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Registry No. $[Zn_2L2]NCS(ClO_4)_3$, 112596-27-7.

Supplementary Material Available: Tables of thermal parameters and complete bond lengths and angles and a table containing the initial quantities of reactants, pH range, number of data points for each titration curve, and the computer output of the program SUPERQUAD giving individual data points for emf measurements (32 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Kinetics of Acid-Catalyzed Dissociation of Nickel(II) Diamino Diamide Complexes

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The kinetics and mechanism of acid-catalyzed dissociation reactions of copper(II) diamino diamide complexes have been described.[1] We now report the kinetics and mechanism of the dissociation reactions of nickel(II) diamino diamide complexes at low pH

$$NiL^{2+} + 2H^+ \rightarrow Ni^{2+} + H_2L^{2+} \qquad (1)$$

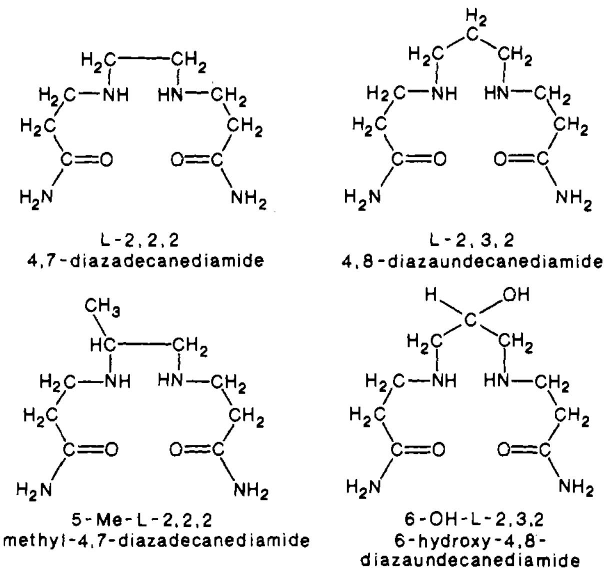
where L is the diamino diamide depicted in Chart I. The stability constants of the nickel(II) complexes of these four ligands and the complexation kinetics of these nickel(II) complexes have been reported.[2,3]

Experimental Section

Reagents. The complexes Ni(L-2,2,2)$(ClO_4)_2$, Ni(5-Me-L-2,2,2)-$(ClO_4)_2$, Ni(L-2,3,2)$(ClO_4)_2$, and Ni(6-OH-L-2,3,2)$(ClO_4)_2$ were the same as those reported previously.[4-9] All other chemicals used were of GR grade from Merck or Fluka.

Kinetic Measurements. The kinetics of the acid-catalyzed dissociation reactions of the nickel complexes were followed at 25.0 ± 0.1 °C with the use of a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment and a Hitachi U-3200 UV-vis spectrophotometer. Absorbance vs time data were collected at 363, 364, 372, and 369 nm for the dissociation reactions of Ni(L-2,2,2)$^{2+}$, Ni(5-Me-L-2,2,2)$^{2+}$, Ni(L-2,3,2)$^{2+}$, and Ni(6-OH-L-2,3,2)$^{2+}$, respectively.[2,3] Pseudo-first-order conditions were maintained by using at least a 10-fold excess of acid in each run. Good first-order kinetics were observed in all cases. The rate constants were obtained by a linear least-squares fit for the data by using the CDC Cyber-172 computer. Recrystallized $NaClO_4$ was used to maintain constant ionic strength at μ = 4.0 M in all solutions. The concentration of the nickel(II) complex employed for the kinetic work is 5.00×10^{-3} M. The concentrations of acid are in the range of 0.05-2.00 M.

Chart I



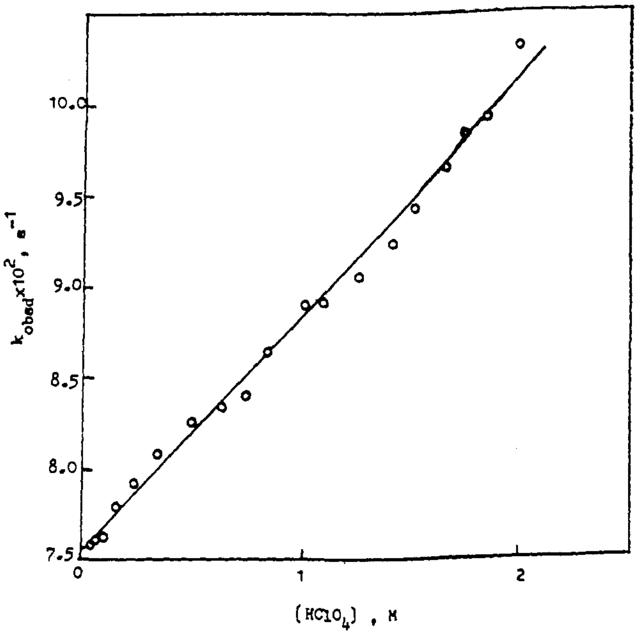


Figure 1. Plot of k_{obsd} vs $[H^+]$ for the dissociation of Ni(L-2,3,2)$^{2+}$ at 25.0 ± 0.1 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$).

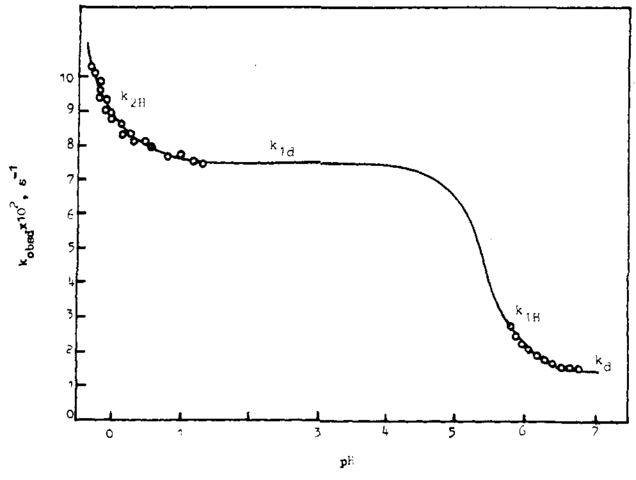


Figure 2. pH dependence for the dissociation of Ni(L-2,3,2)$^{2+}$ at 25.0 ± 0.1 °C.

Results

The kinetics of the dissociation reactions of these nickel(II) diamino diamide complexes were studied at 25.0 °C, with μ = 4.0 M ($HClO_4$ + $NaClO_4$), and in 0.05-2.00 M $HClO_4$. Under these conditions, the dissociation reactions of these complexes were found to proceed to completion. Some of the observed pseudo-

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0020-1669/88/1327-1107$01.50/0

Table I. Kinetic Data for the Dissociation of Nickel(II) Diamino Diamide Complexes in Acid at 25.0 ± 0.1 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$)

acid	$[HB]_T$, M	$[H^+]$, M	10^2k_{obsd}, s^{-1}	acid	$[HB]_T$, M	$[H^+]$, M	10^2k_{obsd}, s^{-1}
	Ni(L-2,2,2)$^{2+}$[a]				Ni(L-2,3,2)$^{2+}$[c]		
H_3O^+		0.050	2.65 ± 0.03	H_3O^+		0.050	7.58 ± 0.04
		0.10	2.70 ± 0.04			0.10	7.64 ± 0.03
		0.15	2.81 ± 0.04			0.15	7.81 ± 0.04
		0.25	2.96 ± 0.03			0.25	7.92 ± 0.04
		0.35	3.12 ± 0.05			0.35	8.13 ± 0.03
		0.50	3.36 ± 0.04			0.50	8.26 ± 0.03
		0.65	3.41 ± 0.03			0.65	8.35 ± 0.04
		0.85	3.61 ± 0.03			0.85	8.63 ± 0.03
		1.00	3.79 ± 0.03			1.00	8.88 ± 0.05
		1.25	3.94 ± 0.03			1.25	9.06 ± 0.04
		1.50	4.15 ± 0.04			1.50	9.42 ± 0.03
		1.65	4.46 ± 0.03			1.65	9.64 ± 0.04
		1.75	4.64 ± 0.03			1.75	9.83 ± 0.04
		1.85	4.72 ± 0.05			1.85	9.92 ± 0.03
		2.00	4.86 ± 0.04			2.00	10.3 ± 0.4
CH_3COOH	0.0922	1.00	3.81 ± 0.04	CH_3COOH	0.0922	1.00	8.91 ± 0.03
	0.256	1.00	3.72 ± 0.03		0.256	1.00	8.86 ± 0.04
	0.578	1.00	3.76 ± 0.04		0.578	1.00	8.81 ± 0.05
	0.965	1.00	3.84 ± 0.05		0.965	1.00	8.83 ± 0.04
$CH_2ClCOOH$	0.184	1.00	3.70 ± 0.05	$CH_2ClCOOH$	0.184	1.00	8.68 ± 0.04
	0.537	1.00	3.68 ± 0.04		0.537	1.00	8.63 ± 0.03
	1.23	1.00	3.73 ± 0.03		1.23	1.00	8.76 ± 0.05
	1.98	1.00	3.78 ± 0.04		1.98	1.00	8.72 ± 0.04
$CHCl_2COOH$	0.201	1.00	3.83 ± 0.04	$CHCl_2COOH$	0.201	1.00	8.87 ± 0.04
	0.576	1.00	3.75 ± 0.03		0.576	1.00	8.92 ± 0.05
	1.02	1.00	3.71 ± 0.04		1.02	1.00	8.78 ± 0.04
	1.87	1.00	3.68 ± 0.05		1.87	1.00	9.01 ± 0.03
	Ni(5-Me-L-2,2,2)$^{2+}$[b]				Ni(6-OH-L-2,3,2)$^{2+}$[d]		
H_3O^+		0.050	1.70 ± 0.03	H_3O^+		0.050	69.2 ± 0.3
		0.10	1.75 ± 0.04			0.10	69.5 ± 0.4
		0.15	1.82 ± 0.03			0.15	71.4 ± 0.4
		0.25	1.88 ± 0.04			0.25	72.6 ± 0.3
		0.35	1.96 ± 0.04			0.35	73.8 ± 0.3
		0.50	2.14 ± 0.05			0.50	75.1 ± 0.4
		0.65	2.20 ± 0.04			0.65	76.3 ± 0.4
		0.85	2.31 ± 0.03			0.85	78.1 ± 0.3
		1.00	2.38 ± 0.04			1.00	78.9 ± 0.4
		1.25	2.51 ± 0.05			1.25	83.4 ± 0.5
		1.50	2.72 ± 0.04			1.50	86.2 ± 0.3
		1.65	2.84 ± 0.03			1.65	86.8 ± 0.4
		1.75	2.91 ± 0.03			1.75	87.6 ± 0.2
		1.85	3.06 ± 0.04			1.85	89.1 ± 0.3
		2.00	3.19 ± 0.04			2.00	91.2 ± 0.4
CH_3COOH	0.0922	1.00	2.43 ± 0.05	CH_3COOH	0.0922	1.00	80.1 ± 0.4
	0.256	1.00	2.48 ± 0.06		0.256	1.00	81.1 ± 0.3
	0.578	1.00	2.34 ± 0.03		0.578	1.00	82.1 ± 0.5
	0.965	1.00	2.37 ± 0.04		0.965	1.00	82.6 ± 0.4
$CH_2ClCOOH$	0.184	1.00	2.47 ± 0.05	$CH_2ClCOOH$	0.184	1.00	79.6 ± 0.3
	0.537	1.00	2.51 ± 0.04		0.537	1.00	79.1 ± 0.5
	1.23	1.00	2.39 ± 0.04		1.23	1.00	80.2 ± 0.4
	1.98	1.00	2.42 ± 0.03		1.98	1.00	80.6 ± 0.3
$CHCl_2COOH$	0.201	1.00	2.40 ± 0.04	$CHCl_2COOH$	0.201	1.00	82.4 ± 0.3
	0.576	1.00	2.52 ± 0.05		0.576	1.00	80.6 ± 0.4
	1.02	1.00	2.48 ± 0.03		1.02	1.00	79.6 ± 0.5
	1.87	1.00	2.45 ± 0.04		1.87	1.00	78.6 ± 0.4

[a] [Ni(L-2,2,2)$^{2+}$] = 5.00 × 10^{-3} M; λ = 363 nm. [b] [Ni(5-Me-L-2,2,2)$^{2+}$] = 5.00 × 10^{-3} M; λ = 364 nm. [c] [Ni(L-2,3,2)$^{2+}$] = 5.00 × 10^{-3} M; λ = 372 nm. [d] [Ni(6-OH-L-2,3,2)$^{2+}$] = 5.00 × 10^{-3} M; λ = 369 nm.

first-order rate constants are given in Table I. Some of the observed rate constants are deposited as supplementary material (Table Is). Plots of k_{obsd} vs $[H^+]$ give straight lines according to eq 2.

$$k_{obsd} = k_{1d} + k_{2H}[H^+] \qquad (2)$$

The plot of the dissociation reaction of Ni(L-2,3,2)$^{2+}$ is shown in Figure 1; the other complexes show a similar behavior. The values of k_{1d} and k_{2H} obtained in these plots are listed in Table II. It is interesting to note that the rates of the dissociation reactions of these nickel(II) complexes do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids. The pH dependence for the dissociation reaction of Ni(L-2,3,2)$^{2+}$ is shown in Figure 2; the other complexes show a similar behavior. The symbols of the rate constants k_d, k_{1H}, k_{1d}, and k_{2H} in this figure are the same as those used by Read and Margerum.[10] As shown in this figure, the dissociation of this nickel(II) complex was accelerated when the pH was lowered from 6.5 to 4.5. This pH dependence is designated by the rate constant k_{1H}. When the pH was above 7.0, the rate constant for the water dissociation pathway is k_d.[10] The values of k_d and k_{1H} for these nickel(II) complexes reported previously are given in Table II. Between pH 4.5 and 1.5, a limiting rate was observed with the rate constant given by k_{1d} (Table II).[10] At pH values below 1.5, the rate increased with the acid concentration. This direct protonation pathway is designated by the rate constant k_{2H} (Table II).

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Table II. Summary of Measured Rate Constants Defined in Terms of the Rate Constants for Individual Steps in the Dissociation of Nickel(II) Diamino Diamide Complexes at 25.0 °C

measd rate const	mechanistic rate const	$Ni(L\text{-}2,2,2)^{2+}$	$Ni(L\text{-}2,3,2)^{2+}$	$Ni(5\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$	$Ni(6\text{-}OH\text{-}L\text{-}2,3,2)^{2+}$
k_d, s^{-1} [a]	$(k_1k_2/k_{-1}k_{-2})k_3$	2.09×10^{-3}	1.41×10^{-2}	1.58×10^{-3}	1.12×10^{-1}
k_{1d}, s^{-1} [b]	$(k_1/k_{-1})k_2$	2.66×10^{-2}	7.54×10^{-2}	1.69×10^{-2}	6.91×10^{-1}
k_{1H}, M^{-1} s^{-1} [a]	$(k_1k_2/k_{-1}k_{-2})k_4$	1.73×10^{2}	8.51×10^{3}	1.86×10^{2}	1.35×10^{4}
k_{2H}, M^{-1} s^{-1} [b]	$(k_5/k_{-5})k_6$	1.09×10^{-2}	1.30×10^{-2}	7.14×10^{-3}	1.09×10^{-1}
k_{2H}/k_{1d}		0.410	0.172	0.422	0.158
k_{1d}/k_d	k_{-2}/k_3	1.27×10^{1}	5.3	1.07×10^{1}	6.17
k_{1d}/k_{1H}, M	k_{-2}/k_4	1.54×10^{-4}	8.86×10^{-6}	9.09×10^{-5}	5.12×10^{-5}
k_{1H}/k_d, M^{-1}	k_4/k_3	8.28×10^{4}	6.03×10^{5}	1.18×10^{5}	1.21×10^{5}

[a] $\mu = 0.1$ M ($NaClO_4$). [b] $\mu = 4.0$ M ($NaClO_4 + HClO_4$).

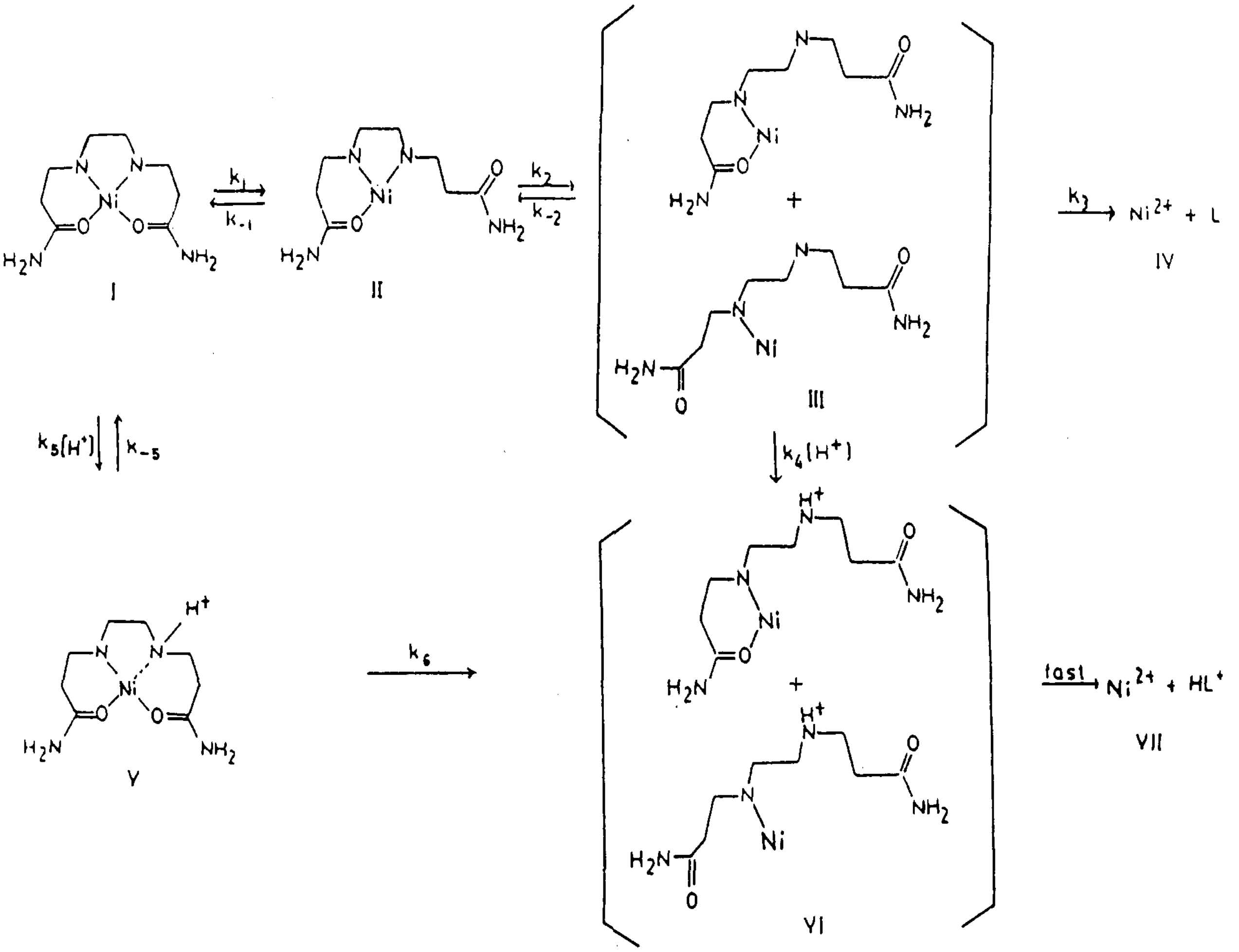

Figure 3. Proposed mechanism for the dissociation reactions of nickel(II) diamino diamide complexes.

Discussion

The kinetic results for these reactions can be explained by the mechanism proposed for the dissociation reactions of the analogous copper(II) diamino diamide complexes (Figure 3). The measured rate constants listed in Table II are defined in terms of the mechanistic rate constants shown in this figure. As the pH is larger than 6.5, the main reaction pathway is the solvent dissociation pathway (I → II → III → IV). The rate-determining step for this pathway is the breakage of the second Ni–N bond (III → IV), and the limiting rate constant k_d corresponds to $k_1k_2k_3/k_{-1}k_{-2}$. Between pH 1.0 and 6.0, the main pathway is the proton-assisted pathway (I → II → III → VI → VII). In the range of pH 5.0 and 6.0, the rate-determining step is the protonation of the released amino group (III → VI), and the rate constant for this pathway k_{1H} corresponds to $k_1k_2k_4/k_{-1}k_{-2}$. At pH <4.5, $k_4[H^+] > k_{-2}$; thus, the breakage of the first nickel–nitrogen bond (II → III) becomes rate determining for this pathway with the limiting rate constant k_{1d}, which corresponds to k_1k_2/k_{-1}.

At pH values below 1.0, both the proton-assisted pathway (I → II → III → VI → VII) and the direct protonation pathway (I → V → VI → VII) make contributions to the rates of these reactions. The direct protonation pathway of these specific-acid-catalyzed reactions involves a rapid equilibration of the nickel complexes with hydrogen ion to form a protonated species V, which then in a slow, rate-determining step reacts to give VI. The last step of this pathway (VI → VII) is fast. The overall rate constant, k_{2H}, corresponds to k_5k_6/k_{-5}.

As shown in Table II, the values of these four rate constants, k_d, k_{1H}, k_{1d}, and k_{2H}, vary in the order $Ni(6\text{-}OH\text{-}L\text{-}2,3,2)^{2+} > Ni(L\text{-}2,3,2)^{2+} > Ni(L\text{-}2,2,2)^{2+}$, $Ni(5\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$. This sequence of labilities parallels the order of aqueous solution instabilities of these complexes, and is related to two factors: (1) the girdle strains among the three linked consecutive chelate rings and (2) the basicity of the ligand. The girdle strains among the linked consecutive chelate rings for the complexes with the 6,6,6-membered ring system are much larger than those for the complexes with the 6,5,6-membered ring system. Thus, the rate constants for the complexes with 6,6,6-membered rings are much larger than those for the complexes with 6,5,6-membered rings. The very large dissociative rate constant for $Ni(6\text{-}OH\text{-}L\text{-}2,3,2)^{2+}$

is attributed to both the large steric strains among the three linked six-membered rings and the low basicity of the ligand.

At pH values lower than 1.0, both the direct protonation pathway and the proton-assisted pathway make contributions to the rate. The ratio k_{2H}/k_{1d} represents the relative rate of dissociation at high acid concentration by the direct protonation and the proton-assisted pathways. As pointed out by Read and Margerum,[10] if the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. The restrictions to hold the donor in the first coordination sphere imposed by the 6,5,6-membered chelate rings are larger than those imposed by the 6,6,6-membered chelate rings. Consequently, ring opening is easier for the 6,6,6-membered rings, making the direct protonation pathway less important. The results tabulated in Table II substantiate this point of view.

The acid dissociation reaction of $Ni(en)^{2+}$ has been studied by Read and Margerum.[10] This reaction is catalyzed by specific and general acids. In contrast with the behavior of $Ni(en)^{2+}$, the results tabulated in Table I indicate that the rates of the dissociation reactions of these nickel(II) diamino diamide complexes do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids. As shown in Figure 3, the rate-determining steps for both the direct protonation pathway (V → VI) and the proton-assisted pathway at low pH (II → III) do not involve a transfer of hydrogen ion from a Brønsted acid to the nickel(II) diamino diamide complex.

The values of k_{1d} and k_{2H} for the reactions of these nickel(II) diamino diamide complexes are smaller than those for the reactions of the corresponding copper(II) complexes; however, the values of k_d for the reactions of these nickel(II) diamino diamide complexes are larger than those for the reactions of the corresponding copper(II) diamino diamide complexes.[1] Of the transition-metal ions, copper(II) is one of the most kinetically labile. Each mechanistic rate constant for the reaction of the copper(II) complex is larger than that for the reaction of the corresponding nickel(II) complex; however, the value of $k_1k_2/k_{-1}k_{-2}$ for the reaction of the copper(II) complex is much smaller than that of the corresponding nickel(II) complex. In summation, k_d for the reaction of a copper(II) complex is smaller than that of the corresponding nickel(II) complex, consistent with a strong Cu(II)-N bond compared to the Ni(II)-N bond.

Acknowledgment. The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 75-0208-M007-04 and NSC 76-0208-M007-66 is gratefully acknowledged.

Registry No. $Ni(L\text{-}2,2,2)(ClO_4)_2$, 112816-41-8; $Ni(5\text{-}Me\text{-}L\text{-}2,2,2)(ClO_4)_2$, 112816-45-2; $Ni(L\text{-}2,3,2)(ClO_4)_2$, 112816-43-0; $Ni(6\text{-}OH\text{-}L\text{-}2,3,2)(ClO_4)_2$, 112816-47-4; CH_3COOH, 64-19-7; $CH_2ClCOOH$, 79-11-8; $CHCl_2COOH$, 79-43-6.

Supplementary Material Available: Table Is, giving part of the kinetic data for the dissociation of nickel(II) diamino diamide complexes in acid at 25.0 ± 0.1 °C and μ = 4.0 M ($NaClO_4$ + $HClO_4$) (2 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of $H_3Os_3(CO)_9(\mu_3\text{-}CF)$. ^{13}C NMR Comparison of Triosmium- and Tricobalt-Substituted Methylidyne Complexes

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Alkylidynetrimetal clusters have been synthesized and studied extensively in recent years,[1] in part since they may be related to species occurring on metal surfaces during heterogeneous catalysis.[2] Though compounds of the formula $M_3(\mu_3\text{-}CX)$ have been prepared for a variety of substituents X, the known examples for X = F are limited to $Co_3(CO)_9(\mu_3\text{-}CF)$[3] and certain of its carbonyl-[4] or metal-substituted[5] derivatives together with $Fe_3(CO)_9(\mu_3\text{-}CF)_2$.[6] Since ^{19}F is NMR active, the fluoromethylidyne ligand is a valuable probe for examining the electronic properties and bonding in $M_3(\mu_3\text{-}CX)$ in clusters. We now report the synthesis and NMR characterization of the first fluoromethylidynetriosmium cluster together with a ^{13}C NMR comparison of analogous substituted methylidynetriosmium and -tricobalt clusters.

Experimental Section

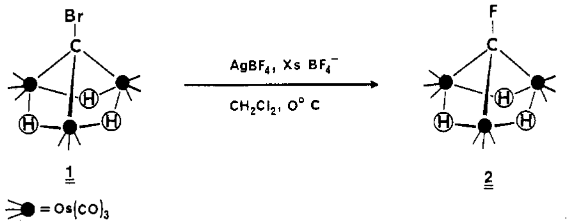
Reactions were conducted under a nitrogen atmosphere. Glassware was heated under vacuum prior to use in order to remove any moisture. Dichloromethane was freshly distilled from phosphorus pentoxide. $AgBF_4$ and $[Et_4N]BF_4$ were purchased from Aldrich Chemical Co. and used as received; both were handled in a N_2-filled glovebox. Preparative TLC plates were prepared with E. Merck silica gel 60-GF 254. $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**) was prepared by a published procedure.[7] A ^{13}C-enriched sample was prepared analogously, starting from ^{13}CO-enriched $Os_3(CO)_{12}$. ^1H and ^{19}F NMR spectra were obtained with a Varian EM-390 spectrometer. ^{13}C NMR spectra were obtained with a General Electric GN-500 NMR spectrometer at 125 MHz. Elemental analysis and mass spectra were obtained by the respective staffs of the Microanalytical Laboratory and of the Mass Spectrometry Laboratory in the School of Chemical Sciences.

Synthesis of $H_3Os_3(CO)_9(\mu_3\text{-}CF)$ (2). A solution of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**) (23.5 mg, 0.026 mmol) and $[Et_4N]BF_4$ (150 mg, 0.69 mmol) in dry dichloromethane (30 mL) was degassed by evacuation and then placed under nitrogen. The flask was cooled in an ice bath, and then a solution of $AgBF_4$ (33.7 mg, 0.17 mmol) in dichloromethane (10 mL) was added via syringe. The solution color immediately turned yellow. The mixture was stirred for 50 min at 0 °C, during which time the solution color changed to dark yellow and then to light tan while a brown precipitate formed. The solution was filtered and separated by TLC. This provided white, solid **2** (13.8 mg, 63%). Two minor products observed on the TLC plate were not characterized.

Anal. Calcd for **2**: C, 14.02; H, 0.35, F, 2.22. Found: C, 13.95; H, 0.39, F, 2.10. ^1H NMR ($CDCl_3$): δ – 18.80. ^{13}C NMR ($CDCl_3$): δ 212.45 (μ_3-*C*F,*J*(^{13}C,^{19}F) = 370.9 Hz), 165.9 (3 CO), 165.5 (6 CO). ^{19}F NMR ($CDCl_3$): –77.73 ppm (relative to external $CFCl_3$). IR (C_6H_{12}): ν(CO) 2083 (vs), 2076 (w, sh), 2027 (vs), 2015 (m), 1986 (m) cm^{-1}. MS (EI, ^{192}Os): *m/z* 862 (M^+) and (M^+ – *x*CO, *x* = 1–9).

Results and Discussion

The reaction of **1** with $AgBF_4$ in dry dichloromethane in the presence of excess $[NEt_4]BF_4$ affords, after TLC purification, the fluoromethylidyne cluster **2** in 63% isolated yield (eq 1). The formulation of **2** is established by microanalysis and mass spectrometry. The carbonyl IR spectrum is very similar to that of **1**, i.e., a typical pattern for such a symmetrical cluster.[7] The ^1H NMR spectrum features a single hydride resonance at δ –18.80.



(1)

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