Kinetic Studies on Copper(II) Complexes with 1,5-Diazacyclooctane (= daco): Uncatalyzed and Base-catalyzed Acid Dissociation of $Cu(daco)_2^{2+}$ and Ligand Replacement by EDTA

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Abstract

Stopped-flow spectrophotometry was used to study the acid dissociation of the complexes $Cu(daco)_2^{2+}$ and $Cu(daco)^{2+}$ (daco = 1,5-diazacyclooctane) with several acids HA at 20 °C and $I = 0.1$ M ($NaClO_4$). The rate of acid dissociation is independent of $[H^+]$ in the pH range 1.5–6.5 and independent of [HA]. It is base-catalyzed and follows a two-term rate law, rate = $(k_0 + k_A[A^-]) \times$ [$Cu(daco)_2^{2+}$] with $k_0 = 0.173 \pm 0.003$ s^{-1} and $k_A = 0$ ($A^- = ClO_4^-$, Cl^-, I^-, NO_3^-, sulfonate), 16.3 ± 1.3 (acetate), 4.6 ± 0.2 (formiate), 3.1 ± 0.3 (chloroacetate), 1.02 ± 3 ($H_2PO_4^-$), 139 ± 12 (HPO_4^{2-}) M^{-1} s^{-1}. Acid dissociation of the species $Cu(daco)^{2+}$ is by a factor of 7 slower than that of the species $Cu(daco)_2^{2+}$. The ratio $k_0(Cu(daco)_2^{2+}):k_0(Ni(daco)_2^{2+})$ is $5 \times 10^4:1$. There is a LFE relationship between $\log k_A$ and the pK_a of the corresponding acids HA. Ligand replacement in $Cu(daco)_2^{2+}$ by EDTA as studied at pH 8 follows the rate law: rate = $(k_0 + k_L[L])[Cu(daco)_2^{2+}]$ with $k_0 = 0.15 \pm 0.01$ s^{-1} and $k_L = 27.4 \pm 0.8$ M^{-1} s^{-1} (L $\hat{=}$ HEDTA^{3-}). Rate constant k_L also fits reasonably well into the LFE relationship between $\log k_A$ and pK_a. A unifying mechanistic interpretation is presented for both acid dissociation and ligand replacement.

Introduction

The eight-membered heterocycle 1,5-diazacyclooctane (I), first introduced as a bidentate ligand by Musker and Hussain [1], represents a diamine with remarkable properties in the sense that, due to its cyclic structure, coordination of two molecules of I to a metal centre leads to planar N_4 coordination geometry around the metal with strong shielding in the axial positions. The thermodynamic stability of

H — N   N — H = I = daco
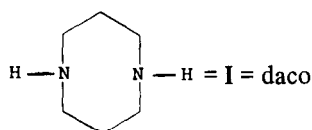
the four-coordinate complexes $Ni(daco)_2^{2+}$ and $Cu(daco)_2^{2+}$ is rather high, with $\log \beta_2 = 18.7$ and 17.8, respectively [1].

Billo demonstrated [2] that the reaction of the diamagnetic cation $Ni(daco)_2^{2+}$ with cyanide, which leads to $Ni(CN)_4^{2-}$ via $Ni(daco)(CN)_2$, is rather fast (stopped-flow time scale), whereas the rate of acid dissociation in dilute $HClO_4$ and in acetate buffer is surprisingly small. This kinetic stability of $Ni(daco)_2^{2+}$ towards acids was confirmed by Hay *et al.* [3] who found rate law (1) to govern acid dissociation in 1–4 M $HClO_4$, with $k_0 = 2 \times 10^{-5}$ s^{-1} (solvolytic pathway) and $k_H = 2 \times 10^{-5}$ M^{-1} s^{-1} (acid-catalyzed pathway) at 60 °C.

$$\text{rate} = k_{obs}[Ni(daco)_2^{2+}]$$
$$= (k_0 + k_H[H^+])[Ni(daco)_2^{2+}] \qquad (1)$$
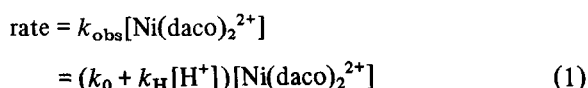
The exceptional inertness of $Ni(daco)_2^{2+}$ led us to study the kinetics of uncatalyzed and base-catalyzed acid dissociation of the corresponding copper(II) species $Cu(daco)_2^{2+}$ and $Cu(daco)^{2+}$ according to (2), as well as the kinetics of ligand substitution with EDTA.

$$Cu(daco)_2^{2+} \xrightleftharpoons{+acid} Cu(daco)^{2+} + daco \xrightleftharpoons{+acid}$$
$$Cu^{2+} + 2daco \qquad (2)$$
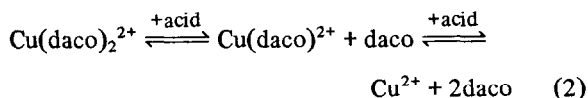
Experimental

The ligand I was obtained from the disodium salt of ditosyl 1,3-diaminopropane and the ditosylate of 1,3-propanediol on the basis of published procedures

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[3–5] and isolated as I·2HBr. The complex [Cu-(daco)₂](ClO₄)₂·2H₂O was prepared as reported in the literature [1]. The C,H,N data proved its correct composition and the data obtained for the absorptivity of $Cu(daco)_2^{2+}$ ($\epsilon = 297$ M^{-1} cm^{-1} at $\lambda_{max} = 500$ nm) and $Cu(daco)^{2+}$ ($\epsilon = 99$ M^{-1} cm^{-1} at $\lambda_{max} = 648$ nm) were in good agreement with those reported in the literature [1].

Instrumentation

UV–Vis spectra: diode array spectrophotometer (HP 8451A); pH data: pH meter (Metrohm 654) with glass electrode (Schott). The proton concentration was calculated according to (3); the correction term of −0.11 for $I = 0.1$ M (as reported in the literature [6a]) was experimentally confirmed.

$$-\log[H^+] = pH - 0.11 \qquad (3)$$

Kinetics

An ionic strength of $I = 0.1$ M (NaClO₄, acid, buffer) was maintained in all experiments. The pH was adjusted with NaOH, HClO₄ or various buffers (MES = 2-(N-morpholino)ethane sulfonic acid; LutSO₃H = 2,6-lutidine-3-sulfonic acid [7, 8]; HOAc; MOPS = 3-(N-morpholino)propane sulfonic acid; HOAcCl = chloroacetic acid).

The calculation of the concentration of buffer salt (see Tables 3 and 4) is based on the following pK_a values [6b]: 4.56 (HOAc), 3.55 (HCO₂H), 2.68 (HOAcCl), 6.87 (H₂PO₄⁻), 1.82 (H₃PO₄).

The kinetic measurements were carried out with a modified [9] DURRUM (D 110) stopped-flow spectrophotometer. The absorbance/time data were fitted to the function $(A - A_\infty)/(A_0 - A_\infty) = \exp(-k_{obs}t)$ with a computer program based on the least-squares method.

Results and Discussion

Spectrophotometric Titration

Titration of a solution of the complex [Cu-(daco)₂](ClO₄)₂ (pH 8.5) with HClO₄ or NaOH and observation of the absorbance A at λ_{max} (Cu-(daco)₂²⁺) = 500 nm and λ_{max}(Cu(daco)²⁺) = 648 nm [1] shows that (i) A^{500} decreases continuously when the pH is lowered from 8.5 to pH 6, (ii) A^{648} passes a maximum at pH 6 upon stepwise pH change from 8.5 to 4, and (iii) a stepwise pH increase from 8.5 to 12.5 reduces A^{500} continuously from pH 10.5 on. These findings are in line with an acid dissociation according to $Cu(daco)_2^{2+} \to Cu(daco)^{2+} \to Cu^{2+}$ for pH 8.5 → 4 and with the formation of hydroxo species at pH > 10.5. The vacant coordination sites in the species $Cu(daco)^{2+}$ are probably occupied by water molecules and/or hydroxyl ions.

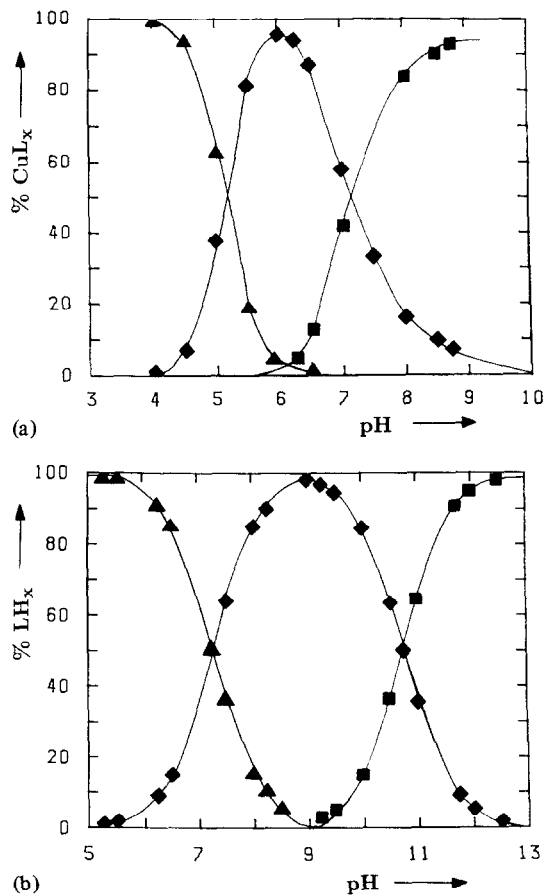On the basis of the data resulting from these titrations and in combination with the formation

Fig. 1. Distribution curves for solutions of the complex $Cu(daco)_2^{2+}$ (a) and the ligand I = L (b) as a function of pH (symbols: ■, ♦ and ▲ for CuL_2^{2+}, CuL^{2+} and Cu^{2+} in (a); ■, ♦ and ▲ for L, LH⁺ and LH_2^{2+} in (b)).

constants and pK_a values reported in the literature [1] for the species CuL_2^{2+}, CuL^{2+}, LH_2^{2+} and LH⁺ (L = I) the pH dependence of the relative distribution in solutions of the complex and of the ligand was calculated (see Fig. 1(a) and (b)). One learns that in the pH range 8–10 the bis complex $Cu(daco)_2^{2+}$ dominates, whereas at pH 6 the mono complex $Cu(daco)^{2+}$ is the predominant species.

Kinetics of Uncatalyzed Acid Dissociation

It follows from Fig. 1(a) that a pH jump from 8.5 to pH ⩽ 5 leads to the species Cu^{2+}_{aq} as the dominating one, i.e. to complete hydrolysis of the complex $Cu(daco)_2^{2+}$. For a smaller jump from 8.5 to 6 the reaction $Cu(daco)_2^{2+} \to Cu(daco)^{2+}$ takes place. Since the absorptivity of $Cu(daco)^{2+}$ at 500 nm is negligibly small, observation at 500 nm allows monitoring of the disappearance of the species $Cu(daco)_2^{2+}$, independent of whether Cu^{2+}_{aq} or $Cu(daco)^{2+}$ is formed.

The absorbance/time data obtained in such pH jump studies at 500 nm can be fitted to a single

TABLE 1. Rate constant k_{obs} for acid dissociation of $Cu(daco)_2^{2+}$ and $Cu(daco)^{2+}$ according to (2) at different concentrations of acid or buffer[a]

System	HA [b]	[HA] [c] (M)	pH[d]	k_{obs} (s^{-1})	$\bar{k}_{obs}$ (s^{-1})
$Cu(daco)_2^{2+}$ (1 × 10^{-3} M; pH 8.5[e])					
I	HClO$_4$	0.01	2.11[f]	0.161 ± 0.001	0.159 ± 0.001
		0.02	1.81[f]	0.160 ± 0.001	
		0.03	1.63[f]	0.157 ± 0.001	
		0.04	1.51[f]	0.158 ± 0.001	
		0.05	1.41[f]	0.158 ± 0.001	
II	HMES/NaMES (1:1)	0.02	6.24	0.176 ± 0.002	0.175 ± 0.003
		0.04	6.16	0.174 ± 0.001	
		0.05	6.14	0.171 ± 0.001	
		0.07	6.13	0.171 ± 0.001	
		0.08	6.12	0.173 ± 0.001	
		0.10	6.13	0.173 ± 0.001	
III	HMES/NaMES	0.15(2:1)[g]	5.81	0.190 ± 0.001	0.188 ± 0.002
		0.13(1.6:1)[g]	5.92	0.182 ± 0.001	
		0.12(1.4:1)[g]	5.97	0.180 ± 0.001	
		0.1(1:1)[g]	6.13	0.183 ± 0.001	
		0.085(1:1.4)[g]	6.27	0.194 ± 0.001	
		0.08(1:1.6)[g]	6.35	0.197 ± 0.001	
		0.075(1:2)[g]	6.41	0.189 ± 0.002	
IV	LutSO$_3$H/LutSO$_3$Na (1:1)	0.01	5.33	0.196 ± 0.001	0.191 ± 0.004
		0.05	4.90	0.192 ± 0.001	
		0.10	4.83	0.180 ± 0.001	
V	LutSO$_3$H/LutSO$_3$Na	0.15(2:1)[g]	4.51	0.167 ± 0.001	0.173 ± 0.002
		0.1(1:1)[g]	4.83	0.180 ± 0.001	
		0.075(1:2)[g]	5.17	0.173 ± 0.002	
$Cu(daco)^{2+}$ (1 × 10^{-3} M; pH 5.94[h])					
VI	HClO$_4$	0.005	2.41[f]	0.0219 ± 0.0001	0.0223 ± 0.0001
		0.02	1.81[f]	0.0224 ± 0.001	
		0.03	1.63[f]	0.0227 ± 0.001	
		0.04	1.51[f]	0.0222 ± 0.001	
		0.05	1.41[f]	0.0226 ± 0.001	

[a]At 20 °C and I = 0.1 M.   [b]Acid or buffer applied.   [c]In the case of a buffer, [HA] denotes the total buffer concentration, [HA]$_T$ = [buffer acid] + [buffer salt].   [d]pH in the reaction mixture after the stopped-flow experiment.   [e]pH of the solution of the complex before mixing in the stopped-flow experiment; reaction monitored at 500 nm.   [f]Calculated from [HClO$_4$] according to (3).   [g]Buffer ratio [buffer acid]:[buffer salt] with [buffer salt] = 0.05 M.   [h]pH of the solution of the complex before mixing in the stopped-flow experiment; reaction monitored at 650 nm.

exponential function which means that eqn. (4) is valid

$$\text{rate} = -d[Cu(daco)_2^{2+}]/dt = k_{obs}[Cu(daco)_2^{2+}] \quad (4)$$

The data for the experimental rate constant k_{obs} at 20 °C and constant ionic strength (I = 0.1 M) are compiled in Table 1. As one can see for HA = HClO$_4$ (system I) the size of k_{obs} is independent of proton concentration in the range [H$^+$] = 0.01–0.05 M with a mean of $\bar{k}_{obs}$ = 0.159 s^{-1}. In the presence of the 'non-coordinating' buffers HMES (pH jump from 8.5 to approx. 6) and LutSO$_3$H (pH jump from 8.5 to approx. 5) the bis complex $Cu(daco)_2^{2+}$ disappears at practically the same rate with $\bar{k}_{obs}$ = 0.175 (system

II), 0.188 (system III), 0.191 (system IV) and 0.173 s^{-1} (system V), respectively. So, it is again found that $k_{obs} \neq f([H^+])$ and, moreover, that the size of k_{obs} is also not affected by the nature of the buffer and its concentration ($k_{obs} \neq f([HA]_T)$. The overall result is, therefore, that there is neither specific nor general acid catalysis in the hydrolysis of $Cu(daco)_2^{2+}$ with HClO$_4$ and various non-coordinating buffers. The mean rate constants $\bar{k}_{obs}$ obtained for systems I–V amounts to $\bar{k}_{obs}$(mean) = 0.177 ± 0.013 s^{-1}.

As pointed out earlier, in a solution of the complex $Cu(daco)_2^{2+}$ adjusted to pH 6 the mono complex $Cu(daco)^{2+}$ dominates (see Fig. 1(a)). When such a solution is reacted with an excess of perchloric acid,

TABLE 2. Summary of rate constants for acid hydrolysis of complexes $Cu(daco)_2^{2+}$ and $Ni(daco)_2^{2+}$ in dilute perchloric acid and acetate buffer

| Complex	Acid or buffer	T ($^\circ$C)	k_0 (s^{-1})	$k_{acetate}$ ($M^{-1} s^{-1}$)	Reference
$Cu(daco)_2^{2+}$	$HClO_4$	20	0.159 ± 0.001		this work
$Cu(daco)_2^{2+}$	HOAc/NaOAc	20	0.159 ± 0.041	16.3 ± 1.3	this work
$Ni(daco)_2^{2+}$	$HClO_4$	25	3.3×10^{-6}		2
$Ni(daco)_2^{2+}$	HOAc/NaOAc	25	3.2×10^{-6}	6.2×10^{-5}	2
$k(Cu):k(Ni)$	HOAc/NaOAc	20/25	$5 \times 10^4:1$	$26 \times 10^4:1$	

monitoring at 650 nm provides data for the acid hydrolysis of the species $Cu(daco)^{2+}$ (see system VI in Table 1). It turns out that the reaction Cu-$(daco)^{2+} \rightarrow Cu^{2+}_{aq}$ is again independent of proton concentration and that the mean rate constant, $\bar{k}_{obs} = 0.0223$ s^{-1}, is by a factor of 7.1 smaller than that for the species $Cu(daco)_2^{2+}$ (see system I).

Summarizing these findings and comparing them with those obtained for the complex $Ni(daco)_2^{2+}$ [2, 3] one learns that acid hydrolysis of both Cu-$(daco)_2^{2+}$ and $Ni(daco)_2^{2+}$ follows the simple rate law (5) (M = Cu(II), Ni(II)). Up to proton concentrations of 0.05 M the rate-determining step in the hydrolysis of the species $Cu(daco)_2^{2+}$ (and also $Cu(daco)^{2+}$) is obviously not proton-assisted. The difference in rate between $Cu(daco)_2^{2+}$ and its nickel analogue is quite dramatic with a factor of 5×10^4 for k_0 (see Table 2).

$$rate = k_{obs}[M(daco)_2^{2+}] = k_0[M(daco)_2^{2+}] \qquad (5)$$

The stereochemistry of the planar complex cation $Ni(daco)_2^{2+}$ as derived from the crystal structure of $[Ni(daco)_2](ClO_4)_2 \cdot 2H_2O$ [10, 11] and general stereochemical considerations [1] implies some kind of an asymmetric twin 'butterfly' shape, the actual conformation of the two eight-membered rings being such that the hydrogen atoms on C_3 (one daco ring) and C_7 (second daco ring) provide shielding of the axial sites, thus preventing octahedral coordination on steric grounds.
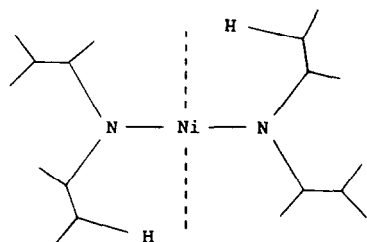
The crystal structure of the complex $Pd(dtco)_2^{2+}$ (dtco = 1,5-dithiacyclooctane) also corresponds to this type of ligand arrangement [12]. Hay et al. [3] describe the extreme inertness of the cation Ni-$(daco)_2^{2+}$ by assuming that step (2b) controls the

(2a)

(2b)

(2c)
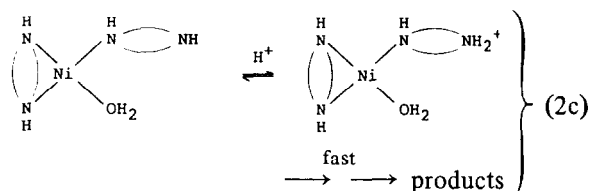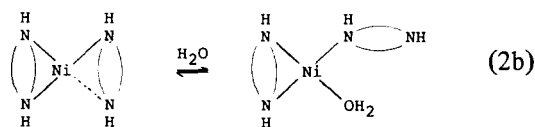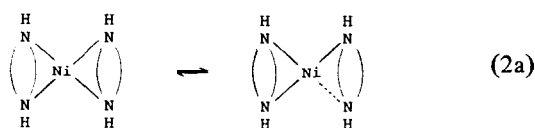
rate of the solvolytic pathway. Both steps (2a) and (2b) have to do with the loosening and/or breaking of a Ni–N bond. Since the strength of the metal–nitrogen bond in $Ni(daco)_2^{2+}$ and $Cu(daco)_2^{2+}$ cannot be very different, sequence (2a)–(2c) appears to be not very suitable to explain the factor of 5×10^4 by which the copper complex reacts faster than the nickel complex. A more convincing explanation for this dramatic difference in rate would arise from the assumption that the steric arrangement of the two cyclic ligands in $Cu(daco)_2^{2+}$ and $Ni(daco)_2^{2+}$ is quite different. Unfortunately, there is no crystal structure analysis of $Cu(daco)_2(ClO_4)_2 \cdot 2H_2O$ available so far. On the basis of the higher energy and higher intensity of the d–d transitions observed for the chromophore $Cu(daco)_2^{2+}$ (as compared to $Cu(en)_2^{2+}$ and similar complexes) Musker and Hussain [1] pointed out, however, that the complex Cu-$(daco)_2^{2+}$ is probably subject to a strong tetragonal distortion. In contrast to the species $Cu(dach)_2^{2+}$ (dach = 1,4-diazacycloheptane) [13] the complex $Cu(daco)_2^{2+}$ does not add anions X^- to form penta-coordinate cations $Cu(daco)_2X^+$. It is nevertheless

TABLE 3. Rate constants for acid dissociation of $Cu(daco)_2^{2+}$ according to (2) as studied with different acids and buffers[a]

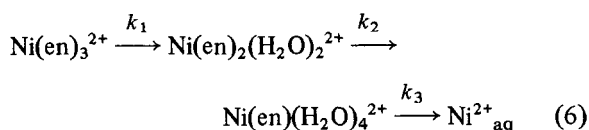| System	HA [b]	[HA] [c] (M)	[A⁻] (M)	pH[d]	k_{obs} (s⁻¹)	k_0 [e] (s⁻¹)	k_A [e] (M⁻¹ s⁻¹)
VII	HOAc/NaOAc	0.01	0.005	5.05	0.280 ± 0.002	0.159 ± 0.041	16.3 ± 1.3
		0.03	0.015	4.67	0.360 ± 0.002		
		0.07	0.035	4.58	0.720 ± 0.002		
		0.1	0.05	4.53	0.990 ± 0.004		
VIII	HOAc/NaOAc	0.15	0.05	4.24	0.985 ± 0.004	0.970 ± 0.050	–
		0.1	0.05	4.53	0.990 ± 0.004		
		0.075	0.05	4.88	0.938 ± 0.005		
IX	HCO₂H	0.005	0.004	4.4	0.192 ± 0.001		
		0.025	0.006	3.2	0.203 ± 0.001	0.173 ± 0.002	4.6 ± 0.2
		0.05	0.009	3	0.213 ± 0.002		
X	HCO₂H/HCO₂Na	0.004	0.004	6.45	0.207 ± 0.001		
		0.01	0.009	4.85	0.208 ± 0.001		
		0.02	0.016	4.2	0.295 ± 0.001	0.184 ± 0.02	5.1 ± 1.2
		0.03	0.022	4.1	0.285 ± 0.002		
		0.04	0.027	4	0.319 ± 0.002		
XI	HOAcCl/NaOAcCl	0.01	0.008	3.3	0.182 ± 0.001		
		0.025	0.018	3.2	0.208 ± 0.001		
		0.04	0.027	3.1	0.226 ± 0.001	0.165 ± 0.004	2.5 ± 0.1
		0.05	0.034	3.1	0.255 ± 0.001		
		0.075	0.050	3.1	0.290 ± 0.001		
		0.1	0.067	3.1	0.326 ± 0.001		
XII	NaOAcCl[f]		0.005	5.1	0.188 ± 0.001		
			0.015	5.05	0.226 ± 0.001		
			0.025	5	0.285 ± 0.001	0.175 ± 0.01	3.7 ± 0.3
			0.04	4.9	0.317 ± 0.002		
			0.05	4.8	0.338 ± 0.002		
			0.06	4.65	0.422 ± 0.003		
			0.07	4.45	0.419 ± 0.003		

[a]At 20 °C and $I = 0.1$ M; the pH of the solution of the complex ($[Cu(daco)_2]^{2+} = 1 \times 10^{-3}$ M) was 8.5 before mixing in the stopped-flow experiment; reaction monitored at 500 nm.   [b]Acid or buffer applied.   [c][HA] = total concentration; in the case of a buffer, [HA] denotes the total buffer concentration, $[HA]_T$ = [buffer acid] + [buffer salt].   [d]pH in the reaction mixture after the stopped-flow experiment.   [e]The data obtained for $k_{obs} = k_0 + k_A[A^-]$.   [f]Solution buffered with LutSO₃H/ LutSO₃Na.

well conceivable that the tetragonal distortion in $Cu(daco)_2^{2+}$ makes this complex much more susceptible to the attack of water according to steps (2a) and (2b) than the corresponding planar complex $Ni(daco)_2^{2+}$. In addition, one has of course to be aware of the fact that the nickel complex contains a d^8 metal centre, whereas the copper complex is a d^9 system.

The fact that the mono complex $Cu(daco)^{2+}$ is hydrolyzed slower than the bis complex $Cu(daco)_2^{2+}$ (k_0(bis):k_0(mono) = 7:1; see Table 1) could be due to several factors. As a matter of fact, the individual stability constant of $Cu(daco)^{2+}$ is by 3.3 orders of magnitude greater than that of $Cu(daco)_2^{2+}$ [1]. On the other hand the species $Cu(daco)^{2+}$ (as produced by adjusting the solution of $Cu(daco)_2^{2+}$ to pH 6; see Fig. 1(a)) is probably present in the form of $Cu(daco)(OH)_n^{(2-n)+}$ with a reduced positive charge. In addition, it is generally known that the individual rate of stepwise loss of chelate ligands upon hydrolysis decreases with decreasing number of ligands still coordinated. For reaction (6) the rate constants for acid hydrolysis decrease in the order $k_1:k_2:k_3 = 533:30:1$ [14].

$$Ni(en)_3^{2+} \xrightarrow{k_1} Ni(en)_2(H_2O)_2^{2+} \xrightarrow{k_2}$$

$$Ni(en)(H_2O)_4^{2+} \xrightarrow{k_3} Ni^{2+}_{aq} \qquad (6)$$

Kinetics of Base-catalyzed Acid Dissociation

When the acetate buffer is applied (see systems VII and VIII in Table 3) the results are different in the sense that k_{obs} depends on the size of $[AcO^-]$ (see system VII and also Fig. 2) although $k_{obs} \neq f([H^+])$
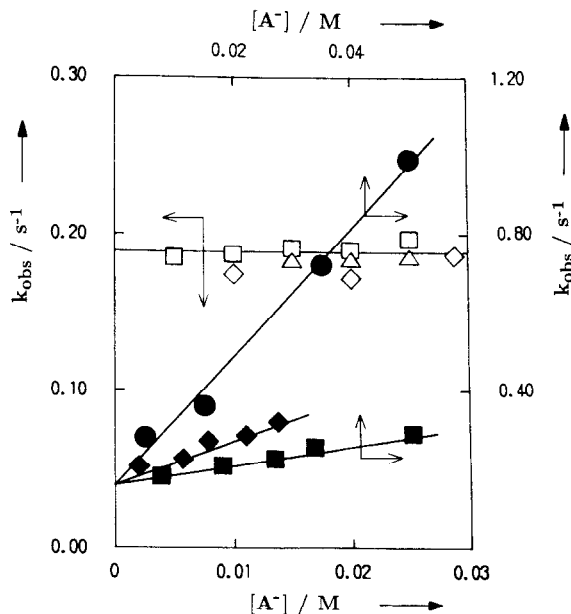
Fig. 2. Rate constants k_{obs} for acid hydrolysis of Cu-(daco)$_2^{2+}$ at different concentrations of various anions at 20 °C (data for carboxylate anions taken from Table 3; pH = 5 for A$^-$ = Cl$^-$, I$^-$, NO$_3^-$ as adjusted with LutSO$_3$H/LutSO$_3$-Na; ● = AcO$^-$, ♦ = HCO$_2^-$, ■ = ClAcO$^-$, □ = Cl$^-$, △ = I$^-$, ◇ = NO$_3^-$; the open and filled symbols refer to the left/lower and right/upper axis, respectively).

at [AcO$^-$] = constant 0.05 M (see system VIII in Table 3). It is important to note that the size of k_{obs} is not affected by chloride, iodide and nitrate ions (see Fig. 2), which means that there is a specific acetate catalysis (as observed also for acid hydrolysis

of the complex Ni(daco)$_2^{2+}$ [2]) which follows rate law (7) (A$^-$ ≙ acetate anion). As found for k_0, the difference in k_A for Cu(daco)$_2^{2+}$ and for its nickel analogue is dramatic with k_A(Cu):k_A(Ni) = 26 × 10^4:1 (see Table 2).

$$\text{rate} = (k_0 + k_A[\text{A}^-])[\text{Cu(daco)}_2^{2+}] \tag{7}$$

The observed catalytic effect of acetate ions led us to introduce carboxylic acids HA other than acetic acid. The results obtained for HA = HCO$_2$H (formic acid) and HOAcCl (chloroacetic acid) are compiled in Table 3. As one can see (systems IX–XII) both formiate ion and chloroacetate ion (see also Fig. 2) catalyze reaction (2) and the kinetic data obtained follow rate law (7). Again, rate constant k_0 is independent of [H$^+$], [HA] and the nature of HA, whereas rate constant k_A ranges from approx. 3 (ClAcO$^-$) and 5 (HCO$_2^-$) to 16 (AcO$^-$).

The conclusion is, therefore, that not only acetate ions but carboxylate ions in general are able to catalyze reaction (2) considerably. One could imagine that this has to do with the bidentate character of the carboxylate ion, since for both chloride and iodide ions there is no such effect (see Fig. 2). The fact, however, that the potentially bidentate nitrate ion does not produce any catalytic effects either (see Fig. 2) points more to the basicity of the carboxylate ion as catalysis-controlling factor.

To obtain further information on this question acid hydrolysis of the complex Cu(daco)$_2^{2+}$ was studied in the presence of phosphate ions. The results (see Table 4) are very interesting: (i) rate constant k_{obs} increases with increasing concentration of total phosphate, [phosphate]$_T$, at pH 4.9 (system XIII)

TABLE 4. Rate constants for acid dissociation of Cu(daco)$_2^{2+}$ according to (2) as studied in the presence of phosphate[a]

System	[phosphate]$_T$ [b] (M)	pH[c]	[H$_2$PO$_4^-$] (M)	[HPO$_4^{2-}$] (M)	k_{obs} (s^{-1})
XIII	0.005[d]	4.9	4.958 × 10^{-3}	4.12 × 10^{-5}	0.187 ± 0.001
	0.01[d]	4.9	9.918 × 10^{-3}	8.24 × 10^{-5}	0.207 ± 0.001
	0.025[d]	4.9	2.479 × 10^{-2}	2.06 × 10^{-4}	0.260 ± 0.001
	0.05[d]	4.9	4.959 × 10^{-2}	4.12 × 10^{-4}	0.327 ± 0.001
XIV	0.05[e]	6	4.526 × 10^{-2}	4.739 × 10^{-3}	0.679 ± 0.003
	0.05[e]	6.2	4.288 × 10^{-2}	7.116 × 10^{-3}	0.986 ± 0.002
	0.05[e]	6.25	4.215 × 10^{-2}	7.849 × 10^{-3}	1.510 ± 0.001
	0.05[e]	6.45	3.860 × 10^{-2}	1.139 × 10^{-2}	1.630 ± 0.002
	0.05[e]	6.5	3.756 × 10^{-2}	1.244 × 10^{-2}	2.010 ± 0.001
XV	0.005[e]	6.85	3.079 × 10^{-3}	1.921 × 10^{-3}	0.415 ± 0.001
	0.015[e]	6.4	1.188 × 10^{-2}	3.124 × 10^{-3}	0.564 ± 0.001
	0.025[e]	6.3	2.068 × 10^{-2}	4.320 × 10^{-3}	0.837 ± 0.001
	0.05[e]	6.25	4.215 × 10^{-2}	7.850 × 10^{-3}	1.510 ± 0.001

[a]At 20 °C and I = 0.1 M; the pH of the solution of the complex ([Cu(daco)$_2$]$^{2+}$ = 1 × 10^{-3} M) was 8.5 before mixing in the stopped-flow experiment; reaction monitored at 500 nm.   [b]Phosphate was introduced as KH$_2$PO$_4$.   [c]pH in the reaction mixture after the stopped-flow experiment.   [d]Phosphate solution buffered with LutSO$_3$H/LutSO$_3$Na.   [e]pH of phosphate solution adjusted with NaOH.

and at pH = 6.2–6.8 (system XV), and, (ii) even for [phosphate]$_T$ = constant rate constant k_{obs} increases with increasing concentration of [HPO$_4{}^{2-}$] (system XIV). The data obtained clearly prove that there is base catalysis through both the $H_2PO_4{}^-$ and the $HPO_4{}^{2-}$ ion. Calculation of [H$_2$PO$_4{}^-$] and [HPO$_4{}^{2-}$] (from [phosphate]$_T$ and the pH values listed in Table 4) and computer fitting of all the data (systems XIII–XV) to eqn. (8) leads to the following results:

$$k_0 = 0.172 \pm 0.08 \text{ s}^{-1}$$

$$k_{H_2PO_4} = 1.02 \pm 3 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{HPO_4} = 139 \pm 12 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{obs} = k_0 + k_{H_2PO_4}[H_2PO_4{}^-] + k_{HPO_4}[HPO_4{}^{2-}] \quad (8)$$

One learns that there is a minor catalytic effect of the $H_2PO_4{}^-$ ion and a very pronounced one of the $HPO_4{}^{2-}$ ion which exceeds even the catalytic activity of the acetate ion. The idea that rate constant k_A can be correlated with the pK_a value of the corresponding acid HA (i.e. with the basicity of the anion A^-) is convincingly confirmed by plotting log k_A versus pK_a for all systems studied (see Fig. 3). The linear relationship obtained covers even the $H_2PO_4{}^-$ ion, which is a very weak base only (pK_a (H$_3$PO$_4$) = 1.82).

The interesting overall result is, therefore, that acid dissociation of Cu(daco)$_2{}^{2+}$ according to (2) is clearly base-catalyzed by carboxylate and phosphate ions, the strong base $HPO_4{}^{2-}$ being the most effective one. It would of course be very interesting at this point to study further bases with donor atoms other than oxygen. Such studies could possibly prove that, mechanistically, the observed base-catalysis is due to the bond breaking attack of the base A^- (instead of
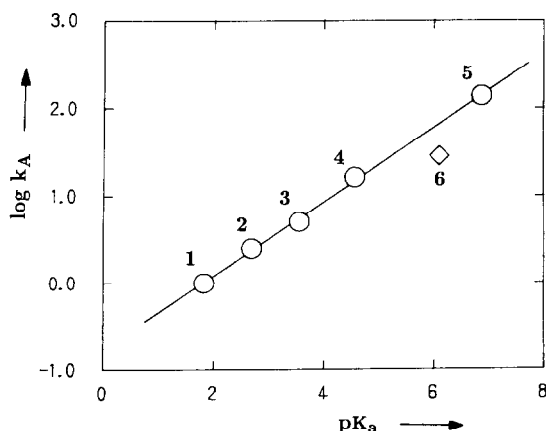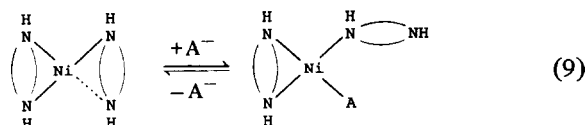

Fig. 3. Plot of the LFE relationship between log k_A and pK_a of the corresponding acids HA (data for k_A and pK_a taken from Tables 3 and 4 and refs. 6b and 15, respectively; 1 = H$_3$PO$_4$, 2 = HOAcCl, 3 = HCO$_2$H, 4 = HOAc, 5 = H$_2$PO$_4{}^-$, 6 = H$_2$EDTA^{2-}).

water, as in reaction (2b); see discussion above on solvolysis) according to (9).

In acidic medium, the species thus formed decomposes in a series of fast consecutive steps to form $Ni^{2+}{}_{aq}$.

Finally, it is important to point out that water-initiated acid dissociation, as characterized by rate constant k_0, is observed in all systems as a parallel and base-independent pathway. For the carboxylate-catalyzed systems VII–XII a mean of $\bar{k}_0 = 0.171 \pm 0.010$ s^{-1} is obtained, which is very close to $\bar{k}_{obs}$(mean) = 0.177 ± 0.013 s^{-1} found for systems I–V. In addition, the phosphate-catalyzed systems XIII–XV yield $k_0 = 0.172 \pm 0.08$ s^{-1}.

Ligand Substitution with EDTA

The reaction of the complex Cu(daco)$_2{}^{2+}$ with EDTA was studied at pH 8 (solution buffered with MOPS) to avoid hydrolysis of the complex. Monitoring of the disappearance of Cu(daco)$_2{}^{2+}$ under pseudo-first-order conditions ([EDTA]$_T \gg$ [Cu(daco)$_2{}^{2+}$]) at 500 nm proves an exponential decay of the Cu(daco)$_2{}^{2+}$ signal, i.e. the reaction is first-order in complex and goes to completion. In addition, the spectral changes prove the formation of the EDTA complex of copper(II). The data obtained for k_{obs} at different concentrations of the entering ligand L $\hat{=}$ EDTA are plotted in Fig. 4. They follow two-term rate law (10) with $k_0 = 0.15 \pm 0.01$ s^{-1} and $k_L = 27.4 \pm 0.8$ M^{-1} s^{-1} (20 °C). Although the ionic strength was higher (0.5 M instead of 0.1 M in the case of acid hydrolysis) the size of k_0 corresponds convincingly to the data obtained for k_0 in systems I–V and VII–XV with an overall mean of $k_0 = 0.173$ s^{-1}. This means that there is a ligand-independent reaction pathway for ligand substitution in Cu(daco)$_2{}^{2+}$ by EDTA, the size of which is identical with the size of the water-initiated solvolytic pathway in acid dissociation. One can therefore draw the conclusion that, mechanistically, the formation of the species [(daco)(H$_2$O)Cu–N-N]$^{2+}$ (N-N $\hat{=}$ daco) according to (2b) controls the rate of both reactions.

$$\text{rate} = -d[Cu(daco)_2{}^{2+}]/dt$$

$$= k_{obs}[Cu(daco)_2{}^{2+}]$$

$$= (k_0 + k_L[L])[Cu(daco)_2{}^{2+}] \quad (10)$$

The ligand-dependent rate contribution $k_L[L]$ in rate law (10) with $k_L = 27.4$ M^{-1} s^{-1} is very interest-
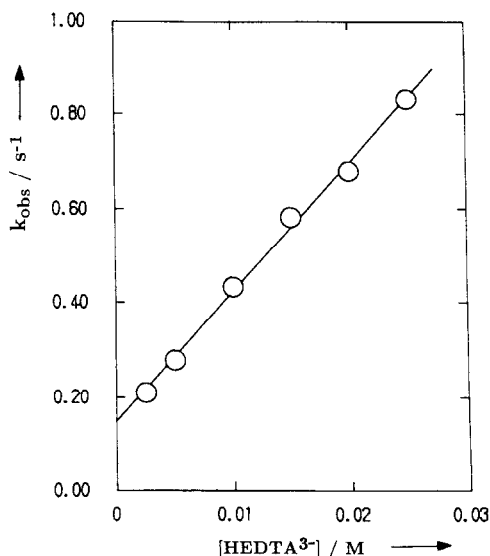
Fig. 4. Dependence of the experimental rate constant k_{obs} on ligand concentration for ligand replacement in Cu-$(daco)_2^{2+}$ by EDTA (conditions: 20 °C; I = 0.5 M $(NaClO_4)$; [complex] = 5 × 10^{-4} M; pH 7.94 (solution buffered with MOPS); reaction monitored at 500 nm).

ing in the sense that the size of k_L is of the same order of magnitude as the data obtained for k_A in the studies on base-catalyzed acid dissociation of Cu-$(daco)_2^{2+}$. Considering the fact that base-catalysis is brought about by carboxylate ions and that, on the other hand, EDTA is a carboxylate group carrying ligand, one is tempted to correlate rate constant k_L for ligand replacement by EDTA with the pK_a value of the corresponding acid.

At pH 8 the ligand EDTA is present predominantly in the form of the HEDTA^{3-} ion (approx. 99%). The species HEDTA^{3-} is the corresponding base A$^-$ of the acid HA $\hat{=}$ H$_2$EDTA^{2-} with a pK_a value of 6.1 [15]. As in the case of carboxylate-catalyzed and phosphate-catalyzed acid dissociation, rate constant k_L for ligand replacement can also be reasonably well correlated with the corresponding pK_a value (see Fig. 3). One can conclude, therefore, that only the most basic carboxyl group in HEDTA^{3-} contributes significantly.

These findings are of great importance for the mechanistic interpretation of the kinetic behavior of the species Cu$(daco)_2^{2+}$. For both acid dissociation and ligand replacement there are two independent pathways, as described by the general rate law (11).

$$v = k_{obs}[\text{complex}] = (k_0 + k_A[A])[\text{complex}] \qquad (11)$$

Rate constant k_0 is the same for acid dissociation as well as for ligand replacement at pH 8, which means that there is a solvent-assisted reaction such as (2b) which contributes to both processes. In acid dissociation, strong bases A (such as carboxylate and phosphate ions) can contribute to the rate of dissociation according to (11), with reaction (9) being rate-controlling. In the case of ligand replacement with A = HEDTA^{3-}, reaction (9) again controls the rate, but due to the high pH of 8, the product of reaction (9), the species [(daco)(A)Cu–N-N] (N-N $\hat{=}$ daco), does not dissociate (as it does at lower pH) and forms the EDTA complex of copper(II) instead. The size of rate constant k_A is governed by the pK_a value of the corresponding acid HA, as proven by the LFE relationship shown in Fig. 3.

Conclusions

The extreme inertness of the complex Ni$(daco)_2^{2+}$ towards acid hydrolysis is not paralleled by the corresponding copper(II) complex Cu$(daco)_2^{2+}$, which is probably also due to a tetragonal distortion of the coordination geometry in Cu$(daco)_2^{2+}$ as compared to the planar N_4 arrangement in Ni$(daco)_2^{2+}$. The copper complex dissociates in acids at a proton-independent rate which is by a factor of 5 × 10^4 higher than the rate observed for the nickel complex. The acid dissociation of the complex Cu$(daco)_2^{2+}$ is subject to carboxylate ion and phosphate ion catalysis. There is a LFE relationship between the rate constants for base-catalysis and the corresponding pK_a values. The kinetic data obtained for ligand replacement in Cu$(daco)_2^{2+}$ by EDTA suggest that the mechanism of acid hydrolysis and of ligand substitution with EDTA is practically the same in the sense that the attack of water (solvolytic pathway) and the attack of carboxylate or phosphate ions open two separate reaction channels.

Acknowledgements

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