the solution becoming practically colorless. The reactions ultimately led to the synthesis of new compounds (vide Experimental Section) that analyze as $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ as obtained from KSCN and NH_4SCN, respectively, providing an access to mixed-ligand fluoro(sulfato)ferrates(III). Presumably, here again an intermediate peroxyfluoroferrate(III) species is first generated, which then participates, through its coordinated peroxy group, in the oxidation of SCN^- finally to afford the heteroligand fluoroferrates(III).

A study of the vibrational spectra of the reaction products revealed the complete absence of ν(CN) at ca. 2120 cm^{-1}, and the IR and laser Raman (lR) spectral patterns were very similar to other metal sulfato complexes. When sulfate is coordinated, its symmetry is lowered from T_d to C_{3v} or C_{2v}[18] depending on whether it binds the metal center in a monodentate or a bidentate fashion.[18] In the case of C_{2v} symmetry of sulfate, its ν_3 and ν_4 modes are split into three bands each while the ν_1 and ν_2 modes appear with medium intensity. Although both bridging and chelating sulfato ligands have C_{2v} symmetry, they can generally be distinguished on the basis of their IR and Raman spectra since ν_3 vibrations for chelating bindate sulfato complexes occur at higher energies than those of bridging sulfato complexes.[18] In the IR and lR spectra of the newly synthesized compounds each of the ν_3 and ν_4 vibrations was split into three bands with the ν_3 modes lying at ca. 1225, ca. 1130, and ca. 1020 cm^{-1}. A comparison with other types of sulfato complexes[19] indicates that these vibrations fall at rather high energies for ν_3 modes and therefore suggests that SO_4^{2-} binds the iron(III) center in a chelating bidentate manner. Another common feature of fluoro(sulfato)ferrates(III) is the band at ca. 495 cm^{-1}, which has been assigned to the ν(Fe–F) mode arising from the presence of coordinated fluoride ligands.

For further characterization, the oxidation state of iron was estimated chemically by an iodometric method and magnetic moments were measured at room temperature. While the chemically estimated oxidation state of iron was found to be 3, the magnetic moments of the compounds were found to be ca. 5.7 μ_B, suggesting the occurrence of high-spin iron(III). These results adduce additional support to the identity of the fluoro(sulfato)ferrates(III).

Concluding Remarks. Under the appropriate experimental conditions hexafluoroferrates(III) of the type A_3FeF_6 (A = Na, K, or NH_4) can be directly synthesized in high yields, providing an easy access to such compounds. Reactions of potassium or ammonium thiocyanate with iron(III) hydroxide, aqueous hydrofluoric acid, and hydrogen peroxide have resulted in the production of hitherto unknown fluoro(sulfato)ferrates(III). These compounds provide excellent prospects as materials for further studies of their physical properties and for a comparison with those of the binary fluorometalates(III). In this way an insight into the fluorochemistry of iron may be gained.

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Registry No. Na_3FeF_6, 20955-11-7; K_3FeF_6, 13815-30-0; $(NH_4)_3FeF_6$, 13815-28-6; $K_3[Fe(SO_4)F_4]$, 103852-34-2; $(NH_4)_2[Fe(SO_4)F_3]$, 103852-35-3; KSCN, 333-20-0; NH_4SCN, 1762-95-4.

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Complexation Kinetics of Highly Substituted Acyclic, Monocyclic, and Bicyclic Tetraamines with Copper(II) in Basic Aqueous Media

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The complex formation kinetics of copper(II) with 1,1,10,10-tetramethyl-1,4,7,10-tetraazadecane (Me_4trien), 1,1,4,7,10,10-hexamethyl-1,4,7,10-tetraazadecane (Me_6trien), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ((*N*-Me)$_4$cyclam), and 1,4,7,10-tetraaza-13,18-dioxabicyclo[8.5.5]eicosane (cryptand $2_N.1_O.1_O$) have been studied in strongly basic media (0.075–0.40 M NaOH) at 25.0 °C. All ligands, with the possible exception of (*N*-Me)$_4$cyclam, react with both $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, and for a given ligand, $Cu(OH)_3^-$ is 10 to >300 times more reactive than $Cu(OH)_4^{2-}$. For Me_4trien reacting with either $Cu(OH)_3^-$ or $Cu(OH)_4^{2-}$ and Me_6trien reacting with $Cu(OH)_3^-$, the rate-determining step is proposed to be Jahn–Teller inversion after formation of the first Cu(II)–nitrogen bond. The rate-determining step appears to shift to second-bond formation for the reaction of Me_6trien with $Cu(OH)_4^{2-}$. For the cyclic ligands, (*N*-Me)$_4$cyclam and $2_N.1_O.1_O$, second-bond formation or multiple desolvation is proposed as the rate-determining step for reactions with $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$. The kinetics of the hydroxide-catalyzed dissociation of the copper(II) complex of 1,4,7,10-tetraaza-13,16,21,24-tetraoxabicyclo[8.8.8]hexacosane (cryptand $2_N.2_O.2_O$) have been studied at $I = 0.5$ ($NaClO_4$–NaOH) and 25.0 °C. For 0.12–0.25 M hydroxide, the reaction shows a third-order dependence on hydroxide ion concentration. The effects of methyl substitution at nitrogen and bicyclic ligand structure on the formation rate constants are discussed.

Introduction

There has been renewed interest in the kinetics of the reactions of divalent copper ion with linear and cyclic polyamines. The earlier studies have been reviewed,[2] and recent work has focused on the acid-catalyzed dissociation of Cu(II) polyamine complexes[3–11] and the formation and isomerization reactions of Cu(II) with cyclic tetraamines in strongly basic media.[12–14] The latter studies are an extension of the work of Lin et al.,[15] who employed highly basic media to avoid the effects of ligand protonation in

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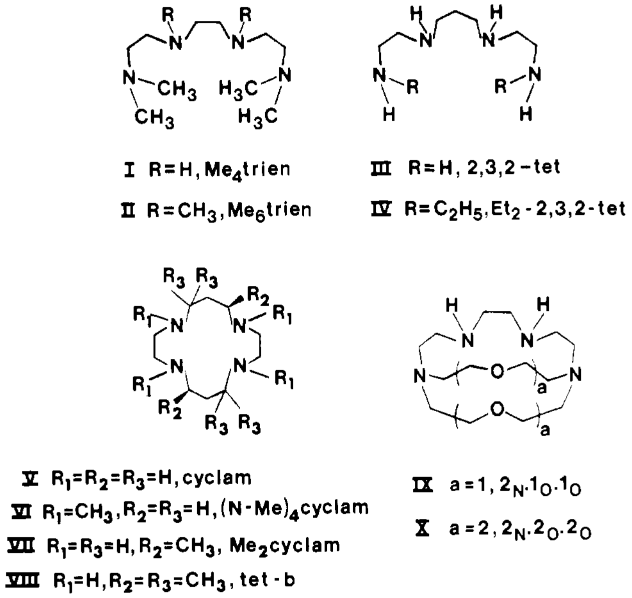

Figure 1. Linear, monocyclic, and bicyclic tetraamines employed in current and previous studies.

their study of the role of ligand cyclization on the formation kinetics of tetraamine ligands with hydroxycuprate(II) species. Those authors found that the effects of alkyl substitution at the nitrogen donor atoms were more significant than ligand cyclization when the proper compounds were chosen for study (see Figure 1; III, IV, V). They also found that methyl substitution (VII, VIII) at the carbon atoms of cyclam (V) caused significant decreases in the formation rate constant, although the steric factors were not calculated. The major effect of ligand cyclization appeared to be to shift the rate-determining step of the complexation reaction from the rearrangement following first-bond formation to second-bond formation as the reactant goes from $Cu(OH)_3^-$ to $Cu(OH)_4^{2-}$.[15] Chung and co-workers have studied the formation and isomerization[12-14] reactions of several highly substituted cyclic tetraamines (for example, Figure 1, VIII) and have found that the high degree of alkyl substitution appears to shift the rate-determining step of the formation reaction to second-bond formation for both $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ species.[14]

In terms of their topological properties, the linear and monocyclic ligands studied represent structures with cyclic order of zero and one and dimensionality of one and two, respectively.[16] The next higher level of ligand topology would be represented by a tridimensional structure with a cyclic order of two. An example of a class of ligands with these properties are the macrobicyclic polyaza-polyethers, cryptands, synthesized by Lehn and co-workers,[16-18] which provide a three-dimensional lattice of donor atoms. Ligands of this type form stable complexes in water with alkali, alkaline-earth, and heavy-metal cations.[19-21] A "macrobicyclic effect" (K_{ML}(bicycle)/K_{ML}(monocycle)) of ~10^5 has been reported for the complexation of K^+ with cryptand 2.2.2 relative to the macrocyclic analogue.[19] Replacement of an $-OCH_2CH_2O-$ segment of cryptands 2.1.1 and 2.2.2 with $-NHCH_2CH_2NH-$ results in the bicyclic tetraamine cryptands $2_N.1_O.1_O$ (IX) and $2_N.2_O.2_O$) (X), respectively.[22] This structural modification increases the stability constants for the complexation of aquocopper(II) by approximately 10 and 6 orders of magnitude for cryptands $2_{NH}.1_O.1_O$ and $2_{NCH_3}.2_O.2_O$ compared with the parent diaza polyethers, respectively.[21,23] The only previous report on the complexation kinetics of Cu(II) with a bicyclic ligand was a study of cryptand 2.2.1 in $(CH_3)_2SO$.[24]

The current study was carried out to evaluate the effects of bicyclic topology on the complexation kinetics of tetraamine ligands. To provide a basis of comparison and to further investigate the effects of N-substitution the tetra- and hexamethyl derivatives of 1,4,7,10-tetraazadecane, Me$_4$trien (I) and Me$_6$trien (II), respectively, were included. (*N*-Me)$_4$cyclam (VI) was included to evaluate the effects of N-substitution of cyclam and to complement the results of previous studies on C-substitution (V, VII, VIII) of cyclam. Cryptand $2_N.2_O.2_O$ (X) did not form a stable complex with Cu(II) in strong base ($[OH^-] > 0.02$ M). However, the dissociation kinetics of $Cu(2_N.2_O.2_O)^{2+}$ in strong base were studied. The ligands included in this investigation (I, II, VI, IX, X) as well as others from previous studies are shown in Figure 1.

Experimental Section

Materials. Ligands Me$_4$trien (Ames Laboratories) and Me$_6$trien (ICN Pharmaceutical) were distilled at reduced pressure. Cryptands $2_N.2_O.2_O$ and $2_N.1_O.1_O$ were synthesized according to literature procedures.[22] Stock solutions of the ligands were standardized by potentiometric titration with HCl or spectrophotometric titration with copper. $Cu(ClO_4)_2$ (G. F. Smith) solutions were standardized by titration with EDTA.[25] Tetraethylammonium hydroxide (Aldrich) was purified by ion exchange using Dowex-1 (Sigma), and stock solutions were standardized against HCl. All solutions were prepared with freshly boiled doubly distilled water.

Spectral Measurements. A Cary 118 or Hitachi 100-80 spectrophotometer equipped with a thermostated cell compartment was used to record the spectra of reactants and the copper complexes.

Kinetic Measurements. All reactions were rapid and were studied on a Durrum-Dionex stopped-flow system interfaced to a Cromenco Z2-D computer. The reactions of Cu(II) with Me$_6$trien and $2_N.1_O.1_O$ were monitored at 272 nm while those with Me$_4$trien and (*N*-Me)$_4$cyclam were monitored at 270 and 305 nm, respectively. The reactions were carried out at 25.0 ±0.1 °C in basic media containing 0.075–0.40 M $(C_2H_5)_4NOH$. The ionic strength of the solutions was dependent on the concentration of $(C_2H_5)_4NOH$ present. The reactions of Me$_6$trien, (*N*-Me)$_4$cyclam and $2_N.1_O.1_O$ were carried out under pseudo-first-order conditions employing at least a tenfold excess of ligand or Cu(II). The reactions of Me$_4$trien were carried out under second-order conditions employing equal concentrations of ligand and Cu(II). The hydroxide-catalyzed dissociation of $Cu(2_N.2_O.2_O)^{2+}$ was monitored at 272 nm. The observed reactions were pseudo first order for the range of hydroxide (NaOH) concentrations employed (0.08–0.25 M). Ionic strength was adjusted to 0.5 with $NaClO_4$.

All reaction traces were analyzed by using standard least-squares techniques. Three to six replicate runs were recorded at each set of reaction conditions.

Results

The log values of the first protonation constants for Me$_4$trien, Me$_6$trien, (*N*-Me)$_4$cyclam, and $2_N.1_O.1_O$ are 9.19, 9.11, 10.10, and 10.25, respectively.[23,26,27] Therefore, the ligands exist predominately (≥99.6%) in the unprotonated form for the conditions employed in this study. Likewise, copper(II) exists as a mixture of $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ in equilibrium, described by the expressions[28]

$$Cu(OH)_3^- + OH^- \rightleftarrows Cu(OH)_4^{2-} \qquad (1)$$

and

$$K_4^c = [Cu(OH)_4^{2-}]/[Cu(OH)_3^-][OH^-] \qquad (2)$$

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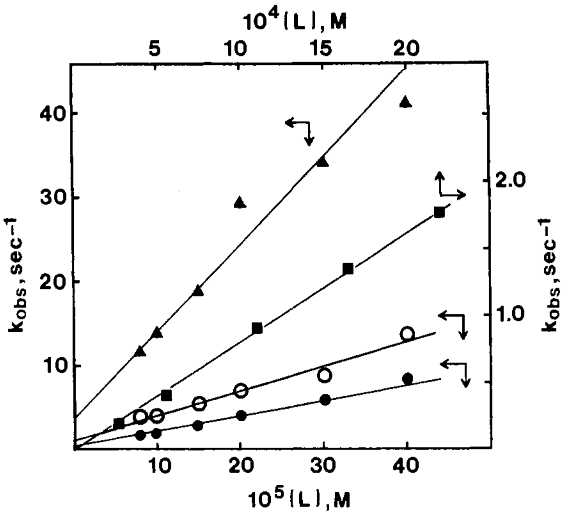

Figure 2. Plots of observed rate constants, k_{obsd}, vs. ligand, L, concentration for reactions of Cu(II) in strongly basic media at 25.0 °C: ▲, Me$_6$trien ([OH$^-$] = 0.20 M); ■, (N-Me)$_4$cyclam ([OH$^-$] = 0.211 M); ○, $2_N.1_O.1_O$ ([OH$^-$] = 0.10 M); ●, $2_N.1_O.1_O$ ([OH$^-$] = 0.20 M).

Table I. Observed Rate Constant Values for Copper(II) Reacting with Me$_4$trien in Basic Solution at 25.0 ± 0.1 °C ([Cu]$_T$ = [L] = A)

$[(C_2H_5)_4NOH]$, M	10^5A, M	$10^{-5}k_{obsd}$, M^{-1} s^{-1}
0.10	2.5	19.0 ± 0.3
	3.5	21.8 ± 1.5
	5.0	28.7 ± 3.8
0.20	2.5	9.5 ± 0.8
	3.5	8.9 ± 0.9
	5.0	12.7 ± 1.1
0.30	2.5	12.5 ± 1.1
	3.5	10.3 ± 0.3
	5.0	9.0 ± 0.6
0.40	3.5	11.8 ± 3.7
	5.0	9.8 ± 1.9
	7.5	7.1 ± 0.5

Table II. Observed Rate Constant Values for Copper(II) Reacting with Me$_6$trien in Basic Solution at 25.0 ± 0.1 °C

$[(C_2H_5)_4NOH]$, M	$10^5[Cu]_T$, M	$10^5[L]$, M	k_{obsd}, s^{-1}
0.075	0.8	8.0	29.0 ± 0.4
	1.0	10	34.5 ± 1.1
	1.5	15	47.9 ± 2.9
	2.0	20	68.2 ± 3.9
	2.0	30	81.4 ± 2.2
	2.0	40	91.4 ± 7.0
0.10	0.8	8.0	18.4 ± 0.8
	1.0	10	27.4 ± 2.0
	2.0	20	46.3 ± 3.9
	2.0	28	50.1 ± 3.8
	2.0	30	65.8 ± 3.8
	2.0	40	80.0 ± 1.6
	2.0	60	95.0 ± 8.5
0.15	0.8	8.0	17.3 ± 0.1
	1.0	10	19.7 ± 0.6
	1.5	15	22.9 ± 0.7
	2.0	20	37.2 ± 1.1
	2.0	30	47.9 ± 0.9
	2.0	40	57.6 ± 0.6
0.20	0.8	8.0	11.6 ± 0.2
	1.0	10	14.0 ± 0.3
	1.5	15	19.0 ± 1.7
	2.0	20	29.6 ± 0.9
	2.0	30	34.4 ± 1.4
	2.0	40	41.3 ± 0.8

Table III. Observed Rate Constant Values for Copper(II) Reacting with (N-Me)$_4$cyclam in Basic Solution at 25.0 ± 0.1 °C

$[(C_2H_5)_4NOH]$, M	$10^5[Cu]_T$, M	$10^4[L]$, M	k_{obsd}, s^{-1}
0.1058	1.34	4.12	0.537 ± 0.015
		8.26	1.18 ± 0.03
		13.76	1.94 ± 0.04
		20.63	2.78 ± 0.16
		27.51	3.85 ± 0.09
0.2115	1.34	2.75	0.184 ± 0.009
		5.50	0.391 ± 0.018
		11.00	0.886 ± 0.018
		16.50	1.35 ± 0.08
		22.0	1.77 ± 0.05
0.3218	1.34	4.12	0.183 ± 0.009
		6.88	0.313 ± 0.005
		11.00	0.538 ± 0.009
		17.88	0.915 ± 0.006
		24.76	1.30 ± 0.01
0.4291	1.34	4.12	0.140 ± 0.004
		6.88	0.235 ± 0.004
		11.00	0.391 ± 0.005
		16.50	0.596 ± 0.010
		22.00	0.833 ± 0.013
0.5364	1.34	11.00	0.301 ± 0.007
	2.68	11.00	0.293 ± 0.003
0.6873	1.34	11.00	0.234 ± 0.003
0.8461	1.34	11.00	0.197 ± 0.006

Table IV. Observed Rate Constant Values for Copper(II) Reacting with $2_N.1_O.1_O$ in Basic Solution at 25.0 ± 0.1 °C

$[(C_2H_5)_4NOH]$, M	$10^5[Cu]_T$, M	$10^5[L]$, M	k_{obsd}, s^{-1}
0.075	0.8	8.0	4.74 ± 0.22
	1.0	10	5.48 ± 0.26
	1.5	15	8.08 ± 0.32
	2.0	20	10.2 ± 0.5
	2.0	30	11.1 ± 1.0
	2.0	40	17.8 ± 0.5
0.10	0.8	8.0	3.98 ± 0.33
	1.0	10	4.01 ± 0.06
	2.0	15	5.42 ± 0.07
	2.0	20	7.09 ± 0.12
	2.0	30	8.73 ± 0.05
	2.0	40	13.65 ± 0.04
0.15	0.8	8.0	2.27 ± 0.07
	1.0	10	2.88 ± 0.04
	1.5	15	4.07 ± 0.10
	2.0	20	4.79 ± 0.18
	2.0	30	7.06 ± 0.19
	2.0	40	9.46 ± 0.23
0.20	0.8	8.0	1.79 ± 0.12
	1.0	10	2.03 ± 0.03
	1.5	15	3.04 ± 0.09
	2.0	20	4.07 ± 0.05
	2.0	30	6.05 ± 0.03
	2.0	40	8.56 ± 0.18
0.40	8.0	0.8	0.246 ± 0.01
	10	1.0	0.300 ± 0.01
	15	1.5	0.323 ± 0.01
	20	2.0	0.360 ± 0.03
	30	3.0	0.536 ± 0.01
	40	4.0	0.632 ± 0.01

The overall reaction of the hydroxycopper species with the various ligands, L, may be represented by the general expression

$$Cu(OH)_n^{2-n} + L \rightleftarrows CuL(OH)_m^{2-m} + (n-m)OH^- \qquad (3)$$

All of the reactions were found to be first order with respect to each reactant. The reactions involving Me$_4$trien and (N-Me)$_4$cyclam proceeded to completion and obeyed the rate expression

$$d[CuL]/dt = k_f[Cu]_T[L]_T \qquad (4)$$

where $[Cu]_T = [Cu(OH)_3^-] + [Cu(OH)_4^{2-}]$ and $k_{obsd} = k_f$ for Me$_4$trien and $k_{obsd} = k_f[L]_T$ for (N-Me)$_4$cyclam. The reactions of Me$_6$trien and $2_N.1_O.1_O$ were reversible (see Figure 2), and the values of k_{obsd} correspond to $k_f[L] + k_d$. Plots of k_{obsd} vs. $[L]_T$ gave straight lines with slope k_f and intercept k_d as shown in Figure 2. The values of k_{obsd} displayed an inverse relationship to [OH$^-$] for all the systems studied. The values of k_{obsd} for all four ligands at each hydroxide concentration are listed in Tables I–IV.

Table V. Observed Rate Constant Values[a] for the Dissociation of $Cu(2_N.2_O.2_O)^{2+}$ in Strong Base at 25.0 ± 0.1 °C

$[OH^-]$, M	k_{obsd}, s^{-1}	$k_{obsd}/[OH^-]^3$, $M^{-3}\ s^{-1}$
0.080	1.07 ± 0.08	2090
0.10	1.80 ± 0.05	1800
0.12	2.34 ± 0.06	1360
0.15	4.02 ± 0.05	1190
0.20	8.86 ± 0.06	1110
0.25	18.36 ± 0.50	1180

[a] μ = 0.5 M ($NaOH/NaClO_4$); $[Cu(2_N.2_O.2_O)^{2+}] = 2.0 \times 10^{-5}$ M.

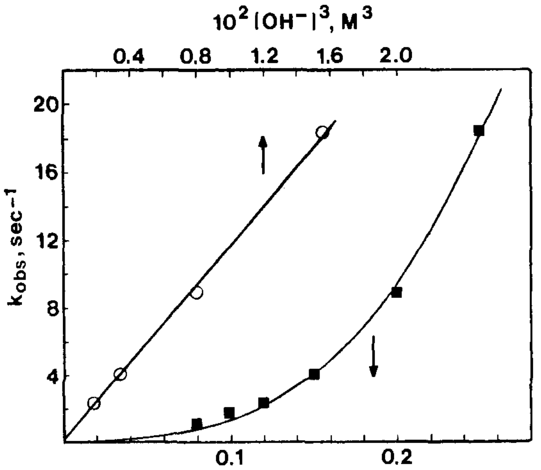

Figure 3. Plots of k_{obsd} vs. $[OH^-]$ (■) and $[OH^-]^3$ (○) for the dissociation of $Cu(2_N.2_O.2_O)^{2+}$ in strongly basic media, μ = 0.5 M ($NaOH/NaClO_4$) at 25.0 °C.

The dissociation reactions of $Cu(2_N.2_O.2_O)^{2+}$ in strong base were pseudo first order overall. For $[OH^-] \leq 0.12$ M the dissociation reactions did not go to completion (≥90%). The observed rate constants at each hydroxide concentration are listed in Table V. Figure 3 shows that k_{obsd} has a hydroxide dependence that is greater than first order. For reactions with $[OH^-] \geq 0.12$, the values of $k_{obsd}/[OH^-]^3$ are essentially constant, suggesting a rate law of the form

$$\frac{-d[CuL]}{dt} = k_{OH}[OH^-]^3[CuL] = k_{obsd}[CuL] \qquad (5)$$

Figure 3 shows that a plot of k_{obsd} vs. $[OH^-]^3$ is indeed linear, and least-squares analysis of the data yield $k_{OH} = 1150 \pm 20\ M^{-3}\ s^{-1}$ (R = 0.9982, n = 15).

Discussion

Examination of Tables I–IV reveals that the observed rate constants decrease with increasing hydroxide concentration. Similar behavior has been reported for other polyamine ligands in strongly basic solution.[14,15] Since the ligands are unprotonated under the conditions employed, the observed kinetic behavior has been attributed to lower reactivity of the $Cu(OH)_4^{2-}$ species relative to $Cu(OH)_3^-$ for a given ligand.[14,15] The observed kinetic behavior may be accounted for by

$$\begin{array}{lcl} Cu(OH)_4^{2-} + L & \xrightarrow{k_{Cu(OH)_4}{}^{L}} & CuL(OH)_x^{2-x} + (4-x)OH^- \\ K_4^c \downarrow\uparrow & & \\ OH^- + Cu(OH)_3^- + L & \xrightarrow{k_{Cu(OH)_3}{}^{L}} & CuL(OH)_x^{2-x} + (3-x)OH^- \end{array} \qquad (6)$$

where L represents one or more reactive conformation(s) of the ligand.

Assuming that the equilibrium involving $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ is rapidly established, the following relationship is obtained by combining eq 2, 4, and 6:

$$k_f(1 + K_4^c[OH^-]) = k_{Cu(OH)_3}{}^{L} + k_{Cu(OH)_4}{}^{L}K_4^c[OH^-] \qquad (7)$$

Table VI. Resolved Formation Rate Constants for Hydroxycuprate(II) Species Reacting with Acyclic and Cyclic Tetraamine Ligands at 25.0 °C

ligand	$k_{Cu(OH_3}{}^{L}$, $M^{-1}\ s^{-1}$	$k_{Cu(OH)_4}{}^{L}$ $M^{-1}\ s^{-1}$	$k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_4}{}^{L}$ ($R_{3,4}$)
2,3,2-tet[a]	$(1.0 \pm 0.7) \times 10^7$	$(4.3 \pm 0.2) \times 10^6$	2.4
Et_2-2,3,2-tet[a]	$(3.0 \pm 0.3) \times 10^6$	$(2.9 \pm 0.6) \times 10^5$	10
Me_4trien	$(4.1 \pm 0.6) \times 10^6$	$(4.2 \pm 1.3) \times 10^5$	10
Me_6trien	$(3.4 \pm 0.4) \times 10^5$	$<10^4$	>30
cyclam[a]	$(2.7 \pm 0.4) \times 10^6$	$(3.8 \pm 0.9) \times 10^4$	72
Me_2cyclam[a]	5.6×10^5	0.9×10^4	60
(N-Me)$_4$cyclam	$(3.1 \pm 0.4) \times 10^3$	<10	>300
tet-b[b]	3.1×10^4	1.1×10^2	290
$2_N.1_O.1_O$	$(6.6 \pm 0.3) \times 10^4$	$(3.8 \pm 0.7) \times 10^3$	17

[a] Reference 15. [b] Reference 14.

For the studies involving $2_N.1_O.1_O$ and Me_6trien, the individual values of k_f may be calculated from

$$k_f = (k_{obsd} - k_d)/[L]_T \qquad (8)$$

where k_d is obtained as the intercept from a plot of k_{obsd} vs. $[L]_T$. The values of K_4^c utilized were interpolated from the reported equilibrium constants.[15,28] Those values were derived from the expression

$$K_4 = \frac{a_{Cu(OH)_4}}{a_{Cu(OH)_3}a_{OH}} = K_4^c\gamma_{NaOH}^2 = 7.86 \qquad (9)$$

where γ_{NaOH} is the mean activity coefficient for NaOH.[29] Corresponding values of $\gamma_{(C_2H_5)_4NOH}$ were not available, so the estimates of K_4^c are based on the calculations utilizing γ_{NaOH}. The values of $k_{Cu(OH)_3}{}^{L}$ and $k_{Cu(OH)_4}{}^{L}$ obtained from least-squares analysis of eq 7 are listed in Table VI.

Inspection of the rate constants listed in Table VI reveals that the ligands utilized in the current study display the following features in common with those from earlier studies.

1. The resolved rate constants are less than the diffusion-controlled limit and, on the basis of comparisons with $Cu(H_2O)_6^{2+}$, are less than the value expected for simple axial H_2O substitution of tetragonal Cu(II).

2. For each of the ligands, the values of $k_{Cu(OH)_3}{}^{L}$ are consistently larger than the corresponding values of $k_{Cu(OH)_4}{}^{L}$ with the ratio of rate constants $k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_4}{}^{L}$ ranging from 10 to >300.

3. With the possible exception of (N-Me)$_4$cyclam, $Cu(OH)_4^{2-}$ is a reactant with each ligand. Since a seven-coordinate copper species is unlikely,[15] the latter finding suggests that the rate-determining step for reactions involving $Cu(OH)_4^{2-}$ occurs before the third Cu–N bond is formed.

As noted in the previous studies,[14,15] these observations suggest that the position of the rate-determining step lies after the first axial H_2O substitution and before formation of the third Cu–N bond. A modified version of the reaction mechanism proposed by Lin et al.[15] to explain the reactions of multidentate polyamine ligands with hydroxycuprate(II) species is shown in Figure 4.

In order to assign the position of the rate-determiing step, it has proven useful to examine the rate constant ratios $k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_4}{}^{L}$ ($R_{3,4}$) for a given ligand L and $k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_3}{}^{2,3,2tet}$ (R_s) for each ligand reacting with $Cu(OH)_3^-$.[14,15] Values of $R_{3,4}$, listed in Table VI, are expected to be greater than unity since the Jahn–Teller inversion step (k_{1b} or k_{2b}) for $Cu(OH)_4^{2-}$ requires that two Cu–OH bonds be lengthened instead of one for $Cu(OH)_3^-$. Small values of $R_{3,4}$ imply that the rate-determining step is the same for $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$. Large values (i.e., >10) of $R_{3,4}$ for a given ligand suggest a shift of the rate-determining step from first- to second-bond formation for $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, respectively.

If Jahn–Teller inversion following first-bond formation is the rate-determining step for the reactions involving $Cu(OH)_3^-$, the differences among the resolved values of $k_{Cu(OH)_3}{}^{L}$ may be at-

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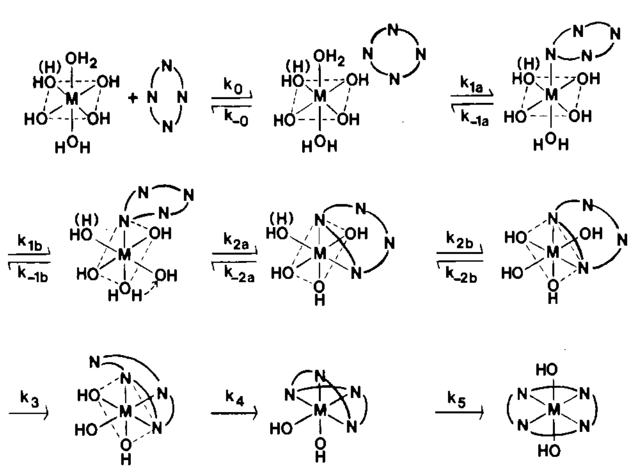

Figure 4. Schematic representation of the complexation of $Cu(OH)_n(H_2O)_m^{2-n}$ by a tetradentate polyamine ligand.[15] In this scheme, the first Cu(II)-N bond is formed by replacement of an axial solvent molecule (k_{1a}) followed by Jahn-Teller inversion (k_{1b}) to bring the coordinated nitrogen into an equatorial position. Second-bond formation is proposed to occur by a similar two-step sequence (k_{2a} and k_{2b}). The coordination number of species with two or more nitrogens bonded may be less than six.

Table VII. Rate Constant Ratios for Acyclic and Cyclic Tetraamine Ligands Reacting with $Cu(OH)_3^-$ at 25.0 °C

	$k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_3}{}^{2,3,2tet}$		
ligand	obsd[a]	predicted[b]	comments[c]
2,3,2-tet[d]	1.0	1.0	acyclic, PSSP
Et_2-2,3,2-tet[d]	0.30	0.22	acyclic, SSSS
Me_4trien	0.41	0.25	acyclic, TSST
Me_6trien	0.034	0.065	acyclic, TTTT
cyclam[d]	0.27	0.22	cyclic, SSSS
Me_2cyclam[d]	0.056	0.22	cyclic, SSSS
(*N*-Me)$_4$cyclam	3.1×10^{-4}	$(5-30) \times 10^{-3}$	cyclic, TTTT
tet-b[e]	3.2×10^{-3}	0.22	cyclic, SSSS
$2_N.1_O.1_O$	6.6×10^{-3}	0.11	bicyclic, TSST

[a] Ratios calculated from values from Table VI. [b] Predicted value for each ligand calculated as described in ref 15 from the following steric factors based on reactions of substituted amines (Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6071-6076) and monoprotonated diamines (Turan, T. S.; Rorabacher, D. B. *Inorg. Chem.* **1972**, *11*, 288-295. Turan, T. S. *Inorg. Chem.* **1974**, *13*, 1584-1590): $Et'NH_2/Et'N(H)Et \cong 8$, $Et'N(Me)_2/Et'N(Me)Et' \cong 0.4-1.2$, $Et'N(H)Et'/Et'N(Me)Et' \cong 8-50$ ($Me = -CH_3$, $Et' = -C_2H_4-$, $Et = C_2H_5$). Thus, for Et_2-2,3,2-tet, $R_s = (1 + 1 + 1 + 1)/(8 + 1 + 1 + 8) = 0.22$, etc. [c] Ligand type and N-substitution pattern: P = primary, S = secondary, T = tertiary. [d] Reference 15. [e] Reference 14.

tributed to steric effects of N-substitution. Table VII lists observed values of R_s for each ligand and the corresponding values predicted on the basis of estimated steric effects of N-substitution.

For those ligands where R_s(observed) ≪ R_s(predicted) steric factors alone are not sufficient to account for the difference between $k_{Cu(OH)_3}{}^{L}$ and $k_{Cu(OH)_3}{}^{2,3,2tet}$,and this may indicate a shift in the rate-determining step to second-bond formation or the subsequent inversion process.

On the basis of this type of analysis, Lin et al.[15] have proposed that Jahn-Teller inversion following first-bond formation (k_{1b}) is the rate-determining step of the formation reactions of $Cu(OH)_3^-$ with 2,3,2-tet, Et_2-2,3,2-tet, cyclam, and Et_4dien (1,1,7,7-tetraethyl-1,4,7-triazaheptane) and of $Cu(OH)_4^{2-}$ with 2,3,2-tet and Et_2-2,3,2-tet. They also postulate that the rate-determining step shifts to second-bond formation for the reactions of $Cu(OH)_4^{2-}$ with cyclam and Et_4dien. Utilizing the same approach, with cyclam as the reference ligand ($R_s' = k_{Cu(OH)_3}{}^{L}/k_{Cu(OH)_3}{}^{cyclam} = 0.012$), Chen et al.[14] proposed that second-bond formation is the rate-determining step for the reaction of tet-b with $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$.

The rate-determining step for the reactions of Me_4trien and Me_6trien with $Cu(OH)_3^-$ appears to be inversion following formation of the first axial Cu-N bond. The relatively low value (~10) of $R_{3,4}$ for Me_4trien suggests the same position of the rate-determining step for the reaction with $Cu(OH)_4^{2-}$. Although Me_4trien has tertiary terminal nitrogen donors, the rate constants for the reactions with $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ are slightly larger than the corresponding values for Et_2-2,3,2-tet. The reaction of Me_6trien with $Cu(OH)_4^{2-}$ is considerably slower than the corresponding reaction with $Cu(OH)_3^-$ ($R_{3,4} > 30$), implying that the rate-determining step shifts to the formation of the second Cu-N bond.

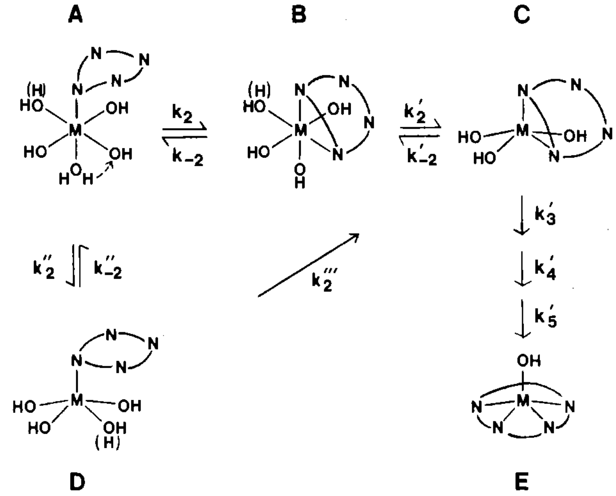

Figure 5. Schematic representation of possible multiple-desolvation processes in the complexation of Cu(II) by a tetradentate polyamine. Only steps subsequent to first-bond formation are shown, and Jahn-Teller inversions have been omitted.

Formation of the first chelate ring is likely to be more difficult for Me_6trien than for Me_4trien since the former ligand contains only tertiary nitrogen donor atoms. Thus, the value of k_{2a} is expected to be less than the corresponding value for Me_4trien. Also, the value of k_{-1b} is presumably larger for reactions of $Cu(OH)_4^{2-}$ than those of $Cu(OH)_3^-$.[15] Thus, the introduction of methyl substituents to the interior nitrogens of Me_4trien to give Me_6trien appears to shift the rate-determining step to second-bond formation for the reaction of $Cu(OH)_4^{2-}$ with Me_6trien. The fact that the observed value of $k_{Cu(OH)_3}{}^{L}$ for Me_6trien is slightly less than that predicted based on steric effects associated with N-substitution may indicate some influence of the ring closure step.

The observed value of R_s for (*N*-Me)$_4$cyclam is about 16-100 times smaller than the calculated values. Thus, it appears that the rate-determining step for the reaction of this ligand with $Cu(OH)_3^-$ has shifted to the formation of the second Cu-N bond or the subsequent inversion/rearrangement process. It should be pointed out, however, that the geometry of the final product may not be six-coordinate. Solid-state and solution structural studies of the zinc and nickel complexes of (*N*-Me)$_4$cyclam indicate that species with square-pyramidal and trigonal-bipyramidal geometries are formed.[30-32] Micheloni et al. have shown that several unidentate ligands (N_3^-, OCN^-, SCN^-) form weak ternary complexes with $Cu[(N\text{-}Me)_4cyclam]^{2+}$.[33] Thus, the mechanism shown in Figure 4 may not strictly apply to the complexation reaction of (*N*-Me)$_4$cyclam, particularly for the steps after first or second Cu-N bond formation. In order to achieve a coordination number of 5 for the product, a step involving multiple desolvation is required. This possibility has been suggested regarding the reactions of tet-b with hydroxycuprate(II) species.[14] Figure 5 represents a modified version of the reaction scheme shown in Figure 4 expanded to include a possible multiple-desolvation

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process. Such a process is not likely for the first Cu–N bond formation but may occur prior to formation of the third Cu–N bond.

As the ligands become more highly substituted, the observed rate constants may reflect an increasing contribution from the multiple-desolvation process due to crowding between the partially bound ligand and remaining solvent molecules, i.e., $k_2' \simeq k_{-2}$, path ABC or $k_2''' \approx k_{-2}''$, path ADC in Figure 5. The large values of $R_{3,4}$ for tet-b and (N-Me)$_4$cyclam are also consistent with the scheme shown in Figure 5 and suggest that multiple desolvation subsequent to first-bond formation affects reactions involving $Cu(OH)_4^{2-}$ to a larger extent than reactions of $Cu(OH)_3^-$. A multiple-desolvation step for $Cu(OH)_4^{2-}$ subsequent to first Cu(II)–N bond formation would require the loss of at least one coordinated hydroxide molecule from the $Cu(OH)_n$–ligand intermediate species. Presumably, this process would be energetically less favorable than the corresponding step for $Cu(OH)_3^-$ where water molecules could be lost.

The macrobicyclic tetraamine $2_N.1_O.1_O$ forms very stable complexes with aquocopper(II) with log K_{CuL} = 17.9.[23] Furthermore, like most other tetraaza macrocycles, the dissociation of the copper complex is very sluggish, with a half-life of ~33 h in 1.5 M $HClO_4$.[34] These facts suggest that the cupric ion is inside the ligand cavity and coordinated to all four nitrogen donor atoms. Although no X-ray crystal structure has been reported for $Cu(2_N.1_O.1_O)^{2+}$, studies on related systems suggest that the copper(II) ion could be located inside the ligand cavity. For example, the structure of the lithium ion complex with the analogous tetraoxa cryptate $2_O.1_O.1_O$ has been reported,[35] and the lithium cation resides inside the ligand cavity coordinated to all donor atoms (4O, 2N) with what has been described as very distorted octahedral geometry. In addition, we have recently solved the structure of the Cu(II) complex of the dithia cryptand 1,10-diaza-13,16,21,24-tetraoxa-4,7-dithiabicyclo[8.8.8]hexacosane, $2_S.2_O.2_O$, where the coordination geometry of the copper ion was octahedral (1N, 2S, 2O, $1H_2O$).[42]

The low value for R_s(obsd) relative to R_s(calcd) indicates that the rate-determining step is most likely formation of the second Cu(II)–N bond or the subsequent rearrangement. The relatively low value of $R_{3,4}$ (~17) indicates that the rate-determining step for the reaction of $Cu(OH)_4^{2-}$ with $2_N.1_O.1_O$ is also formation of the second Cu(II)–N bond or the associated rearrangement. If a multiple-desolvation step is required, as suggested for tet-b and (N-Me)$_4$cyclam, it appears to have little effect on the formation rate constants of $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ and may occur after the rate-determining step.

Comparison of the values of $k_{Cu(OH)_3}{}^L$ and $k_{Cu(OH)_4}{}^L$ for $2_N.1_O.1_O$ with the corresponding values of the acyclic analogue Me_4trien reveals a decrease of 60–110-fold for the bicyclic ligand. The proposed shift of the rate-determining step to second Cu(II)–N bond formation for $2_N.1_O.1_O$ is most likely due to the more rigid bicyclic structure of this ligand. Unlike the acyclic analogue Me_4trien, the terminal (bridgehead) nitrogens of $2_N.1_O.1_O$ are probably quite unreactive due to steric hindrance, and the interior nitrogens of $2_N.1_O.1_O$ may be held in a much less reactive conformation(s) than those of the more flexible acyclic tetraamine.

The values of the ratio $k_{Cu(OH)_3}{}^L{:}k_{Cu(OH)_3}{}^{2,3,2\text{-tet}}$ listed in Table VII are based on the assumption that the ligands exist in one conformation or as a mixture of equally reactive conformers. However, the ligands may exist in several conformations with varying reactivity. For example, the cryptands (IX, X) may exist in three forms differing by the orientation of the bridgehead nitrogen lone pairs; endo–endo (i,i), endo–exo (i,o), and exo–exo (o,o).[16] Ultrasonic absorption studies of cryptand 2.2.2 in water reveal two concentration-independent relaxation processes consistent with

$$L \underset{}{\overset{K_c}{\rightleftarrows}} L' \underset{}{\overset{K_c'}{\rightleftarrows}} L'' \tag{10}$$

where L, L′, and L″ represent different conformers of the ligand and K_c and K_c' are the conformational equilibrium constants.[36] The relaxation data for cryptand 2.2.2 indicate that the conformational rearrangements are fast, $k_{conf} \simeq 4 \times 10^7$–$4 \times 10^8$ s^{-1}.[36] If cryptands $2_N.2_O.2_O$ and $2_N.1_O.1_O$ behave in a similar fashion, it seems unlikely that ligand rearrangement is the rate-determining step of the complexation reaction. Conformational analysis by molecular mechanics calculations also supports the idea that the cryptands may exist as a mixture of conformers. One study finds four conformations of cryptand 2.2.2 (o,o; o,i; i.i; i.i') with similar values of strain energy[37] while another study indicates that the i,i isomer is more stable than the o,o form.[38] All metal ion cryptates for which X-ray structures are available exist as the endo–endo conformer[39] and the presence of an acid-promoted dissociation pathway for cryptates provides indirect evidence for an endo–exo cryptate isomer.[40,41] Thus, the effects of conformational equilibria on the complexation reactions of cryptands must be considered. The observed value of the rate constant ratio for the reaction of $Cu(OH)_3^-$ with $2_N.1_O.1_O$ and 2,3,2-tet is a factor of ~17 lower than the corresponding predicted ratio (see Table VII). Therefore, if either L′ and/or L″ are the reactive species in eq 10 and the values of K_c and K_c' are in the range 0.06–0.28, a 17-fold decrease in the observed rate constant would be expected relative to a system in which L is the only reactive species. Although the values of K_c and K_c' have not been rigorously determined, estimates in the range 0.1–0.2 were required to obtain reasonable values of $\Delta H^\ddagger$ and ΔV from the relaxation data for cryptand 2.2.2.[36]

At the present time, the lack of quantitative conformational equilibrium constant values for cryptands in aqueous solution and the relative reactivities of the various conformers preclude a more detailed treatment of this aspect of the complexation process. However, the possibility cannot be ruled out that the relatively low value of the rate constant ratio for cryptand $2_N.1_O.1_O$ is due to unfavorable conformational equilibria. Similar considerations may also apply to the more highly substituted macrocyclic tetraamines (VI–VIII).

The failure of cryptand $2_N.2_O.2_O$ to form a stable complex with hydroxycuprate(II) species under the conditions employed is consistent with the fact that the value of the stability for aquocopper(II) with $2_{NCH_3}.2_O.2_O$ is ~2000 times lower than the corresponding value with $2_{NCH_3}.1_O.1_O$.[23] The third-order hydroxide dependence for the rate dissociation of $Cu(2_N.2_O.2_O)^{2+}$ in strong base is consistent with the reaction scheme shown in Figure 4 since a transition-state complex composed of a copper cation, three hydroxides, and a partially bound tetraamine is proposed for the formation reactions of several other tetraamines.[14,15] A single reaction accounts for the observed absorbance change, suggesting that no appreciable amounts of hydroxy–cryptate intermediates are formed under the conditions employed. This behavior is qualitatively similar to that reported for the base-catalyzed dissociation of Cu(*trans*-Me_6-18-diene-N_4)$^{2+}$ at low hydroxide concentrations (0.01–0.05 M), where a second-order hydroxide dependence is observed.[6] The range of [OH^-] employed in the current study may not be wide enough to observe the fourth-order hydroxide dependence indicative of the $Cu(OH)_4$–ligand reaction intermediate.

The difference in the stability constants of the Cu(II) cryptates of $2_N.2_O.2_O$ and $2_N.1_O.1_O$ may be a consequence of the bicyclic topology of these ligands. The longer polyether bridging strands of $2_N.2_O.2_O$, relative to those of $2_N.1_O.1_O$, make it difficult for all four nitrogen donor atoms to interact with the copper ion. Space-filling molecular models of $2_N.1_O.1_O$ indicate that the ligand

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can adopt a conformation with all four nitrogen donor atoms in a distorted square-planar array. In contrast, models of $2_N.2_O.2_O$ show that only one bridgehead nitrogen and two bridge nitrogens can readily coordinate to a metal ion with square-planar or tetragonal geometry. Further evidence in support of this hypothesis is provided by the crystal structure of $Cu(2_S.2_O.2_O)^{2+}$, where the cupric ion is coordinated to only one of the bridgehead nitrogen atoms, to the two sulfur atoms in one bridge, and to one oxygen atom adjacent to the coordinated nitrogen in each of the other two bridges. The sixth coordination site of Cu(II) is occupied by a water molecule.[42]

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Chemical and Structural Studies of Azaboranes

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Reaction of $B_{10}H_{14}$ with sodium nitrite in THF at room temperature forms $Na[B_9H_{12}NH]$, $Na[B_9H_{14}]$, and $Na[B_{10}H_{15}]$ as the major products. A single-crystal X-ray structure study of the Lewis base adduct $B_9H_{11}NH{\cdot}CN(C_6H_{11})$ has been completed. The arachno open cage structure of this azaborane derivative is very similar to that previously reported for the isoelectronic compound $9\text{-}N(C_2H_5)_3\text{-}6\text{-}SB_9H_{11}$. Slow passage of $B_9H_{11}NH$ through an evacuated hot tube (400 °C) formed *closo*-B_9H_9NH and H_2. Some of the chemical and spectral properties of this first *closo*-azaborane are described.

In the last two decades there has been considerable progress in understanding the chemistry of thiaboranes,[1-10,17] as well as the chemistry of selenium and tellurium analogues.[11-14] While the initial syntheses of azaboranes were reported in the same paper as those of the first thiaboranes,[1] progress with the nitrogen-containing boranes has been very slow. Decaborane was found to react with (thionitroso)dimethylamine, $(CH_3)_2NN{=}S$, to give both $B_{10}H_{11}S^-$ and $B_9H_{12}NN(CH_3)_2^-$.[1] The yield of the azaborane anion was low, which precluded any extensive study of its chemistry.

Even so, some derivative chemistry was reported.[1] The $B_9H_{12}NN(CH_3)_2^-$ ion reacted with methyl iodide to form the inner salt $B_9H_{12}NN(CH_3)_3$. The N–N bond of $B_9H_{12}NN(CH_3)_2^-$ was broken by reaction with excess sodium in tetrahydrofuran to form $Na[B_9H_{12}NH]$. Salts of $B_9H_{12}NH^-$ are stable enough to survive recrystallization from hot aqueous or ethanol solutions. Bromine oxidation of $B_9H_{12}NH^-$ in acetonitrile solution formed $CH_3CN{\cdot}B_9H_{11}NH$. Treatment of the acetonitrile complex with either lithium aluminum hydride or lithium borohydride re-formed the $B_9H_{12}NH^-$ ion.

At a later date it was reported that sodium nitrite reacted with decaborane in tetrahydrofuran to give an intermediate assumed to be $B_{10}H_{12}NO_2^-$. Treatment of this product with 4 M HCl, with a layer of hexane present, formed the neutral azaborane, $B_8H_{12}NH$.[15] An X-ray structure determination of this compound has been reported.[15] The structure can be described as that of the *arachno*-borane, *i*-B_9H_{15}, in which a BH unit and two bridge hydrogen atoms have been replaced by an NH unit (Figure 1). Subsequently it was reported that treatment of the proposed $B_{10}H_{12}NO_2^-$ intermediate with concentrated sulfuric acid, with a layer of hexane present, formed $B_9H_{11}NH$.[16]

Controlled hydrolysis of $B_9H_{11}NH$ produced $B_8H_{12}NH$ in good yield. This azaborane chemistry is summarized in eq 1.

$$\begin{tikzcd}
B_{10}H_{14} + Na[ON{=}O] \arrow[rr, "THF"] & & Na[B_{10}H_{12}NO_2] \arrow[dl, "H_2SO_4/pentane"'] \arrow[d, "HCl/H_2O"] \\
& B_9H_{11}NH \arrow[r, "H_2O"] & B_8H_{12}NH
\end{tikzcd} \qquad (1)$$

We report herein additional details of the sodium nitrite–decaborane reaction and related chemistry, as well as the synthesis and chemistry of the first *closo*-azaborane.

Results and Discussion

Observations Concerning the Reaction of $B_{10}H_{14}$ with $NaNO_2$ with THF as Solvent. As soon as decaborane was added to the $NaNO_2$/THF slurry, a yellow color developed. This may be due to the formation of $NaB_{10}H_{13}$ and nitrous acid. While $NaB_{10}H_{12}NO_2$ may form as a transient intermediate in the reaction of $B_{10}H_{14}$ with $NaNO_2$ in THF, it is not one of the major final products of this complex reaction. The ^{11}B NMR spectrum of the products, after the reaction mixture was stirred for 3 days at room temperature, showed the presence of $B_9H_{12}NH^-$, $B_9H_{14}^-$,

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