shapes of the emissions are similar for the solid-state and solution spectra, the four-coordinate structure of M(dppp)₂ appears to be intact in solution.[18] Because of the low solubility of the M(dppp)₂ complexes, absorptions attributable to spin-forbidden transitions could not be established with certainty.[19] The M(dppp)₂ emission lifetimes in 2-MeTHF (≤20 ns) are much shorter than those measured for M(PPh₃)₃ complexes. Assignment of the emissive state of M(dppp)₂ to $^{3}([t_2(d\sigma^*)]^5[t_2(\pi^*,p\sigma^*)]^1)$ is suggested.

Depopulation of dσ* in the emissive excited state should lead to a distortion toward a square-planar ML_4 structure.[20] It is reasonable to suggest that this distortion is related to the rapid excited-state decay that is observed.

Registry No. Pd(PPh₃)₃, 28516-49-6; Pt(PPh₃)₃, 13517-35-6; Pd-(dppp)₂, 31989-49-8; Pt(dppp)₂, 54206-19-8.

Supplementary Material Available: Tables V–VIII, listing thermal parameters, the derived hydrogen positions, and complete distances and angles in the molecule (3 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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(18) ³¹P NMR spectra show no resonances attributable to free phosphine (see ref 4). For a number of ML₄ complexes (M = Pd, Pt and L = bulky phosphine ligand), extensive dissociation takes place in solution: Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119.

(19) A very weak band at ~520 nm in each excitation spectrum might represent a triplet ← singlet transition.

(20) Irradiation (≥340 nm) of Pd(dppp)₂ in degassed 5% CH₂Cl₂/THF at room temperature gives [Pd(dppp)₂]Cl₂ and ethylene (2:1 mole ratio). The photoreaction differs from those reported¹ for Pd(PPh₃)₃ and Pd₂(dppm)₃ in that no phosphine is eliminated: Harvey, P. D.; Gray, H. B., unpublished results.

Contribution from the Departments of Chemistry, University of Florence, I-50144 Firenze, Italy, University of Siena, Siena, Italy, and Facultad de Ciencias Quimicas, University of Valencia, Valencia, Spain

Polynuclear Zinc(II) Complexes with Large Polyazacycloalkanes. Equilibrium Studies and Crystal Structure of the Binuclear [Zn₂([30]aneN₁₀)(NCS)](ClO₄)₃ Complex

Andrea Bencini,[1a] Antonio Bianchi,[1a] Enrique Garcia-España,[1b] Stefano Mangani,[1c] Mauro Micheloni,*[1a] Pierluigi Orioli,[1a] and Piero Paoletti*[1a]

Large polyazacycloalkanes, defined as saturated aza macrocycles with more than six secondary nitrogens as donor atoms, are interesting ligand molecules. The cyclic nature, the elevated number of donor atoms available, and the molecular flexibility make these ligands very versatile for the formation of polynuclear metal complexes. In earlier papers we have reported the synthesis and the copper(II) complexes of many large poly-azacycloalkanes.[2-5] In this paper we have investigated the for-

(1) (a) University of Florence. (b) University of Valencia. (c) University of Siena.

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Table I. Crystal and Refinement Data

mol formula	C₂₁H₅₀Cl₃N₁₁O₁₂S₁Zn₂
mol wt	917.86
a, Å	15.615 (3)
b, Å	13.678 (3)
c, Å	9.473 (2)
α, deg	78.85 (5)
β, deg	82.62 (5)
λ, deg	79.53 (5)
V, Å³	1942.9
Z	2
space gp	$P\bar{1}$ [a]
D_{calcd}, g cm⁻³	1.56
radiation	Mo Kα, graphite monochromated
λ, Å	0.7107
temp, °C	25
μ, cm⁻¹	14.7
scan tech	θ/2θ
scan speed, deg min⁻¹	2.4
scan width, deg	1.0 + 0.3 tan θ
scan range, deg	5.0 < 2θ < 50.0
cutoff of obsd data	3.5σ(*I*)
no. of obsd. reflcns	2128
no. of refined params	275
R[b]	0.109
R_w[c]	0.110

[a] Based on centric distribution of *E* values. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_0)^2]^{1/2}$.

mation equilibria of binuclear zinc(II) complexes of the three large polyazacycloalkanes 1,4,7,10,13,16,19,22,25-nonaazacyclohepta-cosane ([27]aneN₉), 1,4,7,10,13,16,19,22,25,28-decaazacyclo-triacontane ([30]aneN₁₀), and 1,4,7,10,13,16,19,22,25,28,31-un-decazacyclotritriacontane ([33]aneN₁₁) (hereafter abbreviated as L1, L2, and L3, respectively). In the case of L2 a solid binuclear zinc(II) complex has been isolated and characterized by X-ray analysis.
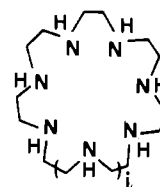
i = 3   L1
i = 4   L2
i = 5   L3

Experimental Section

Synthesis of the Zinc(II) Complex. Well-formed colorless prismatic crystals of the complex [Zn₂L2]NCS(ClO₄)₃ were obtained by slow evaporation at room temperature of a solution of L2 (0.01 mol dm⁻³) containing Zn(ClO₄)₂ (0.02 mol dm⁻³), KCNS (0.02 mol dm⁻³), and NaClO₄ (2 mol dm⁻³). The solution was maintained at pH ~12. The crystals were collected, rapidly washed with water and methanol, and then dried in vacuo. Anal. Calcd for Zn₂C₂₁N₁₁H₅₀SCl₃O₁₂: C, 27.48; H, 5.49; N, 16.79. Found: C, 27.4; H, 5.6; N, 16.7.

Emf Measurements. All potentiometric measurements were carried out in 0.15 mol dm⁻³ NaClO₄ (C. Erba ACS grade). Purification and standardization of solutions used in the potentiometric titrations were performed according to the procedure described in ref 6. Hydrochloride salts of L1, L2, and L3 have been obtained as described in ref 4, 5, and 7, respectively. Aqueous solutions of zinc(II) perchlorate were obtained by dissolving the solid hydrate salt in water. The concentration of zinc(II) was determined gravimetrically by the standard method. The potentiometric titrations were carried out by using equipment (poten-tiometer, buret, stirrer, cell, microcomputer, etc.) that has been fully described.[8] Two titration curves for each systems investigated were used.

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Table II. Positional Parameters and Their Estimated Standard Deviations in Parentheses ($\times 10^4$)

atom	x/a	y/b	z/c
Zn1	2409 (2	173 (3)	7867 (3)
Zn2	2639 (2)	4513 (3)	3974 (4)
N1	2275 (13)	1213 (16)	9247 (22)
C2	2911 (20)	805 (23)	10347 (34)
C3	3770 (21)	441 (25)	9534 (36)
N4	3726 (15)	−214 (20)	8555 (29)
C5	3815 (23)	−1305 (28)	9218 (41)
C6	3320 (25)	−1861 (27)	8666 (40)
N7	2408 (21)	−1397 (23)	8607 (29)
C8	1826 (29)	−1671 (32)	7779 (47)
C9	1040 (30)	−1018 (37)	7633 (52)
N10	1229 (17)	31 (24)	7059 (31)
C11	1443 (30)	189 (35)	5473 (50)
C12	1872 (26)	983 (31)	4948 (44)
N13	2708 (14)	895 (16)	5733 (22)
C14	2994 (18)	1866 (21)	5750 (30)
C15	3470 (22)	2258 (27)	4286 (37)
N16	3685 (15)	3275 (21)	4439 (26)
C17	4320 (37)	3439 (44)	3261 (66)
C18	4465 (33)	4223 (39)	2511 (57)
N19	3604 (15)	4889 (22)	2184 (29)
C20	3618 (31)	5916 (38)	1852 (52)
C21	3538 (27)	6324 (31)	3001 (50)
N22	2566 (30)	6077 (24)	3902 (31)
C23	2374 (48)	6139 (60)	5130 (81)
C24	2088 (32)	5520 (39)	6422 (56)
N25	1957 (21)	4527 (21)	6166 (27)
C26	1039 (27)	4213 (32)	6385 (47)
C27	739 (31)	3908 (37)	7881 (53)
N28	1220 (17)	3110 (21)	8655 (32)
C29	817 (22)	2249 (27)	8999 (37)
C30	1343 (18)	1493 (21)	9990 (31)
N31	1723 (18)	4127 (20)	3015 (33)
C32	1201 (23)	3708 (26)	2852 (35)
S	415 (7)	3159 (9)	2594 (14)
Cl1	5752 (7)	995 (8)	6115 (11)
Cl2	8857 (8)	1553 (9)	7606 (13)
Cl3	6216 (11)	6329 (13)	1207 (19)
O1	5915 (19)	1014 (22)	4630 (33)
O2	5678 (24)	49 (32)	6753 (42)
O3	5062 (33)	1654 (37)	6445 (52)
O4	6312 (71)	1220 (85)	6763 (83)
O5	9368 (22)	827 (26)	8577 (37)
O6	8609 (25)	2430 (32)	8185 (42)
O7	9350 (25)	1795 (26)	6413 (43)
O8	8237 (36)	1056 (40)	7444 (56)
O9	5575 (33)	6918 (36)	493 (51)
O10	6673 (46)	6900 (54)	1654 (73)
O11	5932 (30)	6034 (34)	2688 (56)
O12	6692 (28)	5564 (36)	768 (46)

The experimental details of the emf measurements have been reported in the supplementary material. The computer program SUPERQUAD[9] was used to process data and calculate the stability constants. For each ligand the two titration curves either were treated as a single set or were treated separately without significant variation in the values of the equilibrium constants.

Collection and Reduction of X-ray Intensity Data. A colorless elongated prism with approximate dimensions 0.4 × 0.1 × 0.1 mm was mounted on a Philips PW 1100 computer-controlled diffractometer and used for data collection. A summary of the crystallographic data is reported in Table I. Unit-cell dimensions were determined from the angular settings of 25 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects[10] (transmission factors ranged between 0.9015 and 0.8357). The intensities of three standard reflections were monitored periodically for stability control during data collection.

Solution and Refinement of the Structure. The space group $P1$ was assumed on the basis of the centric distribution of the E values. The structure was solved by the heavy-atom technique, with the use of Patterson and electron density syntheses. Refinement was performed by

Table III. Formation Constants for the Systems Zinc(II)/L (L = L1, L2, L3) in Aqueous Solution (25 °C in 0.15 mol dm^{-3} NaClO$_4$)

reaction	log K		
	L = L1	L = L2	L = L3
$2Zn^a + L = Zn_2(L)$	20.55 (6)^b	22.51 (5)	23.91 (4)
$2Zn + L + H = Zn_2(L)H$	26.98 (6)		
$2Zn + L + 2H = Zn_2(L)H_2$	32.79 (7)	35.22 (5)	36.66 (5)
$2Zn + L + 3H = Zn_2(L)H_3$		40.41 (6)	42.17 (4)
$2Zn + L + H_2O = Zn_2(L)OH + H$	13.56 (6)	14.16 (5)	15.40 (4)
$2Zn + L + 2H_2O = Zn_2(L)(OH)_2 + 2H$	4.71 (5)	3.19 (6)	4.87 (4)
$Zn_2(L) + H = Zn_2(L)H$	6.4		
$Zn_2(L)H + H = Zn_2(L)H_2$	5.8		
$Zn_2(L)H_2 + H = Zn_2(L)H_3$		5.2	5.5
$Zn_2(L)H_2O = Zn_2(L)OH + H$	−7.0	−8.4	−8.5
$Zn_2(L) + OH = Zn_2(L)OH$	6.7	5.4	5.2
$Zn_2(L)OH + OH = Zn_2(L)(OH)_2$	4.9	2.7	3.2

^{a} Charges omitted for clarity. ^{b} Values in parentheses are standard deviations in the last significant figure.
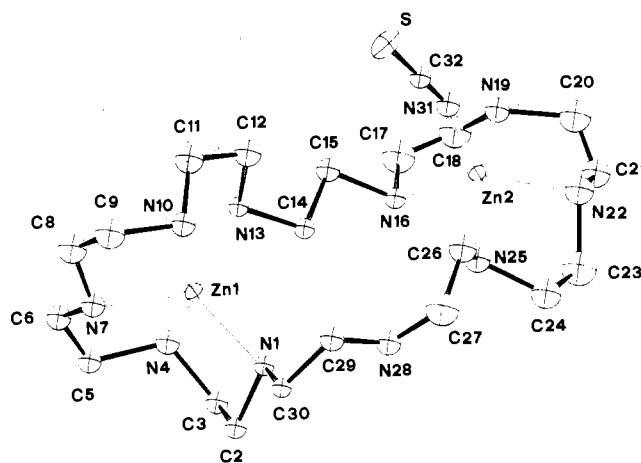
Figure 1. ORTEP drawing of the [Zn$_2$(L2)NCS]$^{3+}$ cation. Thermal ellipsoids are shown at 15% probability.

means of the full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = a/\sigma^2(F) + bF^2$), where a and b are adjustable parameters. Isotropic thermal parameters were used for the carbon atoms and the perchlorate ions. Zinc, sulfur, and nitrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions with an overall temperature factor. During the refinement the presence of some static or dynamic disorder became evident by inspection of the atom thermal parameters, both in the macrocycle chain and in the perchlorate ions. Data were then collected on a second crystal, from a different crystallization batch, but disorder was still persistent. An attempt to refine the structure in the acentric $P1$ space group failed because of the high correlations between the least-squares parameters. With both sets of data the difference synthesis did not show definite peaks, and no reasonable model could be fit to the data to account for disorder. It should be pointed out, however, that the structure is essentially correct and the presence of disorder is shown by the large values of the atomic temperature factors and of the standard deviations of the refined atomic parameters. All calculations were performed on an IBM 4361/3 computer with the SHELX-76 set of programs[10] that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 11. Table II reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plot was produced by the program OR-TEP.[12]

Results and Discussion

Equilibrium Studies. In Table III are reported the formation constants of the polynuclear zinc(II) species of macrocycles L1,

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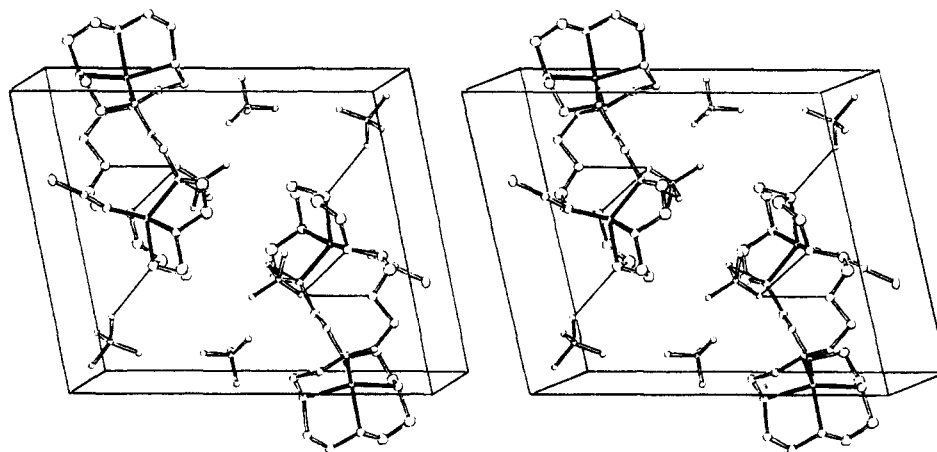
Figure 2. Stereoview of the crystal packing approximately down the *c* axis. Only the shortest hydrogen-bond interactions (3.00–3.25 Å) are displayed as thin lines. The perchlorate atoms are drawn as spheres of arbitrary radius. The hydrogen atoms have been omitted for clarity.

L2, and L3. Very rarely does zinc(II) form binuclear complexes in aqueous media, but in spite of this consideration, the large macrocycles studied here show a great tendency to form stable binuclear zinc(II) complexes. None of these ligands forms mononuclear species. The stabilities of the $[Zn_2L]^{4+}$ species are high, indicating that a strong overall interaction between the two zinc(II) ions and the donor atoms takes place. It is difficult to compare these results because to our knowledge the only stability constant of a binuclear zinc(II) complex with a macrocyclic ligand is the one reported by Martell et al.[13] for mixed oxo–aza 22-membered macrocycle BISDIEN. The value found for the logarithm of the overall stability constant for $[Zn_2BISDIEN]^{4+}$ is 16.46 and it is much smaller than those found for the larger aza macrocycles L1, L2, and L3 (see Table III). If we take the logarithms of the equilibrium constants of the binuclear species $[Zn_2L]^{4+}$ and divide these values by 2, we obtain values that can be considered the average contribution of each zinc(II) ion to the overall stability constants. These values are comparable with those that have been found for mononuclear zinc(II) complexes with tetraaza macrocycles,[14] indicating that the macrocycles investigated are large and flexible enough to well accommodate two zinc(II) ions quite apart from each other with little mutual interaction. There is a slight increase in the stability of the $[Zn_2L]^{4+}$ species going from the smaller macrocycle L1 to the larger L3. A similar trend has been found also for binuclear copper(II) complexes[2–5,7] and can be explained in terms of increase in the overall number of donor atoms involved in the coordination to the metal ions and increase of the ligand flexibility as the ligand size increases. Another small contribution to the above trend may be arise from the decrease in the electrostatic repulsions between the zinc(II) ions. In all cases, many species, both protonated and hydroxo, are present in the equilibrium mixture. It is well-known that zinc(II) in its amino complexes shows a tendency to form hydroxo species, but in our case the hydroxo species are very stable and important. The equilibrium constants for the reaction involving the stepwise addition of a hydroxide ion to the complex $[Zn_2L]^{4+}$ to form $[Zn_2LOH]^{3+}$ and $[Zn_2L(OH)_2]^{2+}$ are high (see Table III). At pH >8 the above mentioned species are the only ones present at equilibrium. The equilibrium constants relative to the ionization of the metal-bound water molecule, reported in Table III, indicate that the complex with macrocycle L1 has the lowest pK_a (7 log units), whereas 8.4 and 8.5 are the values found for the complexes with L2 and L3, respectively. This trend is expected since the complex $[Zn_2L1]^{4+}$ with the smaller macrocycle is probably more strained than the complexes with larger macrocycles $[Zn_2L2]^{4+}$ and $[Zn_2L3]^{4+}$ and will bind the water molecule more tightly. It should be noted the pK_a for $[Zn_2L1]^{4+}$ is remarkably low and very close to the one found for carbonic anhydrase model systems.[15]

Table IV. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Zn1–N1	2.08 (2)	Zn2–N16	2.15 (2)
Zn1–N4	2.18 (2)	Zn2–N19	2.17 (2)
Zn1–N7	2.13 (2)	Zn2–N22	2.11 (3)
Zn1–N10	2.14 (2)	Zn2–N25	2.21 (2)
Zn1–N13	2.11 (2)	Zn2–N31	1.98 (3)
N16–Zn2–N22	131.1 (13)	N4–Zn1–N10	160.2 (10)
N16–Zn2–N25	100.0 (8)	N4–Zn1–N13	99.0 (8)
N22–Zn2–N25	84.5 (10)	N7–Zn1–N10	80.8 (10)
N22–Zn2–N31	115.3 (13)	N7–Zn1–N13	127.2 (9)
N25–Zn2–N31	99.9 (10)	N10–Zn1–N13	83.5 (9)
N1–Zn1–N4	82.5 (8)	N16–Zn2–N19	79.3 (8)
N1–Zn1–N7	123.3 (8)	N16–Zn2–N31	111.7 (10)
N1–Zn1–N10	115.4 (8)	N19–Zn2–N22	78.4 (11)
N1–Zn1–N13	109.0 (8)	N19–Zn2–N25	156.0 (11)
N4–Zn1–N7	82.2 (9)	N19–Zn2–N31	102.7 (10)

In the case of the most symmetric macrocycle L2, the solid, binuclear complex $[Zn_2(L2)NCS](ClO_4)_3$ has been isolated and characterized by X-ray analysis.

Description of the Structure. The structure of $[Zn_2(L2)$-$NCS](ClO_4)_3$ consists of $[Zn_2(L2)NCS]^{3+}$ cations (see Figure 1) and perchlorate anions. In the dimeric cation, the two zinc atoms show essentially the same five-coordinate stereochemistry, which can be described in terms of a distorted trigonal bipyramid. However, Zn1 is coordinated by five nitrogen atoms of the macrocyclic ligand, whereas Zn2 is coordinated by four nitrogen atoms of the macrocycle and the nitrogen atom of the thiocyanate group. Binding of N28 to Zn2 is probably precluded by steric strains of macrocyclic ring. The different coordinations assumed by the two zinc ions, in spite of the presence of an equimolar ratio Zn^{2+}/NCS^- in the crystallization solution, are the most surprising feature of this structure. It is difficult to explain this experimental result in terms of simple balance between the stronger donor character of the macrocyclic amino nitrogens compared with that of the thiocyanate group and the decrease of the electrostatic repulsion achieved through the binding of an anion. In the analogous complex[5] $[Cu_2(L2H)Cl_2]^{2+}$ the two copper ions show identical coordination spheres, binding four nitrogens of the macrocycle and a chloride anion. In the present structure the Zn–Zn distance is 6.40 Å while in the $[Cu_2(L2H)Cl_2]^{2+}$ complex the Cu–Cu distance is 7.26 Å. The macrocyclic ring wraps around the two zinc ions in a rather strained configuration, but the high values of the thermal parameters of the macrocyclic atoms cause several bond distances to shrink noticeably, thus preventing any detailed discussion of bond distances and angles. Bond lengths and angles in the coordination polyhedra are reported in Table IV. Several hydrogen bonds are formed between the perchlorate ions and the nitrogen atoms of the ligand (see Figure 2).

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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

$$NiL^{2+} + 2H^+ \rightarrow Ni^{2+} + H_2L^{2+} \qquad (1)$$
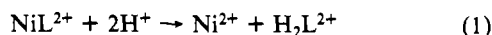
where L is the diamino diamide depicted in Chart I. The stability constants of the nickel(II) complexes of these four ligands and the complexation kinetics of these nickel(II) complexes have been reported.[2,3]

Experimental Section

Reagents. The complexes Ni(L-2,2,2)(ClO₄)₂, Ni(5-Me-L-2,2,2)-(ClO₄)₂, Ni(L-2,3,2)(ClO₄)₂, and Ni(6-OH-L-2,3,2)(ClO₄)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 NaClO₄ was used to maintain constant ionic strength at $\mu = 4.0$ 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.

Results

The kinetics of the dissociation reactions of these nickel(II) diamino diamide complexes were studied at 25.0 °C, with $\mu = 4.0$ M (HClO₄ + NaClO₄), and in 0.05-2.00 M HClO₄. Under

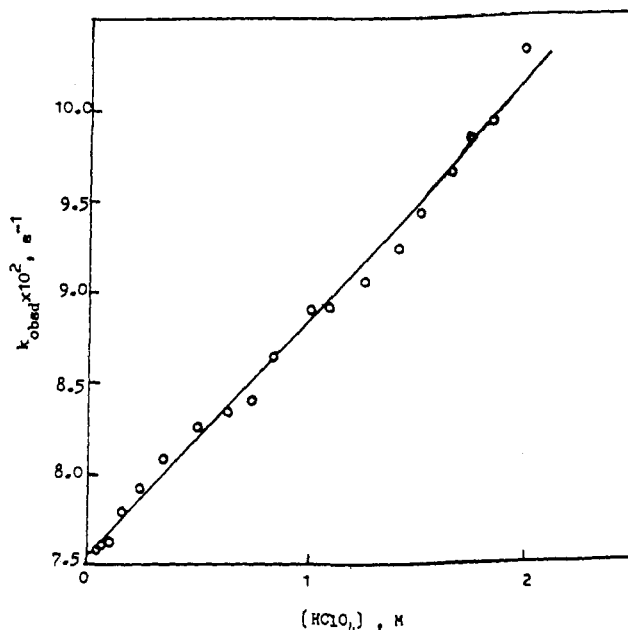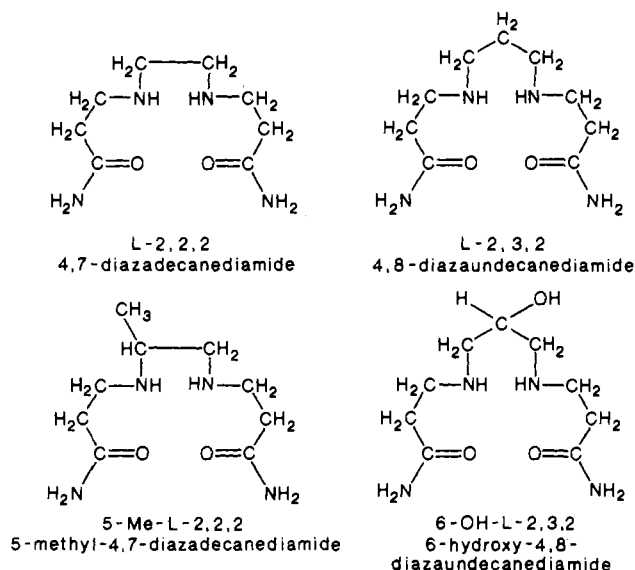(1) Chao, M.-S.; Chung, C.-S. *Inorg. Chem.* **1987**, *26*, 3600–3604.
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Chart I

L-2,2,2
4,7-diazadecanediamide

L-2,3,2
4,8-diazaundecanediamide

5-Me-L-2,2,2
5-methyl-4,7-diazadecanediamide

6-OH-L-2,3,2
6-hydroxy-4,8-diazaundecanediamide

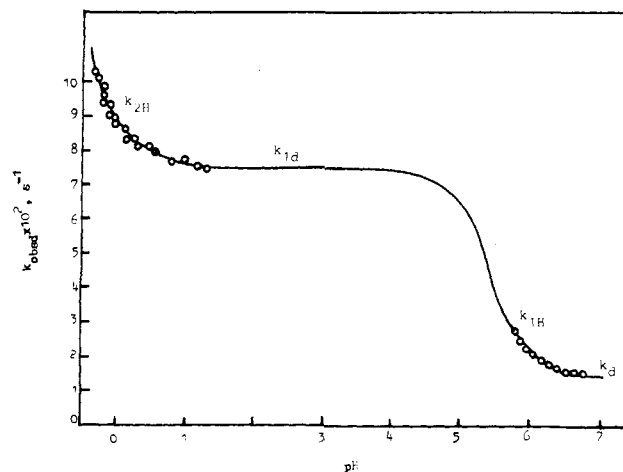**Figure 1.** Plot of k_{obsd} vs [H⁺] for the dissociation of Ni(L-2,3,2)²⁺ at 25.0 ± 0.1 °C and $\mu = 4.0$ M (NaClO₄ + HClO₄).

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

these conditions, the dissociation reactions of these complexes were found to proceed to completion. Some of the observed pseudo-