

# Kinetics and Mechanism of the Formation and Acid Dissociation of Cobalt(II), Nickel(II), and Copper(II) Complexes with the Highly Enolized $\beta$ -Diketone 3-(*N*-Acetylamido)pentane-2,4-dione (=Hamac) in Aqueous Solution<sup>†</sup>

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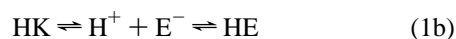
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Received March 8, 1995<sup>⊗</sup>

The  $\beta$ -diketone Hamac = 3-(*N*-acetylamido)pentane-2,4-dione was characterized by potentiometric, spectrophotometric, and kinetic methods. In water, Hamac is very soluble (2.45 M) and strongly enolized, with [enol]/[ketone] =  $2.4 \pm 0.1$ . The  $pK_a$  of Hamac is  $7.01 \pm 0.07$ , and the rate constants for enolization,  $k_e$ , and ketonization,  $k_k$ , at 298 K are  $0.0172 \pm 0.0004 \text{ s}^{-1}$  and  $0.0074 \pm 0.0015 \text{ s}^{-1}$ , respectively. An X-ray structure analysis of the copper(II) complex  $\text{Cu}(\text{amac})_2 \cdot \text{toluene}$  (=C<sub>21</sub>H<sub>28</sub>CuN<sub>2</sub>O<sub>6</sub>; monoclinic, C2/c;  $a = 20.434(6)$ ,  $b = 11.674(4)$ ,  $c = 19.278(6)$  Å;  $\beta = 100.75(1)^\circ$ ;  $Z = 8$ ;  $R_w = 0.0596$ ) was carried out. The bidentate anions  $\text{amac}^-$  coordinate the copper via the two diketo oxygen atoms to form a slightly distorted planar  $\text{CuO}_4$  coordination core. Rapid-scan stopped-flow spectrophotometry was used to study the kinetics of the reaction of divalent metal ions  $\text{M}^{2+}$  ( $\text{M} = \text{Ni}, \text{Co}, \text{Cu}$ ) with Hamac in buffered aqueous solution at variable pH and  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ ) under pseudo-first-order conditions ( $[\text{M}^{2+}]_0 \gg [\text{Hamac}]_0$ ) to form the mono complex  $\text{M}(\text{amac})^+$ . For all three metals the reaction is biphasic. The absorbance/time data can be fitted to the sum of two exponentials, which leads to first-order rate constants  $k_f$  (fast initial step) and  $k_s$  (slower second step). The temperature dependence of  $k_f$  and  $k_s$  was measured. It follows from the kinetic data that (i) the keto tautomer of Hamac, HK, does not react with the metal ions  $\text{M}^{2+}$ , (ii) the rate constant  $k_f$  increases linearly with  $[\text{M}^{2+}]_0$  according to  $k_f = k_0 + k_2[\text{M}^{2+}]_0$ , and (iii) the rate constant  $k_s$  does not depend on  $[\text{M}^{2+}]_0$  and describes the enolization of the unreactive keto tautomer HK. The pH dependence of the second-order rate constant  $k_2$  reveals that both the enol tautomer of Hamac, HE, and the enolate,  $\text{E}^-$ , react with  $\text{M}^{2+}$  in a second-order reaction to form the species  $\text{M}(\text{amac})^+$ . At 298 K rate constants  $k_{\text{HE}}$  are  $18 \pm 6$  (Ni),  $180 \pm 350$  (Co), and  $(9 \pm 5) \times 10^4$  (Cu)  $\text{M}^{-1} \text{ s}^{-1}$  and rate constants  $k_{\text{E}}$  are  $924 \pm 6$  (Ni),  $(7.4 \pm 0.6) \times 10^4$  (Co), and  $(8.4 \pm 0.2) \times 10^8$  (Cu)  $\text{M}^{-1} \text{ s}^{-1}$ . The acid dissociation of the species  $\text{M}(\text{amac})^+$  is triphasic. Very rapid protonation (first step) leads to  $\text{M}(\text{Hamac})^{2+}$ , which is followed by dissociation of  $\text{M}(\text{Hamac})^{2+}$  and  $\text{M}(\text{amac})^+$ , respectively (second step). The liberated enol Hamac ketonizes (third step). The mechanistic implications of the metal dependence of rate constants  $k_{\text{HE}}$ ,  $k_{\text{E}}$ ,  $k_{-\text{HE}}$ , and  $k_{-\text{E}}$  are discussed.

## Introduction

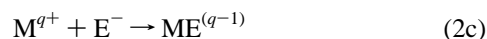
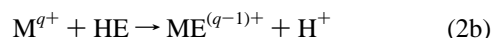
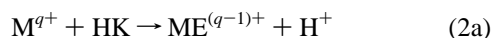
The reaction of metal ions with  $\beta$ -diketones are more complicated than many other complex formation reactions in which the rate of complexation is controlled by the rate of solvent exchange. The complications arise from the fact that  $\beta$ -diketones HL are subject to a keto/enol tautomerism according to (1). The keto tautomer HK is in equilibrium with the enol



HE, and both tautomers can dissociate to form the enolate  $\text{E}^-$ , so that a given metal ion can react with either HK, HE, or  $\text{E}^-$ .

The kinetics and mechanisms of complex formation with  $\beta$ -diketones have been thoroughly discussed by Hynes in a recent review.<sup>1</sup> In particular, the work carried out by Pearson and Anderson,<sup>2</sup> Sutin et al.,<sup>3,4</sup> and Hynes et al.<sup>5–18</sup> provides a

lot of mechanistic information concerning reactions 2a–c. It is



nevertheless still a matter of dispute<sup>1</sup> as to which ligand-based and/or metal-based factors control the intimate mechanism of these reactions.

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<sup>†</sup> Dedicated to Prof. Dr. K.-H. Lieser on the occasion of his 75th birthday.

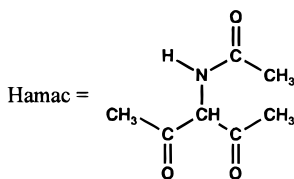
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<sup>§</sup> Fachbereich Materialwissenschaft.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 1, 1996.

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Our work<sup>19</sup> on the coordination chemistry of "isonitrosoacetylacetone" (=3-(hydroxyimino)pentane-2,4-dione) led us to the substituted  $\beta$ -diketone 3-(*N*-acetylamido)pentane-2,4-dione = Hamac,<sup>20</sup> the copper complex of which was prepared by



Fackler and Cotton.<sup>21</sup> This ligand is a remarkable  $\beta$ -diketone in that it is very soluble in water, much more strongly enolized than any of the  $\beta$ -diketones studied so far, and rather acidic. We decided to study the kinetics of mono complex formation according to (3) in aqueous solution for  $M = \text{Co}, \text{Ni},$  and  $\text{Cu}$



and thus contribute to the understanding of the mechanism of the enol-based and enolate-based reactions 2b and 2c.

### Experimental Section

**Chemicals.** The various metal perchlorates and buffers (HMOPS,<sup>20</sup> HMES,<sup>20</sup> HLUS<sup>20,22</sup>) were reagent grade. The solvent water was purified by double distillation of deionized water in a quartz apparatus. The ligand Hamac (mp 99–100 °C) was prepared from Hacac<sup>20</sup> in a two-step procedure as described.<sup>21,23</sup>

**Cu(amac)<sub>2</sub> and Cu(amac)<sub>2</sub>·toluene.** A solution of 0.65 g of Cu-(AcO)<sub>2</sub>·H<sub>2</sub>O (3.25 mmol) in 25 mL of warm ethanol was slowly added to a solution of 1.02 g of Hamac (6.5 mmol) in 25 mL of warm ethanol. After 10 min of stirring at 60 °C, the hot green solution was filtered. Cooling of the filtrate led to a green precipitate, which was recrystallized from ethanol, washed with cyclohexane, and dried in vacuo over silica gel at 60 °C to yield crystalline Cu(amac)<sub>2</sub> (yield 40%; dec pt > 150 °C). Cu(amac)<sub>2</sub>·toluene was prepared analogously, with a 1:1 mixture of ethanol/toluene instead of ethanol serving as solvent. Cooling of the reaction mixture led to green needles of Cu(amac)<sub>2</sub>·toluene (yield 40%; dec pt > 180 °C).

The results of elemental analysis (C,H,N) of Hamac and the two copper complexes were in good agreement with calculated data. The magnetic moments of Cu(amac)<sub>2</sub> and Cu(amac)<sub>2</sub>·toluene at 20 °C were found to be 1.91 and 1.93  $\mu_B$ , respectively. The solubility of Hamac (2.45 M) and Cu(amac)<sub>2</sub> (0.54 M) in water at 25 °C was determined spectrophotometrically.

**Instrumentation.** Magnetic susceptibility: magnetic susceptibility balance (Johnson-Matthey, type MSB-MKI). UV/vis spectra: diode array spectrophotometer (Hewlett-Packard, type 8451). pH: pH meter (Metrohm, type 654) in combination with a glass electrode (Ingold, type 405-88-S7), calibrated at  $I = 0.5 \text{ M}$  (NaClO<sub>4</sub>) to yield the relationship  $-\log[H^+] = \text{pH} - 0.11$ . Potentiometric titration: apparatus (Metrohm) consisting of potentiograph, automatic titrator, and Ag/AgCl reference glass electrode. Kinetic measurements: modified<sup>24</sup> stopped-flow spectrophotometer (Durrum, D 110) and rapid-scan stopped-flow spectrophotometer.<sup>25</sup>

(19) Elias, H.; Wiegand, D.; Wannowius, K. J. *Inorg. Chim. Acta* **1992**, *197*, 21.

(20) Abbreviations: Hamac = 3-(*N*-acetylamido)pentane-2,4-dione; HMOPS = 3-(*N*-morpholino)propanesulfonic acid; HMES = 2-(*N*-morpholino)ethanesulfonic acid; HLUS = 2,6-dimethylpyridine-3-sulfonic acid; Hacac = acetylacetone = pentane-2,4-dione; Htfdp = 1,1,1-trifluoropentane-2,4-dione; Hhptd = heptane-3,5-dione; Htftbd = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione.

(21) Fackler, J. P., Jr.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 102.

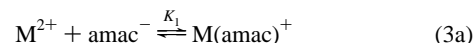
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**pK<sub>a</sub> of Hamac.** The pK<sub>a</sub> of the ligand in water ( $I = 0.5 \text{ M}$ , NaClO<sub>4</sub>) was determined by potentiometric and spectrophotometric titration with NaOH at 25 °C. The potentiometric method<sup>26</sup> led to pK<sub>a</sub> = 7.08 and the spectrophotometric titration,<sup>27</sup> based on  $\lambda_{\text{max}}(\text{Hamac}) = 278 \text{ nm}$  ( $\epsilon = 6700 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $\lambda_{\text{max}}(\text{amac}^-) = 296 \text{ nm}$  ( $\epsilon = 15\,400 \text{ M}^{-1} \text{ cm}^{-1}$ ), led to pK<sub>a</sub> = 6.93. The mean of these two independent determinations is thus pK<sub>a</sub> = 7.01 ± 0.07.

**Stability Constants.** Equilibrium constant K<sub>1</sub> for mono complex formation according to (3a) was determined by spectrophotometric



titration of solutions of Hamac and the metal perchlorate ( $M = \text{Co}, \text{Ni}, \text{Cu}$ ) and NaOH at  $I = 0.5 \text{ M}$  (NaClO<sub>4</sub>) and 298 K. Complex formation was monitored in the UV range as well as in the d–d range, as based on the following absorption data [ $\lambda_{\text{max}}$ , nm ( $\epsilon_{\text{max}}$ , M<sup>-1</sup> cm<sup>-1</sup>): Hamac, 278 (6700); amac<sup>-</sup>, 296 (15 400); Co(amac)<sup>+</sup>, 298 (9400) and 508 (14); Ni(amac)<sup>+</sup>, 302 (12 350) and 648 (3.4); Cu(amac)<sup>+</sup>, 302 (11 850) and 724 (32); Cu(amac)<sub>2</sub>, 298 (22 600) and 648 (44). Computer fitting of the data<sup>28</sup> led to the following stability constants.

M	K <sub>1</sub> , M <sup>-1</sup> (UV)	K <sub>1</sub> , M <sup>-1</sup> (d–d)	K <sub>1</sub> , M <sup>-1</sup> (mean)
Co	2.44 × 10 <sup>4</sup>	1.93 × 10 <sup>4</sup>	(2.18 + 0.25) × 10 <sup>4</sup>
Ni	7.02 × 10 <sup>4</sup>	6.57 × 10 <sup>4</sup>	(6.79 + 0.22) × 10 <sup>4</sup>
Cu	1.70 × 10 <sup>7</sup>	1.17 × 10 <sup>7</sup>	(1.43 ± 0.27) × 10 <sup>7</sup>

Titration of the system Cu<sup>2+</sup>/Hamac and NaOH up to pH 7 led to K<sub>2</sub> = (5.32 ± 3.2) × 10<sup>5</sup> M<sup>-1</sup> for the formation of the bis complex Cu(amac)<sub>2</sub>. In the case of cobalt and nickel, bis complex formation was not detectable.

### Rate of Enolization/Ketonization and the Ratio [enol]/[ketone].

The rate constant  $k_e$  for enolization was determined by the bromination method described elsewhere.<sup>3</sup> The bromination of the enol is too fast to be monitored by the stopped-flow technique at ambient temperature. The stopped-flow spectrophotometric investigation of the reaction of Hamac with Br<sub>2</sub> at 452 nm ( $\epsilon_{\text{max}}(\text{Br}_2) = 103 \text{ M}^{-1} \text{ cm}^{-1}$ ) led therefore to a sharp initial drop in absorbance,  $\Delta A (= A_{\text{init}} - A_0)$ , followed by a first-order decay of  $A$  from  $A_0$  to  $A_\infty$ . This first-order reaction, which corresponds to the enolization of the keto tautomer initially present, was studied at  $[\text{Hamac}]_0 = [\text{Br}_2]_0 = 2.5 \times 10^{-3} \text{ M}$  in the pH range 0.80–1.68 ( $I = 0.5 \text{ M}$ , NaClO<sub>4</sub>). The absorbance/time data were computer-fitted to eq 4, to obtain the parameters  $k_e$ ,  $A_0$ , and  $A_\infty$  (Table

$$A = (A_0 - A_\infty) \exp(-k_e t) + A_\infty \quad (4)$$

1). Rate constant  $k_e$  is pH-independent and averages to  $k_e = 0.0172 \pm 0.0004 \text{ s}^{-1}$  at 25 °C. The ratio [enol]/[ketone], following from the ratio of amplitudes (see Table 1), averages to 2.4 ± 0.1.

The rate constant of ketonization,  $k_k$ , was also determined by stopped-flow spectrophotometry. A solution of Hamac at pH 8.5, containing exclusively the enolate, was reacted with dilute HClO<sub>4</sub> to produce

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(26) Stepwise titration with NaOH changes the pH, from which the degree of protonation,  $n = [\text{Hamac}]/[\text{Hamac}]_0$ , was calculated. Computer-fitting of the  $n/[\text{H}^+]$  data<sup>22</sup> to  $n = ([\text{H}^+]/K_a)/(1 + [\text{H}^+]/K_a)$  led to K<sub>a</sub>.

(27) The species Hamac and amac<sup>-</sup> differ in their UV absorption. Stepwise titration with NaOH led to  $A/[\text{H}^+]$  data ( $A =$  absorbance), which were computer-fitted to  $A = [A_0(\text{Hamac}) + A_0(\text{amac}^-)K_a/[\text{H}^+]]/(1 + K_a/[\text{H}^+])$ . The symbols  $A_0(\text{Hamac})$  and  $A_0(\text{amac}^-)$  stand for the absorbance of the species Hamac and amac<sup>-</sup> at  $[\text{Hamac}]_0$ .

(28) The absorbance/[H<sup>+</sup>] data were fitted to eq I (monitoring in the UV range) or eq II

$$A = (A_0^{\text{HL}} + A_0^{\text{ML}}K_1[M^{2+}]_0K_a/[\text{H}^+])/(1 + K_1[M^{2+}]_0K_a/[\text{H}^+]) \quad \text{I}$$

$$A = (A_0^{\text{M}} + A_0^{\text{ML}}K_1[\text{HL}]_0K_a/[\text{H}^+])/(1 + K_1[\text{HL}]_0K_a/[\text{H}^+]) \quad \text{II}$$

(monitoring in the d–d range) with  $A_0^{\text{HL}}$ ,  $A_0^{\text{ML}}$ , and  $A_0^{\text{M}}$  being the absorbance of the species HL, ML, and M at concentrations  $[M^{2+}]_0$  (eq I) and  $[\text{HL}]_0$  (eq II), respectively.

**Table 1.** Rate Constants for the Enolization and Ketonization of Hamac at 298 K ( $I = 0.5$  M)

pH	$k_e, s^{-1}$ <sup>a</sup>	$(k_e + k_k), s^{-1}$ <sup>b</sup>	$\Delta A, \%$ <sup>c</sup>	$A_0 - A_\infty, \%$ <sup>c</sup>	$\Delta A/(A_0 - A_\infty) = [\text{enol}]/[\text{ketone}]$
0.80	0.0175		69.6	30.4	2.29
1.06	0.0167		70.9	29.1	2.44
1.68	0.0175		71.2	28.8	2.47
1.09		0.0247			
1.45		0.0240			
2.34		0.0240			
3.02		0.0256			

<sup>a</sup> Obtained by fitting the  $A/t$  data to eq 4;  $[\text{Hamac}]_0 = [\text{Br}_2]_0 = 2.5 \times 10^{-3}$  M. <sup>b</sup> Obtained by fitting the  $A/t$  data to eq 5;  $[\text{Hamac}]_0 = 5 \times 10^{-5}$  M. <sup>c</sup> The parameters  $\Delta A$  and  $(A_0 - A_\infty)$  are described in the Experimental Section.

**Table 2.** Crystallographic Data for  $\text{Cu}(\text{amac})_2 \cdot \text{toluene}$ 

$\text{C}_{21}\text{H}_{28}\text{CuN}_2\text{O}_6$	$Z = 8$
fw = 467.98	$T = 26.0$ °C
space group: $C2/c$ (No. 15)	$\lambda = 0.710\ 69$ Å
$a = 20.434(6)$ Å	$\rho(\text{calcd}) = 1.38$ g cm <sup>-3</sup>
$b = 11.674(4)$ Å	$\mu = 10.0$ cm <sup>-1</sup>
$c = 19.278(6)$ Å	$R(F_o)^a = 0.0742$
$\beta = 100.75(1)^\circ$	$R_w(F_o)^b = 0.0596$
$V = 4517.85 \pm 4.2$ Å <sup>3</sup>	

$${}^a R(F_o) = \sum |F_o - F_c| / \sum F_o, {}^b R_w(F_o) = \sum w^{1/2} |F_o - F_c| / \sum w^{1/2} F_o.$$

exclusively the enol. The ketonization of the enol, which is a reversible first-order reaction with  $k_{\text{obsd}} = k_e + k_k$ , was followed at different pH values ( $I = 0.5$  M,  $\text{NaClO}_4$ ). The  $A/t$  data were fitted to eq 5 to obtain

$$A = (A_0 - A_{\text{eq}}) \exp[-(k_e + k_k)t] + A_{\text{eq}} \quad (5)$$

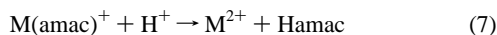
the pH-independent sum of  $k_e$  and  $k_k$  (Table 1). The averaged values of  $(k_e + k_k) = 0.0246 \pm 0.0015$  s<sup>-1</sup> and  $k_e = 0.0172$  s<sup>-1</sup> (see above) led to  $k_k = 0.0074 \pm 0.0015$  s<sup>-1</sup> at 25 °C.

**Kinetics of Complex Formation.** Reaction 3 was followed by stopped-flow or rapid-scan-stopped-flow spectrophotometry at  $I = 0.5$  M ( $\text{NaClO}_4$ ) and variable pH in buffered solution under pseudo-first-order conditions ( $[\text{M}^{2+}]_0 \geq 10[\text{Hamac}]_0$ ). The  $A/t$  data, resulting from the increase in absorbance at 300–315 nm with time, were computer-fitted to eq 6 (irreversible biphasic consecutive reaction). The fitting

$$A = a_f[\exp(-k_f t)] + a_s[\exp(-k_s t)] + A_\infty \quad (6)$$

procedure, based on the least-squares method, led to  $a_f$ ,  $a_s$ ,  $A_\infty$ ,  $k_f$ , and  $k_s$  ( $k_f$ ,  $k_s$  = rate constants for the fast and slow reaction;  $a_f$ ,  $a_s$  = corresponding amplitudes in units of absorbance).

**Kinetics of Acid Hydrolysis.** Reaction 7 was followed as described for complex formation according to (3), with  $\text{HClO}_4$  being the excess



partner ( $[\text{HClO}_4]_0 \geq 10[\text{M}(\text{amac})^+]_0$ ). The  $A/t$  data of the biphasic process were computer-fitted with eq 6.

**X-ray Structure Determination.** The green crystal of  $\text{Cu}(\text{amac})_2 \cdot \text{toluene}$ , as grown from the ethanol/toluene reaction mixture, was needle-shaped and had the dimensions  $0.15 \times 0.16 \times 1.2$  mm. Intensities were measured on a four-circle diffractometer (Stoe-Stadi-4) using graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.710\ 69$  Å; scan  $2\theta/\omega = 1:1$ ). Cell constants were determined by the least-squares method from the  $2\theta$  angles of 94 reflections ( $T = 299$  K) on the same instrument.  $Lp$  and background corrections and a numerical absorption correction (EMPIR and REDU4 (Stoe);  $T_{\text{min}} = 0.935$  and  $T_{\text{max}} = 1.000$ ) were applied.

The structure was solved by direct methods with SHELXS-86 (PATT) and refined by least-squares to the  $R$  values given in Table 2. Hydrogen atoms were positioned geometrically (C–H distance =  $0.96$  Å) and not refined. An empirical extinction correction was applied. All crystallographic calculations were performed with the programs SHELX-76 and SHELXS-86 on an IBM 3090 computer at the

**Table 3.** Atomic Parameters ( $\times 10^4$ ) for  $\text{Cu}(\text{amac})_2 \cdot \text{toluene}$  (Excluding H)

atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}, \text{Å}^2$ <sup>a</sup>
Cu1	4846(1)	4721(1)	4150(1)	417(5)
O1	4209(2)	5911(5)	3991(2)	473(31)
C1	3250(4)	6987(7)	3525(5)	785(56)
C2	3628(4)	5854(7)	3646(3)	472(40)
C3	3301(3)	4849(7)	3361(3)	412(39)
C4	3617(4)	3776(7)	3450(3)	463(43)
C5	3237(4)	2728(7)	3123(5)	741(54)
O2	4206(2)	3586(4)	3776(2)	498(31)
N1	2638(3)	4931(6)	2964(3)	467(35)
C6	2093(3)	4816(7)	3270(4)	516(44)
O3	2118(3)	4752(6)	3895(2)	821(38)
C7	1438(3)	4797(8)	2739(4)	714(49)
O4	5517(2)	3567(4)	4232(2)	492(31)
C8	6539(4)	2648(7)	4320(4)	663(51)
C9	6150(4)	3714(7)	4377(3)	417(42)
C10	6451(3)	4766(8)	4541(3)	400(38)
C11	6120(3)	5769(7)	4616(3)	426(42)
C12	6478(4)	6884(7)	4784(4)	662(50)
O5	5481(2)	5849(4)	4553(2)	512(31)
N2	7170(3)	4826(6)	4672(3)	449(34)
C13	7528(4)	4899(7)	4160(4)	481(43)
O6	7285(2)	4838(6)	3535(2)	682(35)
C14	8268(3)	5051(7)	4417(3)	508(43)

$${}^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

Technische Hochschule Darmstadt. Scattering factors  $f_0$ ,  $f'$ , and  $f''$  for C, H, N, and O are stored in SHELX-76.<sup>29</sup> The final positional parameters are given in Table 3.

## Results

**The  $\beta$ -Diketone Hamac.** Hamac is a colorless solid which, due to the polar acetamido group in 3-position, is well soluble in water. The solubility (2.45 M) exceeds that of Hacac by a factor of 1.5. Moreover, the complex  $\text{Cu}(\text{amac})_2$  can be dissolved in water up to 0.56 M, which is 700 times higher than for  $\text{Cu}(\text{acac})_2$ . The  $\text{pK}_a$  of Hamac, as determined independently by potentiometric and spectrophotometric titration, is  $7.01 \pm 0.07$  (mean of 7.08 and 6.93). Hamac is thus by almost two  $\text{pK}$  units more acidic than Hacac (see Table 4).

The rate of enolization of Hamac ( $k_e = 0.0172$  s<sup>-1</sup>) is rather close to that of Hacac and Htfpd<sup>20</sup> ( $k_e = 0.015$  s<sup>-1</sup>), but the rate of ketonization is considerably smaller (Table 4). This means that the enol/ketone equilibrium is much more shifted toward the enol tautomer, with  $K = k_e/k_k = 2.3 \pm 0.4$ . The spectrophotometric investigation of the kinetics of enolization according to the bromination method leads to the reaction amplitudes  $\Delta A$  and  $(A_0 - A_\infty)$ , the ratio of which corresponds to  $K$  (see Table 1). This independently obtained value amounts to  $K = 2.4 \pm 0.1$  and is in good agreement with the value following from the ratio  $k_e/k_k$ . To our knowledge, the ligand Hamac is thus the most strongly enolized  $\beta$ -diketone so far studied kinetically.

**Structure of the Complex  $\text{Cu}(\text{amac})_2 \cdot \text{toluene}$ .** The ligand Hamac carries three donor oxygen atoms in total so that the question of O(acetyl) coordination cannot be excluded. It follows from Figure 1, however, that in the complex unit  $\text{Cu}(\text{amac})_2$  the ligand prefers the normal coordination with the two  $\beta$ -diketone oxygens being bound to the copper. The complex is centrosymmetric and crystallizes in the monoclinic space group  $C2/c$  with 8 formula units per unit cell. Half of the toluene is located on a 2-fold axis; the other half is located close

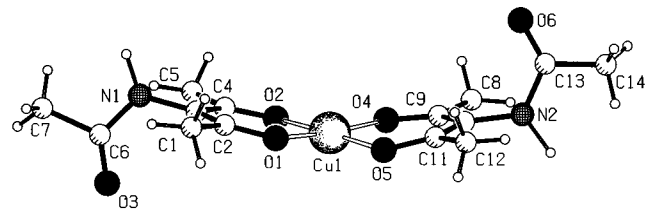
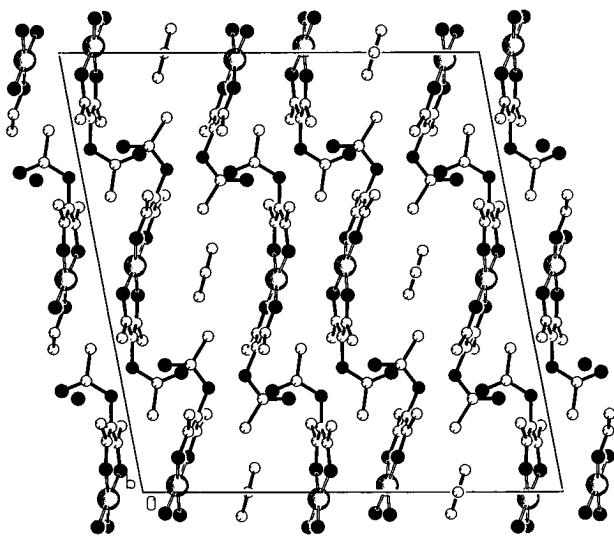
(29) Data for Cu was taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV.

(30) Pearson, R. G.; Moore, J. W. *Inorg. Chem.* **1966**, *5*, 1528.

**Table 4.** Parameters Characterizing the  $\beta$ -Diketone Hamac<sup>a</sup>

$\beta$ -diketone <sup>20</sup>	solubility, M	pK <sub>a</sub>	$k_e$ , s <sup>-1</sup>	$k_k$ , s <sup>-1</sup>	$K = k_e/k_k = [\text{enol}]/[\text{ketone}]$	ref
Hamac	2.45	7.01 ± 0.07	0.0172 ± 0.0004	0.0074 ± 0.0015	2.3 ± 0.4 2.4 ± 0.1 <sup>b</sup>	this work
Hacac	1.6	9.00	0.015	0.114	0.13	30
Htfpd		6.06	0.015	1.5	0.01	10
Hhptd		10.0	0.0058	0.048	0.12	7

<sup>a</sup> The data refer to the solvent water,  $I = 0.5$  M, and 298 K. <sup>b</sup> As determined from the ratio of amplitudes (see Table 1).

**Figure 1.** View of the coordination geometry in the complex Cu(amac)<sub>2</sub>.**Figure 2.** Projection of the unit cell of the complex Cu(amac)<sub>2</sub>·toluene along [010].

to a center of symmetry and is highly disordered, which limited the refinement to  $R_w = 0.0596$  (Table 2).

The copper coordinates the two ligands in a planar fashion. The planes of the two chelate rings are slightly bent off the CuO<sub>4</sub> coordination plane though, with the two *N*-acetyl amino groups pointing into opposite directions (Figure 1). As shown in Figure 2, the units of Cu(amac)<sub>2</sub> form dimers (Cu–Cu distance = 329 pm; shortest intermolecular Cu–O distance = 279 pm). The dimeric units are stabilized by weak intermolecular hydrogen bonds between N2 and O3 (distance = 291 pm) and the dimers are stacked along [001] via weak hydrogen bonds between N1 and O6 (distance = 292 pm). The toluene located on the twofold axis is sitting between the stacked dimers. The Cu–Cu distance of 329 pm and the normal magnetic moment of 1.93  $\mu_B$  point to the absence of metal–metal interactions. The planar arrangement of the CuO<sub>4</sub> coordination core is slightly distorted (see angles and distances in Table 5). The average Cu–O distance (190.3 pm), C–O distance (127.3 pm), and C–C distance within the chelate rings (139.3 pm; see Table 5) is rather close to what is found for similar  $\beta$ -diketone copper complexes of the type bis(3-*R*-pentane-2,4-dionato)-copper(II) with *R* = phenyl<sup>31</sup> or methyl.<sup>32</sup> The C–C and C–O

**Table 5.** Selected Distances (pm) and Bond Angles (deg) for Cu(amac)<sub>2</sub>·toluene

Distances			
Cu–O1	188.9(5)	C1–C2	152.8(10)
Cu–O2	190.6(5)	C4–C5	152.1(10)
Cu–O4	190.7(5)	C8–C9	149.3(10)
Cu–O5	191.1(5)	C11–C12	149.8(10)
O1–C2	124.9(8)	C3–N1	142.7(8)
O2–C4	126.9(8)	C10–N2	144.5(8)
O4–C9	128.3(8)	N1–C6	135.6(9)
O5–C11	129.1(8)	N2–C13	133.6(8)
C2–C3	141.0(10)	C6–C7	152.6(9)
C3–C4	140.4(10)	C13–C14	151.1(9)
C9–C10	138.3(10)	C6–C3	120.0(8)
C10–C11	137.3(10)	C13–O6	121.8(8)
		Cu–Cu <sup>a</sup>	328.6(2)

Angles			
O1–Cu–O2	92.7(2)	O4–Cu–O5	91.7(2)
Cu–O2–C4	125.9(5)	Cu–O4–C9	127.1(5)
Cu–O1–C2	127.2(5)	Cu–O5–C11	125.9(5)
O2–C4–C3	126.0(7)	O4–C9–C10	123.8(7)
O1–C2–C3	125.9(7)	O5–C11–C10	124.1(7)
C2–C3–C4	121.4(6)	C9–C10–C11	125.0(6)

<sup>a</sup> Distance between neighboring complex units.

distances lie in between those for single and double bonds and reflect delocalization of electron density within the chelate rings formed, which is typical for  $\beta$ -diketone complexes.

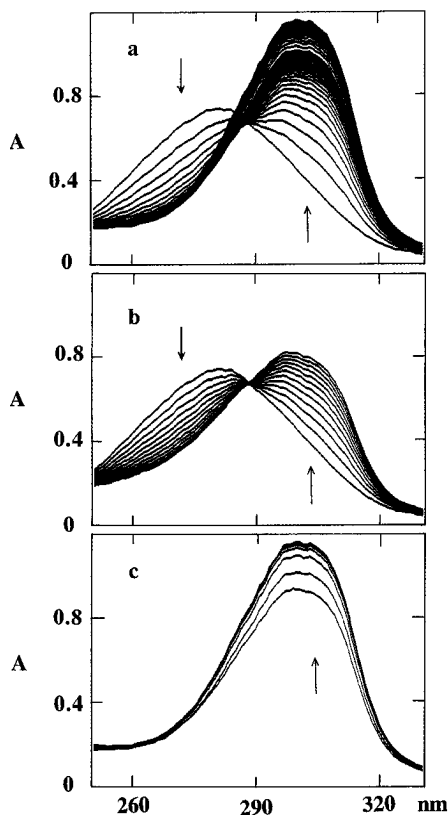
**Kinetics of Complex Formation.** The reaction of Hamac with an excess of the divalent metal ions M<sup>2+</sup> (M = Co, Ni, Cu) leads to the species M(amac)<sup>+</sup>. These species absorb strongly in the UV and have weak d–d transitions in the visible range (see Experimental Section). The strong absorption at about 300 nm corresponds to the  $\pi \rightarrow \pi^*$  transition of the enolate amac<sup>-</sup>, which is bathochromically shifted and intensified upon coordination to the metal. Monitoring of the formation of the species M(amac)<sup>+</sup> at 300–315 nm should therefore result in an increase in absorbance.

As an example, Figure 3a shows the series of spectra obtained for the reaction of an excess of Ni<sup>2+</sup> ions with Hamac at pH 6.2. The first 50 spectra were recorded every second, the second set of 50 spectra every 5 s. The reaction is obviously biphasic. As shown in Figure 3b, the first set of spectra is characterized by a sharp isosbestic point at 288 nm, with a decrease in absorbance below 288 nm and an increase above. This initial reaction step is followed by a slower reaction (see Figure 3c), associated with a gradual increase of the absorption peak at 302 nm, typical for Ni(amac)<sup>+</sup>. The  $A/t$  data can be fitted to the sum of two exponentials (eq 6), which leads to rate constants  $k_f$  (fast initial step) and  $k_s$  (slower second step). For M = Co, Cu the same type of biphasic kinetics is observed.

Variation of [M<sup>2+</sup>]<sub>0</sub> at constant pH leads to the data summarized in Table 6. Rate constant  $k_f$  increases with increasing [M<sup>2+</sup>]<sub>0</sub> and, for a given concentration of the metal, its size depends on the nature of the metal according to  $k_f(\text{Cu}) > k_f(\text{Co}) > k_f(\text{Ni})$ . Rate constant  $k_s$  is independent of [M<sup>2+</sup>]<sub>0</sub>, nearly of the same size for M = Ni, Co and somewhat larger for M = Cu. These findings suggest that the  $k_f$  step describes complex formation and that the  $k_s$  step has to do with the

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(32) Robertson, J.; Truter, M. R. *J. Chem. Soc. A* **1967**, 309.



**Figure 3.** Spectral changes in the UV range associated with the reaction of  $\text{Ni}^{2+}$  ions ( $[\text{Ni}^{2+}]_0 = 5 \times 10^{-3} \text{ M}$ ) with Hamac ( $[\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ ) in water at pH 6.2, 298 K, and  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ ). Key: (a) 100 consecutive spectra, with  $\Delta t = 1 \text{ s}$  for spectra 1–50 and  $\Delta t = 5 \text{ s}$  for spectra 51–100 (every second spectrum omitted for clarity); (b) spectra 1–12; (c) spectra 25, 50, 60, 70, 80, 90, and 100.

**Table 6.** Rate Constants  $k_f$  and  $k_s$  for the Reaction of Hamac with  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  Ions According to Eq 3 at 298 K<sup>a,b</sup>

$[\text{M}^{2+}]$ , mM	pH <sup>c</sup>	$k_f$ , s <sup>-1</sup>	$k_s$ , s <sup>-1</sup>
M = Ni			
0.50	4.94	0.0485	0.0104
1.25	4.87	0.0654	0.0231
2.50	4.85	0.0850	0.0237
3.75	4.84	0.104	0.0249
5.00	4.84	0.121	0.0243
12.5	4.85	0.233	0.0246
25.0	4.83	0.396	0.0248
M = Cu			
0.050	3.49	18.2	0.144
0.125	3.47	20.3	0.162
0.250	3.48	23.7	0.154
0.500	3.47	28.8	0.150
1.00	3.47	42.7	0.138
2.00	3.45	64.7	0.128
M = Co			
0.50	4.89		0.0066
1.25	4.87	8.67	0.0115
2.50	4.84	9.70	0.0237
3.75	4.86	10.1	0.0238
5.00	4.83	11.2	0.0255
12.5	4.81	15.7	0.0259
25.0	4.80	23.4	0.0265

<sup>a</sup> Conditions  $[\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ ;  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ ). <sup>b</sup>  $k_f$  and  $k_s$  obtained by computer-fitting of the  $A/t$  data to eq 6. <sup>c</sup> The pH was adjusted with the buffers HLU<sup>20</sup> (Ni, Co) and formic acid (Cu) at  $[\text{buffer}] = 0.1 \text{ M}$ .

tautomerism of the ligand Hamac. Convincing support for this interpretation comes from two experiments. In the first one, excess  $\text{Ni}^{2+}$  ions were reacted exclusively with the enol tautomer

**Table 7.** First-Order Rate Constant for the Reaction of  $\text{Ni}^{2+}$  Ions with Exclusively the Enol Tautomer of Hamac<sup>33</sup> and for the Reaction of  $\text{Co}^{2+}$  Ions with an Excess of Hamac at 298 K ( $I = 0.5 \text{ M}$ )

$[\text{Ni}^{2+}]$ , mM <sup>a</sup>	pH <sup>b</sup>	$k$ , s <sup>-1</sup> <sup>c</sup>	$[\text{Hamac}]$ , M <sup>d</sup>	pH <sup>e</sup>	$k$ , s <sup>-1</sup> <sup>f</sup>
1.00	5.50	0.0831	0.0375	4.65	21.4
2.50	5.51	0.116	0.050	4.67	25.2
5.00	5.51	0.179	0.075	4.60	35.3
10.0	5.43	0.295	0.10	4.61	43.4
25.0	5.45	0.660	0.15	4.55	51.8
50.0	5.50	1.26			

<sup>a</sup>  $[\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ . <sup>b</sup> Adjusted with HME<sup>20</sup>. <sup>c</sup> Obtained by fitting eq 4 to the  $A/t$  data recorded at 300 nm. <sup>d</sup>  $[\text{Co}^{2+}]_0 = 0.00375 \text{ M}$ . <sup>e</sup> Adjusted with HLU<sup>20</sup>. <sup>f</sup> Obtained by fitting eq 4 to the  $A/t$  data recorded at 500 nm.

of Hamac at pH 5.5.<sup>33</sup> The  $A/t$  data thus obtained could be well fitted to a single exponential according to (4); i.e. only one step was observed. The first-order rate constant resulting from this experiment increases with increasing  $[\text{Ni}^{2+}]_0$  (Table 7), as does  $k_f$ . This result indicates that the  $k_s$  step obviously describes the (slow) enolization of the keto tautomer of Hamac after the enol tautomer has been consumed in (fast) complex formation with the nickel present in excess. In addition, the fact that  $k_s \neq f([\text{Ni}]_0)$  is consistent with the interpretation that the keto tautomer as such does not add to the nickel. The second experiment concerns the reaction of  $\text{Co}^{2+}$  ions with an excess of Hamac, as monitored in the d–d range. In this case the  $A/t$  data could also be fitted to a single exponential according to (4). The resulting first-order rate constant increases with increasing  $[\text{Hamac}]_0$  (Table 7). These findings suggest that, for  $[\text{Hamac}]_0 \geq 10[\text{Co}^{2+}]_0$ , there is an excess of enolic Hamac present to completely convert the  $\text{Co}^{2+}$  ions into the species  $\text{Co}(\text{amac})^+$  in a pseudo-first-order reaction.

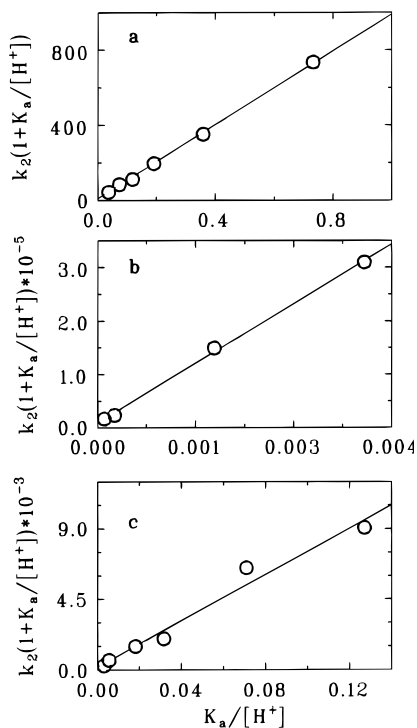
The reaction of Hamac with copper is much faster than that with nickel and cobalt. For experimental reasons the concentration of excess copper had therefore to be kept low. As shown in Table 6, for some of the copper experiments the pseudo-first-order condition ( $[\text{Cu}^{2+}]_0 \geq 10[\text{Hamac}]_0$ ) was not fulfilled. The surprising result was however that even for  $[\text{Cu}^{2+}]_0 : [\text{Hamac}]_0 = 1:1$  and 2.5:1 the  $A/t$  data could be well fitted to eq 6.<sup>34</sup> A simple interpretation of this finding would come from the assumption that the species  $\text{Cu}(\text{amac})^+$  is mainly formed via the reaction of the  $\text{Cu}^{2+}$  ion with the enolate  $\text{amac}^-$ , for which the condition  $[\text{Cu}^{2+}]_0 \gg [\text{amac}^-]$  is of course fulfilled in the pH range 3–4.7.

Figure 4 shows the plot of the dependence  $k_f = f([\text{Ni}^{2+}]_0)$  and  $k_s = f([\text{Ni}^{2+}])$ , respectively, for the system  $\text{Ni}^{2+}/\text{Hamac}$  at three different pH values. The rate constant  $k_s$  for the slower second reaction step is independent of  $[\text{Ni}^{2+}]_0$  (Figure 4b) and increases weakly with increasing pH. The averaged size of  $k_s$  is close to that of the rate constant for the enolization of Hamac,  $k_e = 0.0172 \text{ s}^{-1}$  (Table 4), but is somewhat larger. An explanation for this comes from the study of the rate of enolization at variable pH in the presence of buffers.<sup>35</sup> This study shows that the enolization of Hamac is subject to general base catalysis. Hydroxyl ions and the  $\text{B}^-$  ions of added buffers HB affect  $k_e$  according to  $k_e = k_{\text{HOH}}[\text{H}_2\text{O}] + k_{\text{OH}}[\text{OH}^-] + k_{\text{B}}[\text{B}^-]$ . The term  $k_{\text{HOH}}[\text{H}_2\text{O}]$  amounts to  $0.017 \pm 0.001 \text{ s}^{-1}$  at

(33) The solution of Hamac used for this stopped-flow experiment was set to pH 8.4 to convert Hamac completely to  $\text{amac}^-$ . This solution was reacted with solutions of nickel perchlorate of pH 5.5 (as adjusted with the buffer HME<sup>20</sup>) to produce reaction mixtures of pH 5.5 containing only the enol tautomer of Hamac upon mixing.

(34) In the case of the experiment with the stoichiometry  $[\text{Cu}^{2+}]_0 : [\text{Hamac}]_0 = 1:1$  it was attempted to fit the  $A/t$  data for the fast initial step to the equation valid for a 1:1 second-order reaction,  $A = A_\infty + (A_0 - A_\infty)/(1 + [\text{Cu}^{2+}]_0 kt)$ . The quality of the fit was very poor though.





**Figure 5.** Plot of the term  $k_2(1 + K_a/[H^+])$  vs  $K_a/[H^+]$  according to eq 11 for nickel (a), copper (b), and cobalt (c).

**Table 9.** Rate and Equilibrium Constants for the Formation and Acid Dissociation of the Species  $M(\text{amac})^+$  ( $M = \text{Ni}, \text{Co}, \text{Cu}$ ) at 298 K and  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ )

	$M = \text{Ni}$	$M = \text{Co}$	$M = \text{Cu}$
$k_{\text{HE}}, \text{M}^{-1} \text{s}^{-1}$	$18 \pm 6$	$180 \pm 350$	$(9 \pm 5) \times 10^4$ $(1.3 \pm 0.7) \times 10^4$ <sup>a</sup>
$k_{\text{E}}, \text{M}^{-1} \text{s}^{-1}$	$924 \pm 6$	$(7.4 \pm 0.6) \times 10^4$	$(8.4 \pm 0.2) \times 10^8$
$k_{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$			$(3.0 \pm 0.1) \times 10^8$ <sup>a</sup>
$k_{-\text{HE}}, \text{s}^{-1}$	$\geq 10.3$ <sup>b</sup>	$240 \pm 43$	$1330 \pm 210$
$k_{-\text{E}}, \text{s}^{-1}$	$0.054 \pm 0.005$	$9.5 \pm 2.3$	$15.7 \pm 1.6$
$K_{\text{MEH}}, \text{M}$	$\geq 0.5$ <sup>b</sup>	$0.0038 \pm 0.0013$	$0.22 \pm 0.05$
$k_{\text{E}}/k_{-\text{E}}, \text{M}^{-1}$	$1.7 \times 10^4$	$0.91 \times 10^4$	$5.4 \times 10^7$
$K_1, \text{M}^{-1}$	$6.79 \times 10^4$	$2.18 \times 10^4$	$1.6 \times 10^7$
$k_{\text{ex}}, \text{s}^{-1}$ <sup>c</sup>	$3.2 \times 10^4$	$3.2 \times 10^6$	$4.4 \times 10^9$
$k_{i,\text{E}}/k_{\text{ex}}$ <sup>e</sup>	0.048	0.039	0.32
$k_{i,\text{HE}}/k_{\text{ex}}$ <sup>f</sup>	$1.9 \times 10^{-3}$	$1.9 \times 10^{-4}$	$6.8 \times 10^{-5}$

<sup>a</sup> As obtained by fitting eq 16b to the  $k_2/[H^+]$  data. <sup>b</sup> Estimated on the basis of the condition  $[H^+]/K_{\text{MEH}} \leq 0.1$ . <sup>c</sup> Spectrophotometrically determined formation constant for the species  $M(\text{amac})^+$  according to eq 3a. <sup>d</sup> Rate constant for water exchange at 298 K.<sup>44,45</sup> <sup>e</sup> Calculated on the basis of  $k_{i,\text{E}} = k_{\text{E}}/K_{\text{OS}}$  for  $K_{\text{OS}} = 0.6 \text{ M}^{-1}$ .<sup>46</sup> <sup>f</sup> Calculated on the basis of  $k_{i,\text{HE}} = k_{\text{HE}}/K_{\text{OS}}$  for  $K_{\text{OS}} = 0.3 \text{ M}^{-1}$ .<sup>46</sup>

**Kinetics of Acid Hydrolysis.** The acid hydrolysis of the mono complex  $M(\text{amac})^+$  ( $M = \text{Co}, \text{Ni}, \text{Cu}$ ), as monitored spectrophotometrically in the UV range, was found to be a three-step process. The first step is a sharp change in absorbance,  $\Delta A$ , too fast to be monitored by the stopped-flow technique. This initial rapid step is followed by a change in absorbance with time to which eq 6 can be fitted satisfyingly. The fitting procedure leads to first-order rate constants  $k_f$  for a fast second step and  $k_s$  for a third slower step (see Table 11). The rate constant  $k_s$  is pH-independent and found to be the same for  $M = \text{Co}, \text{Ni}, \text{and Cu}$ ; its size corresponds to  $(k_e + k_k)$  (see Table 1). This means that the  $k_s$  step is indeed the final third step describing the ketonization of enolic Hamac liberated by the acid hydrolysis of the species  $M(\text{amac})^+$ .

The very rapid initial change in absorbance,  $\Delta A$ , increases with decreasing pH. It is therefore suggested that, according to Scheme 1, the first step consists in the fast protonation of

**Table 10.** Temperature Dependence of Rate Constants  $k_f$  and  $k_s$  for the Formation of the Species  $M(\text{amac})^+$  According to Eq 3 at  $I = 0.5 \text{ M}$  and Activation Parameter  $\Delta H^\ddagger$

$T, \text{K}$	$M = \text{Ni}^a$		$M = \text{Co}^b$		$M = \text{Cu}^c$	
	$k_f, \text{s}^{-1}$	$k_s, \text{s}^{-1}$	$k_f, \text{s}^{-1}$	$k_s, \text{s}^{-1}$	$k_f, \text{s}^{-1}$	$k_s, \text{s}^{-1}$
285	0.204	0.0297				
288	0.261	0.0325	12.9	0.0416	9.98	0.00739
291	0.353	0.0411				
293	0.439	0.0543	19.3	0.0594	13.6	0.0166
298	0.687	0.0703	29.0	0.0832	17.6	0.0241
303	1.08	0.0995	43.6	0.120	24.2	0.0366
308	1.60	0.136	60.3	0.164	29.2	0.0444
313	2.40	0.188	86.3	0.231	44.2	0.0605

$\Delta H^\ddagger, \text{kJ mol}^{-1}$ <sup>d</sup>  $63.4 \pm 1$   $47.6 \pm 2$   $54.7 \pm 2$   $48.7 \pm 1$   $40.6 \pm 2$   $46.4 \pm 3$

<sup>a</sup> At pH 6.2 (buffer: HMES),  $[\text{Ni}^{2+}]_0 = 0.005 \text{ M}$ ,  $[\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ . <sup>b</sup> At pH 6.2 (buffer: HMES),  $[\text{Co}^{2+}]_0 = 0.0025 \text{ M}$ ,  $[\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ . <sup>c</sup> At pH 4.2 (buffer: HLUS),  $[\text{Cu}^{2+}]_0 = [\text{Hamac}]_0 = 5 \times 10^{-5} \text{ M}$ . <sup>d</sup> Obtained from the slope of the plot of  $\ln(k_f/T)$  and  $\ln(k_s/T)$ , respectively, vs  $1/T$ . The data for  $\Delta S^\ddagger$  are not presented. Due to the fact that both  $k_f$  (see eqs 10 and 12) and  $k_s (=k_e + k_k)$ <sup>35</sup> are composite parameters the data for  $\Delta S^\ddagger$  are rather meaningless.

the complex  $M(\text{amac})^+ = \text{ME}^+$ . The concentration of the species  $\text{MEH}^{2+}$  thus formed is governed by the pH. The decay of  $\text{ME}^+$  and  $\text{MEH}^{2+}$  liberates the enol HE (second step;  $k_f$ ), which finally ketonizes (third step;  $k_s = k_e + k_k$ ). If so, the experimental rate constant  $k_f$  for the observable fast step of acid hydrolysis should follow relationship 12. The plot of  $k_f = f(\text{pH})$

$$k_f = (k_{-\text{E}} + k_{-\text{HE}}[H^+]/K_{\text{MEH}})/(1 + [H^+]/K_{\text{MEH}}) \quad (12)$$

for  $M = \text{Co}$ , as shown in Figure 6, indicates the expected saturation type behavior of  $k_f$ .<sup>38</sup> Computer-fitting of eq 12 to the data leads to the parameters  $k_{-\text{E}}$ ,  $k_{-\text{HE}}$  and  $K_{\text{MEH}}$  for  $M = \text{Co}$  and  $\text{Cu}$ , albeit with large errors for  $k_{-\text{HE}}$  and  $K_{\text{MEH}}$  (see Table 9). In the case of nickel the dependence of  $k_f$  on  $[H^+]$  is linear up to pH 1.3. A linear dependence of  $k_f$  on  $[H^+]$  follows from eq 12 for the condition  $[H^+]/K_{\text{MEH}} \leq 0.1$ . This in turn means for pH 1.3 that the condition  $K_{\text{MEH}} \geq 0.5$  has to be fulfilled. It follows from the numbers obtained for  $K_{\text{MEH}}$  that, compared to the complex cation  $\text{Co}(\text{amac})^+$ , the species  $\text{Ni}(\text{amac})^+$  and  $\text{Cu}(\text{amac})^+$  are only weakly protonated.

## Discussion

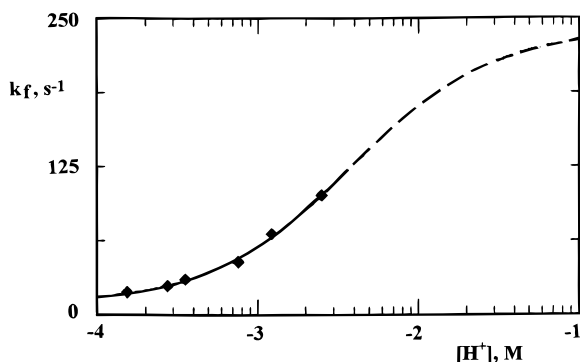
In aqueous solution the ligand Hamac is present mainly in its enolic form (70%). In the complex  $\text{Cu}(\text{amac})_2$ -toluene (see Figure 1) and, most probably, in all of the species  $M(\text{amac})^+$  studied the ligand behaves like an unsubstituted  $\beta$ -diketone and coordinates the metal via the two diketo oxygens. The kinetic results are consistent with the interpretation that the keto tautomer of Hamac does not add to the metal. The coordination of the enol tautomer, as studied with an excess of metal ion, is biphasic. There is a fast initial step ( $k_f$ ), describing "fast"  $M(\text{amac})^+$  formation, and a slower consecutive step ( $k_s$ ), describing "slow"  $M(\text{amac})^+$  formation, as controlled by the enolization of the "unreactive" keto tautomer. The rate of the latter process is subject to general base catalysis. The activation enthalpies  $\Delta H^\ddagger$  for the slower second step ( $k_s$ ) of the reaction with nickel, cobalt, and copper agree within the limits of error (see Table 10). This result supports the interpretation that the  $k_s$  step describes the enolization of the keto tautomer of Hamac. For a given pH, rate constant  $k_f$  for complex formation increases linearly with the metal concentration according to eq 8, which

(38) It would have been most desirable to extend the measurements to higher proton concentrations. This was however limited by the  $k_f$  step becoming too fast for observation.

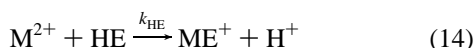
**Table 11.** Experimental Rate Constants for the Acid Hydrolysis<sup>a</sup> of the Species M(amac)<sup>+</sup> at Variable pH, 298 K, and *I* = 0.5 M (NaClO<sub>4</sub>)

M = Co <sup>b</sup>				M = Cu <sup>c</sup>				M = Ni <sup>d</sup>			
pH <sup>e</sup>	k <sub>f</sub> , s <sup>-1 f</sup>	k <sub>s</sub> , s <sup>-1 f</sup>	ΔA <sup>g</sup>	pH <sup>e</sup>	k <sub>f</sub> , s <sup>-1 f</sup>	k <sub>s</sub> , s <sup>-1 f</sup>	ΔA <sup>g</sup>	pH <sup>e</sup>	k <sub>f</sub> , s <sup>-1 f</sup>	k <sub>s</sub> , s <sup>-1 f</sup>	ΔA <sup>g</sup>
3.81	18.8	0.0283	0.054	2.86	22.9	0.0220	0.030	3.70	0.065	0.0194	0.017
3.56	24.7	0.0266	0.103	2.50	34.5	0.0236	0.114	2.63	0.101	0.0241	0.049
3.45	30.3	0.0258	0.079	2.27	47.9	0.0235	0.119	2.34	0.148	0.0252	0.045
3.12	45.1	0.0258	0.100	2.04	66.8	0.0242	0.218	1.61	0.548	0.0269	0.051
2.91	68.3	0.0262	0.101	1.89	86.4	0.0234	0.236	1.30	1.09	0.0248	0.085
2.60	101	0.0266	0.112	1.64	136	0.0234	0.307				
2.29		0.0263	0.184	1.48	187	0.0225	0.374				
				1.36	229	0.0231	0.487				

<sup>a</sup> In the stopped-flow experiment, the solution containing the ligand Hamac and an excess of the metal perchlorate at pH 5–6 was mixed with perchloric acid of variable concentration. <sup>b</sup> [Co<sup>2+</sup>] = 1 × 10<sup>-2</sup> M, [Hamac] = 7.5 × 10<sup>-5</sup> M, monitoring at 275 nm. <sup>c</sup> [Cu<sup>2+</sup>] = 5 × 10<sup>-4</sup> M, [Hamac] = 7.5 × 10<sup>-5</sup> M, monitoring at 325 nm. <sup>d</sup> [Ni<sup>2+</sup>] = 7.5 × 10<sup>-3</sup> M, [Hamac] = 7.5 × 10<sup>-5</sup> M, monitoring at 275 nm. <sup>e</sup> pH after mixing. <sup>f</sup> As obtained by computer-fitting of eq 6 to the exponential absorbance/time data. <sup>g</sup> Initial drop in absorbance; too fast to be followed by the stopped-flow technique.

**Figure 6.** Plot of the experimental rate constant *k<sub>f</sub>* vs log[H<sup>+</sup>] according to eq 12 for the fast step of the acid dissociation of the species Co(amac)<sup>+</sup> at 298 K.

leads to rate constants *k<sub>2</sub>* and *k<sub>0</sub>*.<sup>39</sup> According to Scheme 1, the observed pH dependence of *k<sub>2</sub>* is due to the participation of the enolate in complex formation. Alternatively, the dependence of *k<sub>2</sub>* on pH could also be due to the mono hydroxo species M(OH)<sup>+</sup> being involved. The acidity of the hydrated cations M<sup>2+</sup>, as described by their p*K*<sup>\*</sup> values,<sup>40</sup> increases from Ni<sup>2+</sup> (10.3) to Co<sup>2+</sup> (9.7) to Cu<sup>2+</sup> (7.7).<sup>41</sup> At least for copper it is therefore conceivable that complex formation takes place according to (13)–(15). For [M<sup>2+</sup>] = constant = [M<sup>2+</sup>]<sub>0</sub>, [H<sup>+</sup>]



= constant ≥ 10<sup>-5</sup> M, and [M(OH)<sup>+</sup>] ≪ [M<sup>2+</sup>], the corresponding rate law is given by (16). Rate constants *k<sub>HE</sub>* and *k<sub>OH</sub>*, as

$$d[ME^+]/dt = k_2[M^{2+}]_0([HE]_0 - [ME^+]) \quad (16a)$$

$$k_2 = k_{HE} + k_{OH}K^*/[H^+] \quad (16b)$$

obtained from the plot of *k<sub>2</sub>* vs *K*<sup>\*</sup>/[H<sup>+</sup>], are also listed in Table 9 for M = Cu. The ratio *k<sub>OH</sub>*/*k<sub>HE</sub>* is found to be 2.3 × 10<sup>4</sup>,

(39) Rate constant *k<sub>0</sub>*, describing the back reaction (*k<sub>0</sub>* ≡ *k*<sub>-HE</sub>[H<sup>+</sup>]/*K*<sub>MEH</sub>), is obtained from the intercept with large limits of error, so that the detailed discussion of its size does not make much sense.

(40) The parameter p*K*<sup>\*</sup> describes the equilibrium M<sup>2+</sup>(aq) ⇌ M(OH)<sup>+</sup> + H<sup>+</sup>.

(41) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4, p 6.

which is too high to make sense.<sup>42</sup> The interpretation of the pH dependence of *k<sub>2</sub>* on the basis of reactions (13)–(15) is therefore rejected. The interpretation based on Scheme 1 is obviously more appropriate. Support for this comes also from the comparison of the parameters *K*<sub>1</sub> and *k<sub>E</sub>*/*k*<sub>-E</sub>. Complex formation constant *K*<sub>1</sub>, as determined by spectrophotometric titration (see Experimental Section), should agree with the ratio *k<sub>E</sub>*/*k*<sub>-E</sub>, as obtained kinetically from the study of complex formation and dissociation, respectively. The data listed in Table 9 show that *K*<sub>1</sub> and *k<sub>E</sub>*/*k*<sub>-E</sub> differ by factors of about 4 (Ni), 2.4 (Co), and 3.4 (Cu), which are acceptable in view of the different methods applied.

In a general sense, the results of the present study are in line with those of earlier studies on complex formation with β-diketones.<sup>1</sup> It is found that the enolate of Hamac reacts faster with a given metal than the enol, *k<sub>E</sub>* > *k<sub>HE</sub>*, and that there is a strong metal effect on the rate of complexation with both species, namely Cu<sup>2+</sup> ≫ Co<sup>2+</sup> > Ni<sup>2+</sup>. The more specific questions to be addressed concern the aspect of rate-control through water exchange on the metal (Eigen–Wilkins mechanism) and the aspect of first bond formation versus second bond formation (chelate ring closure).

Rate constants *k<sub>ex</sub>* for water exchange on the metal are listed in Table 9. In the framework of the Eigen–Wilkins mechanism for complex formation with monodentate ligands X it is expected that *k<sub>i</sub>*, the rate constant for the interchange step (X substitutes coordinated H<sub>2</sub>O), is close to *k<sub>ex</sub>*. In the present study, *k<sub>i,HE</sub>* can be estimated according to *k<sub>HE</sub>* = *k<sub>i,HE</sub>**K*<sub>os</sub> (see Table 9). The ratio *k<sub>i,HE</sub>*/*k<sub>ex</sub>* ranges from 1.9 × 10<sup>-3</sup> (Ni) to 6.8 × 10<sup>-5</sup> (Cu). It is much too small to be indicative of solvent exchange controlling the rate of the reaction of HE with the metal. Rate constant *k<sub>E</sub>* however leads to *k<sub>i,E</sub>*/*k<sub>ex</sub>* = 0.32 for copper, which would allow us to invoke solvent exchange to control the reaction of the enolate with copper. Surprisingly, for cobalt

(42) Rate constant *k<sub>ex</sub>* for the exchange of coordinated water is a measure for the reactivity of hydrated metal ions M<sup>n+</sup> toward ligand substitution. The ratio *k*(M(OH)<sup>2+</sup>)/*k<sub>ex</sub>*(M<sup>3+</sup>) is found to be on the order of 500 for M = Cr, Fe, and Ga.<sup>43</sup> To our knowledge there are no data available for water exchange in divalent metal cations and the corresponding monohydroxo species, i.e. for the ratio *k<sub>ex</sub>*(M(OH)<sup>+</sup>)/*k<sub>ex</sub>*(M<sup>2+</sup>).

(43) Van Eldik, R. Ed. *Inorganic High Pressure Chemistry*; Studies in Inorganic Chemistry 7; Elsevier: Amsterdam, 1986; pp 82 and 85.

(44) Ducommun, Y.; Zbinden, D.; Merbach, A. E. *Helv. Chim. Acta* **1982**, *65*, 1385.

(45) Powell, D. H.; Helm, L.; Merbach, A. E. *J. Chem. Phys.* **1991**, *95*, 9258.

(46) The calculated ion pair formation constants *K*<sub>OS</sub> for divalent 3d cations pairing with singly charged anions are 0.81 M<sup>-1</sup> for *I* = 0.1 M and 0.54 M<sup>-1</sup> for *I* = 1.0 M for the medium water and 298 K.<sup>47</sup>

(47) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*; Oxford University Press: Oxford, England, 1991; p 33.



and nickel the ratio  $k_{i,E}/k_{ex}$  is smaller by about one order of magnitude (0.039 and 0.048, respectively). Considering the  $pK^*$  values of the aqua metal ions under study, one is tempted to suggest that the reaction of the enolate with the  $M^{2+}$  cation is "acidity-assisted" in the sense that formation of the first M–O bond with the enolate is initiated and facilitated by the formation of a more or less strong hydrogen bond between a coordinated water molecule and the attacking enolate. This would at least explain as to why the ratio  $k_{i,E}/k_{ex}$  is highest for copper ( $pK^* = 7.7$ ) and lower for cobalt ( $pK^* = 9.7$ ) and nickel ( $pK^* = 10.3$ ).<sup>48</sup> In summary, the ratio  $k_{i,E}/k_{ex} = 0.32$  for copper could suggest the operation of the Eigen–Wilkins mechanism with formation of the first Cu–O bond with the enolate  $E^-$  being controlled by the rate of water exchange on the copper. The low values of  $k_{i,E}/k_{ex}$  obtained for cobalt and nickel however are not in line with this interpretation and point to intermolecular hydrogen bond formation as being rate-affecting.

For the reaction of the enol HE with the metal it is found that  $k_{i,HE}/k_{ex} \ll 1$ , which means that the rate of this reaction is obviously not governed by the rate of solvent exchange on the metal cation. In addition, the ratio  $k_{i,HE}/k_{ex}$  is more strongly metal-dependent than the ratio  $k_{i,E}/k_{ex}$  (see Table 9). The existence of the  $k_{HE}$  pathway as such indicates, however, that the rate-determining step occurs prior to the formation of the second M–O bond with the entering ligand. The question of why the formation of the first M–O bond with the enol HE occurs so slowly is as open to speculation as it has been all the time.<sup>1</sup> It is reasonable to assume that the enol HE is substantially stabilized by intramolecular hydrogen bond formation, producing a six-membered heterocyclic ring. The symmetry of this ring and the charge distribution within it will be rather close to the symmetry and charge delocalization in the mono complex species  $ME^+$ . This means that the reaction of the enol HE with the metal corresponds to the substitution of the cation  $H^+$  by the cation  $M^{2+}$ . From the kinetic point of view, this process is found to be a second-order reaction. Its slowness cannot simply be due to the fact that the enol is a poor entering ligand.<sup>49</sup> If that were the case, the ratio  $k_{HE}/k_{ex}$  should not be so much metal-dependent as it is. Some characteristic property of the metal has to be involved, and one might again suggest that the different acidity of the hydrated metal cations is essential. The most acidic copper ion is the one providing most

easily the mono hydroxo species, which is able to support the breaking of the hydrogen bond stabilized cyclic enol.

The acid hydrolysis of the species  $M(\text{amac})^+ = ME^+$  is triphasic. Very fast proton addition, leading to the cation  $MEH^{2+}$ , is followed by the dissociation of  $MEH^{2+}$  and  $ME^+$  to form  $M^{2+}$  and the enol HE, which finally ketonizes. The pH dependence of the dissociation reaction leads to the acid dissociation constant  $K_{MEH}$  (see Scheme 1) for copper ( $K_{MEH} = 0.22$  M) and cobalt ( $K_{MEH} = 0.0038$  M). In the case of nickel one can estimate  $K_{MEH} \geq 0.5$  M. These data mean that the species  $Co(\text{amac})^+$  is the most basic one and that the species  $Ni(\text{amac})^+$  and  $Cu(\text{amac})^+$  are much weaker proton acceptors. From the chemical point of view one has to assume that the cation  $MEH^{2+}$  corresponds to a species in which the enol Hamac coordinates in a monodentate fashion. This unstable species is involved in complex formation as well as in complex dissociation as an intermediate.

## Conclusions

The  $\beta$ -diketone Hamac, a modified acetylacetone with a *N*-acetylamido group in the 3-position, is very soluble in water, strongly enolized ( $[\text{enol}]/[\text{ketone}] = 2.4$ ), and rather acidic ( $pK_a = 7.1$ ). Hamac coordinates metal ions such as  $Cu^{2+}$  in a normal fashion, i.e. via the two diketo oxygens. It follows from the kinetic investigation of the formation of the mono complex  $M(\text{amac})^+$  with  $M = Ni, Co, \text{ and } Cu$  at variable pH that the enol tautomer of Hamac, HE, and the enolate anion,  $E^-$ , are the reactive species to form  $M(\text{amac})^+$ , with second-order rate constants  $k_E > k_{HE}$ . In both,  $k_{HE}$  and  $k_E$  are strongly metal-dependent, the order of reactivity being  $Ni < Co \ll Cu$ . The kinetic data suggest that (i) in the reaction of the divalent metal ions  $M^{2+}$  with both the enol HE and the enolate  $E^-$  formation of the first M–O bond is rate-controlling and (ii) the acidity of the coordinated water in the cations  $M_{aq}^{2+}$  is rate-affecting. The study of the acid dissociation leads to the equilibrium constant  $K_{MEH}$  for the protonation of the complex  $ME^+$ . The protonated species  $MEH^{2+}$  with Hamac coordinated in a monodentate fashion is an intermediate in both complex formation and complex dissociation.

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**Supporting Information Available:** Tables S1–S4, listing complete crystallographic data, calculated coordinates of hydrogens, distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(48) Interestingly, the ratio  $k_E/k_{HE}$  also follows qualitatively the acidity of the aqua cations in that  $k_E/k_{HE}$  for copper is by a factor of 183 and 23 larger than for nickel and cobalt, respectively.

(49) It is of interest to note that rate constants  $k_{HE}$  for the reaction of  $Ni^{2+}$  ions with the enol tautomers of Hacac, Hamac, Hhptd,<sup>20</sup> Htfdp,<sup>20</sup> and Htftbd<sup>20</sup> lie within the narrow range of 1.7 (Htfdp) to 19.3 (Hacac)  $M^{-1} s^{-1}$  (298 K).<sup>50</sup>

(50) The data for  $k_{HE}$  were taken from Table 2 of ref 1.