

been estimated to be -0.59 V (NHE).¹⁸ This indicates that the cobalt ion in our ligand Mabiq⁻ is somewhat less solvated than in the corrin system of vitamin B₁₂.

Conclusions

We have shown that a corrin type macrocyclic ligand, containing an additional diimine type coordination site, can be synthesized from commercially available materials in a few inexpensive steps. Its dicyano-cobalt(III) complex was shown to be

comparable to dicyanocobalamin in its spectroscopic and electrochemical properties. Further investigation is needed to elucidate the behavior of the diimine coordination site of the new ligand HMabiq, as well as the photochemical and catalytic properties of the corresponding simple and mixed complexes, e.g. those of the [Cu^I(Mabiq)Co^{III}] type. It is felt that new and interesting "molecular machines" could be constructed upon this principle.

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Supplementary Material Available: A full table of crystal data, intensity measurement, and structure refinement parameters (Table V), full tables of bond distances and angles, and listings of atomic coordinates and displacement parameters for both structures (32 pages); tables of structure factors in the format of ref 21 (38 pages). Ordering information is given on any current masthead page.

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Syntheses and Characterization of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic Acid (HL¹) and Its Transition-Metal Complexes: Crystal Structures of HL¹·2HBr·H₂O, [NiL¹(H₂O)]Br, and [NiL¹(NCS)]H₂O[†]

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A simple stereospecific synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid (HL¹) is reported. The Ni²⁺, Co³⁺, and Cu²⁺ complexes of HL¹ have been prepared and characterized. HL¹·2HBr·H₂O (1) crystallizes in the orthorhombic space group *Pbca* with $a = 16.079$ (3) Å, $b = 16.918$ (3) Å, $c = 17.837$ (4) Å, and $Z = 8$. The structure was refined to $R = 0.060$ with 2001 reflections. [NiL¹(H₂O)]Br (3) crystallizes in the monoclinic space group *P2₁/n* with $a = 9.214$ (2) Å, $b = 19.972$ (3) Å, $c = 12.580$ (4) Å, $\beta = 106.34$ (2)°, and $Z = 4$. The structure was refined to $R = 0.041$ with 2971 reflections. [NiL¹(NCS)]H₂O (6) crystallizes in the monoclinic space group *P2₁/a* with $a = 12.746$ (3) Å, $b = 11.809$ (2) Å, $c = 15.568$ (2) Å, $\beta = 102.29$ (2)°, and $Z = 4$. The structure was refined to $R = 0.044$ with 2999 reflections. In both complexes 3 and 6, the nickel ion coordination is approximately octahedral with the second ligand coordinated at axially on the octahedron, while the four nitrogen atoms of the macrocycle are essentially coplanar and the nickel ion shows +0.002 and -0.04 Å deviation from the least-squares plane, respectively. Complexes [NiL¹(H₂O)]X react with X₂ (X = Br, I) to yield the novel five-coordinated low-spin species containing trihalide counteranions, [NiL¹]X₃. The pH-dependent coordination geometry change of metal complex 3 accompanied by the change of its electrochemical behavior is also discussed.

The field of coordination chemistry of polyazamacrocycles has undergone spectacular growth after the early 1960s due to the pioneering independent contributions of Curtis¹ and Busch.² Since then a large number of synthetic polyazamacrocyclic ligands have been reported.³ Their metal complexes often exhibit properties that are distinctly different from those of complexes with analogous open-chain ligands.

Recently, many efforts⁴⁻⁹ have been made to introduce additional ligating groups into macrocycles in order to obtain new types of ligands that have the relatively rigid and kinetically stable structural element of the macrocycle as well as the more flexible and kinetically labile open-chain structural elements.

The synthesis of per-*N*-substituted tetraazamacrocycles is straightforward. The reaction of a macrocyclic tetraamine such as cyclam with an excess of chloroacetic acid or ethylene oxide usually gives the per-substituted product.⁷ However, the synthesis of partial-*N*-substituted macrocycles is generally more complicated and necessitates several steps.⁹ Recently Kaden and Studer¹⁰ presented a one-step preparation method to obtain some mono-

N-substituted polyazamacrocycles containing a carboxyalkyl or carboxyaryl side chain. We present here a simple stereospecific synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid (HL¹) and discuss its metal complexes.

HL¹ is a pentadentate ligand, in which the relative rigidity of the macrocyclic ring and the flexibility of the pendent carboxylate group should give rise to square-pyramidal or octahedral complexes. It forms metal complexes with Co³⁺ and Ni²⁺ of the type MLY, in which Y is the second monodentate ligand. Our interest in this paper is to study the influences of the second ligand on the structure of the complexes, and we report the novel five-coordinated low-spin nickel complexes containing trihalide counteranions [NiL¹]X₃ (X = Br, I) and the structures of HL¹·2HBr·H₂O, [NiL¹(H₂O)]Br, and [NiL¹(NCS)]H₂O. Preliminary accounts describing some of our results have been published.^{11,12}

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Experimental Section

Materials and Methods. All chemicals were analytical grade and were not purified further. The macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a) was prepared as described.¹³ Proton NMR spectra were recorded with a JEOL FX90Q spectrometer. Infrared and UV-visible spectra were obtained with Nicolet 170Sx and Shimadzu UV-240 spectrometers respectively. Microanalyses were performed by the Centre of Structure and Elemental Analysis of the China University of Science and Technology. Electrochemical studies were done with the help of a HDV 7B potentiostat, a 79-1 voltammeter, and a Da Hua LZ-3 X-Y recorder.

Preparation of the Ligand. The synthesis of HL¹ has been reported previously.⁸ We present an improved stereospecific synthesis with about 75% yield as follows.

HL¹·2HBr·H₂O (1). To 14 g (0.1 mol) of bromoacetic acid in 50 mL of dry methanol was added 5.6 g (0.1 mol) of KOH in 100 mL of dry methanol. Then 32 g (0.1 mol) of tet a in 650 mL of dry methanol and 12 g (0.11 mol) of powdered anhydrous sodium carbonate were added, and the mixture was stirred at 45 °C for 6 h, and then heated at 60 °C for 16 h. The reaction mixture was cooled, and the white precipitate of NaHCO₃ was filtered off. After nearly complete evaporation of the solvent on a rotary evaporator, the residue was dissolved in water and the solution was filtered to remove any unreacted cyclic polyamine. The filtrate was acidified to pH 4.5 with concentrated hydrobromic acid. The product HL¹·2HBr·H₂O precipitated upon standing (yield 75%). IR (KBr, cm⁻¹): 3360, 3400 (OH); 3200 (NH); 2650–2900 (NH₂⁺); 1730 (COOH). ¹H NMR (D₂O): δ 0.95–1.04 (3 H, d, CH₃-C-N), 1.13–1.20 (3 H, d, CH₃-C-N), 1.30–1.41 (12 H, t, CH₂-C-N), 1.72–1.93 (4 H, m, C-CH₂-C), 2.85 (2H, s, CH₂COOH), 2.90–3.20 (8 H, m, CH₂-N), 3.64 (1 H, s, C-CH-N), 3.85 (1 H, s, C-CH-N). Anal. Calcd for C₁₈H₄₂Br₂N₄O₃: C, 41.39; H, 8.10; N, 10.73. Found: C, 41.38; H, 8.09; N, 10.57.

HL¹·2.5HClO₄·H₂O (2). The sparingly soluble, white perchloric acid adduct of HL¹ was prepared as for compound 1, substituting concentrated perchloric acid for the concentrated hydrobromic acid. Alternatively, a concentrated aqueous solution of 1 was added to an aqueous solution containing excess sodium perchlorate. IR (KBr, cm⁻¹): 1730 (COOH); 1144, 1106–1093 (ClO₄⁻). Anal. Calcd for C₁₈H₄₃Cl_{2.5}N₄O₁₃: C, 35.31; H, 7.08; N, 9.15. Found: C, 35.23; H, 7.15; N, 8.92.

Preparation of Metal Complexes. [NiL¹(H₂O)]Br (3). First, 522 mg (1 mmol) of 1 and 490 mg (1.5 mmol) of NiBr₂·6H₂O were dissolved in 25 mL of water, and the pH was adjusted to 5 with NaOH. After the mixture was heated for several hours, light violet crystals precipitated. These were collected and air-dried to give 400 mg (80%) of product. IR (KBr, cm⁻¹): 1614, 1423 (COO⁻). Anal. Calcd for C₁₈H₃₉BrNiN₄O₃: C, 43.40; H, 7.89; N, 11.25; Ni, 11.78. Found: C, 43.50; H, 8.03; N, 11.10; Ni, 11.57.

[NiL¹(H₂O)]I (4). First 350 mg (0.7 mmol) of 3 was dissolved in 400 mL of water, and then the Br⁻ ions were removed with a strong basic ion-exchange resin 201X4 (OH⁻ form). Sodium iodide (3.5 mmol) was added to the concentrated eluate whereupon the light violet product crystallized. These were collected and air-dried to give 325 mg (85%) of product. IR (KBr, cm⁻¹): 1608, 1424 (COO⁻). Anal. Calcd for C₁₈H₃₉INiN₄O₃: C, 39.66; H, 7.21; N, 10.28. Found: C, 39.58; H, 7.29; N, 10.56.

[NiL¹(H₂O)]ClO₄·H₂O (5). This compound was prepared by following the [NiL¹(H₂O)]I procedure, but a saturated aqueous solution of sodium perchlorate was substituted for the sodium iodide. IR (KBr, cm⁻¹): 1588, 1425 (COO⁻); 1105 (ClO₄⁻). Anal. Calcd for C₁₈H₄₁ClNiN₄O₈: C, 40.36; H, 7.71; N, 10.46; Ni, 10.96. Found: C, 40.40; H, 7.61; N, 10.50; Ni, 10.81.

[NiL¹(NCS)]H₂O (6). This preparation followed that for [NiL¹(H₂O)]I, with a saturated aqueous solution of sodium thiocyanate substituted for the sodium iodide. IR (KBr, cm⁻¹): 2086 (NCS⁻); 1590 (COO⁻). Anal. Calcd for C₁₈H₃₉NiN₅O₃S: C, 47.91; H, 8.25; N, 14.70; Ni, 12.32. Found: C, 48.18; H, 8.25; N, 14.61; Ni, 12.17.

[NiL¹]Br₃ (7). First 500 mg (1 mmol) of 3 was dissolved in 100 mL of warmed dry acetonitrile, and then anhydrous bromine (0.2 g, 1.2 mmol) was added with stirring with the resulting mixture then allowed to cool to 0 °C. The pale yellow-brown product was filtered off, washed with dry acetonitrile, and dried in vacuo; yield 380 mg (60%). IR (KBr, cm⁻¹): 1590 (COO⁻); 196 (Br₃⁻). Anal. Calcd for C₁₈H₃₇Br₃NiN₄O₂: C, 33.78; H, 5.83; N, 8.76; Ni, 9.17; Br, 37.46. Found: C, 33.71; H, 5.81; N, 8.57; Ni, 9.1; Br, 37.20.

An alternative synthesis was achieved by exhaustive electrolysis of a saturated solution (0.1 mol L⁻¹ NaBr as solvent, pH = 2) of 3 in a thermostated cell (323 K) at a constant potential of 0.8 V (vs SCE). The electrolyzed product deposits on the platinum electrode. Its IR and composition are identical with that obtained from the above synthesis.

[NiL¹]I₃ (8). 4 (545 mg, 1 mmol) was dissolved in 200 mL of water, potassium triiodide (5 mmol) was added, and the brown-yellow product was filtered off, washed with cold ethanol, and dried in vacuo; yield 625 mg (80%). IR (KBr, cm⁻¹): 1587 (COO⁻); 148 (I₃⁻). Anal. Calcd for C₁₈H₃₇I₃NiN₄O₂: C, 27.69; H, 4.78; N, 7.17; Ni, 7.52; I, 48.75. Found: C, 27.60; H, 4.85; N, 7.01; Ni, 7.4; I, 48.6.

CoL¹Br₂·1.5H₂O (9). 1 (522 mg, 1 mmol) and 750 mg (2 mmol) of CoBr₂·6H₂O were dissolved in 30 mL of water; the pH was adjusted to 4 with NaOH. After being heated for several hours, the solution turned intensely purple, and scalelike crystals were obtained when the solution was allowed to stand. These were collected and air-dried to give 290 mg (46%) of product. IR (KBr, cm⁻¹): 1687 (COO⁻). Anal. Calcd for C₁₈H₄₀Br₂CoN₄O_{3.5}: C, 36.81; H, 6.87; N, 9.54; Co, 10.03. Found: C, 36.77; H, 6.65; N, 9.68; Co, 9.70.

CoL¹(ClO₄)₂·H₂O (10). First 612 mg (1 mmol) of 2 and 530 mg (2 mmol) of Co(ClO₄)₂·6H₂O were dissolved in 50 mL of water, and then the pH was adjusted to 4.5 with NaOH. After being heated for several hours, the intensely purple solution was concentrated in a bath, and cubic purple-brown crystals were obtained upon standing. These were collected and air-dried to give 250 mg of product (37%). IR (KBr, cm⁻¹): 1630 (COO⁻); 1108 (ClO₄⁻). Anal. Calcd for C₁₈H₃₉Cl₂CoN₄O₁₁: C, 35.02; H, 6.37; N, 9.07; Co, 9.54. Found: C, 35.21; H, 6.49; N, 9.00; Co, 9.45.

CuL¹(ClO₄)₂·4H₂O (11). After 612 mg (1 mmol) of 2 and 270 mg (1 mmol) of Cu(ClO₄)₂·6H₂O were dissolved in 25 mL of water, the pH was adjusted to 4.5 with NaOH. After being heated for several hours, blue crystals were obtained when the solution was allowed to stand. These were collected and air-dried to give 220 mg (75%) of product. IR (KBr, cm⁻¹): 1630 (COO⁻); 1116 (ClO₄⁻). Anal. Calcd for C₁₈H₄₅ClCuN₄O₁₀: C, 37.50; H, 7.87; N, 9.72; Cu, 11.02. Found: C, 37.54; H, 7.56; N, 9.69; Cu, 11.10.

Cu₂L¹Br₃·H₂O (12). 1 (522 mg, 1 mmol) and 1.01 g (3 mmol) of CuBr₂·6H₂O were dissolved in 20 mL of water, the pH was adjusted to 2 with hydrobromic acid. After being heated for several hours in a bath, black crystals precipitated. These were collected and air-dried to give 290 mg (40%) of product. IR (KBr, cm⁻¹): 1637 (COO⁻). Anal. Calcd for C₁₈H₃₉Br₃Cu₂N₄O₃: C, 29.77; H, 5.41; N, 7.71; Cu, 17.50. Found: C, 29.86; H, 5.43; N, 7.81; Cu, 17.20.

Structural Determinations. Three-dimensional X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using an ω - 2θ scan mode. In each case corrections were made for Lorentz, polarization, and empirical X-ray absorption effects. The structure of each crystal was solved by direct methods and difference Fourier syntheses. The positional and thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares method. Hydrogen atom positions were calculated but not included in refinement. Details of crystal data, intensity measurements and refinements are given in Table I. Final atomic fractional coordinates are given in Tables II–IV. All calculations were performed on a PDP 11/34 computer with Enraf-Nonius SDP program package.

Results and Discussions

We have reported⁸ that the alkylation of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a) with an excess of bromoacetic acid in alkaline alcoholic medium gave only the mono- and di-N-substituted macrocycles HL¹ and H₂L². Lately we have found¹⁴ that the alkylation of *C-meso*-2,2,4,13,13,15-hexamethyl-1,5,12,16-tetraazacyclodocosane, an analogue of tet a, with a large excess of bromoacetic acid in alkaline methanol medium gave only the di-N-substituted product H₂L³.

These results reveal that in alcoholic medium the alkylation of hexamethyltetraazatetradecanes does not take place in the 4- and 11-positions, but takes place in the 1- and 8-positions, although the nitrogen atoms in the 4- and 11-positions have stronger basicity than those in the 1- and 8-positions. Such a selectivity is most likely due to the fact that the nitrogen atoms in the 1- and 8-positions, which are less sterically hindered, are more nucleophilic than those in the 4- and 11-positions. It may be concluded that

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Table I. Data for Crystal Structure Analyses^a

	HL ¹ ·2HBr·H ₂ O	[NiL ¹ (H ₂ O)]Br	[NiL ¹ (NCS)]H ₂ O
mol formula	C ₁₈ N ₄ O ₂ H ₃₈ 2HBrH ₂ O	[NiC ₁₈ N ₄ O ₂ H ₃₇ (H ₂ O)]Br	[NiC ₁₈ N ₄ O ₂ H ₃₇ (NCS)]H ₂ O
<i>M_r</i>	522.37	498.15	476.32
cryst color	colorless	light violet	light reddish violet
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/a</i>
<i>a</i> /Å	16.079 (3)	9.214 (2)	12.746 (3)
<i>b</i> /Å	16.918 (3)	19.972 (3)	11.809 (2)
<i>c</i> /Å	17.837 (4)	12.580 (4)	15.568 (2)
<i>α</i> /deg	90	90	90
<i>β</i> /deg	90	106.34 (2)	102.29 (2)
<i>γ</i> /deg	90	90	90
<i>V</i> /Å ³	4852 (3)	2221 (2)	2290 (2)
<i>Z</i>	8	4	4
<i>D_c</i> /g cm ⁻³	1.422	1.486	1.382
<i>F</i> (000)	2151	1044	1024
cryst size/mm	0.1 × 0.45 × 0.45	0.075 × 0.3 × 0.8	0.26 × 0.3 × 0.8
<i>μ</i> (Mo Kα)/cm ⁻¹	33.306	26.820	9.665
no. of data recorded	4752	4209	4022
no. of data used	2001	2971	2999
criterion of observn, <i>n</i> [<i>I</i> ≥ <i>nσ</i> (<i>I</i>)]	2.0	3.0	3.0
final <i>R</i> (<i>R_w</i>)	0.060 (0.071) ^b	0.041 (0.044)	0.044 (0.045)
residual extrema in final difference map/e Å ⁻³	0.74	0.67	0.64

^aDetails common to all three compounds: scan range (2θ), 2–50°. ^b*w* = 4|*F_o*|²/[*σ* + (*p*|*F_o*|²)]²; *p* = 0.06.

Table II. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of HL¹·2HBr·H₂O

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> , Å ²
Br(1)	0.10794 (8)	0.18362 (6)	0.84210 (7)	4.48 (3)
Br(2)	0.35911 (8)	0.10687 (6)	0.06498 (6)	4.27 (2)
O(1)	0.2994 (4)	-0.0035 (3)	0.4420 (3)	3.0 (1)
O(2)	0.3973 (5)	-0.0826 (4)	0.4884 (4)	5.0 (2)
O(w)	0.3045 (5)	0.3139 (4)	0.4048 (5)	5.9 (2)
N(1)	0.3268 (5)	0.1082 (4)	0.5553 (4)	2.9 (2)
N(4)	0.3569 (5)	0.1565 (4)	0.3958 (4)	2.9 (2)
N(8)	0.1923 (5)	0.1212 (4)	0.3578 (4)	2.6 (2)
N(11)	0.1547 (5)	0.0784 (4)	0.5154 (4)	2.7 (2)
C(2)	0.3954 (7)	0.1589 (6)	0.5310 (6)	3.7 (2)
C(3)	0.4251 (7)	0.1441 (6)	0.4531 (6)	3.9 (3)
C(5)	0.3814 (6)	0.1461 (5)	0.3154 (5)	2.7 (2)
C(6)	0.3024 (6)	0.1615 (6)	0.2702 (5)	3.2 (2)
C(7)	0.2268 (6)	0.1077 (5)	0.2833 (5)	2.7 (2)
C(9)	0.1272 (6)	0.0636 (6)	0.3777 (6)	3.5 (2)
C(10)	0.0915 (6)	0.0854 (6)	0.4553 (6)	4.3 (3)
C(12)	0.1374 (7)	0.1274 (5)	0.5845 (6)	4.1 (3)
C(13)	0.2060 (7)	0.1070 (6)	0.6425 (5)	3.8 (2)
C(14)	0.2927 (7)	0.1363 (5)	0.6307 (5)	3.2 (2)
C(15)	0.3561 (7)	0.0246 (5)	0.5628 (5)	3.5 (2)
C(16)	0.3463 (6)	-0.0209 (5)	0.4902 (5)	2.6 (2)
C(17)	0.4467 (7)	0.2075 (6)	0.2953 (6)	4.4 (3)
C(18)	0.4149 (7)	0.0622 (6)	0.3021 (6)	3.9 (3)
C(19)	0.1643 (7)	0.1222 (6)	0.2187 (6)	4.3 (3)
C(20)	0.1410 (8)	0.2145 (6)	0.5634 (7)	5.5 (3)
C(21)	0.0526 (8)	0.1054 (7)	0.6182 (7)	5.5 (3)
C(22)	0.3478 (8)	0.1191 (6)	0.6958 (6)	4.9 (3)

Table III. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of [NiL¹(H₂O)]Br

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> , Å ²
Br	-0.30316 (7)	0.13545 (3)	0.39962 (5)	3.84 (1)
Ni	-0.31303 (6)	0.26584 (3)	0.10338 (5)	2.01 (1)
O(1)	-0.1898 (4)	0.2598 (2)	0.2825 (3)	2.85 (7)
O(2)	-0.4166 (3)	0.2739 (2)	-0.0645 (3)	2.65 (7)
O(3)	-0.3920 (5)	0.3173 (2)	-0.2205 (3)	4.9 (1)
N(1)	-0.1673 (4)	0.3370 (2)	0.0660 (3)	2.43 (8)
N(4)	-0.1590 (4)	0.1935 (2)	0.0826 (3)	2.38 (8)
N(8)	-0.4620 (4)	0.1961 (2)	0.1348 (3)	2.28 (8)
N(11)	-0.4660 (4)	0.3372 (2)	0.1313 (3)	2.43 (8)
C(2)	-0.0223 (5)	0.2985 (2)	0.0884 (4)	2.9 (1)
C(3)	-0.0508 (5)	0.2298 (3)	0.0366 (4)	3.1 (1)
C(5)	-0.2106 (6)	0.1263 (3)	0.0326 (4)	2.8 (1)
C(6)	-0.3282 (6)	0.0990 (3)	0.0876 (4)	3.1 (1)
C(7)	-0.4810 (6)	0.1339 (3)	0.0673 (4)	2.8 (1)
C(9)	-0.6054 (5)	0.2330 (3)	0.1244 (4)	3.0 (1)
C(10)	-0.5682 (6)	0.2996 (3)	0.1817 (4)	3.2 (1)
C(12)	-0.4158 (6)	0.4051 (3)	0.1822 (4)	3.2 (1)
C(13)	-0.3016 (7)	0.4326 (3)	0.1266 (4)	3.4 (1)
C(14)	-0.1509 (6)	0.3978 (3)	0.1386 (4)	2.9 (1)
C(15)	-0.2194 (6)	0.3545 (3)	-0.0550 (4)	3.1 (1)
C(16)	-0.3521 (5)	0.3121 (3)	-0.1177 (4)	2.9 (1)
C(17)	-0.0754 (7)	0.0774 (3)	0.0591 (5)	4.2 (1)
C(18)	-0.2763 (6)	0.1300 (3)	-0.0924 (4)	3.7 (1)
C(19)	-0.5936 (7)	0.0857 (3)	0.0959 (5)	4.3 (1)
C(20)	-0.3445 (7)	0.4000 (3)	0.3072 (5)	3.8 (1)
C(21)	-0.5503 (7)	0.4530 (3)	0.1591 (5)	4.5 (1)
C(22)	-0.0328 (7)	0.4469 (3)	0.1207 (5)	4.5 (1)

the reaction of a hexamethyltetraazamacrocycle (tet a or its analogues) with an alkylating agent is stereospecific. Therefore the monosubstituted product could be prepared relatively easily by selective alkylation under suitable conditions. In this paper we present a simple stereospecific preparation of HL¹. The synthesis consists in the alkylation of tet a with an equimolar ratio of bromoacetic acid in dry methanol in the presence of anhydrous Na₂CO₃ as base and the use of a relatively low reaction temperature to reduce the nucleophilicity of the cyclic polyamine.

The complexes of HL¹ were studied in part in solution but were mainly studied by preparing several crystalline compounds. According to the element analyses, HL¹ forms with Co³⁺, Ni²⁺, and Cu²⁺ complexes with a metal to ligand ratio of 1:1; the 2:1 complex Cu₂L¹Br₃ was also isolated.

Molecular Structure. In order more fully to characterize HL¹ and its transition-metal complexes, as well as to study the influence of the second ligands on the structure of its nickel complexes, the molecular structures of HL¹·2HBr·H₂O, [NiL¹(H₂O)]Br and

Chart I

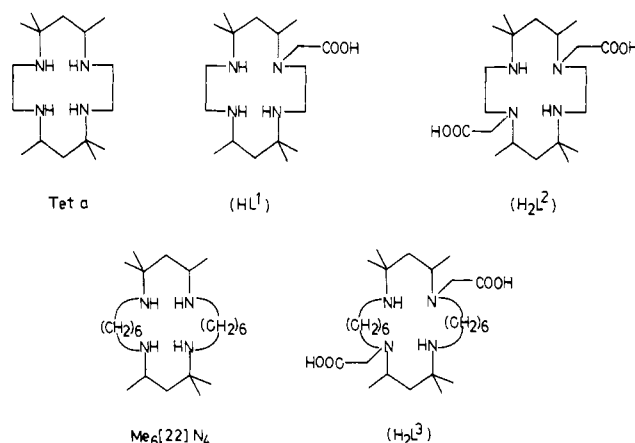
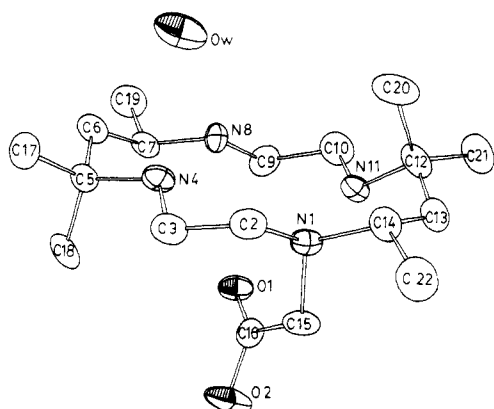


Table IV. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of $[\text{NiL}^1(\text{NCS})]\text{H}_2\text{O}$

atom	x	y	z	B_{eq} , Å ²
Ni	-0.24447 (4)	0.04876 (4)	-0.24598 (4)	2.508 (9)
S	0.1043 (1)	-0.0659 (1)	-0.07376 (9)	4.66 (3)
O(1)	-0.3926 (2)	0.0963 (2)	-0.3198 (2)	3.05 (6)
O(2)	-0.4779 (3)	0.1419 (3)	-0.4555 (2)	4.91 (8)
O(w)	0.4644 (3)	-0.0982 (4)	-0.3726 (3)	6.8 (1)
N(1)	-0.2065 (3)	0.0378 (3)	-0.3707 (2)	2.83 (7)
N(4)	-0.1840 (3)	0.2163 (3)	-0.2415 (2)	3.11 (8)
N(5)	-0.0903 (3)	0.0090 (3)	-0.1751 (3)	3.64 (9)
N(8)	-0.2946 (3)	0.0649 (3)	-0.1279 (2)	2.93 (7)
N(11)	-0.3051 (3)	-0.1173 (3)	-0.2487 (2)	2.94 (7)
C(2)	-0.1248 (4)	0.1289 (4)	-0.3661 (3)	3.7 (1)
C(3)	-0.1623 (4)	0.2374 (4)	-0.3298 (4)	4.1 (1)
C(5)	-0.2350 (3)	0.3116 (4)	-0.2017 (3)	3.4 (1)
C(6)	-0.2576 (4)	0.2701 (4)	-0.1142 (3)	3.6 (1)
C(7)	-0.3414 (3)	0.1769 (4)	-0.1135 (3)	3.20 (9)
C(9)	-0.3671 (4)	-0.0325 (4)	-0.1263 (3)	3.7 (1)
C(10)	-0.3177 (4)	-0.1374 (4)	-0.1573 (3)	3.9 (1)
C(12)	-0.2568 (4)	-0.2135 (4)	-0.2896 (3)	3.5 (1)
C(13)	-0.2382 (4)	-0.1737 (4)	-0.3792 (3)	3.7 (1)
C(14)	-0.1608 (3)	-0.0764 (4)	-0.3851 (3)	3.4 (1)
C(15)	-0.3032 (3)	0.0656 (4)	-0.4318 (3)	3.5 (1)
C(16)	-0.3986 (3)	0.1061 (4)	-0.4015 (3)	3.20 (9)
C(17)	-0.0097 (3)	-0.0201 (4)	-0.1314 (3)	2.99 (9)
C(18)	-0.1566 (4)	0.4116 (4)	-0.1823 (4)	4.9 (1)
C(19)	-0.3380 (4)	0.3524 (4)	-0.2626 (3)	3.9 (1)
C(20)	-0.3805 (4)	0.1828 (5)	-0.0279 (3)	4.5 (1)
C(21)	-0.1527 (5)	-0.2558 (4)	-0.2313 (4)	4.8 (1)
C(22)	-0.3371 (3)	-0.3124 (4)	-0.3073 (4)	5.2 (1)
C(23)	-0.1257 (4)	-0.0833 (5)	-0.4726 (4)	5.0 (1)

Table V. Selected Interatomic Distances (Å) and Angles (deg) in $\text{HL}^1 \cdot 2\text{HBr} \cdot \text{H}_2\text{O}$

Distances			
O(1)-C(16)	1.181 (9)	N(11)-C(10)	1.480 (11)
O(2)-C(16)	1.327 (9)	N(11)-C(12)	1.511 (11)
N(1)-C(2)	1.463 (11)	C(2)-C(3)	1.492 (13)
N(1)-C(14)	1.528 (11)	C(5)-C(6)	1.527 (12)
N(1)-C(15)	1.497 (10)	C(6)-C(7)	1.537 (11)
N(4)-C(3)	1.514 (11)	C(9)-C(10)	1.543 (13)
N(4)-C(5)	1.498 (10)	C(12)-C(13)	1.551 (13)
N(8)-C(7)	1.460 (10)	C(13)-C(14)	1.495 (13)
N(8)-C(9)	1.473 (10)	C(15)-C(16)	1.515 (11)
Angles			
N(1)-C(2)-C(3)	114.7 (8)	N(11)-C(12)-C(13)	106.9 (7)
C(2)-C(3)-N(4)	111.9 (8)	C(12)-C(13)-C(14)	119.7 (8)
C(3)-N(4)-C(5)	116.0 (7)	N(1)-C(14)-C(13)	110.8 (7)
N(4)-C(5)-C(6)	105.4 (7)	C(2)-N(1)-C(14)	110.4 (7)
C(5)-C(6)-C(7)	118.5 (7)	C(2)-N(1)-C(15)	110.1 (7)
C(6)-C(7)-N(8)	110.3 (7)	C(14)-N(1)-C(15)	109.1 (6)
C(7)-N(8)-C(9)	112.7 (6)	N(1)-C(15)-C(16)	111.7 (7)
N(8)-C(9)-C(10)	108.8 (7)	O(1)-C(16)-O(2)	125.0 (8)
C(9)-C(10)-N(11)	112.1 (7)	O(1)-C(16)-C(15)	124.2 (8)
C(10)-N(11)-C(12)	114.9 (7)	O(2)-C(16)-C(15)	110.8 (7)

**Figure 1.** Molecular structure of the macrocycle of the compound $\text{HL}^1 \cdot 2\text{HBr} \cdot \text{H}_2\text{O}$.**Table VI.** Deviations (Å) from Least-Squares Planes for 1, 3, and 6

compound	atom	deviation (Å)	atom	deviation (Å)
compound 1	N(1)	0.027 (7)	N(4)	-0.028 (7)
	N(8)	0.029 (7)	N(11)	-0.028 (7)
	C(15)	1.453 (9)	C(17)	-0.111 (11)
	C(18)	2.062 (10)	C(19)	0.426 (10)
	C(20)	-2.441 (11)	C(21)	-1.249 (12)
	C(22)	-0.593 (11)		
compound 3	N(1)	0.037 (4)	N(4)	-0.038 (4)
	N(8)	0.038 (4)	N(11)	-0.038 (4)
	Ni	0.002 (1)		
	O(1)	-2.211 (3)	O(2)	2.048 (3)
	C(17)	0.141 (6)	C(18)	2.177 (5)
	C(19)	0.840 (6)	C(20)	-2.279 (6)
C(21)	-0.261 (6)	C(22)	-0.942 (6)	
compound 6	N(1)	0.044 (3)	N(4)	-0.044 (4)
	N(8)	0.045 (3)	N(11)	-0.044 (4)
	Ni	-0.044 (1)		
	O(1)	2.012 (3)	N(5)	-2.120 (4)

Table VII. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{NiL}^1(\text{H}_2\text{O})]\text{Br}$

Distances			
Ni-O(1)	2.223 (2)	N(8)-C(7)	1.488 (5)
Ni-O(2)	2.065 (2)	N(8)-C(9)	1.486 (4)
Ni-N(1)	2.097 (3)	N(11)-C(10)	1.479 (5)
Ni-N(4)	2.093 (3)	N(11)-C(12)	1.515 (5)
Ni-N(8)	2.070 (3)	C(2)-C(3)	1.509 (6)
Ni-N(11)	2.103 (3)	C(5)-C(6)	1.540 (5)
O(2)-C(16)	1.267 (4)	C(6)-C(7)	1.526 (5)
N(1)-C(2)	1.498 (5)	C(9)-C(10)	1.506 (6)
N(1)-C(14)	1.501 (5)	C(12)-C(13)	1.520 (6)
N(1)-C(15)	1.502 (4)	C(13)-C(14)	1.522 (6)
N(4)-C(3)	1.476 (5)	C(15)-C(16)	1.513 (5)
N(4)-C(5)	1.502 (5)		
Angles			
O(1)-Ni-O(2)	176.1 (1)	Ni-N(8)-C(7)	115.2 (2)
O(1)-Ni-N(1)	95.1 (1)	Ni-N(8)-C(9)	105.7 (2)
O(1)-Ni-N(4)	85.3 (1)	Ni-N(11)-C(10)	105.3 (2)
O(1)-Ni-N(8)	87.0 (1)	Ni-N(11)-C(12)	122.5 (2)
O(1)-Ni-N(11)	92.4 (1)	N(1)-C(2)-C(3)	110.3 (3)
O(2)-Ni-N(1)	81.9 (1)	N(1)-C(14)-C(13)	112.1 (3)
O(2)-Ni-N(4)	93.5 (1)	N(4)-C(3)-C(2)	109.4 (3)
O(2)-Ni-N(8)	96.2 (1)	N(4)-C(5)-C(6)	108.0 (3)
O(2)-Ni-N(11)	88.8 (1)	N(8)-C(7)-C(6)	109.4 (3)
N(1)-Ni-N(4)	86.6 (1)	N(8)-C(9)-C(10)	108.6 (3)
N(1)-Ni-N(8)	178.0 (1)	N(11)-C(10)-C(9)	109.3 (3)
N(1)-Ni-N(11)	94.6 (1)	N(11)-C(12)-C(13)	107.3 (3)
N(4)-Ni-N(8)	94.0 (1)	O(2)-C(16)-C(15)	119.5 (3)
N(4)-Ni-N(11)	177.6 (1)	C(2)-N(1)-C(15)	108.9 (3)
N(8)-Ni-N(11)	85.0 (1)	C(2)-N(1)-C(14)	111.6 (3)
Ni-O(2)-C(16)	115.9 (3)	C(14)-N(1)-C(15)	112.3 (3)
Ni-N(1)-C(2)	101.7 (2)	C(3)-N(4)-C(5)	116.4 (3)
Ni-N(1)-C(14)	111.9 (2)	C(9)-N(8)-C(7)	113.9 (3)
Ni-N(1)-C(15)	110.0 (2)	C(10)-N(11)-C(12)	115.4 (3)
Ni-N(4)-C(3)	105.4 (2)	C(5)-C(6)-C(7)	119.7 (3)
Ni-N(4)-C(5)	121.5 (2)	C(12)-C(13)-C(14)	121.3 (3)

$[\text{NiL}^1(\text{NCS})]\text{H}_2\text{O}$ have been determined by X-ray crystallography.

A view of the macrocycle structure of $\text{HL}^1 \cdot 2\text{HBr} \cdot \text{H}_2\text{O}$ is shown in Figure 1. Table V contains selected bond distances and angles for $\text{HL}^1 \cdot 2\text{HBr} \cdot \text{H}_2\text{O}$.

The macrocycle adopts a conformation with the nitrogen atoms essentially coplanar. The deviations of C(15) and the six methyl carbon atoms from the least-squares plane of the four nitrogen atoms are listed in Table VI. It is seen that the pendent arm and two methyl groups of the macrocycle are on the same side of the least-squares plane, while the other four methyl groups are on the other side. The water molecule is attached to the macrocycle through O(w)···H-N(4) hydrogen bonds. The position of such a hydrogen atom was found on the difference Fourier map, but not refined. The distance of O(w)···H is 1.95 Å while that of H-N(4) is 0.866 Å. The angle of O(w)···H-N(4) is 165.91°, obviously, such a hydrogen atom must be an amino H atom.

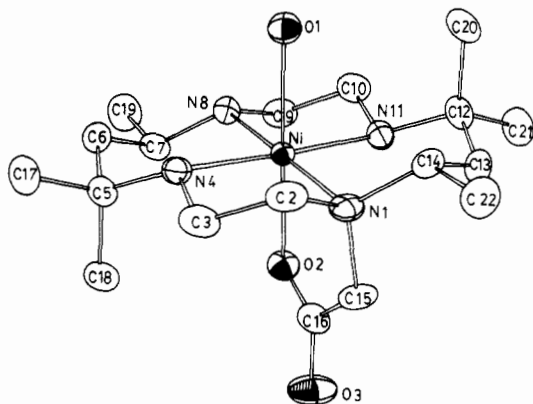


Figure 2. Molecular structure of the cation of the complex $[\text{NiL}^+(\text{H}_2\text{O})]\text{Br}$.

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{NiL}^+(\text{NCS})]\text{H}_2\text{O}$

Distances			
Ni-O(1)	2.068 (2)	N(11)-C(10)	1.484 (5)
Ni-N(1)	2.102 (3)	N(11)-C(12)	1.497 (4)
Ni-N(4)	2.119 (3)	S-C(17)	1.629 (4)
Ni-N(5)	2.092 (3)	O(1)-C(16)	1.263 (4)
Ni-N(8)	2.079 (3)	O(1)-O(w)	2.938 (4)
Ni-N(11)	2.105 (3)	O(2)-C(16)	1.243 (4)
N(1)-C(2)	1.489 (4)	O(2)-O(w)	2.767 (5)
N(1)-C(14)	1.504 (4)	C(2)-C(3)	1.518 (5)
N(1)-C(15)	1.479 (4)	C(5)-C(6)	1.531 (5)
N(4)-C(3)	1.480 (5)	C(6)-C(7)	1.536 (5)
N(4)-C(5)	1.499 (4)	C(9)-C(10)	1.514 (5)
N(5)-C(17)	1.158 (4)	C(12)-C(13)	1.538 (5)
N(8)-C(7)	1.487 (4)	C(13)-C(14)	1.530 (5)
N(8)-C(9)	1.480 (4)	C(15)-C(16)	1.524 (5)
Angles			
O(1)-Ni-N(1)	82.3 (1)	Ni-N(11)-C(10)	104.1 (2)
O(1)-Ni-N(4)	92.7 (1)	Ni-N(11)-C(12)	122.2 (2)
O(1)-Ni-N(5)	176.3 (1)	N(1)-C(2)-C(3)	110.8 (3)
O(1)-Ni-N(8)	92.9 (1)	N(1)-C(15)-C(16)	114.6 (3)
O(1)-Ni-N(11)	87.4 (1)	N(1)-C(14)-C(13)	112.9 (3)
N(1)-Ni-N(4)	86.2 (1)	N(4)-C(5)-C(6)	107.9 (3)
N(1)-Ni-N(8)	175.2 (1)	N(8)-C(9)-C(10)	109.1 (3)
N(1)-Ni-N(11)	94.6 (1)	N(11)-C(12)-C(13)	108.1 (3)
N(4)-Ni-N(5)	95.6 (1)	N(4)-C(3)-C(2)	109.8 (3)
N(4)-Ni-N(8)	84.1 (1)	N(8)-C(7)-C(6)	109.5 (3)
N(4)-Ni-N(11)	93.6 (1)	N(11)-C(10)-C(9)	108.3 (3)
N(8)-Ni-N(11)	179.2 (1)	O(1)-C(16)-O(2)	125.4 (4)
Ni-O(1)-C(16)	115.9 (2)	O(1)-C(16)-C(15)	117.7 (3)
Ni-N(1)-C(2)	102.0 (2)	O(1)-O(w)-O(2)	104.7 (2)
Ni-N(1)-C(14)	111.4 (2)	O(2)-C(16)-C(15)	116.9 (3)
Ni-N(1)-C(15)	108.7 (2)	S-C(17)-N(5)	117.0 (3)
Ni-N(4)-C(3)	105.4 (2)	C(2)-N(1)-C(14)	111.5 (3)
Ni-N(4)-C(5)	121.8 (2)	C(2)-N(1)-C(15)	110.1 (3)
Ni-N(5)-C(17)	173.5 (3)	C(3)-N(4)-C(5)	116.1 (3)
Ni-N(8)-C(7)	115.0 (2)	C(5)-C(6)-C(7)	119.9 (3)
Ni-N(8)-C(9)	104.7 (2)	C(7)-N(8)-C(9)	114.6 (3)
		C(10)-N(11)-C(12)	115.2 (3)
		C(12)-C(13)-C(14)	120.6 (3)
		C(14)-N(1)-C(15)	112.6 (3)

The molecular structure of $[\text{NiL}^+(\text{H}_2\text{O})]\text{Br}$ consists of a discrete $[\text{NiL}^+(\text{H}_2\text{O})]^+$ cation and a bromide ion. The structure of the cation $[\text{NiL}^+(\text{H}_2\text{O})]^+$ is shown in Figure 2. Table VII contains selected bond distances and angles. The central nickel ion is six-coordinated with the water molecule occupying a position trans to the pendent arm, giving an octahedral conformation.

A view of the molecular structure of $[\text{NiL}^+(\text{NCS})]\text{H}_2\text{O}$ is shown in Figure 3. Table VIII contains selected bond distances and angles. The nickel ion is six-coordinated with bonds to the four amine nitrogen atoms and the carboxylic oxygen atom of the macrocyclic ligand and to the nitrogen atom of the terminal isothiocyanate anion, which is coordinated in a linear arrangement.

It is interesting that two macrocycles, related by a center of symmetry, are joined together by two water molecules through

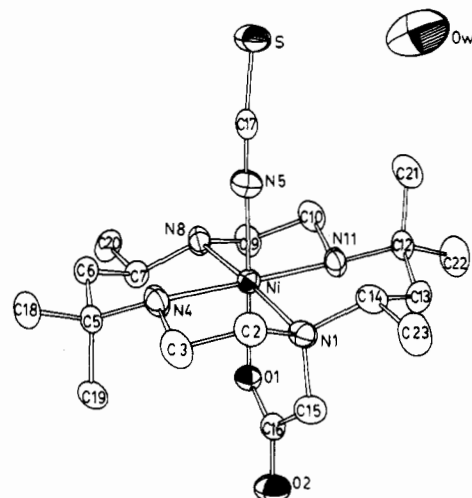


Figure 3. Molecular structure of the complex $[\text{NiL}^+(\text{NCS})]\text{H}_2\text{O}$.

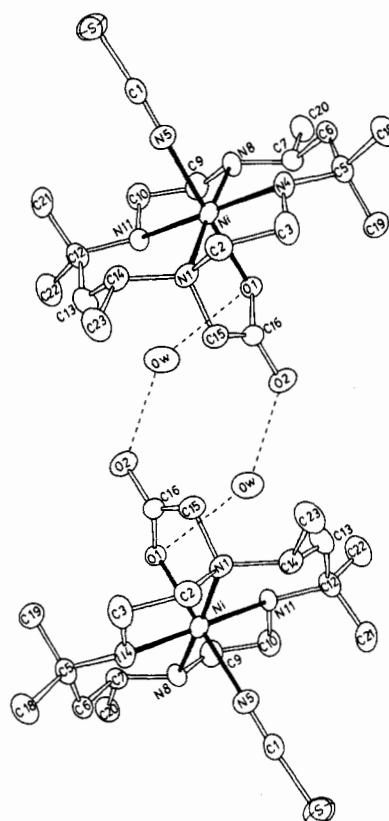


Figure 4. Molecular structure of $[\text{NiL}^+(\text{NCS})]\text{H}_2\text{O}$. Dashed lines correspond to hydrogen bonds.

two $\text{C}=\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{O}-\text{C}$ hydrogen bonds, in which each hydrogen atom of the water molecule is joined to a carboxylate group of a different macrocycle (Figure 4).

The structure of $[\text{NiL}^+(\text{H}_2\text{O})]\text{Br}$ is very similar to that of $[\text{NiL}^+(\text{NCS})]\text{H}_2\text{O}$; in each case, the four nitrogen atoms of the macrocycle are essentially coplanar (Table VI), and the nickel ion deviates +0.002 and -0.04 Å, respectively, from the least-squares plane, while the coordinated carboxylic oxygen atom deviates +2.048 and +2.012 Å, respectively, from the least-squares plane. As can be seen from Figures 2 and 3, both six-membered chelate rings of both complexes adopt chair conformations, while the five-membered chelate rings of both of the complexes are in the gauche conformations.

However, on comparing the structure of $[\text{NiL}^+(\text{H}_2\text{O})]^+$ with that of $[\text{NiL}^+(\text{NCS})]$, we find there is a difference between the distances from nickel atom to the donor atom of the second ligand. In the former (Ni-O(1), 2.223 (2) Å), it is much longer than that

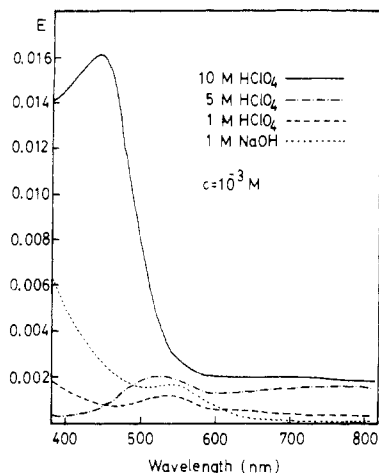


Figure 5. Absorption spectra of $[\text{NiL}(\text{H}_2\text{O})]\text{ClO}_4$ at different pH values.

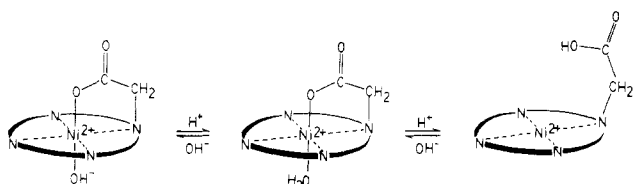


Figure 6. pH-induced structural rearrangement of $[\text{NiL}(\text{H}_2\text{O})]^+$.

in the latter (Ni-N(5), 2.092 (3) Å). Obviously the second ligand NCS^- has a much stronger coordination ability than H_2O . It might be noted that the average Ni-N(macrocycle) distance (2.101 (3) Å) in $[\text{NiL}(\text{NCS})]\text{H}_2\text{O}$ is slightly longer than that in $[\text{NiL}(\text{H}_2\text{O})]\text{Br}$ (2.091 (3) Å). It seems that the combination of the nickel ion with the macrocyclic ligand becomes looser as the coordination ability of the second ligand gets stronger.

pH-Dependent Coordination Geometry Change. Kaden¹⁵ has reported the pH-induced structural rearrangement of some mono-N-substituted macrocyclic complexes. Similar reactions have also been observed for metal complexes with HL^1 . For the nickel complex ion $[\text{NiL}(\text{H}_2\text{O})]^+$ two spectral changes are observed (Figure 5). In 10 mol L^{-1} perchloric acid it has an absorption spectrum which is analogous to that of $[\text{Ni}(\text{tet a})]^{2+}$ in which the nickel ion is in a square-planar field. In 5 mol L^{-1} perchloric acid the absorption bands indicate a pseudooctahedral geometry of the metal ion, while at even higher pH, a second color change is observed. This probably due to the substitution of hydroxide ion for the coordinated water molecule (Figure 6).

We have observed that the pH-dependent coordination geometry change also takes place in a nonaqueous medium, and this change is accompanied by a change in the electrochemical behavior of the complexes. The spectra of $[\text{NiL}(\text{H}_2\text{O})]\text{ClO}_4$ in dry acetonitrile solution indicate pseudooctahedral geometry for the nickel ion, and its cyclic voltammograms show a quasi-reversible charge-transfer process at 0.67 V vs Ag^+/Ag (0.1 mol L^{-1} in acetonitrile). When concentrated sulfuric acid was successively added to this solution, its color eventually turned to yellow, with the absorption bands indicating square-planar geometry, and its cyclic voltammograms (Figure 7) show that the oxidation/reduction peaks of $[\text{NiL}(\text{H}_2\text{O})]^+$ disappear and a new reversible charge-transfer process at 0.89 V vs Ag^+/Ag (0.1 mol L^{-1} in acetonitrile) is observed. This potential is very close to the reduction potential (0.89 V vs Ag^+/Ag 0.1 mol L^{-1}) of the square-planar complex couple $[\text{Ni}(\text{tet a})]^{3+}/[\text{Ni}(\text{tet a})]^{2+}$.¹⁶ It may be concluded that the pH-dependent coordination geometry change of a metal complex with mono-N-substituted polyaza

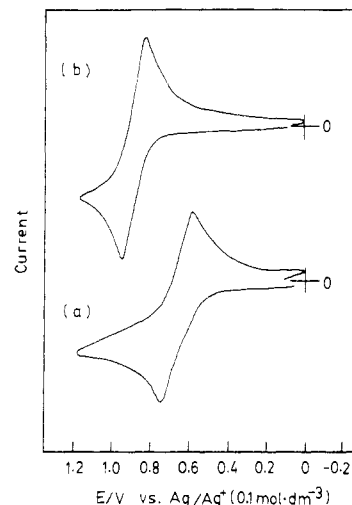


Figure 7. Cyclic voltammogram for $[\text{NiL}(\text{H}_2\text{O})]^+$ in acetonitrile (a) and acidified acetonitrile (b) recorded at a scan rate of 50 mV/s.

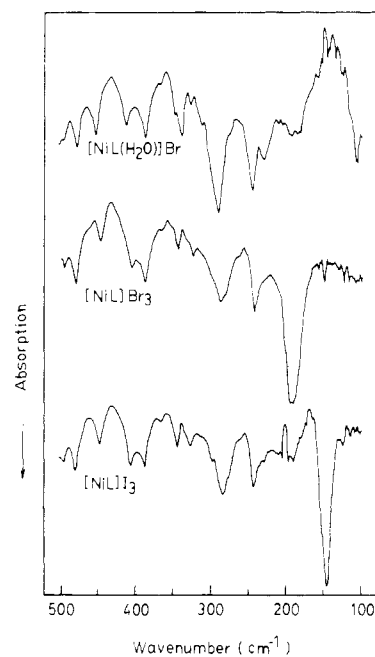


Figure 8. Far-infrared spectra of $[\text{NiL}(\text{H}_2\text{O})]\text{Br}$ and NiLX_3 (X = Br, I).

macrocycle is accompanied by a change in its electrochemical behavior.

Nickel Complexes Containing Trihalide Ions. Reactions of $[\text{NiL}(\text{H}_2\text{O})]\text{X}$ with X_2 (X = Br, I) result in the formation of yellow-brown products with the stoichiometry $[\text{NiL}^1]\text{X}_3$. The infrared spectrum of $[\text{NiL}^1]\text{Br}_3$ is very similar to that of $[\text{NiL}^1]\text{I}_3$, and both of them contain a very strong coordinated COO^- stretching band at about 1590 cm^{-1} . The far-infrared spectra contain strong absorption bands at 196 and 148 cm^{-1} , respectively (Figure 8), while the typical trihalide anion exhibit bands at 210 cm^{-1} for Br_3^- (aqueous solution)¹⁷ and 149 cm^{-1} for I_3^- (solid),^{18,19} respectively.

The careful reduction of $[\text{NiL}^1]\text{X}_3$ with a dilute alkaline solution of hydrogen peroxide below 5 °C gives light violet products, whose IR spectra and composition are identical with those of $[\text{NiL}^1(\text{H}_2\text{O})]\text{X}$ (X = Br, I). The titration of $[\text{NiL}^1]\text{X}_3$ with a standard solution of sodium thiosulfate indicates that $[\text{NiL}^1]\text{X}_3$ reacts with 2 mol of $\text{Na}_2\text{S}_2\text{O}_3$. These facts also suggest the presence of

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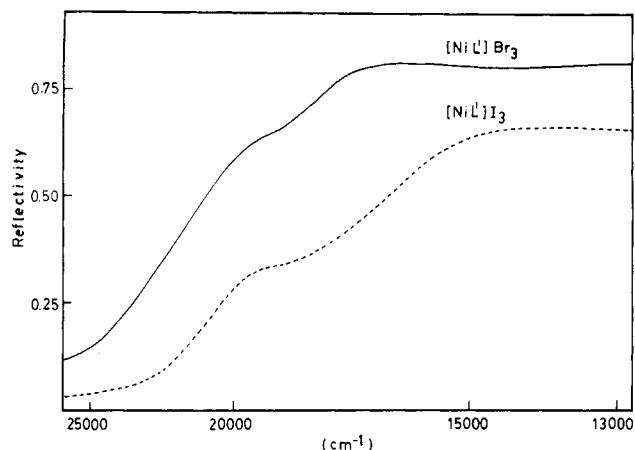


Figure 9. Reflectance spectra of $[\text{NiL}^1]\text{X}_3$ ($\text{X} = \text{Br}, \text{I}$).

trihalide ions, which appear as the counteranions of the complex ion $[\text{NiL}^1]^+$.

Both $[\text{NiL}^1]\text{Br}_3$ and $[\text{NiL}^1]\text{I}_3$ are diamagnetic substances; they are also EPR-silent, and therefore they are neither Ni(III) species nor octahedral Ni(II) complexes.

The reflectance spectra of $[\text{NiL}^1]\text{X}_3$ contain intense bands of counteranions throughout the blue end of the visible region and

a shoulder for $[\text{NiL}^1]^+$ ion at ca. $18\,800\text{ cm}^{-1}$ (Figure 9). The absorption at $18\,800\text{ cm}^{-1}$ is considerably lower in energy than those observed for a large number of the planar diamagnetic tetraamine complexes whose band maxima usually fall in the range $25\,000\text{--}20\,500\text{ cm}^{-1}$. From this and the presence of a coordinated carboxylate group in $[\text{NiL}^1]\text{X}_3$, it is evident that the geometry of $[\text{NiL}^1]\text{X}_3$ about the metal ions is nonplanar. Low-spin five-coordinate nickel(II) complexes usually have only one absorption spectrum in the visible region, generally in the range $20\,000\text{--}16\,660\text{ cm}^{-1}$.²⁰ The reflectance spectra for the complexes $[\text{NiL}^1]\text{X}_3$ indicate that they might have a low-spin five-coordinate structure. This is a rare case for such complexes that contain a pendent tetraazamacrocyclic ligand and a trihalide counteranion. More efforts will be yet required to elucidate this phenomenon.

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Supplementary Material Available: Listings of anisotropic thermal parameters, the derived hydrogen positions, all nonessential bond lengths and angles, and least-squares planes and deviations therefrom for compounds 1, 3, and 6 (11 pages); tables of calculated and observed structure factors for the three compounds (80 pages). Ordering information is given on any current masthead page.

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Vanadium Complexes of the Tridentate Schiff Base Ligand *N*-Salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine: Acid-Base and Redox Conversion between Vanadium(IV) and Vanadium(V) Imino Phenolates

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The reaction of vanadyl sulfate or vanadyl acetylacetonate ($\text{VO}(\text{ACAC})_2$) with *N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine (H_2SHED) affords a wide range of vanadium(IV) and vanadium(V) complexes. The structure of $\text{V}^{\text{IV}}\text{O}(\text{HSBED})(\text{ACAC})$ was determined by an X-ray analysis of red crystals having the following crystallographic parameters: space group *Pbca* (orthorhombic); $a = 11.607(5)$, $b = 25.960(2)$, $c = 11.701(5)$ Å; $V = 3526(2)$ Å³; $Z = 8$. The final *R* indices were $R = 0.051$ and $R_w = 0.040$ for 1485 observed data. The vanadium is six-coordinate with the phenolate, imine, and amine donors of HSBED^- oriented in a meridional geometry. The hydroxyl oxygen remains unbound. The ACAC moiety is a bidentate chelate with one oxygen atom (V1-O5 , 2.194(5) Å) trans to the short $\text{V}=\text{O}$ bond (V1-O1 , 1.596(4) Å). When the complex is dissolved in methanol, ACAC dissociates from a small fraction of $\text{V}^{\text{IV}}\text{O}(\text{HSBED})(\text{ACAC})$, yielding air-sensitive $\text{V}^{\text{IV}}\text{O}(\text{SHED})$ in which an alkoxide oxygen atom of the ligand has been inserted in the coordination sphere. If this green material is left in air for several days, orange blocks and yellow plates are deposited. X-ray analysis of both crystal types reveals that the two materials are weakly associated solid-state dimers of the pervanadyl- HSBED^- complex $\text{VO}_2(\text{HSBED})$, which result from different hydrogen bonding in the crystals. Once again, HSBED^- is a meridional, tridentate chelate with amine, imine, and phenolate ligation. The orange material shows a vanadium-vanadium separation of 3.103(1) Å and a long $\text{V1-O1}'$ distance of 2.298(2) Å. In contrast, the yellow crystals reveal a more weakly associated structure with $\text{V1-V1}'$ of 3.251(1) Å and $\text{V1-O1}'$ equal to 2.455(2) Å. Acidification of an acetonitrile solution of either the yellow or orange compounds results in the formation of a stable oxo-hydroxo- $\text{V}^{\text{V}}\text{HSBED}$ complex, which is red. Further addition of acid generates the deep blue, highly unstable monoxo- $\text{V}^{\text{V}}\text{HSBED}$ complex. A comparison to related V(IV) and V(V) complexes and the potential biological relevance are discussed. Crystallographic parameters for $[\text{VO}_2(\text{HSBED})]_2$ (yellow, 1): space group *P2₁/c* (monoclinic); $a = 11.246(3)$, $b = 6.842(2)$, $c = 17.022(5)$ Å; $\beta = 114.38(6)^\circ$; $V = 1193.0(6)$ Å³; $Z = 4$. The final *R* indices were $R = 0.027$ and $R_w = 0.027$ for 1729 observed data. Crystallographic parameters for $[\text{VO}_2(\text{HSBED})]_2$ (orange, 2): space group *P2₁/c* (monoclinic); $a = 10.249(2)$, $b = 10.999(2)$, $c = 10.578(2)$ Å; $\beta = 119.16(4)^\circ$; $V = 1191.6(4)$ Å³; $Z = 4$. The final *R* indices were $R = 0.029$ and $R_w = 0.029$ for 1265 observed data.

Introduction

Until very recently, the biological chemistry of vanadium had only been established for a novel natural product (amavadin)¹ in the mushroom *A. muscaria*, in the blood of sessile marine organisms known as tunicates,² and as a potent inhibitor of phos-

phoryl transfer enzymes.³ The latter activity results from the formation of a stable pentacoordinate V(V) species generated as an analogue of the phosphorus transition state.^{4,5} Although the chemical structure of amavadin has been elucidated,⁶ its function

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