(7) Bannister, C. E.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 3149.
(8) Bips, H.; Elias, H.; Hauröder, M.; Kleinhans, G.; Pfeifer, S.; Wannowius, K. J. *Inorg. Chem.* **1983**, *22*, 3862.

0020-1669/89/1328-0736$01.50/0

lutidine buffer solutions (except for LS) were prepared by mixing the appropriate amounts of the corresponding lutidine derivative and perchloric acid. The remaining buffers (LS, PS, MES, HOAc) were prepared by mixing with NaOH solution. The pH of the buffer solutions and of the reaction mixtures was measured with a glass electrode (Schott), the proton concentration following from relationship 6,[7] which corrects the measured pH for the ionic strength μ = 0.3 M.

$$-\log [H^+] = pH + 0.1 \quad (6)$$

Kinetic Measurements. The kinetic measurements were done with a modified[9] Durrum stopped-flow spectrophotometer at 298 K by reacting the solution of the metal complex (1 or 2 mM) with the corresponding buffer solution, both being set to μ = 0.3 M ($NaClO_4$). The final pH of the reaction mixtures was measured in 1:1 mixtures of the solutions of the complex and of the buffer after equilibration. The proton concentration was calculated from the mean pH of the various runs at different buffer concentrations according to eq 6.

The absorbance/time data obtained at 430 ($Ni(H_{-2}G_3)^-$), 555 ($Cu(H_{-2}G_3)^-$ and $Cu(H_{-1}G_3)$), 600 ($Cu(H_{-2}G_4)^-$), and 635 nm ($Cu(H_{-1}G_4)$) were stored in a transient recorder and computer-fitted to eq 7 or 8 with a program based on the least-squares method. The rate constants k

$$A = \Delta \exp(-k_{obsd}t) + A_\infty \quad (7)$$

$$A = \Delta_f \exp(-k^f t) + \Delta_s \exp(-k^s t) + A_\infty \quad (8)$$

obtained (k_{obsd}, k^f, k^s), when plotted vs the total buffer concentration, increased linearly according to (9). The second-order rate constant k_{HB}

$$k = k_0 + m[\text{buffer}]_T \quad (9)$$

was calculated from the slope m by using eq 10. The K_a values used in

$$k_{HB} = m(1 + K_a/a(H^+))\varphi \quad (10)$$

eq 10 were taken from the literature and refer to media with an ionic strength of approximately 0.3 M. Correspondingly, the proton activity, $a(H^+)$ (resulting from pH = -log $a(H^+)$), instead of the proton concentration, $[H^+]$, is used in eq 10.

Results and Discussion

One of the major differences between the deprotonated oligopeptide complexes of copper(II) and nickel(II) is that in the case of copper the first protonation step is faster than the second one, whereas for nickel the addition of the first proton is the slowest step.[2,4,7] Consequently, the various consecutive steps of protonation can be observed experimentally for the deprotonated oligopeptide complexes of copper(II) but not for those of nickel(II).[4,6]

The System Copper(II)/Tetraglycine. It was reported for this system[6] that all three steps in reaction sequence 11 are subject to general-acid catalysis, step 1 being very fast, however.[4,6] In

$$Cu(H_{-3}G_4)^{2-} \xrightarrow{1} Cu(H_{-2}G_4)^- \xrightarrow{2} Cu(H_{-1}G_4) \xrightarrow{3} CuG_4^+ \quad (11)$$

the present contribution steps 2 and 3 were therefore studied. At pH 7.9 the species $Cu(H_{-2}G_4)^-$ dominates.[6,10] For a pH jump from 7.9 to 4.8 the absorbance/time data obtained can be fitted best to two exponentials according to eq 8, which means that obviously both steps 2 and 3 of eq 11 are observed under these conditions.

The absorbance/time data obtained from experiments leading to a pH jump from 7.9 to 5.9 can be fitted well to one exponential according to (7) and describe step 2, therefore. These experiments were carried out with buffers based on H(MES) and AC, as well. The data compiled in Table I prove that k_{obsd} is independent of the buffer concentration, which means that there is practically no general-acid catalysis with $H(MES)^\pm$ and $H(AC)^+$ (estimated upper limit: $k_{HB} < 0.3$ M^{-1} s^{-1}).

The addition of increasing amounts of HOAc to the MES buffer increases k_{obsd} and leads to $k_{HOAc} = 834 \pm 97$ M^{-1} s^{-1} (see Table I). The value reported in the literature[6] ($k_{HOAc} = (5.9 \pm 0.2) \times 10^3$ M^{-1} s^{-1}) was derived from studies in the presence of EDTA. The fact that it is so much larger points to an interference of EDTA with the acetate buffer in the earlier study,[6] which was carried out at pH 5.98.

(9) Elias, H.; Fröhn, U.; von Irmer, A.; Wannowius, K. J. *Inorg. Chem.* **1980**, *19*, 869.
(10) Smith, R. M., Martell, A. E., Eds. *Critical Stability Constants*; Plenum Press: New York, 1974; Vol. 1.

Table I. Rate Constants for the Protonation of the Species $Cu(H_{-2}G_4)^-$ According to Step 2 in Eq 11 with Different Acids HB Applied as Buffer Components[a]

HB (pK_a[e])	-log $[H^+]$[b]	$[HB]_T$, M	k_{obsd}, s^{-1}	k_0,[c] s^{-1} (m,[c] M^{-1} s^{-1})	k_{HB},[d] M^{-1} s^{-1}
$H(MES)^\pm$ (6.2[f])	5.96	0.05	0.857	0.851 ± 0.0006 (<0.2[g])	<0.3
		0.1	0.852		
		0.2	0.831		
		0.3	0.842		
		0.4	0.852		
		0.5	0.874		
$H(AC)^+$ (5.91[h])	5.70	0.05	0.900	0.858 ± 0.016 (<0.2[g])	<0.3
		0.1	0.848		
		0.2	0.826		
		0.3	0.828		
		0.4	0.832		
		0.5	0.915		
HOAc[i] (4.64[j])	5.92	0	0.870	1.18 ± 0.20 (51.7 ± 6.0)	834 ± 97 5900 ± 200[k]
		0.01	1.82		
		0.02	2.46		
		0.03	2.90		
		0.04	3.26		
		0.05	3.54		
$H(py)^+$[l] (5.33[m])	5.69	0.05	0.299	0.242 ± 0.027 (0.646 ± 0.088)	1.82 ± 0.25
		0.1	0.304		
		0.2	0.318		
		0.3	0.467		
		0.4	0.490		
		0.5	0.573		

[a] Solution of metal complex adjusted to pH 7.9. [b] Proton concentration in reaction mixture. [c] Obtained by fitting k_{obsd} to eq 9. [d] Obtained from eq 10. [e] pK_a used for calculating k_{HB} from eq 10. [f] Good, N. E.; Winget, G. D.; Winter, W.; Conolly, T. N.; Izawa, S.; Singh, R. M. M. *Biochemistry* **1966**, *5*, 467. [g] Estimated value. [h] Reference 8; μ = 0.5 M (KNO_3). [i] In the presence of $[H(MES)]_T$ = 0.2 M. [j] Feldman, I.; Kovel, L. *Inorg. Chem.* **1963**, *2*, 145. μ = 0.2 M (KNO_3). [k] From ref 6. [l] The vis spectrum points to coordination of py in the product. [m] Kahmann, K.; Martell, A. E. *Inorg. Chem.* **1965**, *4*, 462.

Table II. Rate Constants for the Protonation of the Species $Cu(H_{-1}G_4)$ According to Step 3 in Eq 11 with Different Acids HB Applied as Buffer Components[a]

HB (pK_a[e])	-log $[H^+]$[b]	$[HB]_T$, M	k_{obsd}, s^{-1}	k_0,[c] s^{-1} (m,[c] M^{-1} s^{-1})	k_{HB},[d] M^{-1} s^{-1}
$H(LS)^\pm$ (4.80[f])	4.88	0.05	2.08	2.06 ± 0.04 (1.35 ± 0.12)	2.64 ± 0.22 (2.74 ± 0.32[g])
		0.1	2.23		
		0.2	2.34		
		0.3	2.49		
		0.4	2.65		
		0.5	2.69		
HOAc[h] (4.64[i])	4.87	0	2.37	2.65 ± 0.30 (283 ± 10)	665 ± 24 (610 ± 40[j])
		0.01	5.48		
		0.02	8.33		
		0.03	11.8		
		0.04	14.0		
		0.05	16.4		
$H(py)^+$[k] (5.3[l])	4.45	0.05	1.48	1.54 ± 0.10 (1.02 ± 0.40)	1.33 ± 0.44
		0.1	1.79		
		0.2	1.72		
		0.3	1.90		
		0.4	1.91		

[a] Solution of metal complex adjusted to pH 6.5. [b] Proton concentration in reaction mixture. [c] Obtained by fitting k_{obsd} to eq 9. [d] Obtained from eq 10. [e] pK_a used for calculating k_{HB} from eq 10. [f] Reference 8; μ = 0.5 M (KNO_3). [g] Mean value of two independent measurements. [h] In the presence of $[H(LS)]_T$ = 0.2 M. [i] Feldman, I.; Kovel, L. *Inorg. Chem.* **1963**, *2*, 145. μ = 0.2 M (KNO_3). [j] Reference 6. [k] The vis spectrum points to the coordination of py in the product. [l] Kahmann, K.; Martell, A. E. *Inorg. Chem.* **1965**, *4*, 462.

As compared to that for acetic acid, the general-acid catalytic activity of the species $H(py)^+$ is rather small ($k_{HB} = 1.82 \pm 0.25$ M^{-1} s^{-1}; see Table I). One has to consider, however, that the vis spectra indicate the coordination of pyridine in the product, which is in line with the results reported for similar copper(II) complexes.[5]

Rate constants obtained for protonation step 3 in sequence 11 are compiled in Table II. They were derived from experiments corresponding to a pH jump from 6.5 to approximately 4.8. One

Table III. Rate Constants for the Protonation of the Species $Cu(H_{-2}G_3)^-$ and $Cu(H_{-1}G_3)$ According to Steps 2 and 3 in Eq 12 with Different Acids HB Applied as Buffer Components[a]

			$Cu(H_{-2}G_3)^-$				$Cu(H_{-1}G_3)$			
HB (pK_a[b])	−log $[H^+]$[c]	$[HB]_T$, M	Δ_f[f]	k^f, s^{-1}	k^f_0,[d] s^{-1} (m^f,[d] M^{-1} s^{-1})	k^f_{HB},[e] M^{-1} s^{-1}	Δ_s[f]	k^s, s^{-1}	k^s_0,[d] s^{-1} (m^s,[d] M^{-1} s^{-1})	k^s_{HB},[e] M^{-1} s^{-1}
H(MES)[±] (6.2[f])	6.03	0.05	1748	10.2	9.97 ± 0.15	6.78 ± 0.80	180	1.82	1.55 ± 0.07	<0.3
		0.1	1823	10.4	(4.01 ± 0.48)		181	1.52	(<0.2[g])	
		0.2	1856	10.9			199	1.40		
		0.3	1724	11.1			220	1.46		
		0.4	1802	11.3			241	1.44		
		0.5	1787	12.2			246	1.67		
$H(AC)^+$ (5.91[h])	5.76	0.05	1962	11.2	8.94 ± 0.97	54.7 ± 5.0	232	1.50	0.85 ± 0.09[i]	<0.3
		0.1	2025	12.5	(35.0 ± 3.2)		274	1.20	(<0.2[g])	
		0.2	2023	16.6			371	1.11		
		0.3	2072	17.9			411	0.90		
		0.4	2101	22.0			498	0.93		
		0.5	2168	27.9			560	0.98		
H(LS)[±] (4.80[h])	4.89	0.05						2.51[j]	2.64 ± 0.19	5.5 ± 1.2
		0.1						3.04[j]	(2.78 ± 0.62)	
		0.2						3.43[j]		
		0.3						3.58[j]		
		0.4						3.48[j]		
		0.5						4.07[j]		
HOAc[k] (4.64[l])	5.82	0	2002	10.0	6.1 ± 5.8	22000	320	1.40	1.62 ± 0.20	791 ± 85
		0.01	1732	25.3	(1690 ± 240)	±3100	358	2.62	(60.7 ± 6.5)	
		0.02	1404	30.5			312	2.58		
		0.03	1362	53.3		34000[m]	359	3.60		
		0.04	1274	80.7			365	4.05		
		0.05	*n*	*n*			387	4.58[j]		
HOAc[o] (4.64[l])	4.85	0						3.52[j]	3.39 ± 0.20	691 ± 15
		0.01						6.50[j]	(302 ± 6.7)	
		0.02						9.29[j]		
		0.03						12.0[j]		
		0.04						15.8[j]		
		0.05						18.5[j]		
$H(py)^+$[p] (5.33[q])	5.67	0.05	1251	19.1	6.8 ± 1.7	1080	403	0.307	0.294 ± 0.005	0.58 ± 0.05
		0.1	982	52.3	(394 ± 46)	±130	460	0.311	(0.211 ± 0.018)	
		0.2	684	91.8			280	0.331		
		0.3	558	120			146	0.367		
		0.4	*n*	*n*				0.397[j]		
$H(py)^+$[p] (5.33[q])	4.45	0.05						1.84[j]	2.05 ± 0.11	<0.2
		0.1						2.36[j]	(<0.2[g])	
		0.2						2.12[j]		
		0.3						2.16[j]		
		0.4						1.76[j]		

[a] Solution of metal complex adjusted to pH 9.25. [b] pK_a used for calculating k_{HB} from eq 10. [c] Proton concentration in reaction mixture. [d] Obtained by fitting k^f, k^s, or k_{obsd} to eq 9. [e] Obtained from eq 10. [f] See footnote *f* in Table I. [g] Estimated value. [h] Reference 8; μ = 0.5 M (KNO_3). [i] The observed rate constants for the slow step, k^s, are adequately described by $k^s = (k^s_1 + k^s_0K^s[HB]_T)/(1 + K^s[HB]_T)$. Computer fitting resulted in $k^s_1 = 3.8 \pm 6.3$ s^{-1}, $k^s_0 = 0.85 \pm 0.09$ s^{-1}, and $K^s = 71 \pm 200$ M^{-1}. [j] k_{obsd}. [k] In the presence of $[H(MES)]_T = 0.2$ M. [l] See footnote *j* in Table I. [m] Reference 3. [n] Too fast for accurate stopped-flow detection. [o] In the presence of $[H(LS)]_T = 0.2$ M. [p] The vis spectrum points to coordination of py in the product. [q] See footnote *m* in Table I. [r] Arbitrary units.

learns that the activity of H(LS) in general-acid catalysis is very small indeed, rate constant k_{HB} amounting to only 2.64 ± 0.22 M^{-1} s^{-1}. In contrast to the case for H(LS), acetic acid again is found to have a strong general-acid catalytic activity, namely k_{HB} = 665 ± 24 M^{-1} s^{-1}. The rate constant reported for acetic acid earlier[6] (k_{HB} = 610 ± 40 M^{-1} s^{-1}) is in good agreement with the present result. As observed for the protonation of the species $Cu(H_{-2}G_4)^-$ (see Table I), the general-acid catalytic activity of the acid $H(py)^+$ in step 3 of eq 11 is very small (k_{HB} = 1.13 ± 0.44 M^{-1} s^{-1}). It is important to point out that the vis spectra of the product solution again indicate the coordination of pyridine, whereas in the case of the acid H(LS) no spectral changes are observed. The lutidine derivative LS is obviously not coordinated to the copper at pH 4.8.

The System Copper(II)/Triglycine. With a Cu^{2+}/triglycine solution adjusted to pH 9.25 as the starting material the stopped-flow experiments were carried out in such a way that the final pH of the buffered reaction mixture was either approximately 5.8 or approximately 4.8. In the first case (pH jump from 9.25 to 5.8) the reaction appears to proceed in three steps: a very fast step (observed as a nontraceable jump in absorbance) is followed by two exponential steps which can be fitted to eq 8. The very fast step 1 probably has to be assigned to the protonation of a hydroxo species according to eq 12. Steps 2 and 3 then follow

$$Cu(H_{-2}G_3)(OH)^{2-} \xrightarrow{1} Cu(H_{-2}G_3)^- \xrightarrow{2} Cu(H_{-1}G_3) \xrightarrow{3} CuG_3^+ \quad (12)$$

as traceable consecutive reactions, which means that at the relatively high pH of 5.8 appreciable amounts of the species CuG_3^+ are already formed.

In the experiments with a pH jump from 9.25 to 4.8 even step 2 becomes too fast for the stopped-flow time scale. As a consequence, the initial nontraceable jump in absorbance becomes larger and the observed absorbance/time data describing step 3 in eq 12 can be fitted to one exponential. The results obtained for both types of experiments are summarized in Table III.

The general-acid catalytic activity of H(MES) is such that there is practically no effect on step 3 (k_{HB} < 0.3 M^{-1} s^{-1}) and a small effect on step 2 (k_{HB} = 6.78 ± 0.80 M^{-1} s^{-1}). For the acid $H(AC)^+$ a considerable general-acid contribution is found for step 2 whereas the results obtained for step 3 are somewhat surprising. The rate constant k_{obsd} for step 3 first decreases slightly with increasing buffer concentration and then levels, the corresponding preexponential factor Δ_s increasing clearly. One has to assume that obviously there is some kind of interaction between AC and the copper species involved in step 3, which makes the buffer less suitable for the study of this specific reaction.

The general-acid catalysis produced by the acid $H(py)^+$ is very pronounced for step 2 (k_{HB} = 1080 ± 130 M^{-1} s^{-1}) and very small for step 3 (k_{HB} = 0.58 ± 0.05 and <0.2 M^{-1} s^{-1}, respectively; see Table III). The high catalytic activity of $H(py)^+$ in step 2 is in line with that of 2,6-lutidine (k_{HB} = 390 M^{-1} s^{-1}) found for the pH range 6–8.[1] It was reported[5] that at high pH 2,6-lutidine and pyridine form ternary complexes with the species $Cu(H_{-2}G_3)^-$ (K_{lu}

= 4.0 and K_{py} = 2.1 M^{-1}, respectively). In the presence of pyridine the vis spectrum of the reaction mixture is indeed different from that obtained in solutions buffered with MES. The collidine base AC, however, does not change the vis spectrum.

For the acids $H(MES)^{\pm}$ and $H(AC)^{+}$ the size of Δ_f does not change significantly with increasing buffer concentration $[HB]_T$ (see Table III), which indicates noncoordination of these acids to the species $Cu(H_{-2}G_3)^-$ and which is in line with the observation that the vis spectra do not change with $[HB]_T$. For the acids $H(py)^+$ and HOAc (in the presence of MES), however, Δ_f decreases clearly with $[HB]_T$, which points to coordination to the species $Cu(H_{-2}G_3)^-$. The increase (or decrease) in Δ_s with $[HB]_T$ for $H(MES)^{\pm}$, $H(AC)^+$, and HOAc (or $H(py)^+$) suggests coordination of these acids to the species $Cu(H_{-1}G_3)$. In terms of a general comparison, the species $Cu(H_{-1}G_3)$ appears to offer more "vacant" coordination sites than the species $Cu(H_{-2}G_3)^-$.

The general-acid catalytic effect of the lutidine-type acid H(LS) on step 3 is small (k_{HB} = 5.5 ± 1.2 M^{-1} s^{-1}; see Table III), and admixing of acetic acid with the H(LS) buffer again displays the effectiveness of this acid in general-acid catalysis (k_{HB} = 691 ± 15 M^{-1} s^{-1}; see Table III). Admixing of acetic acid with a MES-buffered solution allows the determination of the general-acid rate constant k_{HB} of acetic acid for both step 2 (k_{HB} = 22000 ± 3100 M^{-1} s^{-1}) and step 3 (k_{HB} = 791 ± 85 M^{-1} s^{-1}). Comparing the k_{HB} values obtained for acetic acid at pH 4.75 (H(LS) buffer; k_{HB} = 691 ± 15 M^{-1} s^{-1}) and pH 5.72 (MES buffer; k_{HB} = 791 ± 85 M^{-1} s^{-1}), one learns that this rate constant seems to be independent of pH. The enormously large k_{HB} value of acetic acid for step 2 (22000 M^{-1} s^{-1}) is somewhat smaller than that reported[3] (34000 M^{-1} s^{-1}). One has to consider, however, that the higher value reported was obtained in the presence of EDTA[3] and for solutions with a smaller ionic strength (μ = 0.1 M ($NaClO_4$)).

The System Nickel(II)/Triglycine. As pointed out above, the rate of protonation of the nickel(II) complex anion $Ni(H_{-2}G_3)^-$ is controlled by the first protonation step and follows eq 13. The

$$Ni(H_{-2}G_3)^- + 3H^+ \rightarrow Ni^{2+} + HG_3^{\pm} \qquad (13)$$

experiments were carried out with solutions of $Ni(H_{-2}G_3)^-$ (adjusted to pH 9.5), which were reacted with a series of buffer solutions with different concentrations in the pH range 4.6–8. In all cases the absorbance/time data obtained could be fitted to eq 7 and the resulting rate constants are summarized in Table IV.

Most of the acids HB applied for buffering are of the 2,6-lutidine type. Before discussing the results in detail, one should therefore consider the following facts: (i) complex formation of the Ni^{2+} aquo cation with 2,6-lutidine is very weak (K_1 = 1.6 M^{-1} [8]); (ii) complex formation of the square-planar species $Ni(H_{-2}G_3)^-$ with 2,6-lutidine to form $Ni(H_{-2}G_3)(lu)^-$ is reported to be considerable (K = 11 M^{-1} [5]); (iii) acid dissociation of the species $Ni(H_{-2}G_3)^-$ was found to be general-acid catalyzed,[7] whereas for the species $Ni(H_{-2}G_3)(lu)^-$ general-acid catalysis was not observed,[5] (iv) acid dissociation of the anion $Ni(H_{-2}G_3)^-$ follows a rather complicated pH profile;[7] (v) the specific-acid catalysis of the dissociation of the species $Ni(H_{-2}G_3)^-$ is reported[7] to follow eq 14. It is very essential for the present study to point out that

$$k_{obsd} = k_{H_2O} + k_H[H^+] + k_{H,H}[H^+]^2 \qquad (14)$$

the formation of ternary complexes with any of the lutidine buffers applied was not spectroscopically observed. This would mean, at least, that the protolytic dissociation of the complex $Ni(H_{-2}G_3)^-$ is faster than ternary complex formation.

It follows from Table IV that, at a given pH, the rate of acid dissociation of the species $Ni(H_{-2}G_3)^-$ is practically independent of the buffer concentration $[HB]_T$ for HB = $H(LS)^{\pm}$, $H(AC)^+$, $H(MES)^{\pm}$, $H(lu)^+$, and $H(ML)^+$. A slight increase in k_{obsd} for HB = $H(MES)^{\pm}$, corresponding to k_{HB} = 0.28 M^{-1} s^{-1}, is close to what was reported earlier[7] (k_{HB} = 0.5 M^{-1} s^{-1}). For H(LS), AC, lu, and ML an upper limit of k_{HB} < 0.4 M^{-1} s^{-1} can be estimated.

The acid $H(py)^+$ was reported to be very effective as a general-acid catalyst in the protonation of $Ni(H_{-2}G_3)^-$[7] (k_{HB} = 66 M^{-1} s^{-1}). Figure 1 compares the catalytic activity of $H(py)^+$, H(LS), and HOAc at pH 4.9 and demonstrates the catalytic nonactivity of H(LS), contrasting the effectiveness of $H(py)^+$ and especially

Table IV. Rate Constants for the Protonation of the Species $Ni(H_{-2}G_3)^-$ According to Reaction 13 with Different Acids HB Applied as Buffer Components[a]

HB (pK_a[e])	$-\log [H^+]$[b]	$[HB]_T$, M	k_{obsd}, s^{-1}	k_0,[c] s^{-1} (m,[c] M^{-1} s^{-1})	k_{HB},[d] M^{-1} s^{-1}
$H(LS)^{\pm}$ (4.80[f])	4.98	0.1	1.11	1.11 ± 0.01 (<0.15[g])	<0.3
		0.15	1.10		
		0.2	1.11		
		0.25	1.12		
		0.3	1.13		
$H(AC)^+$ (5.91[f])	5.91	0.025	0.122	0.124 ± 0.002 (<0.15[g])	<0.3
		0.05	0.129		
		0.1	0.127		
		0.15	0.122		
		0.2	0.124		
		0.25	0.123		
		0.3	0.118		
$H(MES)^{\pm}$ (6.2[h])	6.36	0.036	0.103	0.104 ± 0.005 (0.115 ± 0.028)	0.28 0.5[i]
		0.09	0.120		
		0.21	0.130		
		0.3	0.136		
$H(lu)^+$ (6.96[f])	6.96	0.06	0.053	0.050 ± 0.005 (<0.1[g])	<0.2
		0.09	0.048		
		0.12	0.055		
		0.15	0.043		
$H(ML)^+$ (8.05[f])	8.12	0.03	0.032	0.030 ± 0.003 (<0.2[g])	<0.4
		0.04	0.031		
		0.05	0.029		
		0.07	0.026		
HOAc[j] (4.64[k])	6.16	0	0.098	0.11 ± 0.020 (5.07 ± 0.16)	138 ± 4.4
		0.05	0.362		
		0.1	0.649		
		0.15	0.891		
		0.2	1.101		
HOAc[l] (4.64[k])	6.25	0	0.080	0.074 ± 0.013 (4.207 ± 0.095)	140 ± 3.2
		0.05	0.146		
		0.1	0.478		
		0.15	0.714		
		0.2	0.917		
HOAc[m] (4.64[k])	5.25	0	0.460	0.417 ± 0.034 (125.8 ± 1.6)	533 ± 6.8
		0.005	1.05		
		0.0125	1.92		
		0.025	3.56		
		0.0375	5.16		
HOAc[m] (4.64[k])	4.95	0	0.989	0.940 ± 0.065 (246.4 ± 3.0)	646 ± 7.9 770[l]
		0.005	2.21		
		0.0125	3.94		
		0.025	7.01		
		0.0375	10.27		
HOAc[m] (4.64[k])	4.65	0	2.11	1.92 ± 0.18 (439 ± 8.8)	795 ± 16
		0.005	4.16		
		0.0125	7.22		
		0.025	12.60		
		0.0375	18.6		

[a] Solution of metal complex adjusted to pH = 9.5. [b] Proton concentration in reaction mixture. [c] Obtained by fitting k_{obsd} to eq 9. [d] Obtained from eq 10. [e] pK_a used for calculating k_{HB} from eq 10. [f] Reference 8; μ = 0.5 M (KNO_3). [g] Estimated value. [h] See footnote *f* in Table I. [i] Reference 7. [j] In the presence of $[AC]_T$ = 0.2 M. [k] See footnote *j* in Table I. [l] In the presence of $[H(MES)]_T$ = 0.2 M. [m] In the presence of $[H(LS)]_T$ = 0.15 M.

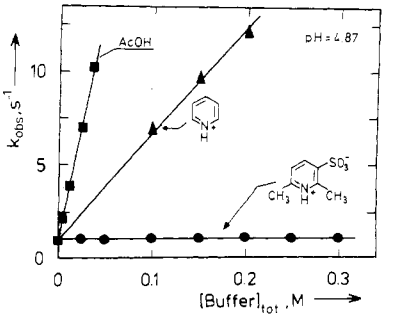

Figure 1. Experimental rate constant k_{obsd} for reaction 13 as studied with different acids HB as buffer components at 298 K (see Table IV; data for $H(py)^+$ taken from ref 7).

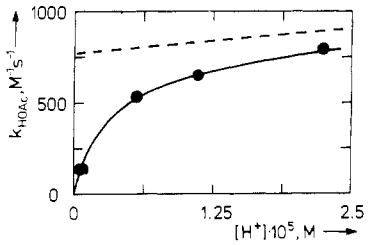

Figure 2. Dependence of rate constant k_{HOAc} for reaction 13 on the concentration of H_3O^+ (see Table IV; dashed line corresponds to eq 15[7]).

HOAc. The rate constant $k_{HB} = 646 \pm 7.9$ M^{-1} s^{-1} obtained for acetic acid at pH 4.95 (in the presence of a sufficiently high concentration of H(LS); see Table IV) is very close to $k_{HB} = 770$ M^{-1} s^{-1} reported earlier.[7]

One could still argue that the nonactivity of the 2,6-lutidine type buffers in general-acid catalysis is due to "axial blocking"[5] as a consequence of lutidine coordination. To rule out this possibility, reaction 13 was studied with acetic acid, at a pH of approximately 6.1, not only with AC but also with MES being present as buffer (see Table IV). The fact that the two rate constants obtained for acetic acid are identical ($k_{HB} = 138 \pm 4.4$ and 140 ± 3.2 M^{-1} s^{-1}, respectively) clearly proves that ternary complexes with the 2,6-lutidine base AC are not formed.

In addition, experiments were carried out with solutions of $Ni(H_{-2}G_3)^-$ containing appropriate amounts of AC to allow complex formation before the stopped-flow experiment. These solutions were then reacted with acid solutions containing either $^1/_2$ equiv of $HClO_4$ or 1 equiv of the cation $H(AC)^+$ (the final pH of the reaction mixtures was the same). These experiments led to identical rate constants, which further proves that neither the free base AC nor the acid $H(AC)^+$ contribute or interfere. The study of reaction 13 with acetic acid at different pH values (adjusted with AC, H(MES), or H(LS) buffer; see Table IV) leads to different values for k_{HOAc} ($=k_{HB}$ for acetic acid). Figure 2 shows that k_{HOAc} increases with increasing proton concentration, but obviously not linearly according to eq 15 as suggested earlier.[7]

$$k_{HOAc} = k_{0,HOAc} + k_{H,HOAc}[H^+] \qquad (15)$$

The dashed line in Figure 2 characterizes the limiting rate at higher proton concentration and follows from published data[7] and eq 15, respectively. One learns that at low proton concentrations the dependence $k_{HOAc} = f([H^+])$ is more complicated and that an extrapolation of eq 15 into this pH range is not allowed. As a consequence, some aspects of the mechanistic interpretation given on the basis of eq 15[7] have to be reconsidered.

The experimental curve shown in Figure 2 is more adequately described by eq 16. For $k_{H,HOAc} = 5.5 \times 10^6$ M^{-2} s^{-1} (as taken

$$k_{HOAc} = \frac{k_1K_1[H^+]}{1 + K_1[H^+]} + k_{H,HOAc}[H^+] \qquad (16)$$

from the literature[7]) computer fitting of eq 16 to the data in Figure 2 leads to $k_1 = 735 \pm 31$ M^{-1} s^{-1} and $K_1 = (3.73 \pm 0.38) \times 10^5$ M^{-1}. The experimental data do not prove the existence of an additional proton-independent term in eq 16; if there is one, it can only be small (<25 M^{-1} s^{-1}).

Margerum et al.[11] have shown for the mechanism of the acid dissociation kinetics of deprotonated polypeptide complexes that so-called "outside" protonation of a coordinated deprotonated carboxamide group[12] is quite common. In line with this the term $k_{H,HOAc}[H^+]$ in eq 15 has been assigned to the rate-controlling attack of HOAc at the outside-protonated complex $Ni(H_{-2}G_3)H$,[7] whereas the term $k_{0,HOAc}$ has been interpreted as describing the attack of HOAc at the species $Ni(H_{-2}G_3)^-$.[7]

Equation 16 suggests a 2-fold outside protonation to be involved, as described by the sequence (17)–(20) (HB = HOAc). As-

$$Ni(H_{-2}G_3)^- + H^+ \overset{K_{1H}}{\rightleftharpoons} Ni(H_{-2}G_3)H \qquad (17)$$

$$Ni(H_{-2}G_3)H + HB \xrightarrow{k_{1H,HB}} Ni(aq)^{2+} + G_3^- + B^- \qquad (18)$$

$$Ni(H_{-2}G_3)H + H^+ \overset{K_{2H}}{\rightleftharpoons} Ni(H_{-2}G_3)H_2^+ \qquad (19)$$

$$Ni(H_{-2}G_3)H_2^+ + HB \xrightarrow{k_{2H,HB}} Ni(aq)^{2+} + G_3^- + HB \qquad (20)$$

suming fast equilibration according to (17) and (19), relationship (21) follows from this sequence of reactions. For $K_{2H}[H^+] \ll 1$,

$$k_{HOAc} = \frac{k_{1H,HB}K_{1H}[H^+] + k_{2H,HB}K_{1H}K_{2H}[H^+]^2}{1 + K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2} \qquad (21)$$

i.e., negligible second protonation in the pH range 3.5–6 (corresponding to $K_{2H} \leq 10^2$ M^{-1}), eq 21 is reduced to eq 22, which

$$k_{HOAc} = \frac{k_{1H,HB}K_{1H}[H^+]}{1 + K_{1H}[H^+]} + \frac{k_{2H,HB}K_{1H}K_{2H}[H^+]^2}{1 + K_{1H}[H^+]} \qquad (22)$$

describes the experimental curve observed for the pH range 4.6–6.2 (see Figure 2) adequately, since the contribution of the second term in eq 22 is only small for this pH range. In addition, it follows for pH $\leq$ 4.5 that $k_{2H,HB}K_{1H}K_{2H}[H^+]^2/(1 + K_{1H}[H^+]) \approx k_{2H,HB}K_{2H}[H^+] = k_{H,HOAc}[H^+]$ (see eq 15 and 16), so that eq 16 and eq 22 become identical with $k_1 \triangleq k_{1H,HB}$, $K_1 \triangleq K_{1H}$, and $k_{H,HOAc} \triangleq k_{2H,HB}K_{2H}$.

Although there is no detectable absorbance change at 430 nm during the mixing time of the stopped-flow apparatus (cf. ref 7), which would point to an appreciable formation of an outside-protonated complex, eq 22 implies the formation of an outside-protonated complex with $\log K_{1H} = 5.6 \pm 0.1$. It is not unexpected that the outside protonation does not necessarily result in an absorbance change in the ligand field band at 430 nm because primarily only peripheral oxygen atoms in the complex are involved.

In earlier work outside-protonation constants have been evaluated by spectroscopic and/or kinetic methods. For similar complexes, e.g. $[Ni(H_{-2}G_3)lu]^+$ ($\log K_{1H} = 3.6$[5]) and $Ni(H_{-3}G_4)^{2-}$ ($\log K_{1H} = 4.2$[12]), somewhat smaller values were found. It has been argued[5,11] that hydrogen bonding within the complexes is responsible for an increase in the stability of the outside-protonated species.

The essential mechanistic information resulting from Figure 2 is an assignment of rate constants that contradicts earlier ones.[7] Margerum et al.[7] studied the effect of general-acid catalysis at pH < 5, where, according to $K_{1H} = 3.7 \times 10^5$ M^{-1} following from the present study, the complex $Ni(H_{-2}G_3)^-$ is more or less fully protonated. As a consequence, the experimental rate constant k_1 in eq 16 (which corresponds to $k_{0,HOAc}$ in eq 15 and to $k_{1H,HB}$ in eq 22) describes the attack of HOAc at the species $Ni(H_{-2}G_3)H$ (*not* $Ni(H_{-2}G_3)^-$[7]). Correspondingly, rate constant $k_{H,HOAc}$ in eq 16 has to be assigned to the attack of HOAc at the doubly protonated species $Ni(H_{-2}G_3)H_2^+$ (*not* $Ni(H_{-2}G_3)H^7$). As to the mechanistic meaning of the specific-acid-catalyzed pathway $k_H[H^+]$ there still remains the ambiguity whether (i) the proton attack is rate-determining at a donor nitrogen, leading to bond cleavage, or (ii) fast outside protonation takes place at the carboxamide oxygen and solvent molecules displace the polypeptide ligand in the species $Ni(H_{-2}G_3)H$ in a rate-determining step. In the latter case the rate constant k_H is a composite, $k_H = k_{1H,HOH}K_{1H}$, where $k_{1H,HOH}$ describes the attack of a water molecule at the outside-protonated species $Ni(H_{-2}G_3)H$. From the experimental data a decision between these two alternatives seems to be impossible at this stage.

Table V and Figure 3 present the k_{obsd} data obtained for reaction 13 when studied in the pH range 3–8 with differently substituted 2,6-lutidines as buffers. Since the buffers applied (lu, AC, H(LS), NL, NC, CL) no not contribute as general-acid catalysts, the dependence $k_{obsd} = f([H^+])$ shown in Figure 3 describes the specific-acid catalysis for reaction 13. It is very satisfying to see that the data obtained with the different buffers complement each

(11) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 497.
(12) Paniago, E. B.; Margerum, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 6704.

Table V. Rate Constants for the Protonation of the Species $Ni(H_{-2}G_3)^-$ According to Reaction 13 with Different Lutidine Type Acids HB Applied as Buffer Components[a]

HB (symbol[c])	$[HB]_T$, M	$-\log [H^+]$[b]	k_{obsd}, s^{-1}
$H(lu)^+$ (□)	0.2	7.84	0.020
		7.74	0.014
		7.68	0.015
		7.32	0.018
		6.99	0.028
		6.83	0.030
		6.66	0.040
		6.38	0.060
		6.26	0.070
		6.07	0.090
		6.03	0.10
		5.96	0.11
$H(AC)^+$ (▲)	0.2	6.62	0.040
		6.50	0.040
		6.16	0.060
		5.69	0.15
		5.28	0.34
$H(LS)^±$ (○)	0.2	5.66	0.26
		4.86	0.98
		4.24	4.06
		3.97	8.20
$H(NL)^+$ (●)	0.05	3.67	21.6
		3.60	26.4
		3.46	35.7
		3.29	49.5
		3.25	53.4
		3.16	66.0
		3.09	70.8
$H(NC)^+$ (◇)	0.012	3.66	22.4
	0.015	3.56	27.4
$H(CL)^+$ (▼)	0.009	3.99	8.94
	0.012	3.96	10.4
	0.015	3.89	11.4

[a] Solution of the metal complex adjusted to pH = 9.5. [b] Proton concentration in reaction mixture. [c] Symbol used for HB in Figure 3.

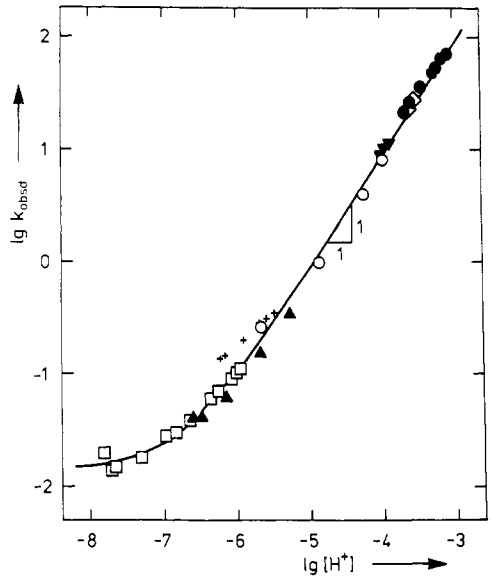

Figure 3. Dependence of the experimental rate constant k_{obsd} at 298 K for reaction 13 on the concentration of H_3O^+ in the pH range 7.4–3.1 (the symbol + corresponds to MES; for the other symbols see Table V).

other and overlap consistently and that the MES data (symbol +) fit in as well. The whole body of data can be fitted to eq 23

$$k_{obsd} = k_{H_2O} + k_H[H^+] \quad (23)$$

with $k_{H_2O} = (1.49 \pm 0.06) \times 10^{-2}$ s^{-1} and $k_H = (8.57 \pm 0.20) \times 10^4$ M^{-1} s^{-1}. On the basis of measurements in the pH range 3–4 in the presence of HOAc and chloroacetic acid (both of which are strong general-acid catalysts), eq 14 was suggested[7] to govern the catalytic activity of protons for reaction 13 ($k_{H_2O} = 8.6 \times 10^{-2}$ s^{-1}, $k_H = 9.5 \times 10^4$ M^{-1} s^{-1}, and $k_{H,H} = 1.1 \times 10^8$ M^{-2} s^{-2}). The agreement in k_H is acceptable (8.57×10^4 and 9.5×10^4 M^{-1} s^{-1}, respectively), whereas the values obtained for k_{H_2O} disagree considerably (0.0149 and 0.086 s^{-1}, respectively) and the term $k_{H,H}[H^+]^2$ is missing in the present study. Due to the absence of general-acid catalysis in the present study one is allowed to assume that the data presented in Table V and Figure 3 are more reliable than those derived earlier[7] under more complicated experimental conditions. This would mean that the squared term in eq 14 can be neglected and that, according to eq 16, the acid dissociation of the species $Ni(H_{-2}G_3)^-$ is initiated simply by bimolecular proton attack followed by a rate-limitng rearrangement reaction.

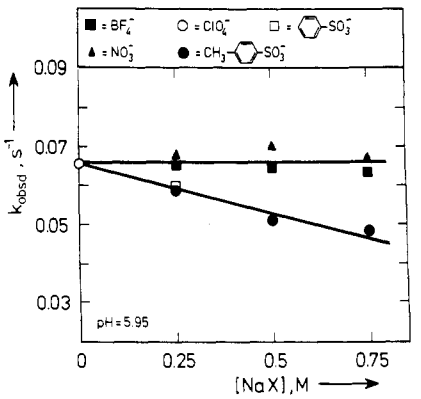

Figure 4. Anion effect on the experimental rate constant k_{obsd} at 298 K for reaction 13 as studied with the buffer system $AC/H(AC)^+X^-$ (μ = 1.0 M ($NaX + NaClO_4$)).

Effect of Anions. The application of 2,6-lutidine type bases such as lu, AC, ML, NL, NC, and CL as buffer components necessitates the introduction of acids HX to prepare mixtures of the free lutidine base and its lutidinium salt. The acid dissociation of the species $Ni(H_{-2}G_3)^-$ was studied with the buffer system $AC/H(AC)^+X^-$ at pH 5.95 (μ = 1.0 M ($NaX + NaClO_4$)), the anion X being perchlorate, nitrate, tetrafluoroborate, and benzenesulfonate as well as *p*-toluenesulfonate. Figure 4 shows that for $X^- = BF_4^-$, NO_3^- the experimental rate constant k_{obsd} is independent of the concentration of NaX. It is somewhat surprising (and not readily understandable) to see that for X = benzenesulfonate, *p*-toluenesulfonate there is a slight decrease in k_{obsd} with increasing salt concentration. It follows from these experiments, however, that the salts $H(AC)^+ClO_4^-$, $H(AC)^+BF_4^-$, and $H(AC)^+NO_3^-$ are well suited from the kinetic point of view. Taking into account the fact that the perchlorate and nitrate tend to explode upon heating, the tetrafluoroborate appears to be the best choice for both buffer preparation and storage of the base AC, which is slightly air-sensitive.

Conclusions

The protonation and dissociation of the oligopeptide complexes $Cu(H_{-2}G_3)^-$, $Cu(H_{-1}G_3)$, $Cu(H_{-2}G_4)^-$, $Cu(H_{-1}G_4)$, and $Ni(H_{-2}G_3)^-$, which were studied in detail by Margerum and coworkers, is known to be subject to specific-acid catalysis as well as to general-acid catalysis. The contribution of the general-acid-catalyzed pathway depends on the nature of the acid applied in the sense that a weakly coordinating acid such as $H(MES)^±$ is much less catalytically effective than carbonic acids such as acetic acid.[7]

The present reinvestigation of the above-mentioned reactions with 2,6-lutidine type buffers, which have a very limited coordination power,[8] was undertaken to study the effect of steric hindrance on the general-acid catalytic activity of buffer acids. The overall result is that buffers based on the 2,6-dimethylpyridine system, with its two methyl groups "shielding" the nitrogen, are indeed very weak general acids. The rate constant k_{HB} is, according to eq 3, a measure for the general-acid catalytic activity of an acid HB. Comparing a typical buffer acid HB such as acetic acid with the 2,6-lutidine type buffer acids applied in the present study, we find the following ratios for the protonation or acid

dissociation of the various complexes at a given pH:

$k_{HOAc}:k_{H(AC)^+} > 2000:1$ ($Cu(H_{-2}G_4)^-$; Table I)

$k_{HOAc}:k_{H(LS)^\pm} = 252:1$ ($Cu(H_{-1}G_4)$; Table II)

$k_{HOAc}:k_{H(LS)^\pm} = 275:1$ ($Cu(H_{-1}G_3)$; Table III)

$k_{HOAc}:k_{H(AC)^+} > 2000:1$ ($Cu(H_{-1}G_3)$; Table III)

$k_{HOAc}:k_{H(AC)^+} = 400:1$ ($Cu(H_{-2}G_3)^-$; Table III)

$k_{HOAc}:k_{H(LS)^\pm} > 2000:1$ ($Ni(H_{-2}G_3)^-$; Table IV)

The data prove the drastically reduced general-acid catalytic activity of H(LS) and $H(AC)^+$ as compared to that of HOAc. The fact that the pK_a values of HOAC and H(LS) are of the same size (4.6 and 4.8, respectively) and the finding that $k_{H(LS)^\pm} < 1$ M^{-1} s^{-1} (or even zero in some cases) makes H(LS), which is now commercially available, an attractive substitute for acetic acid as a buffer in kinetic studies. The role of H(LS) in the pH range 4.3–5.3 could be the same as that of MES in the pH range 5.7–6.7 (the application of the AC buffer as a substitute for the MES buffer is not advisable, since the base AC is of limited stability).

The main advantage of the 2,6-lutidine type buffers such as H(LS) is that, due to the absence of general-acid catalysis, the contribution of specific-acid catalysis and the contribution of general-acid catalysis produced by added acids HB can be determined more accurately.

Acknowledgment. Support by the Deutsche Forschungsgemeinschaft and by the Verband der Chemischen Industrie e.V. is gratefully acknowledged. Some of the buffers were kindly provided by Merck, Darmstadt, FRG.

Registry No. $Cu(H_{-2}G_3)^-$, 20160-84-3; $Cu(H_{-1}G_3)$, 12352-96-4; $Cu(H_{-2}G_4)^-$, 67180-35-2; $Cu(H_{-1}G_4)$, 15628-82-7; $Ni(H_{-2}G_3)^-$, 31011-65-1.

Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany, and Institute of Inorganic Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland

Spectroscopic Studies of Cyclometalated Palladium(II) Complexes: Optical Absorption and Emission of Single-Crystal *cis*-Bis(benzo[*h*]quinolinato)palladium(II)

R. Schwarz,[†] G. Gliemann,*[,†] Ph. Jolliet,[‡] and A. von Zelewsky*[,‡]

Received February 29, 1988

The polarized optical absorption and emission spectra of single-crystal *cis*-bis(benzo[*h*]quinolinato)palladium(II) (≡[Pd(bhq)$_2$]) as functions of temperature (1.9 K ≤ T ≤ 60 K) are reported. The spectra and lifetime of the emission exhibit an unusual temperature dependence, indicating the luminescence to originate from several types of traps located energetically below the triplet exciton band of the crystal. At T = 1.9 K no energy transfer occurs between the traps, and the emission spectra are superpositions of the radiative deactivation of all traps. Raising the temperature depopulates the traps via the exciton band corresponding to the energetic depth of the traps. At T = 60 K only the deepest traps (ΔE = 780 cm^{-1}) are occupied and determine the luminescence.

Introduction

In a series of papers von Zelewsky, Balzani, and co-workers reported on the photochemical, photophysical, and electrochemical properties of several cyclometalated, homoleptic platinum(II) and palladium(II) complexes with C,N ligands.[1-6] The emission and absorption spectra of the corresponding glasses (at T = 77 K) and solutions (at room temperature) are distinctly structured, and the emission lifetimes are on the order of 10^{-6}–10^{-3} s. Depending on the central ions and/or the coordinating ligands the low-energy absorption processes are assigned to MLCT and LC transitions, respectively. Up to now for most of the cyclometalated complexes no detailed interpretations of their electronic structures have been available.

Recently Gliemann, von Zelewsky, and co-workers published the first spectroscopic study on single crystals of a cyclometalated d^8 complex.[7] In contrast to the glass, the crystalline [Pt(phpy)$_2$] (phpy = 2-phenylpyridine) exhibits one structureless phosphorescence band. The wavelength and the intensity of the emission depend as much on temperature as on the strength of an applied magnetic field, a behavior similar to that of other solid platinum(II) compounds.[8-14] By a method originally developed for single crystals of cyanoplatinates(II),[8-13] of binuclear $Pt_2(H_2P_2O_5)_4^{4-}$,[14] and of several $[W(CO)_5X]$ compounds[15,16] the character of the low-energy optical transitions and the energetic order as well as the symmetry of the emitting states could be assigned.

The purpose of this paper is to get further details on the electronic states of single-crystal cyclometalated d^8 complexes. We report on the temperature dependence of the polarized optical absorption and emission of single-crystal [Pd(bhq)$_2$]. A qualitative model of the electronic properties of the crystalline compound is established to rationalize the observed behavior.

Experimental Section

Single crystals of [Pd(bhq)$_2$] were prepared according to ref 1 and 5. The needle-shaped crystals used for the spectroscopic measurements had a size of 3 × 0.1 × 0.05 mm^3.

The polarized crystal emission was measured with a liquid helium bath

[†] Universität Regensburg.
[‡] University of Fribourg.

(1) Chassot, L.; Müller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4289.
(2) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.
(3) Bonafede, S.; Ciano, M.; Bolletta, F.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Phys. Chem.* **1986**, *90*, 3836.
(4) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084.
(5) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.
(6) Balzani, V.; Maestri, M.; Melandri, A.; Sandrini, D.; Chassot, L.; Cornioley-Deuschl, C.; Jolliet, P.; Maeder, U.; von Zelewsky, A. Photochemistry and Photophysics of Coordination Compounds. In *Proceedings of the Seventh International Symposium*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1987. Maestri, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A.; Jolliet, P. *Helv. Chim. Acta* **1988**, *134*, 71.
(7) Bär, L.; Gliemann, G.; Chassot, L.; von Zelewsky, A. *Chem. Phys. Lett.* **1986**, *123*, 264.
(8) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*.
(9) Hidvegi, I.; von Ammon, W.; Gliemann, G. *J. Chem. Phys.* **1982**, *76*, 4361.
(10) Hidvegi, I.; von Ammon, W.; Gliemann, G. *J. Chem. Phys.* **1984**, *80*, 2837.
(11) Dillinger, R.; Gliemann, G.; Pfleger, H. P.; Krogmann, K. *Inorg. Chem.* **1983**, *22*, 1366.
(12) Biedermann, J.; Wallfahrer, M.; Gliemann, G. *J. Lumin.* **1987**, *37*, 323.
(13) Schwarz, R.; Lindner, M.; Gliemann, G. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1233.
(14) Bär, L.; Gliemann, G. *Chem. Phys. Lett.* **1984**, *108*, 14.
(15) Dillinger, R.; Gliemann, G. *Chem. Phys. Lett.* **1985**, *122*, 66.
(16) Dillinger, R.; Gliemann, G. *Z. Naturforsch.* **1986**, *41A*, 1071.

0020-1669/89/1328-0742$01.50/0