hydroxamato)iron(III) and -chromium(III) complexes since the carbonyl oxygen can be considered complexed by H^+ as exemplified by one resonance form of **1**, i.e., $(CH_3)_3N\cdot BH_2C(=O^+\cdot H)NHOH\cdot Cl^-$. The complexation to a +3 metal ion does not substantially affect the C=O stretching frequency since three boranecarbohydroxamato ligands are complexed to the metal.

The second difference between the spectrum of **1** and those of its iron(III) and chromium(III) complexes is the position and intensity of the N—O stretching vibration. The N—O stretching vibration for the hydroxamato group in **1** was assigned to the weak absorption at 935 cm^{-1}. Complexation should shift this N—O bond to higher frequency due to an increase in the $-N=O^-M^+$ contribution since the O–M bond formed is more ionic than the O—H bond that existed before coordination. A slight increase in intensity is also expected for this band due to coordination to the metal ion. The spectrum of each complex reveals a band of medium intensity at 950 cm^{-1}, which is assigned to the N—O stretching vibration. The weak absorption at 935 cm^{-1} due to uncomplexed **1** is absent.

Acid Dissociation Constants and Formation Constants. The acid dissociation constants of **1** were measured so that information concerning the coordinating ability of this novel ligand could be obtained. The pK_a values obtained were $pK_1 = 3.9$ and $pK_2 = 8.3$. The dissociation constants represent the protonated carbonyl oxygen (pK_1) and the hydroxamate hydroxyl proton (pK_2). The pK_2 value for **1** may be compared with the pK_a values for some organic hydroxamic acids, which are listed in Table I.[33] This comparison shows that the acidity of **1** is within the range expected for organic hydroxamic acids.

The formation constants of **1** with cobalt(II), nickel(II), copper(II), zinc(II), and iron(III) are given in Table II. These values are the average of at least four separate determinations. Activity coefficients were taken into account. The data summarized in Table II follow the general order of complex stabilities known as the Irving–Williams order,[34] which is Co(II) < Ni(II) < Cu(II) < Zn(II). This order says nothing about the relative stability of zinc compared to that of the cobalt or nickel complexes. Mellor and Malley[35] have given a more explicit order of stabilities: Zn(II) < Co(II) < Ni(II) < Cu(II), where the relationship between zinc, cobalt, and nickel is established. Inspection of Table II reflects the general agreement of the log K_1K_2 data with the Mellor–Malley order of stabilities.

Summary

The data obtained in this study support the proposed formulation for the first boron analogue of a hydroxamic acid as $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (**1**). The compound may be represented by two resonance forms, $(CH_3)_3N\cdot BH_2C(=O^+H)-NHOH\cdot Cl^-$ and $(CH_3)_3N\cdot BH_2C(OH)=N^+HOH\cdot Cl^-$. The boranecarbohydroxamic acid complexes with transition-metal ions (Fe(III), Cr(III), Co(II), Ni(II), Zn(II)) give observed log K_1K_2 data in accordance with the Mellor–Malley order of stabilities.

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Contribution from the Chemistry Department,
Victoria University of Wellington, Private Bag, Wellington, New Zealand

Kinetics of Acid-Promoted Dissociation of Diamine–Diimine Macrocycle Complex Cations with Nickel(II) and Copper(II)

Neil F. Curtis* and Sarah R. Osvath

The kinetics of the slow acid-promoted dissociation reactions of complex cations of nickel(II) and copper(II) with six diimine–diamine macrocycles, with 14, 15, and 16 ring members, have been studied in HCl–NaCl solutions ($I = 2$ mol L^{-1}) at 25 °C. The reaction rate for (5,5,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene)nickel(II) shows a linear dependence on $[H^+]$, with $k_{obsd} = 1.7$ (2) $\times$ 10$^{-5}[H^+]$ s^{-1}. For several cations the first-order rate constants show a nonlinear dependence on $[H^+]$ with $k_{obsd} = A[H^+]/(1 + B[H^+])$ s^{-1}, with the following parameters ($A/$L mol^{-1} s^{-1} and $B/$L mol^{-1}): (2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene)copper(II), 9.0 (2) $\times$ 10^{-3}, 1.0 (2) ($I = 1$ mol L^{-1}); (5,7,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,12-diene)nickel(II), 1.4 (2) $\times$ 10^{-5}, 0.4 (1) (and 1.2 (2) $\times$ 10^{-4}, 0.17 (5) at 50 °C); (3,5,7,7,13,13,15-heptamethyl-1,4,8,12-tetraazacyclopentadeca-4,12-diene)nickel(II), 5.0 (5) $\times$ 10^{-7}, 0.13 (5). An "activated intermediate in equilibrium with starting material" mechanism is proposed for these reactions. A "protonation preequilibrium" mechanism is excluded by the absence of any spectroscopically detectable protonated tridentate macrocycle species. The reactions of other copper(II) cations show second-order dependence on $[H^+]$, with the following rate constants (L^2 mol^{-2} s^{-1}): (5,7,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene)copper(II), 8.7 (2) $\times$ 10^{-4} ($I = 1$ mol L^{-1}); (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II), 1.3 (2) $\times$ 10^{-7} (and 2.2 (2) $\times$ 10^{-6} at 50 °C); (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)copper(II), 1.5 (2) $\times$ 10^{-6} (and 2.1 (2) $\times$ 10^{-5} at 50 °C).

Introduction

A feature of the chemistry of complex cations of nickel(II) and copper(II) with aza macrocyclic ligands, which has been commented on from the beginnings of studies in this area, is the extreme resistance shown by many to acid hydrolysis.[1] Relatively few detailed kinetic studies of acid-promoted dissociation reactions of these complex cations have been reported,[2] but they can usually be accommodated within the same general mechanistic schemes as for complexes of noncyclic polyamines with these metal ions, although reaction rates may be slower by many orders of magnitude.[3]

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Studies of acid-promoted aquation reactions of aza macrocycle complexes of nickel(II) and copper(II) have revealed a variety of kinetic forms, particularly of the dependence of the rate on the hydrogen ion concentration. Some reactions show first-order dependence of rate on [H⁺], often also with an acid-independent term, with kinetic expressions of the form $k_{obsd} = k_0 + k_H[H^+]$ [4-9] (or consecutive reactions of this type).[10] Copper(II) complexes of some tetraaza macrocycles with amido groups,[11] and of cyclic pentaamines,[9,11-13] show second-order dependence of rate on [H⁺] and, for a cyclic hexaamine, third-order dependence on [H⁺].[12]

For other macrocycles, "acid-limiting" kinetics have been interpreted as indicating the presence of a rapid protonation preequilibrium (equilibrium constant K), with rate-determining dissociation of this protonated species (rate constant k_H), leading to the kinetic expression $k_{obsd} = Kk_H[H^+]/(1 + K[H^+])$.[14,15] This mechanistic scheme has been suggested even for systems that show a linear dependence of rate on [H⁺], as the limiting case when K is small, so that $k_{obsd} \approx k_0 + Kk_H[H^+]$.[5,6] "Acid-limiting" kinetics are also compatible with a mechanism that has rate-determining reaction of [H⁺] with an "activated" species, formed reversibly from the initial complex cation.[16,17]

Hydrolysis rates in 0.3 mol L⁻¹ HClO₄ for nickel(II) complexes of some cyclic tetraamines with 13-16-membered rings show a marked dependence on ring size, with the slowest rate for the 14-membered amine, [14]ane.[18,19] However, rates at a single acid concentration are not very informative if the acid dependence is unknown, and the reaction for the [Ni([13]ane)]²⁺ cation, at least, has been shown to be complex.[20] The rate of acid hydrolysis is significantly different for nitrogen configurational isomers of the nickel(II) complex with [14]ane⁸ and (N-Me)₄[14]ane²¹ and of copper(II) complexes of hexa-C-methyl derivatives of [14]ane.[10]

Acid hydrolysis reactions of copper(II) amine complexes are usually more rapid than those of their nickel(II) analogues, up to 10⁵ times faster when metal ion–donor atom bond breaking is important in the rate-determining step.[17] Pseudo-first-order rate constants for hydrolysis of the copper(II) complexes have been measured in 6.1 mol L⁻¹ HCl at 25 °C for [14]ane, trans-[14]diene (**1**, $m = n = 2$; $k_{obsd} = 1.2 \times 10^{-3}$ s⁻¹), and the meso cyclic tetramine formed by reducing the imine groups of this macrocycle (teta).[21,22] The last complex and the C-rac isomer (tetb), in metastable nitrogen configurations, have shown consecutive reactions of kinetic form $k_{obsd} = k_0 + k_H[H^+]$.[9] The complex of [12]ane in 5 mol L⁻¹ ClO₄⁻ shows a linear dependence of reaction
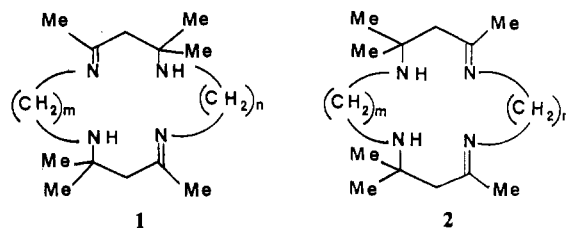
$m = n = 2$, *trans*-[14]diene
$m = 2, n = 3$, *trans*-[15]diene
$m = n = 3$, *trans*-[16]diene
$m = n = 4$, *trans*-[18]diene

1

$m = n = 2$, *cis*-[14]diene
$m = 2, n = 3$, *cis*-[15]diene
$m = n = 4$, *cis*-[18]diene

2

rate on [H⁺].[5] The compounds of 1,4,8,11-tetraazacyclohepta-decane and 1,4,8,11-tetraazacyclohexadecane (with one large chelate ring of eight and nine members, respectively) react relatively rapidly with acid, with "acid-limiting" kinetics.[15]

The copper(II) and nickel(II) compounds of the diimine–diamine macrocycle trans-[18]diene (**1**, $m = n = 4$) react slowly with acid, with "acid-limiting" kinetics.[14,23] For [Cu(trans-[18]diene)]²⁺ an isotope factor (k_H/k_D) of 2.0 was interpreted as indicating slow proton transfer in the rate-determining step. The reaction of the isomeric cation [Cu(cis-[18]diene)]²⁺ (**2**, $m = n = 4$) is much more rapid than that of the trans isomer and shows general-acid catalysis.[14]

This paper reports studies of the rates of reaction with acid of nickel(II) and copper(II) complex cations of the homologous diimine–diamine macrocycles trans-[14]diene and cis-[14]diene (**2**, $m = n = 2$), trans-[15]diene (**1**, $m = 2, n = 3$) and the 3,5,7,7,13,15,15-heptamethyl homologue Me[15]diene, cis-[15]diene (**2**, $m = 2, n = 3$), and trans-[16]diene (**1**, $m = n = 3$) to establish ring size and to determine other structural effects on reaction rate and mechanism.[23]

Experimental Section

Kinetic Measurements. Reaction rates were determined spectrophotometrically, with a Hitachi-Perkin-Elmer Model 330 instrument. Measurements were made in aqueous HCl–NaCl solutions of ionic strength 1 mol L⁻¹ for [Cu(trans-[16]diene)]²⁺ and [Cu(cis-[15]diene)]²⁺ and 2 mol L⁻¹ for the other cations, at 25 °C, unless otherwise specified. Complex cation concentrations were in range 0.01–0.005 mol L⁻¹. Reactions with $t_{1/2}$ less than ca. 12 h were followed by using a constant-temperature cell housing in the spectrophotometer, with continuous monitoring, or repetitive scan measurements. Slower reactions were followed by storing in the solutions in a thermostat bath and periodically measuring the absorbance. Reactions were generally followed for at least 3 half-lives, except for the extremely slow reactions, which were followed for about 6 monmths. Pseudo-first-order rate constants were computed by least-squares fitting of the kinetic data. The parameters for the acid dependence of the rate constants were computed by least-squares linear

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Table I. Kinetic Parameters for Acid Hydrolysis Reactions at 25 °C

cation	$A^{a,d}$	$B = K^{b,d,e}$	$k_H = A/B^{a,e}$	$k'^{a,f}$	$k_0'^{c,f}$
[Cu(trans-[16]diene)]²⁺	9.0 (2) × 10⁻³	1.0 (1)	9.0 (4) × 10⁻³	6.9 (2) × 10⁻³ ᵍ	1.2 (5) × 10⁻⁴ ᵍ
[Cu(trans-[18]diene)]²⁺ ʰ	0.05	10.2	4.8 × 10⁻³	3.6 × 10⁻²	8 × 10⁻⁴
[Cu[16]ane)]²⁺ ⁱ	0.13	2.7	0.48	1.13	
[Cu[17]ane)]²⁺ ʲ	0.7	1.3	0.53	0.60	
[Ni(trans-[15]diene)]²⁺	1.3 (2) × 10⁻⁵	0.4 (1)	3.5 (2) × 10⁻⁵	9.6 (2) × 10⁻⁶ ᵍ	5.1 (5) × 10⁻⁷ ᵍ
				7.1 (2) × 10⁻⁶ ᵏ	1.6 (2) × 10⁻⁶ ᵏ
[Ni(trans-[15]diene)]²⁺ ˡ	1.2 (2) × 10⁻⁴	0.17 (5)	7.1 (2) × 10⁻⁴	1.1 (1) × 10⁻⁴ ᵐ	1.6 (5) × 10⁻⁷ ᵐ
				9.3 (2) × 10⁻⁵ ᵏ	7.3 (5) × 10⁻⁶ ᵏ
[Ni(Me[15]diene)]²⁺	5.0 (5) × 10⁻⁷	0.13 (5)	3.8 (5) × 10⁻⁶	4.0 (1) × 10⁻⁷	1.7 (5) × 10⁻⁸
[Ni(cis-[15]diene)]²⁺				1.7 (2) × 10⁻⁵	7 (2) × 10⁻⁷
[Ni(trans-[18]diene)]²⁺ ⁿ	8.5 × 10⁻⁴	1.7	5 × 10⁻⁴	6 × 10⁻⁴	1.25 × 10⁻⁴

^{a}L mol⁻¹ s⁻¹. ^{b}L mol⁻¹. ^{c}s⁻¹. ^{d}For the expression $k_{obsd} = A[H^+]/(1 + B[H^+])$. ^{e}For the expression $k_{obsd} = k_H K[H^+]/(1 + K[H^+])$. ^{f}For the expression $k_{obsd} = k_0' + k'[H^+]$. ^{g}From first six data points. ^{h}From ref 14, in 1 mol L⁻¹ ClO₄⁻. ^{i}[16]ane = 1,4,8,11-tetraazacyclohexadecane; from ref 15, in 1 mol L⁻¹ ClO₄⁻. ^{j}[17]ane = 1,4,8,11-tetraazacycloheptadecane; from ref 15, in 1 mol L⁻¹ ClO₄⁻. ^{k}For all data. ^{l}At 50 °C. ^{m}For first five data points. ^{n}From ref 14, in 1 mol L⁻¹ NO₃⁻.

fitting of $k_{obsd} = k_0 + k_H[H^+]$, $k_{obsd} = k_0 + k_H[H^+]^2$, or $1/k_{obsd}$ vs $1/[H^+]$. In the last case an initial fitting of $k_{obsd} = k_0 + A[H^+]/(1 + B[H^+])$ showed that k_0 was not significant.

Kinetic Data. Data are given for the wavelength at which absorbance measurements were made, temperature, hydrogen ion concentration, and pseudo-first-order rate constants.

[Cu(trans-[14]diene)]²⁺. λ = 507 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁸ s⁻¹ (25 °C): 0.20, 1.0 (3); 0.50, 3.1 (2); 1.00, 15 (2); 1.40, 19 (2); 1.80, 44 (2); 2.00, 54 (2). [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁷ s⁻¹ (50 °C): 0.68, 9.4 (2); 1.0, 22 (2); 1.6, 60 (2); 2.0, 89 (2).

[Cu(cis-[14]diene)]²⁺. λ = 503 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁷ s⁻¹ (25 °C): 0.20, 0.6 (1); 0.50, 3.9 (2); 1.00, 16 (2); 1.40, 29 (2); 1.80, 49 (2); 2.00, 61 (2). [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁵ s⁻¹ (50 °C): 1.00, 2.3 (2); 1.40 4.4 (2); 1.60, 5.5 (2); 2.00, 8.6 (2). The reaction at 50 °C was followed by repetitive scan measurements. The data gave satisfactory first-order fits over 3 half-lives, but the early part of the reaction showed irregularities, with small deviations from the later established isosbestic points, which may indicate a more rapid initial reaction.

[Ni(trans-[15]diene)]²⁺. λ = 455 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁶ s⁻¹ (25 °C): 0.10, 1.3 (2); 0.20, 2.6 (2); 0.40, 4.5 (2); 0.68, 6.7 (2); 0.80, 8.4 (2); 1.00, 9.0 (1); 1.40, 12 (1); 1.80, 14 (1); 2.00, 15 (1). [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁵ s⁻¹ (50 °C): 0.15, 1.5 (1); 0.20, 2.1 (1); 0.40, 4.7 (1); 0.68, 7.3 (2); 1.00, 10.8 (2); 1.40, 14.2 (2); 1.60 16.0 (2); 1.75, 17.0 (2); 1.86, 17.7 (2); 2.00, 18.3 (2).

[Ni(Me[15]diene)]²⁺. λ = 454 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁸ s⁻¹ (25 °C): 0.10, 3.1 (2); 0.20, 7.8 (2); 0.24, 93 (2); 0.40, 17 (2); 0.50, 23 (2), 0.68, 34 (2); 1.00, 45 (2); 1.60, 65 (2); 2.00, 78 (2).

[Ni(cis-[15]diene)]²⁺. λ = 470 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁶ s⁻¹ (25 °C): 0.20, 3.8 (1); 0.40, 7.4 (2); 0.80, 15.5 (5); 1.60, 29 (1); 2.00, 35 (1).

[Cu(cis-[15]diene)]²⁺. λ = 565 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁵ s⁻¹ (25 °C): 0.20, 1.7 (1); 0.30, 3.9 (1); 0.50, 8.8 (1); 0.80, 22 (2); 1.00, 34 (2).

[Cu(trans-[16]diene)]²⁺. λ = 580 nm. [H⁺]/mol L⁻¹ and k_{obsd}/10⁻⁴ s⁻¹ (25 °C): 0.05, 4.2 (1); 0.072, 5.9 (1); 0.10, 8.3 (1); 0.15, 12.0 (5); 0.20, 15.0 (5); 0.28, 20 (1); 0.40, 26 (1); 0.60, 33 (2); 0.80, 41 (2); 1.00, 44 (2).

Results

The kinetics of the acid-promoted hydrolysis reactions were studied spectrophotometrically; see the Experimental Section for details and measured rate constants. Measurements were made in chloride media since many of the cations are insufficiently soluble in perchlorate media and/or are oxidized in acid nitrate solutions.[30] Acid dissociation rates may be affected by the medium—for example some tetraaza macrocycle complexes of nickel(II) were reported to react at similar rates in 0.7 mol L⁻¹ HCl and 6 mol L⁻⁷ HClO₄,[21] while the reaction of [Cu(trans-[18]diene)]²⁺ is appreciably faster in HCl than in HNO₃.[14]

Plots of pseudo-first-order rate constants k_{obsd} at 25 °C against hydrogen ion concentration for hydrolysis of [Cu(trans-[16]diene)]²⁺, [Ni(trans-[15]diene)]²⁺ (and at 50 °C), [Ni(Me[15]-
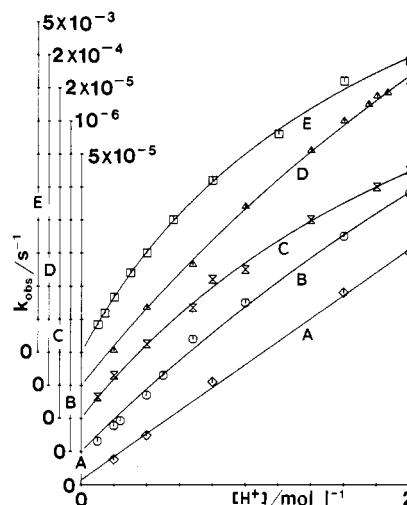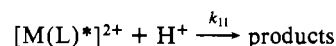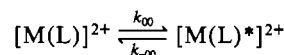
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Figure 1. Plots of observed rate constants vs [H⁺] for acid dissociation reactions in 2 mol L⁻¹ Cl⁻ at 25 °C, unless otherwise specified. The solid lines are least-squares lines of best fit for the expressions $k_{obsd} = k_0 + k_H[H^+]$ for [Ni(cis-[15]diene)]²⁺ and $k_{obsd} = A[H^+]/(1 + B[H^+])$ for the other compounds. Parameters shown are in L mol⁻¹ for A and L mol⁻¹ for B: (A) Ni(cis[15]diene)²⁺, k_{obsd} = 7.2 × 10⁻⁷ + 1.74 × 10⁻⁵[H⁺] s⁻¹; (B) [Ni(Me[15]diene)]²⁺, A = 4.96 × 10⁻⁷, B = 0.13; (C) [Ni(trans-[15]diene)]²⁺, A = 1.27 × 10⁻⁵, B = 0.36; (D) [Ni(trans-[15]diene)]²⁺ at 50 °C, A = 1.24 × 10⁻⁴, B = 0.16; (E) [Cu(trans-[16]diene)]²⁺, [H⁺] scale 0–1 mol L⁻¹, A = 9.19 × 10⁻³, B = 1.06.

diene)]²⁺, and [Ni(cis-[15]diene)]²⁺ are shown in Figure 1.

The relationship is linear for [Ni(cis-[15]diene)]²⁺ with k_{obsd} = 7 (10) × 10⁻⁷ + 1.7 (2) × 10⁻⁵[H⁺] s⁻¹ but shows varying amounts of curvature for the other cations. The data for the reactions with nonlinear relationships were fitted to the expression $k_{obsd} = k_0 + A[H^+]/(1 + B[H^+])$ directly, and since the k_0 terms were found to be small, also as a linear fit of $1/k_{obsd}$ vs $1/[H^+]$, with A evaluated from the slope and B from the intercept (Figure 2). The latter calculation gives greater weight to the rate constants at lower [H⁺]. For [Ni(Me[15]diene)]²⁺, which shows only a small curvature in the k_{obsd}/[H⁺] relationship, the latter plot was nonlinear (see later). Apart from this case, the parameters evaluated by the two methods are in reasonable agreement, and the values shown in Table I are the means of the values calculated by the two procedures (as listed in the legends to the figures).

The kinetic expression $k_{obsd} = A[H^+]/(1 + B[H^+])$ can arise with several mechanisms. For the rapid reactions of some copper(II) polyamine cations that show this kinetic form, a mechanism with the acid-dependent reaction of the "activated" species [M-(L)*]²⁺ has been proposed

$$[M(L)]^{2+} \underset{k_{-00}}{\overset{k_{00}}{\rightleftharpoons}} [M(L)^*]^{2+}$$

$$[M(L)^*]^{2+} + H^+ \xrightarrow{k_{11}} \text{products}$$

which results in the kinetic expression
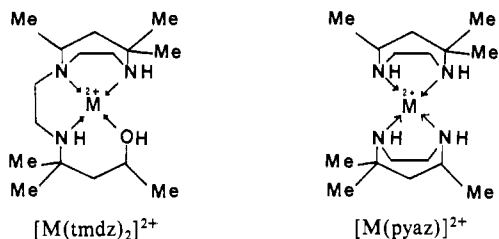
$$k_{obsd} = (k_{00}k_{11}/k_{-00})[H^+]/(1 + (k_{11}/k_{-00})[H^+])$$

if the species $[M(L)*]^{2+}$ is in low, steady-state concentration. Scheme I represents the relevant portion of the dissociation/protonation reaction sequence, with solvation omitted. The parameters have the values $A = k_{00}k_{11}/k_{-00}$ and $B = k_{11}/k_{-00}$, so only k_{00} and k_{11}/k_{-00} can be evaluated from the kinetic data.

The spectroscopic evidence (discussed below) indicates that the species $[M(L)*]^{2+}$ must have a spectrum closely similar to that of $[M(L)]^{2+}$. The most likely candidate is an isomeric form arising from the two chiral secondary amine centers present in these cations. For [Ni(*trans*-[14]diene)]$^{2+}$ the *N-meso* and *N-rac* isomers have comparable stability.[24,33] The salt [Ni(*trans*-[15]diene)](ClO$_4$)$_2$ has the 1*RS*,8*SR* or pseudo-meso configuration, but an isomeric form, which is stable as the solid but rapidly reverts to the original form in solution, was prepared.[27] The equivalent metastable forms are even less stable for the Me-[15]diene and *cis*-[15]diene cations.[27] Equilibria, or consecutive reactions, involving nitrogen configurational isomers have been reported in the acid dissociation reactions of nickel(II) and copper(II) compounds of several cyclic amines.[8,10,21]

"Acid limiting" kinetics can also arise for a protonation preequilibrium (equilibrium constant $K_1 = k_{11}/k_{-11}$), with rate-determining dissociation of the prtonated species (rate constant k_{21}), as proposed for the *trans*-[18]diene complexes,[14] where $A = k_{21}K_1$ and $B = K_1$ (Scheme I, with the "activation" reactions k_{00} and k_{-00} omitted).[14] Values of k_{21} and K_1, evaluated by assuming this mechanism for these reactions, are listed in Table I.

This mechanism requires a rapid equilibration of the complex cation with H$^+$, forming a species with the protonated macrocycle in tridentate coordination, either with three-coordinate metal ions or more probably with water completing the normal coordination shell. These species would be expected to have a d–d absorption spectrum significantly different from that of the tetradentate macrocycle species. For copper(II), the change from CuN$_4$ to CuN$_3$O chromophore would cause a large shift in the band maximum to lower energy (compare the band maxima for [Cu(pyaz)]$^{2+}$, 573 nm,[31] and [Cu(tmdz)$_2$]$^{2+}$, 480 nm[32]). For nick-

el(II), these highly methyl substituted macrocyclic cations exist in aqueous solution exclusively with singlet-ground-state nickel(II), with a single relatively intense d–d band typical of the square-planar NiN$_4$ chromophore. A species with the macrocycle in tridentate coordination would be likely to have triplet-ground-state triaquo-coordinated nickel(II) and have a spectrum typical of a NiN$_3$O$_3$ chromophore. However, even if a singlet-ground-state NiN$_3$O species occurs, the band maximum would be shifted to longer wavelength (compare [Ni(pyaz)]$^{2+}$, 472 nm,[31] and [Ni(tmdz)$_2$]$^{2+}$, 420 nm[32]).

The values of the protonation equilibrium constants calculated from the kinetic data for [Cu(*trans*-[16]diene)]$^{2+}$ and [Ni(*trans*-[15]diene)]$^{2+}$, under the assumption of the protonation preequilibrium mechanism, require that ca. 30% and 50%, respectively, of the cation be in the protonated form at the hydrogen ion concentrations used in the kinetic studies, but the spectra of these cations do not differ significantly in band maximum or absorptivity in water, NaCl, or HCl solutions of these concentrations. The spectra of the nickel(II) cations show only a single
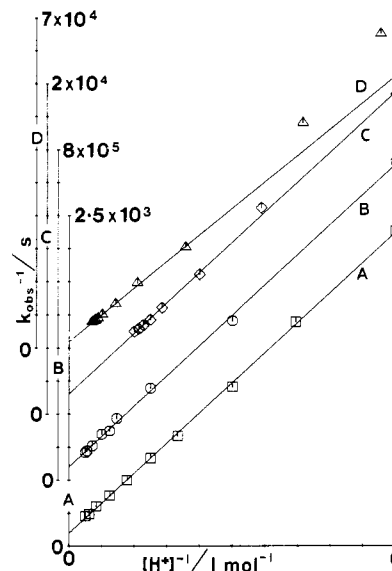
Figure 2. Plots of $1/k_{obsd}$ vs $1/[H^+]$ for acid hydrolysis reactions in 2 mol L^{-1} Cl$^-$ at 25 °C, unless otherwise specified. Parameters listed are in L mol^{-1} for c for the $1/[H^+]$ axes and in L mol^{-1} s^{-1} (A) and L mol^{-1} (B) for the least-squares lines of best fit shown (A and B are for the equation $1/k_{obsd} = (1/A)(1/[H^+]) + B/A$): (A) [Cu(*trans*-[16]diene)]$^{2+}$, $c = 20$, $A = 8.8 \times 10^{-3}$, $B = 0.88$. (B) [Ni(*trans*-[15]diene)]$^{2+}$, $c = 10$, $A = 1.37 \times 10^{-5}$, $B = 0.45$; (C) [Ni(*trans*-[15]diene)]$^{2+}$ at 50 °C, $c = 2.5$, $A = 1.24 \times 10^{-4}$, $B = 0.17$ (excluding two data points at lowest [H$^+$]); (D) [Ni(*trans*-[15]diene)]$^{2+}$ at 50 °C; showing all data points, but twith the two points at lowest [H$^+$] not included in the fit; $c = 7$. The curvature shown in (D) is more accentuated when the data for [Ni(Me[15]diene)]$^{2+}$ are plotted in the same fashion, and a linear fit is not satisfactory.

Scheme I. Part of the Dissociation/Protonation Reaction Sequence for the Tetraaza Macrocycle Complex, Omitting Solvation
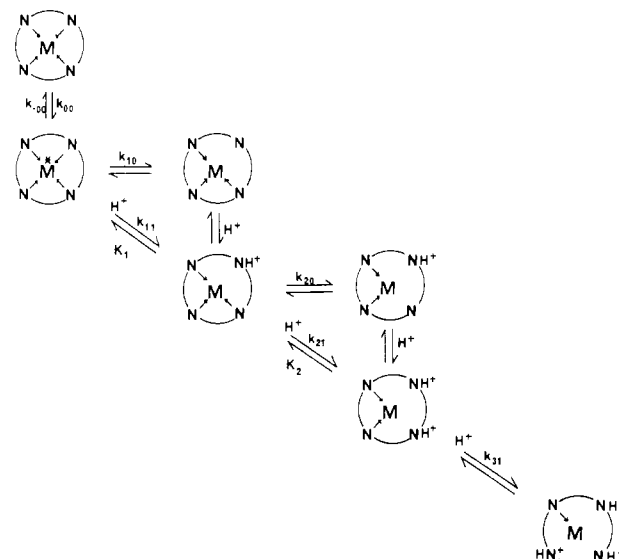
d–d band, typical of compounds with a singlet-ground-state NiN$_4$ chromophore, and show no bands assignable to triplet-ground-state nickel(II) species. It is unlikely that a protonated MN$_3$/aquo species would have a spectrum sufficiently similar to that of the starting complex to explain these observations, and it is therefore concluded that a protonation preequilibrium type mechanism is not responsible for the curvature in the $k_{obsd}/[H^+]$ relation observed for these reactions.

The rates for the acid hydrolysis reactions of the copper(II) cations with *cis*-[15]diene, *cis*-[14]diene, and *trans*-[14]diene all show second-order dependence on [H$^+$], with $k_{obsd} = k_H[H^+]^2$ (Figure 3). The observed rate constants (L^2 mol^{-2} s^{-1}) are as follows: *cis*-[15]diene, 8.7 (2) $\times$ 10^{-4}; *cis*-[14]diene, 1.5 (2) $\times$

[M(tmdz)$_2$]$^{2+}$ [M(pyaz)]$^{2+}$

(33) Curtis, N. F.; Curtis, Y. M. *J. Chem. Soc.* **1966**, 1653. Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 703.
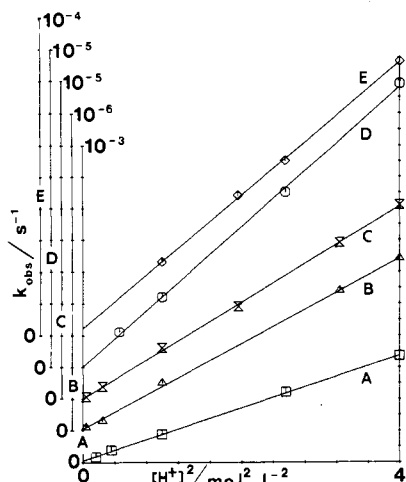
Figure 3. Plots of k_{obsd} vs $[H^+]^2$ for acid hydrolysis reactions at 25 °C in 2 mol L^{-1} Cl^-, unless otherwise specified. Parameters listed are in s^{-1} for k_0 and in L^2 mol^{-2} s^{-1} for k_H for lines of least-squares best fit for k_{obsd} = $k_0 + k_H[H^+]^2$: (A) $[Cu(cis\text{-}[15]diene)]^{2+}$ (1 mol L^{-1} Cl^-, $[H^+]^2$ scale 0–1 mol^2 L^{-2}), $k_0 = 6.3 \times 10^{-6}$, $k_H = 3.3 \times 10^{-5}$; (B) $[Cu(trans\text{-}[14]diene)]^{2+}$, $k_0 = 5.2 \times 10^{-9}$, $k_H = 1.3 \times 10^{-7}$; (C) $[Cu(cis\text{-}[14]diene)]^{2+}$, $k_0 = 1.3 \times 10^{-8}$, $k_H = 1.5 \times 10^{-6}$; (D) $[Cu(trans\text{-}[14]diene)]^{2+}$ at 50 °C, $k_0 = 1.3 \times 10^{-8}$, $k_H = 2.2 \times 10^{-6}$; (E) $[Cu(cis\text{-}[14]diene)]^{2+}$ at 50 °C, $k_0 = 2.3 \times 10^{-6}$, $k_H = 2.1 \times 10^{-5}$.

10^{-6} (and 2.1 (2) $\times$ 10^{-5} at 50 °C); trans-[14]diene, 1.5 (2) $\times$ 10^{-6} (and 2.2 (2) $\times$ 10^{-6} at 50 °C). All of these values have insignificant acid-independent terms. The activation enthalpies for reaction of $[Cu(cis\text{-}[14]diene)]^{2+}$ and $[Cu(trans\text{-}[14]diene)]^{2+}$, calculated from the 25 and 50 °C values, are 78 (5) and 84 (5) kJ mol^{-1}, respectively.

The d–d bands in the spectra of $[Cu(trans\text{-}[14]diene)]^{2+}$ and $[Cu(cis\text{-}[14]diene)]^{2+}$ are not significantly different in band maximum or absorbance in water, 2 mol L^{-1} NaCl, or 2 mol L^{-1} HCl solutions, indicating no appreciable formation of chloro adducts or species with protonated macrocycles.

Second-order dependence of reaction rate on $[H^+]$ has been reported for copper(II) cations with several cyclic pentaamines,[11–13] and for a diamine–diamide macrocycle, [14]diamide,[9,34] all of which react very much more rapidly than the cations of these diamine–diimine macrocycles.

These reactions can be accommodated within a kinetic scheme in which the dissociation reaction of the diprotonated species, formed in successive rapid protonation equilibria, is rate-determining. The reaction rate is given by the expression

$$rate = k_{30}K_1K_2[M(L)][H^+]^2/(1 + K_1[H^+] + K_1K_2[H^+]^2)$$

where K_1 and K_2 are the equilibrium constants for the first and second protonation reactions and k_{30} is the rate constant for dissociation of the diprotonated species. If the protonation constants are small, so that $(1 + K_1[H^+] + K_1K_2[H^+]^2) \approx 1$, then the expression simplifies to

$$rate \approx k_{30}K_1K_2[M(L)][H^+]^2$$

Alternatively, the results are compatible with a scheme in which the protonation reaction of the monoprotonated species, rate constant k_{21}, is rate-determining, which reduces to the same form if the protonation equilibrium constants; K_1, is small.

A preequilibrium involving the reactive species $[Cu(L)^*]^{2+}$ would not change the kinetic form if the equilibrium constant k_{00}/k_{-00} were large or if the rate constants k_{00} and k_{-00} were large compared with subsequent rate constants.

The d–d spectra show no indication of the presence of significant amounts of species with other than a CuN_4 chromophore, which

is compatible with very small protonation constants in these expressions.

These mechanisms would imply rate-determining dissociation of the third (or second) copper–nitrogen bonds, respectively.

The difference between the kinetic expressions for the copper(II) compounds of the larger (16- and 18-membered), and smaller (14- and 15-membered) macrocycles, or between the expressions for the copper(II) and nickel(II) compounds, does not necessarily imply a radically different dissociation mechanism. Any reaction that has successive steps showing first- and second-order dependence, respectively, on hydrogen ion concentration will show kinetics with a rate with dependence on $[H^+]$ at sufficiently high $[H^+]$ and a rate with dependence on $[H^+]^2$ at sufficiently low $[H^+]$. The different rate expressions for the two sets of compounds may merely indicate that different parts of the acid-dependence profile have been examined in the two cases. It is perhaps significant that the observed rate constants at the lower acid concentrations for $[Ni(trans\text{-}[15]diene)]^{2+}$ at 50 °C, and particularly for $[Ni(Me[15]diene)]^{2+}$, are smaller than predicted from a linear extrapolation of the $1/k_{obsd}$ vs $1/[H^+]$ plot, which may indicate the beginnings of a changeover to second-order rate dependence.

The presence of general-acid catalysis, as reported for the reaction of $[Cu(cis\text{-}[18]diene)]^{2+}$,[14] was investigated for $[Ni(trans\text{-}[15]diene)]^{2+}$ and $[Cu(cis\text{-}[14]diene)]^{2+}$ by measuring the reaction rate in 2 mol L^{-1} CH_3COOH, 2 mol L^{-1} NaCl at 50 °C ($[H^+]$ = ca. 7.1 $\times$ 10^{-3} mol L^{-1}).[35] In the former case a very slow hydrolysis reaction was observed, with $k_{obsd} = 1.2$ (3) $\times$ 10^{-6} s^{-1}, indicating the absence of appreciable general-acid catalysis or of a significant acid-independent rate. In the latter case an *extremely* slow reaction was observed, indicating the absence of any appreciable general-acid catalysis or acid-independent reaction.

Discussion

For compounds of nickel(II) and copper(II) with a homologous series of tetraaza macrocycles of varying ring size, acid-promoted dissociation rates are generally smallest for the 14-membered macrocycle, although quantitative kinetic data are sparse.[2] The ring-size dependence of rate has been attributed to the extent of strain inherent in square-planar coordination of the macrocycles, which is least for the symmetrical 14-membered macrocycle, when coordinated to copper(II) or singlet-ground-state nickel(II). However, slow acid dissociation is observed not only for complexes with "girdling" aza macrocycles but also for compounds with the tetraaza macrocycles in folded cis coordination, for compounds of triaza macrocycles, which must coordinate facially,[4] and even for some cyclic diamines, which must coordinate bidentally.[32,36] One common feature of cyclic amines is the absence of a terminal amino group that could initiate an "unzipping" mechanism. However, copper(II) compounds of cyclic pentaamines and cyclic hexaamines react with acid at rates comparable with those of noncyclic polyamines,[10,11] and some nickel(II) and copper(II) compounds of 14-membered cyclic tertiary tetraaza macrocycles also react rapidly,[6,21] so other factors must be involved in determining the reaction rates.

The unusual thermodynamic and ligand field properties of complexes of cyclic tetra(secondary amines), compared with those of linear analogues, can largely be attributed to the substitution of two secondary for two primary amino groups upon cyclization, without the increased inter- and intraligand strain present when terminal secondary amino groups are present.[37] Some of the enhanced kinetic stability of cyclic amine complexes may arise from the slightly stronger metal–nitrogen bonds, but it appears more probable that the very slow reaction rates arise from some organizational process, for example a concerted conformational change required to move a dissociated nitrogen away from the coordination site. A process of this nature is likely to be very

(34) [14]diamide = 1,4,8,11-tetraazacyclotetradeca-5,7-dione.

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(36) Musker, K. W.; Hussain, M. S. *Inorg. Chem.* **1966**, *5*, 1416.
(37) Thom, V. J.; Boyens, J. C. A.; McDougall, G. J.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3198.

dependent on structural features, such as ring size, ring substitution, or ring unsaturation.

With the rate constants from the linear approximation of $k_{obsd}/[\text{H}^+]$ at low [H⁺] for comparison, the rate constant decreases from 6×10^{-4} L mol⁻¹ s⁻¹ for [Ni(*trans*-[18]diene)]²⁺ to 9.6×10^{-6} L mol⁻¹ s⁻¹ for [Ni(*trans*-[15]diene)]²⁺. The reaction for [Ni(*trans*-[16]diene)]²⁺ is kinetically more complex, but the rate is between those of the [18] and [15] homologues.[38] Reaction of [Ni(*trans*-[14]diene)]²⁺ with acid is extremely slow, with a rate constant in 2 mol L⁻¹ HCl at 25 °C of ca. 10⁻⁹ s⁻¹.[38] Preliminary studies on the 13-membered monoimine complex [Ni([13]-ene)]²⁺ [38] show hydrolysis rates comparable to those of [Ni-(*trans*-[15]diene)]²⁺, confirming that the rate minimum occurs for the 14-membered macrocycles.

For the copper(II) compounds the comparison is complicated by the change in kinetic form. However, for the trans macrocycles the rate decreases from the [18] to the [16] species (acid-limiting kinetics), and for the cis macrocycles the rate decreases from the [15] to the [14] species (and then increases for [Cu([13]ene)]²⁺),[38] all with second order dependence on [H⁺]. As for the nickel(II) analogues, available evidence indicates that the hydrolysis rate is a minimum for the 14-membered tetraaza macrocycle cations.

Although metal ion compounds of noncyclic imine ligands are usually very readily hydrolyzed, the compounds of the macrocyclic diimines in this study are clearly very resistant to acid hydrolysis. Studies reported in 6.1 mol L⁻¹ HCl showed that [Cu(*trans*-[14]diene)]²⁺ reacted more rapidly than the compound of the *C-meso* tetraamine formed by reduction of the imine functions.[22] However, measurements at a single acid concentration can be misleading, since the diimine compound shows second-order dependence of rate on [H⁺], while metastable nitrogen isomers of the tetraamine compounds show consecutive reactions with first-order dependence of rate on [H⁺].[8] Studies in progress indicate that the stable isomer of the *C-meso* tetraamine complex reacts more slowly than [Cu(*trans*-[14]diene)]²⁺, and the rate constants show second-order dependence on [H⁺].[38] The nickel(II) compounds of cyclic tetraamines formed by reduction of the imine

functions of *trans*-[16]diene, *trans*-[15]diene, and Me[15]diene all react with acid considerably more rapidly than do their diimine analogues[38] (in line with rates published for the unsubstituted cyclic amines).[18] The presence of rigid imine groups makes the macrocycles much less flexible and could thus make conformational changes associated with movement of a dissociated nitrogen away from the coordination site more difficult. Once freed from coordination, the imine function would be subject to relatively rapid acid hydrolysis, opening the macrocycle. The reaction thereafter should proceed at rates similar to those of compounds of noncyclic polyamines. The kinetic results for the hydrolysis of the copper(II) compounds that show second-order dependence on [H⁺] suggest that the breaking of the second (or third, in the alternative kinetic interpretation, discussed above) copper–nitrogen bond may be rate-determining. This would indicate that the first (or first two) bonds dissociated are to secondary amine groups.

For copper(II) the cis diene macrocycle compounds react more rapidly than their trans isomer, by a factor of 10 for the [14] pair, with a much greater difference for the [18] pair.[8] For nickel(II) the cis isomer for the [15] pair reacts more rapidly by a factor of 1.7, while for the [14] system the cis isomer reacts even more slowly than the trans isomer.[38]

Increased C- or N-substitution of amine ligands generally reduces the rate of reaction with acid of their metal ion complexes.[3] This effect is shown for [Ni(*trans*-[15]diene)]²⁺ and [Ni(Me-[15]diene)]²⁺, where the additional axially oriented methyl group, added to an already crowded coordination environment, reduces the rate by 1 order of magnitude. This effect must be stereochemical in origin and is understandable if a conformational change of the macrocycle is important in determining the rate of the slow dissociation step.

(38) Curtis, N. F., unpublished observations.

Contribution from the Department of Inorganic Chemistry,
The University, Newcastle upon Tyne NE1 7RU, U.K.

Kinetics of the Substitution of Thiocyanate and Oxalate on [Mo₃O₄(H₂O)₉]⁴⁺: High Acidity of the Aqua Ligands and the Dominance of Conjugate-Base Pathways

Bee-Lean Ooi and A. Geoffrey Sykes*

The influence of [H⁺] on substitution reactions of [Mo₃O₄(H₂O)₉]⁴⁺ is addressed. From the kinetic treatment given, the trimer has an exceptionally high acid dissociation constant K_{aM}(25 °C) of 0.42 M (average), $I = 2.00$ M (LiPTS), and as far as can be ascertained substitution with NCS⁻ and HC₂O₄⁻ proceeds solely by the trimer conjugate-base form. Rate constants for NCS⁻ (4.8 M⁻¹ s⁻¹) and HC₂O₄⁻ (3.3 M⁻¹ s⁻¹) reacting with the conjugate base are in close agreement, consistent with an I_d process. Substitution is believed to be at the more labile d-H₂O positions (two to each Mo) trans to the μ_2-oxo's and is influenced by conjugate-base formation at a coordinated H₂O. Aquation steps, and chelation of monodentate HC₂O₄⁻ to give oxalate chelated at two d-H₂O positions, also proceed by conjugate-base pathways. The two stages involving oxalate coordination provide a further (rare) example of two reaction stages becoming interposed.

Introduction

Cotton and colleagues demonstrated for the first time in 1978 the occurrence of the trimeric Mo(IV) core in a crystal study on the complex Cs₂[Mo₃O₄(C₂O₄)₃(H₂O)₃]·4H₂O·0.5H₂C₂O₄.[1] Other crystal studies have been reported since then,[2–5] and it is

now established that the metal–metal-bonded Mo₃O₄⁴⁺ (incomplete cuboidal) cluster is the sole species relevant to the aqueous solution chemistry.[6] Using ¹⁸O-labeling techniques, Murmann and co-workers have demonstrated that the same Mo₃O₄⁴⁺ core is retained in the aqua ion [Mo₃O₄(H₂O)₉]⁴⁺.[7] The latter has

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