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Stepwise Complexation of Ni(II) and Cu(II) Ions by 6,6′-C-spirobi(cyclam) (cyclam = 1,4,8,11-Tetraazacyclotetradecane), L_1. Syntheses and Redox Chemistry of $[M(H_2L_1)]X_4$ ($M = Cu^{2+}$, Ni^{2+}), $[Cu_2(L_1)]X_4$, and $[CuNi(L_1)]X_4$ ($X = ClO_4^-$) and the X-ray Crystal Structure of $[Cu_2(L_1)](ClO_4)_4$

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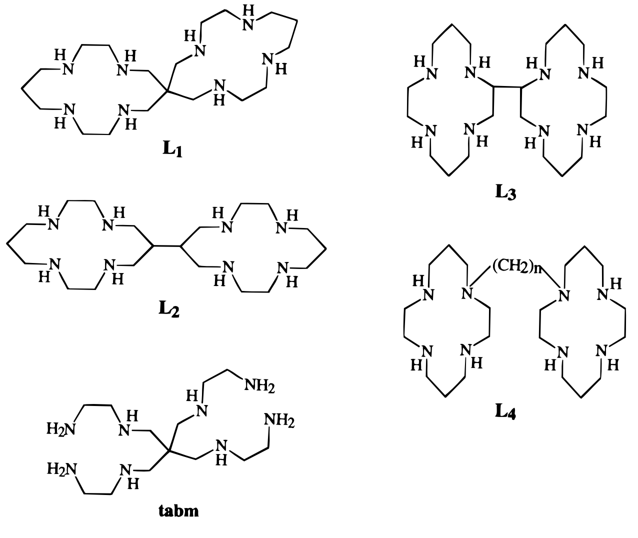
In aqueous $HClO_4$, the cation $[H_4(L_1)]^{4+}$ where L_1 is 6,6′-C-spirobi(cyclam) (cyclam = 1,4,8,11-tetraazacyclotetradecane), complexes Cu^{2+} and Ni^{2+} ions in a stepwise fashion to form $[M(H_2L_1)](ClO_4)_4$ ($M = Cu^{2+}$ and Ni^{2+}) from which $[CuNi(L_1)](ClO_4)_4$ has been prepared selectively. The preparation and the structure of $[Cu_2(L_1)](ClO_4)_4$ (empirical formula, $C_{19}H_{44}N_8Cu_2Cl_4O_{16}$; space group, triclinic; $P\bar{1}$; $a = 8.1815(6)$ Å, $b = 12.6098(9)$ Å, $c = 16.6565(12)$ Å, $\alpha = 80.3890(10)°$, $\beta = 76.5840(10)°$, $\gamma = 87.1750(10)°$, $V = 1647.9(2)$ Å^3, and $Z = 2$; of the 9531 total reflections collected, 6779 reflections with $I > 2\sigma(I)$ on least-squares refinement provided final $R_1 = 0.0657$ and $wR_2 = 0.1424$) are also reported. The cyclic voltammograms (1.0 M NaCl, 0.1 M H^+; Pt electrodes; all $E_{1/2}$ vs NHE) of $[M(H_2L_1)]^{4+}$ ($M = Cu^{2+}$ and Ni^{2+}) ions show single waves for the Cu^{II}/Cu^{III} couple ($E_{1/2} = 0.79$ V, irreversible) and the Ni^{II}/Ni^{III} couple ($E_{1/2} = 0.56$ V, reversible), respectively. In CH_3CN (0.1 M Et_4NClO_4), the $[Cu_2(L_1)]^{4+}$ ion shows a reversible wave for the $Cu^{II}-Cu^{II}/Cu^{II}-Cu^{III}$ couple ($^1E_{1/2} = 1.120$ V) and an irreversible wave for the $Cu^{II}-Cu^{III}/Cu^{III}-Cu^{III}$ couple ($^2E_{1/2} = 1.430$ V). Similarly, a reversible wave for the $Cu^{II}-Ni^{II}/Cu^{II}-Ni^{III}$ couple ($^1E_{1/2} = 0.750$ V) and an irreversible wave for the $Ni^{III}-Cu^{II}/Ni^{III}-Cu^{III}$ couple ($^2E_{1/2} = 1.20$ V) are observed in the case of the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion. The $[Cu_2(L_1)]^{4+}$ ion ($g_\perp = 2.120$, $g_\| = 2.256$ and 2.196, $A_\| = 150$ G, and $D_\| = 75$ G) and the mixed valent species $[Cu^{II}Ni^{III}(L_1)]^{5+}$ (for Cu^{2+}, $g_\perp = 2.060$, $g_\| = 2.219$, and $A_\| = 100$ G; for Ni^{3+} in sulfate media, $g_\perp = 2.204$ and $g_\| = 1.967$) and $[Cu^{II}Cu^{III}(L_1)]^{5+}$ ($g_{xx} = 1.982$, $g_{yy} = 2.155$, $g_{zz} = 2.386$, $A_{yy} = 80$ G, and $A_{zz} = 120$ G) show dipolar−dipolar interaction. In the mixed-valent ions, due to strong electrostatic repulsion from either the Ni(III) or Cu(III) ions, significantly smaller $A_\|$ (or A_{zz}) values are observed for the Cu^{2+} ion compared to 200 G in the mononuclear ions. Also, the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ in aqueous $HClO_4$ and the $[Ni_2(L_1)]^{4+}$ ion in CH_3NO_2 show a tendency to reduce perchlorate very slowly.

Introduction

Homo-binuclear macrocyclic complexes prepared from bis-macrocycles of the type L_2, L_3, and L_4 (Chart 1) have been studied extensively.[1] Generally, these ligands lack metal ion selectivity, and hence, preparation of hetero-binuclear complexes is rather laborious.[2] Open chain ligands that show site specific metal ion selectivity are known, and both homo- and hetero-binuclear complexes of such ligands have been investigated for magnetic interactions.[3] Only recently, macrocyclic analogues of these ligands have been prepared, and selective formation of hetero-binuclear complexes has been studied.[4] Other known hetero-binuclear macrocyclic systems have either ferrocene[5] or

Chart 1



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2,2′-dipyridyl[6] units built into their structure. Ru(II)−Cu(II) complexes of the latter systems show promise as photoantennae and in photo-electron-transfer processes.[7]

Binuclear macrocyclic complexes are potentially good candidates for catalysts.[8a] For example, cofacial porphyrins have been used for the electrocatalytic reduction of oxygen,[8b] and $[Ni_2(L_2)]^{4+}$ cation has been shown to be good for the electrocatalytic reduction of water to hydrogen.[9] Recently, a binuclear Ni(II) complex of a bis(cyclam) derivative has been shown to enhance the photocatalytic reduction of carbon dioxide.[1d] Earlier studies of binuclear complexes focused on intramolecular electron-transfer processes and intervalence charge-transfer spectra of mixed-valent species.[10] In recent years, this focus has shifted to small molecule activation[4c] and application in molecular magnetism and electronics.[11] The hetero-binuclear complexes of the type described here are capable of existing in two different stable oxidation states, and such reversible bistable states are potentially useful for constructing molecular devices.[12]

Fabbrizzi et al. first reported the effects of electrostatic repulsion on the redox behavior of $[CuNi(L_2)](ClO_4)_4$.[13] In a subsequent study, Mochizuki et al.[2a] reported the isolation of $[Ni(L_2)]^{2+}$ by column chromatography and the selective preparation of $Cu^{II}-Ni^{II}$, $Cu^{II}-Co^{II}$, and $Ni^{II}-Co^{II}$ complexes of L_2. Earlier, we reported the structure and redox behavior of the *trans*-III isomer of $[Ni_2(L_1)](ClO_4)_4$.[14] In this paper we describe the formation and isolation of $[M(H_2L_1)]^{4+}$ ($M = Cu^{2+}$ and Ni^{2+}) and their usefulness in the selective synthesis of $[CuNi(L_1)](ClO_4)_4$. Also, the syntheses, UV−vis and EPR spectroscopy, and redox behavior of $[Cu_2(L_1)]^{4+}$, $[CuNi(L_1)]^{4+}$, $[Cu^{II}Ni^{III}(L_1)]^{5+}$, and $[Cu^{II}Cu^{III}(L_1)]^{5+}$ ions and the X-ray structure of $[Cu_2(L_1)](ClO_4)_4$ are presented.

Experimental Section

Caution: Perchlorate salts are potentially explosive when heated or dried on a filter paper. Only small quantities of such materials should be prepared. Extreme care should be taken to avoid contact with combustible organic matter and heat.

Synthesis. The ligands L_1[15] and L_2[1e] were prepared as described in the literature. The tetrahydroperchlorate salts of the ligands were precipitated by dropwise addition of 70% $HClO_4$ to a solution of the free base in 95% EtOH and purified by recrystallization from a minimum amount of hot water.

$[Cu(H_2L_1)](ClO_4)_4$. To a solution of 1.50 g (1.9 mmol) of $[H_4L_1](ClO_4)_4$ dissolved in 250 mL of water, 2 mL of 70% $HClO_4$ was added and maintained at 50−60 °C in a water bath under stirring. To this clear solution, 0.704 g (1.9 mmol) of $Cu(ClO_4)_2\cdot 6H_2O$ in 25 mL of water was added. This mixture was stirred at 60 °C, and the excess acid was neutralized over a period of 2 h to a final pH of 7.0−7.5 by dropwise addition of a saturated solution of $NaHCO_3$. This solution was concentrated to half its original volume and cooled in an ice bath. The crystalline pale pink precipitate which formed was collected, washed successively with CH_3CN and Et_2O, and dried under vacuum. This solid was recrystallized from a 1:1 v/v mixture of CH_3CN and water to yield pale pink crystals of $[Cu(H_2L_1)](ClO_4)_4$. Yield: 1.21 g (75%). Anal. Calcd for $C_{19}H_{46}N_8CuCl_4O_{16}$ (found): C, 26.91 (26.60); H, 5.47 (5.33); N, 13.21 (13.00); Cu, 7.49 (7.41). MS: M^+ calcd for $C_{19}H_{46}N_8CuCl_3O_{12}$, 748.5 (found 748.2); M^{2+} calcd for $C_{19}H_{45}N_8CuClO_4$, 273.7 (found 273.7).

$[Ni(H_2L_1)](ClO_4)_4$. To a solution of 0.392 g (0.5 mmol) of $[H_4L_1](ClO_4)_4$ in 100 mL of water was added 2 mL of 70% $HClO_4$. This mixture was stirred and warmed in a water bath at 60−65 °C to form a clear solution. A solution of 0.220 g (0.6 mmol) of $Ni(ClO_4)_2\cdot 6H_2O$ in 25 mL of water was added, and the solution was slowly neutralized over a period of 4 h to a final pH of 7−7.5 with saturated $NaHCO_3$ solution and stirred overnight.[16] The resulting solution was concentrated to half its original volume and again just made acidic with 20% $HClO_4$. Bright orange crystalline solids that formed on standing were filtered off under suction and dried. The product was ground to a fine powder, digested with CH_3CN at 60 °C, filtered under suction, and air-dried. Yield: 0.245 g (58%). Anal. Calcd for $C_{19}H_{46}Cl_4N_8NiO_{16}$ (found): C, 27.07 (27.63); H, 5.50 (5.67); N, 13.29 (13.43). MS: M^+ calcd for $C_{19}H_{46}N_8NiCl_3O_{12}$, 743.6 (found 743.6); $[M - H(ClO_4)_2]^+$, calcd 643.8 (found 643.8).

$[Cu_2(L_1)](ClO_4)_4$. To 0.1 g (0.26 mmol) of L_1 dissolved in 25 mL of EtOH was added an aqueous solution of 0.193 g (0.52 mmol) of $Cu(ClO_4)_4\cdot 6H_2O$, and the solution was refluxed for about 40 min (instead of L_1, an equivalent amount of $[H_4L_1](ClO_4)_4$ or $[Cu(H_2L_1)](ClO_4)_4$ and 1 mol of Cu(II) can be used with an aqueous solution of a base such as $NaHCO_3$ or Na_2CO_3). The resulting dark purple solution was concentrated to 15 mL and saturated with $NaClO_4$. The complex that precipitated was separated by centrifugation and redissolved in 10 mL of boiling water. Dark purple crystals of $[Cu_2(L_1)](ClO_4)_4$ obtained upon slow cooling were filtered, washed with EtOH, and dried under vacuum. Yield: 0.2 g (83%). Anal. Calcd for $C_{19}H_{44}N_8Cu_2Cl_4O_{16}$

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(16) When the pH was increased beyond 9 and the solution allowed to react overnight, a base-catalyzed inversion at the nitrogen centers occurs with the formation of diastereomers of the mononuclear Ni(II) species. This mixture of species is highly soluble in water and red-brown in color and is not precipitated upon acidification by $HClO_4$, unlike the pure *trans*-III diastereomer which is only sparingly soluble and orange in color. A similar observation has been observed with the bis-Ni(II) species also. The characteristics of these diastereomers are under further investigation.

(found): C, 25.09 (25.06); H, 4.88 (4.86); N, 12.32 (12.00). MS: M$^+$ calcd for $C_{19}H_{44}N_8Cu_2Cl_3O_{12}$, 809.0 (found 809).

Replacing the perchlorate salts with either $CuCl_2$ or $[H_4(L_1)]Cl_4$ resulted in the formation of a dark blue chloro-bridged cationic polymer. The crystal structure of this polymer, $\{[Cu_2(L_1)Cl]_n(ClO_4)_{3n}\}\cdot EtOH$, has been reported earlier.[17]

$[CuNi(L_1)](ClO_4)_4$. Method 1. To a solution of 0.154 g (0.4 mmol) of L_1 in 75 mL of 0.1 M HCl was added 0.095 g (0.4 mmol) of $NiCl_2\cdot 6H_2O$ in 10 mL of water under stirring. To this mixture was added 2 mL of 1 M Na_2CO_3 and the temperature maintained at 60 °C for 30 min. To the resulting bright yellow solution was added 0.068 g (0.4 mmol) of $CuCl_2\cdot 2H_2O$ in 10 mL of water and the mixture maintained under stirring at 60 °C for a further period of 1 h. The pH of this solution was adjusted to 7.0 by dropwise addition of 1 M Na_2CO_3 and maintained at 60 °C for a further period of 30 min. This mixture of complexes was diluted to 200 mL with water and separated on a Sephadex CM C-25 cation exchange column (75 cm × 4 cm diameter). Elution with 0.34 M NaCl provided three distinct well-separated bands. These three bands were collected separately and concentrated, and the complexes were extracted from NaCl by successive washing with MeOH. These methanolic extracts were concentrated to dryness, dissolved in a minimum amount of water, and saturated with $NaClO_4$. The perchlorate salts which precipitated were filtered and recrystallized from a 1:1 CH_3CN/H_2O mixture. The first violet band was found to be $[Cu_2(L_1)](ClO_4)_4$, and the final yellow band was analyzed to be $[Ni_2(L_1)](ClO_4)_4$. The middle pink band was identified to be the hetero-binuclear complex $[NiCu(L_1)](ClO_4)_4$. Yield: 0.15 g (41%).

Method 2. To a solution of 1.0 g (1.18 mmol) of $[Cu(H_2L_1)](ClO_4)_4$ in 100 mL of water was added 0.43 g (1.18 mmol) of $Ni(ClO_4)_4\cdot 6H_2O$ in 10 mL of water, and the mixture was stirred in a hot water bath at 60 °C for 1 h. The acid liberated was neutralized by dropwise addition of saturated Na_2CO_3 solution until the final pH was 7.5−8.0. The solution was filtered, concentrated to 50 mL, and saturated with $NaClO_4$. The light salmon pink precipitate formed was collected by centrifugation and recrystallized from a solution of 1:1 CH_3CN/H_2O. Yield: 0.96 g (90%). Anal. Calcd for $C_{19}H_{44}N_8NiCuCl_4O_{16}$ (found): C, 25.23 (25.21); H, 4.90 (4.90); N, 12.39 (12.34); Ni, 6.49 (6.25); Cu, 7.02 (7.02). MS: M$^+$ calcd for $C_{19}H_{44}N_8CuNiCl_3O_{12}$, 802 (obsd 802). The chloro complex was also analyzed by mass spectrometry. The following peaks were observed: M$^+$ calcd for $C_{19}H_{44}N_8NiCuCl_3$, 610 (obsd 610.0 (45), 612 (100), 614 (45).

Reagent-quality materials (Aldrich Chemical Co.) were used as received. Nonaqueous solvents and electrolytes were purified by standard methods.[18] Tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4) purchased from GFS Chemicals, Ohio, was used as received. Microanalyses were performed by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada. UV−vis spectra were recorded on either a Perkin-Elmer Lambda 4B or a Cary 17 dual beam spectrophotometer. EPR spectra were recorded in an X-band Varian ES-6 spectrometer, at 77 K in solvents as indicated in the text. Diphenyl picryl hydrazide (DPPH, $g = 2.0037$) was used as an external standard. Mass spectra were obtained on a Kratos Concept model 2H mass spectrometer by the FAB or electrospray technique. In all cases, the theoretical isotopic distributions of relevant peaks were found to agree with the experimental spectrum. A three-electrode cell configuration was used in electrochemical experiments. Platinum beads were used as working electrodes. Redox potentials in aqueous media were measured against a saturated calomel electrode (SCE) (0.244 V vs NHE). An Ag/Ag$^+$ reference electrode[19] was used for measurements in nonaqueous media, and the Fc/Fc$^+$ couple was used either as an external or an internal standard. Cyclic voltammetric experiments were performed using a Princeton Applied Research galvanostat/potentiostat model 273 instrument interfaced to an IBM PC. The "HeadStart" program was used to collect data. Corrections for liquid junction potentials were not applied. However, the cell resistance measured using the HeadStart program was used to compensate for internal resistance during nonaqueous measurements. The reversibility of cyclic voltammograms was confirmed as described elsewhere.[20] The accuracy of the measured potentials was within ±5 mV. Linear scan voltammetric experiments were performed on a Metrohm Polarecord 626 instrument. Coulometric experiments were performed using a Princeton Applied Research potentiostat model 173 and model 172 digital coulometer. All electrochemical experiments were performed at 25 ± 0.3 °C.

Table 1. Crystallographic Data for $[Cu_2(L_1)](ClO_4)_4$

empirical formula	$C_{19}H_{44}N_4Cu_2Cl_4O_{16}$
formula weight	901.44
space group	triclinic, $P\bar{1}$
cell params	$a = 8.1815(6)$ Å, $\alpha = 80.3890(10)°$ $b = 12.6098(9)$ Å, $\beta = 76.5840(10)°$ $c = 16.6565(12)$ Å, $\gamma = 87.1750(10)°$ vol = 1647.9(2) Å^3, $Z = 2$
θ range (deg)	1.27−28.0
total no. of reflections	9531
nol of data/restraint/params	6778/0/442
final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0657$, w$R_2 = 0.1420$
R indices (all data)	$R_1 = 0.1424$, w$R_2 = 0.1720$
largest diff peak and hole (e·Å^{-3})	1.088 and −0.753

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Single crystals suitable for X-ray crystallography were obtained by slowly cooling a saturated aqueous solution of $[Cu_2(L_1)](ClO_4)_4$. A dark purple single crystal of dimensions 0.20 × 0.15 × 0.15 mm was mounted on a glass fiber, and the diffraction data were collected over the index range $-10 \leq h \leq 10$, $-11 \leq k \leq 16$, $-16 \leq l \leq 21$ using a graphite-monochromated X-ray of wavelength 0.710 73 Å at 183(2) K on a Siemens SMART/CCD diffractometer equipped with an LT-II low-temperature device. Diffraction data were corrected for absorption using the SADABS program. The absorption coefficient was 1.702 mm^{-1}. SHELXTL[21] was used for the structure solution, and refinement was based on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically on the basis of corresponding C-atoms $[U(H) = 1.2U_{eq}(C)]$. Pertinent crystallographic information is given in Table 1. Fractional coordinates and anisotropic displacement parameters have been deposited as Supporting Information.

Results and Discussion

Synthetic Aspects. Fabbrizzi et al.[22] have reported the stepwise complexation of Cu(II) ion by bis(5,7-dioxocyclam). A similar observation has also been made in this laboratory in the case of 6,6′-spirobi(dioxocyclam).[23] This led us to investigate the complexation properties of $[H_4(L_1)](ClO_4)_4$. In a recent investigation of the $[Ni_2(L_1)]^{4+}$ cation, electrostatic repulsion between the Ni(II) centers was found to be the dominant force controlling electron transfer and coordination geometry changes.[14] Similar factors were expected to influence complexation of metal ions by $[H_4(L_1)]^{4+}$, and a stepwise complex formation (eqs 1 and 2) was expected. This was confirmed experimentally with the isolation of $[Cu(H_2L_1)](ClO_4)_4$ as the predominant product. Further, the insolubility of this species in aqueous ethanolic medium enhanced its isolation in 70−80% yield. Unlike [Cu$_2$-

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$$[H_4(L_1)]^{4+} + M^{2+} \rightarrow [M(H_2L_1)]^{4+} + 2H^+ \qquad (1)$$

$$[M(H_2L_1)]^{4+} + M^{2+} \rightarrow [M_2(L_1)]^{4+} + 2H^+ \qquad (2)$$

$(L_1)](ClO_4)_4$, $[Cu(H_2L_1)](ClO_4)_4$ is highly insoluble in CH_3CN. This difference in solubility provides a very convenient and effective method for separating the mononuclear species from traces of binuclear species. Also, a distinct difference in their EPR spectra aids in identifying these two species very easily (see discussions in the EPR section). Attempts to prepare $[Ni(H_2L_1)](ClO_4)_4$ under identical conditions resulted in a mixture of $[H_4L_1](ClO_4)_4$, $[Ni(H_2L_1)](ClO_4)_4$, and $[Ni_2(L_1)](ClO_4)_4$ due to the sluggish complexation behavior of $[Ni(H_2O)_6]^{2+}$ ion. To avoid problems of separating this mixture, a slight excess of Ni(II) and a longer reaction time were used. This yielded a mixture of $[Ni(H_2L_1)](ClO_4)_4$ and $[Ni_2(L_1)](ClO_4)_4$, which was easily separated like their Cu(II) analogue, by digesting with CH_3CN in which $[Ni_2(L_1)](ClO_4)_4$ alone is soluble.

This difference in the complexation behavior of Ni(II) and Cu(II) ions reflects the rates of substitution of H_2O in the corresponding aqua species.[24] $[Cu(H_2O)_6]^{2+}$ is much more labile than $[Ni(OH_2)_6]^{2+}$, and hence complexation of Cu(II) ion is much faster than that of Ni(II) ion. Also, $[CuN_4]^{2+}$ exerts a much stronger electrostatic repulsion than a $[NiN_4]^{2+}$ ion. In $[Ni(H_2L_1)]^{4+}$, the Ni(II) ion can coordinate two axial ligands (solvents or anions), which can significantly diminish the intramolecular electrostatic repulsion required for the selective formation of $[Ni(H_2L_1)]^{4+}$. This was found to be the case when $[H_4L_1](ClO_4)_4$ was replaced by $[H_4L_1]Cl_4$ and $M(ClO_4)_2$ by MCl_2. An earlier report from this laboratory that described the preparation of a chloro-bridged polymer of $[Cu_2(L_1)]^{4+}$ demonstrated this point.[17] Thus, the properties of counterions are a critical factor in the selective formation of mononuclear species.[25]

Comparison of the two methods described for the preparation of $[CuNi(L_1)](ClO_4)_4$ clearly demonstrates the importance of steric and electrostatic factors. Method 1 is similar to that described by Fabbrizzi et al. for the preparation of $[CuNi(L_2)]^{4+}$.[1e] In this method, a mixture of $[Ni_2(L_1)]^{4+}$, $[Ni(H_2L_1)]^{4+}$, and $[H_4L_1)]^{4+}$ is formed, which upon subsequent complexation with Cu(II) ions leads to the formation of a mixture of $[Ni_2(L_1)]^{4+}$, $[Cu_2(L_1)]^{4+}$, and $[CuNi(L_1)]^{4+}$ cations. However, when Cu(II) is reacted with $[H_2(L_1)]^{4+}$ first, particularly in perchlorate medium, $[Cu(H_2L_1)]^{4+}$ is formed predominantly and can either be isolated or further reacted with Ni(II) to form pure $[CuNi(L_1)](ClO_4)_4$. Reaction of Cu(II) with pure $[Ni(H_2L_1)]^{4+}$ also provides $[CuNi(L_1)](ClO_4)_4$ exclusively. However, method 2 is preferable since the yields and purity of isolated $[Cu(H_2L_1)](ClO_4)_4$ are superior to those of $[Ni(H_2L_1)](ClO_4)_4$. The preparation of the mononuclear species of the ligand L$_2$, reported by Mochizuki,[2b] requires column chromatography for its isolation, an observation which has been confirmed in this laboratory. In the case of $[H_4L_1]^{4+}$, though the formation of $[Ni(H_2L_1)]^{4+}$ is not as exclusive as that of $[Cu(H_2L_1)]^{4+}$, the separation of the mononuclear ions from the binuclear species is easily achieved by their solubility differences in CH_3CN. The isolation of the mononuclear species described here provides an efficient route to hetero-binuclear complexes of the type $[M_1M_2(L_1)](ClO_4)_4$ where M_1 = Cu(II) or Ni(II) and M_2 is any other transition metal ion.

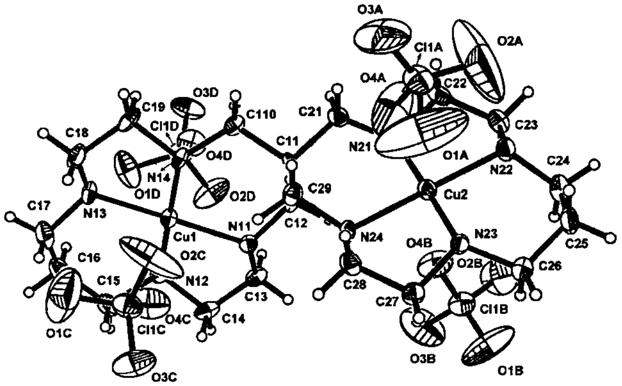

Figure 1. ORTEP (30% thermal ellipsoid) diagram of $[Cu_2(L_1)](ClO_4)_4$.

Table 2. Important Bond Lengths (Å) and Angles (deg) for $[Cu_2(L_1)](ClO_4)_4$

bond lengths		bond angles	
Cu(1)−N(12)	2.012(6)	N(12)−Cu(1)−N(13)	93.8(2)
Cu(1)−N(13)	2.015(5)	N(12)−Cu(1)−N(11)	86.5(2)
Cu(1)−N(11)	2.022(5)	N(13)−Cu(1)−N(11)	178.7(2)
Cu(1)−N(14)	2.022(5)	N(12)−Cu(1)−N(14)	178.9(2)
Cu(2)−N(23)	2.014(5)	N(13)−Cu(1)−N(14)	87.0(2)
Cu(2)−N(21)	2.021(5)	N(11)−Cu(1)−N(14)	92.6(2)
Cu(2)−N(22)	2.020(5)	N(23)−Cu(2)−N(21)	178.2(2)
Cu(2)−N(24)	2.036(5)	N(23)−Cu(2)−N(22)	94.8(2)
		N(21)−Cu(2)−N(22)	86.3(2)
		N(23)−Cu(2)−N(24)	86.4(2)
		N(21)−Cu(2)−N(24)	92.4(2)
		N(22)−Cu(2)−N(24)	178.0(2)

Structure of $[Cu_2(L_1)](ClO_4)_4$. The ORTEP diagram of this complex is shown in Figure 1. Selective bond distances and angles are provided in Table 2. In each cyclam ring, the Cu(II) ion and the four nitrogens are coplanar with an average Cu−N distance of 2.020 Å, similar to that observed in $[Cu(II)(cyclam)](ClO_4)_2$[26] and its derivatives.[27] The cyclam rings adopt the *trans*-III configuration.[28] A Cu−Cu distance of 6.588 Å observed in this cation is slightly longer than the 6.4 Å reported for the related open chain analogue, $[Cu_2(tabm)](NO_3)_4$ (tabm = tetrakis(4-amino-2-azabutyl)methane).[29] Average N−Cu−N angles of 86.6° and 93.4° observed in this complex for the five- and six-membered chelate rings, respectively, are similar to those found in the chloro-bridged polymer[17] and in $[Ni_2(L_1)](ClO_4)_4$.[30] The *trans*-N−Cu−N angles are close to 180°. The two planes containing the CuN_4 chromophore are oriented at an angle of 85.2°. It is interesting to note that $[Ni_2(L_1)](ClO_4)_4$,[30] $[H_4(L_1)](ClO_4)_4$,[31] $[Ni(H_2L_1)](ClO_4)_4$,[31] and the $[Cu_2(L_1)](ClO_4)_4$ described here are all isostructural. In all these systems, the perchlorate ions occupy a position approximately 3.5 Å above and below the plane containing the four nitrogens, indicating weak electrostatic interaction. In the ligand cation $[H_4L_1]^{4+}$, the macrocyclic rings adopt a conformation that is virtually unchanged in the complex cations. Thus, in the $[H_4L_1]^{4+}$ cation, the ligand is preorganized such that complexation of metal ions occurs with little or no change in its structural parameters.

UV−Vis Spectroscopy. The UV−vis spectroscopic data for the complexes are presented in Table 3. The mononuclear

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Table 3. UV−Vis Spectroscopic Data for Complexes of L_1

complex	solvent	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
$[Ni^{II}(H_2L_1)](ClO_4)_4$	H_2O	465	57
$[Cu^{II}(H_2L_1)](ClO_4)_4$	H_2O	520	59
$[Cu^{II}Cu^{II}(L_1)](ClO_4)_4$	H_2O	498	138
	CH_3CN	497	190
	CH_3NO_2	487	120
$[Cu^{II}Cu^{III}(L_1)](ClO_4)_5$	$(CH_3)_2NCHO$	535	160
	$(CH_3)_2NCHO$	400	350
$[Cu^{II}Ni^{II}(L_1)](ClO_4)_4$	H_2O	494	120
	CH_3CN	495	96
	CH_3NO_2	470	130
$[Cu^{II}Ni^{III}(L_1)](ClO_4)_4$	1.0 M H_2SO_4	272	1×10^4
		316	
		376	4×10^3

complexes $[M^{II}(H_2L_1)]X_4$ (M = Ni or Cu and X = ClO_4^-) are insoluble in nonaqueous solvents. In H_2O, they showed the expected features. The λ_{max} for the mononuclear species showed a bathochromic shift compared to the binuclear species. This is due to higher concentrations of pseudooctahedral species, $[NiX_2(H_2L_1)]^{2+}$ (X = solvent or anion). Such species are stabilized by the presence of ammonium centers in the mononuclear species, which are absent in the binuclear complexes. Also, axial ligation in these species dramatically reduces electrostatic repulsion. The perchlorate salts of the binuclear complexes being soluble both in protic and aprotic solvents, their UV−vis spectra were recorded in H_2O, CH_3NO_2, and CH_3CN. Though they showed characteristic features,[1e,32] these were not significantly different. However, their molar adsorptivities, ϵ-values, differed significantly, depending upon the coordinating ability of the solvent. For example, in the poorly coordinating H_2O and CH_3NO_2, the molar absorptivities for $[Cu_2(L_1)]^{4+}$ and $[Cu^{II}Ni^{II}(L_1)]^{4+}$ are practically identical. However, in the strongly coordinating CH_3CN, the ϵ-value for the $[Cu_2(L_1)]^{4+}$ ion is much larger than for the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion. This trend is in accord with the coordination geometry changes expected for these ions. In general, for a Cu(II) ion the ϵ-values increase when the coordination geometry changes from square planar (50−70 M^{-1} cm^{-1}) to octahedral or square pyramidal (90−110 $M^{-1}cm^{-1}$),[32] and for a Ni(II) ion, a decrease in the ϵ-value (75−90 M^{-1} cm^{-1} for the square planar geometry to 8−15 M^{-1} cm^{-1} for the octahedral geometry) is normally expected.

The temperature and anion dependencies of the UV−vis spectra of the binuclear complexes were also studied. In both H_2O (0.1 M $NaClO_4$) and CH_3CN (0.1 M Et_4NClO_4), no temperature-dependent changes were observed in the spectrum of $[Cu_2(L_1)]^{4+}$. However, a chloride-dependent bathochromic shift was noticed due to the formation of the chloro-bridged polymer.[17] In the case of the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion, only a very small temperature dependence was observed in an aqueous medium (0.1 M $NaClO_4$). These changes, due to the square planar−octahedral equilibrium in Ni(II) complexes, are usually significant as observed in the case of $[Ni_2(L_1)]^{4+}$ in CH_3CN (0.1 M Et_4NClO_4).[14] However, in this case, these changes were too small to derive any reliable thermodynamic data. A similar situation in CH_3CN for the related open chain complex ion $[Ni_2(tabm)]^{4+}$ has been reported by us previously.[33] This rather unusual behavior in $[Ni_2(tabm)]^{4+}$ was ascribed to a synergistic interaction between the axial and the equatorial ligands. However, in the case of $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion, this is likely due to the specific geometry demands of the metal ions being satisfied in this solvent. As has been shown in the case of $[Ni_2(L_1)]Cl_4$, owing to steric demands, both metal centers could not adopt six-coordinate geometry simultaneously.[14] In the case of $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion, a compromise is easily achieved with the Cu(II) adopting a five-coordinate and the Ni(II) a six-coordinate geometry. Thus, the steric demands are met fully, and also the electrostatic repulsion between the metal centers is reduced to a significant extent.

Formation of Mixed-Valent Species. Spectroscopic data for the mixed-valent species are also presented in Table 3. Spectrophotometric titration of $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ion consumed exactly 1 equiv of the oxidant ($[Co(H_2O)_6]^{3+}$ in 1.0 M $HClO_4$), indicating quantitative formation of $[Cu^{II}Ni^{III}(L_1)]^{5+}$ ion. This conversion occurred with an isobestic point at 239 nm (see Figure 1 in the Supporting Information). This species can be prepared in nonaqueous media using $NOPF_6$ as the oxidizing agent since the Cu(II) center is not oxidized under these conditions. Also, the large difference in the successive redox potentials of the metal centers and their stability in nonaqueous media (see below) permits the preparation of mixed-valent ions $[Cu^{II}Ni^{III}(L_1)]^{5+}$ and $[Cu^{III}Cu^{II}(L_1)]^{5+}$ by electrolysis. For example, the mixed-valent $[Cu^{II}Cu^{III}(L_1)]^{5+}$ species was prepared by electrolysis of a solution of $[Cu^{II}Cu^{II}(L_1)]^{4+}$ in anhydrous $(CH_3)_2NCHO$ (sluggish in CH_3CN; 0.1 M n-Bu_4NClO_4) at 1.5 V vs a Ag wire with Pt as working electrode. Unlike, the drastic change from salmon pink to dark green that was observed for the oxidation of $[Cu^{II}Ni^{II}(L_1)]^{4+}$ to $[Cu^{II}Ni^{III}(L_1)]^{5+}$, no distinct color change was observed for the conversion of $[Cu^{II}Cu^{II}(L_1)]^{4+}$ to $[Cu^{II}Cu^{III}(L_1)]^{5+}$ ion. Also, since there is no direct electronic delocalization between the metal centers, intervalence bands were not observed in these mixed-valent ions.

Electrochemistry. The solubility characteristics of the mononuclear species permitted electrochemical studies in aqueous chloride (1.0 M NaCl and 1.0 M HCl) medium only. An irreversible wave for the Cu^{II}/Cu^{III} couple ($E_{1/2}$ = 790 mV) and a reversible wave for the Ni^{II}/Ni^{III} couple ($E_{1/2}$ = 569 mV; ΔE_p = 63 mV) were observed for the $[Cu^{II}(H_2L_1)]^{4+}$ and $[Ni^{II}(H_2L_1)]^{4+}$ cations, respectively. Neither of these cations exhibited a proton dependence, suggesting there was no significant dissociation of the secondary ammonium ions of the unoccupied macrocyclic ring.

The redox behavior of $[Cu_2(L_1)](ClO_4)_4$ and $[CuNi(L_1)](ClO_4)_4$ was studied in CH_3CN (in 0.1 M Et_4NClO_4). Differential pulse polarography showed two waves corresponding to the successive oxidation of the metal ions for these complexes. Under identical conditions, the cyclic voltammogram of $[Cu_2(L_1)]^{4+}$ showed a reversible wave for the $Cu^{II}-Cu^{II}/Cu^{II}-Cu^{III}$ couple ($^1E_{1/2}$ = 1.120 V, ΔE_p = 60 mV over the 10−500 mV/s range) and an irreversible wave for the $Cu^{II}-Cu^{III}/Cu^{III}-Cu^{III}$ couple ($^2E_{1/2}$ = 1.430 V from differential pulse polarography). Similarly, a reversible wave for $Cu^{II}-Ni^{II}/Cu^{II}-Ni^{III}$ ($^1E_{1/2}$ = 0.75 V, ΔE_p = 60 mV, 10−500 mV/s range) couple and an irreversible wave for $Cu^{II}-Ni^{III}/Cu^{III}-Ni^{III}$ ($^2E_{1/2}$ = 1.20 V from differential pulse polarography) were also observed in the case of $[CuNi(L_1)]^{4+}$ cation.

A comparison of the electrochemical behavior of these complexes, with those of $[Cu_2(L_2)]^{4+}$ and $[CuNi(L_2)]^{4+}$, clearly demonstrates that the influencing factor in these complexes is electrostatic repulsion.[34] Unlike the complexes of L_2 which are freely soluble in aqueous acidic perchlorate medium, the complexes of L_1 are only sparingly (see below) soluble in this medium. Hence, their electrochemistry was investigated only in CH_3CN (0.1 M Et_4NClO_4). Due to the low dielectric constant

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Table 4. EPR Spectroscopic Parameters for the Complexes of L_1

complex cation	$g_\perp$	$g_\parallel$	$A_\parallel$ (G)	$D_\parallel$ (G)
$[Cu^{II}(H_2L_1)]^{4+}$	2.043	2.179	200	
$[Cu^{II}Cu^{II}(L_1)]^{4+}$				
Cu1	2.120	2.256	150	75
Cu2	2.120	2.196		
$[Cu^{II}Cu^{III}(L_1)]^{5+}$	1.982 (g_{xx})	2.116 (g_{yy})	80 (A_{yy})	
		2.386(g_{zz})	120 (A_{zz})	
$[Ni^{III}Cl_2(H_2L_1)]^{5+}$				
a	2.169	2.026	30	
b	2.235 (g_{xx})	2.120 (g_{yy})		
		2.073 (g_{zz})		
$[Cu^{II}Ni^{II}(L_1)]^{4+}$				
Cu^{II}	2.080	2.200	200	
$[Cu^{II}Ni^{III}(L_1)]^{5+}$				
Cu^{II} [c]	2.060	2.219	100	
Ni^{III} [c]	2.204	1.967		
Cu^{II} [d]	2.077	2.149	95	
Ni^{III} [d]	2.346 (g_{xx})	1.967	30	
	2.226 (g_{yy})			

[a,b] These two species are present together, depending upon how the Ni(II) was prepared. See the text and ref 17. [c] In sulfate medium. $[Co(OH_2)_6]^{3+}$ was used as oxidant. [d] In chloride medium. Slow axial ligation occurs, and hyperfine due to chloride was observed.

of this medium, the effect of electrostatic repulsive forces is also magnified. This is clearly noticeable, when the redox potentials[35] of $[Ni(cyclam)]^{2+/3+}$ ($E_{1/2}$ for $Ni^{II/III} = 0.6$ V) and $[Cu(cyclam)]^{2+/3+}$ ($E_{1/2}$ for $Cu^{II/III} = 0.968$ V) couples are compared with those of the hetero-binuclear ions $[Cu^{II}Ni^{II}(L_1)]^{4+}$ and $[Cu^{II}Ni^{II}(L_2)]^{4+}$. Under identical conditions, the $Ni^{II/III}$ couple[34] in $[Cu^{II}Ni^{II}(L_2)]^{4+}$ is not shifted relative to $[Ni(cyclam)]^{2+}$. However, the same couple in $[Cu^{II}Ni^{II}(L_1)]^{4+}$ experiences an anodic shift of 150 mV. Similarly, the $Cu^{II/III}$ couple[34] in $[Cu^{II}Ni^{II}(L_2)]^{4+}$ is more anodic by only 30 mV compared to that of $[Cu(cyclam)]^{2+}$, whereas the same couple in $[Cu^{II}Ni^{II}(L_1)]^{4+}$ exhibited an anodic shift of 230 mV. Among the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ and $[Cu^{II}Ni^{II}(L_2)]^{4+}$ ions, the successive redox potentials for $Ni^{II/III}$ ($^1E_{1/2}$) and $Cu^{II/III}$ ($^2E_{1/2}$) are separated ($^2E_{1/2} - {}^1E_{1/2}$) by 398 mV for $[Ni^{II}Cu^{II}(L_2)]^{4+}$ and by 450 mV for $[Cu^{II}Ni^{II}(L_1)]^{4+}$. This clearly reflects the electrostatic repulsion which is related directly to intermetal ion distances in these complexes. Compared to an intermetal ion distance of approximately 8.3 Å in the complexes of the L_2 type of ligand,[1c,d,36] in the complexes of L_1, such distances are shorter (approximately 6.4−6.6 Å, depending upon the coordination geometry).[17,30] While $[Cu_2(L_2)]^{4+}$ does not appear to show any reversible redox activity in CH_3CN,[14] $[Cu_2(L_1)]^{4+}$ does show two waves separated by 310 mV. The irreversibility of the second wave is anticipated, since the formation of two adjacent square-planar Cu(III) centers (d^8) would dramatically increase electrostatic repulsion.

EPR Spectroscopy. The EPR spectroscopic parameters for the complexes of L_1 are presented in Table 4. For the purpose of comparison, EPR spectra of $[Cu^{II}Cu^{II}(L_2)](ClO_4)_4$, $[Cu^{II}Ni^{II}(L_2)](ClO_4)_4$, and $[Cu^{II}Ni^{III}(L_2)](ClO_4)_4$ were also studied (available as Supporting Information). EPR spectra of the Cu^{2+} ion in $[Cu^{II}(H_2L_1)]^{4+}$, $[Ni^{II}Cu^{II}(L_1)]^{4+}$, $[Cu^{II}(L_2)]^{4+}$, and $[Ni^{II}Cu^{II}(L_2)]^{4+}$ are practically indistinguishable and comparable to that of $[Cu^{II}(cyclam)]^{2+}$.[35,37] However, a dramatic change is observed when the neighboring metal ion is Cu^{2+}, Cu^{3+}, or Ni^{3+}. This is clearly seen in Figure 2, where EPR spectra of $[Cu^{II}Ni^{II}(L_1)]^{4+}$, $[Cu^{II}Cu^{II}(L_1)]^{4+}$, $[Cu^{III}Cu^{II}(L_1)]^{5+}$, and $[Cu^{II}Ni^{III}(L_1)]^{5+}$ ions are compared. In all these cases, there is no evidence for direct spin−spin interaction between the ions since the structure of the ligand precludes such pathways. For the $[Cu^{II}Cu^{II}(L_1)]^{4+}$ ion, two sets of $g_\parallel$ features corresponding to the two Cu^{2+} ions are observed. In this cation, though the two Cu(II) centers have structurally identical environments, the CuN_4 planes are oriented approximately orthogonal (about 85°) to each other and further tilted toward each other due to the chair conformation adopted by the six-membered rings on the quaternary carbon. This generates a local anisotropy that differentiates these two Cu(II) centers. As has been shown in similar cases,[29,38] the nature of the interaction in this type of cation is purely dipolar in origin. The barycenters of these two Cu(II) signals are separated by a zero field splitting ($D_\parallel$) of 75 G in the case of $[Cu^{II}Cu^{II}(L_1)]^{4+}$ and by 90 G in the case of $[Cu^{II}Cu^{II}(L_2)]^{4+}$ ion. While the nature of the interaction is very similar, the relative orientation of CuN_4

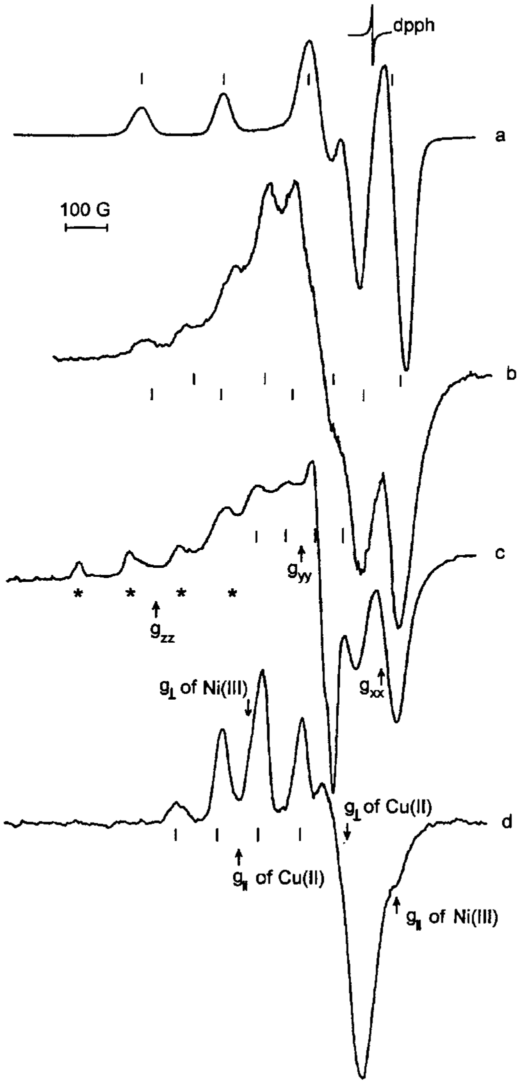

Figure 2. EPR spectra at 77 K: (a) $[Cu^{II}(H_2L_1)](ClO_4)_4$, (b) $[Cu^{II}Cu^{II}(L_1)](ClO_4)_4$, (c) $[Cu^{II}Cu^{III}(L_1)](ClO_4)_4$, and (d) $[Cu^{II}Ni^{III}(L_1)](ClO_4)_4$ ((a) and (b) in EtOH/$(CH_3)_2NCHO$ (1:1), (c) in anhydrous $(CH_3)_2NCHO$), and (d) in 1 M $HClO_4$).

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planes and the distances between the Cu^{2+} ions are distinctly different, and this is clearly reflected in their EPR spectra. When one of the Cu^{2+} centers in $[Cu^{II}Cu^{II}(L_1)]^{4+}$ is oxidized to Cu^{3+}, a dramatic change in the spectrum is observed (see Figure 2c). Owing to the presence of a square planar Cu(III) ion, the Cu^{2+} experiences significant electrostatic effect and anisotropy. As a result, the g_{xx}, g_{yy}, and g_{zz} features are fully discernible. An A_{zz} value of only 120 G was observed compared to 150 G ($A_{\|}$) observed in $[Cu^{II}Cu^{II}(L_1)]^{4+}$. The g_{yy} features also show hyperfine interactions with an $A_{yy} = 80$ G.

In the $[Cu^{II}Ni^{II}(L_1)]^{4+}$ ions, the Ni^{2+} ion is diamagnetic and hence did not influence the Cu^{2+} spectrum. However, when the Ni^{2+} ion is oxidized to Ni^{3+}, a dramatic decrease in the $A_{\|}$ value, of 100 G, for the Cu^{2+} ion in $[Ni^{III}Cu^{II}(L_1)]^{5+}$ was observed, compared to 200 G in the parent ion. The Ni^{3+} features of this cation were influenced by the nature of the solvent and counterions as observed in the case of the bis-Ni(III) cation $[Ni^{III}Ni^{III}(L_1)]^{6+}$.[14] Also, these features were found to change slowly with time due to slow axial ligation. Soon after formation (in sulfate media) the Ni(III) features showed characteristics typical of rhombic symmetry, but no hyperfine splitting from axial ligands was observed. However, when allowed to stand in the presence of chloride ion or oxidized in the presence of chloride, the gradual appearance of an axially symmetrical Ni(III) species was observed with a hyperfine splitting pattern indicative of chloride substitution.

Spontaneous Reduction of Perchlorate. The perchlorate salts of $[M^{II}M^{II}(L_1)]^{4+}$ ($M = Cu^{2+}$ or Ni^{2+}) are quite stable in the solid state. However, in solution, $[CuNi(L_1)]^{4+}$ slowly reduces perchlorate ions. In general, the complex cations of L_1 show a strong tendency to form ion pairs with perchlorate. This is evident from their low solubility in aqueous perchlorate medium (for example, even a 1×10^{-3} M solution in 0.1 M $NaClO_4$ tends to precipitate within hours). Though very weak, a definite axial interaction through one of the oxygens of perchlorate ions with the metal centers is observed in the solid-state structure of $[Cu_2(L_1)](ClO_4)_4$ described here. A similar observation has also been made in the structure of $[Ni_2(L_1)](ClO_4)_4$[30] and also in other complexes of L_1.[31] Under favorable conditions (in acidic aqueous perchlorate medium), the heterobinuclear cation $[Cu^{II}Ni^{II}(L_1)]^{4+}$ shows evidence for the spontaneous formation of a Ni(III) center (see Figure 3a). The slow and gradual appearance of the Ni(III) species also broadened the Cu^{2+} EPR features with the eventual formation of the fully oxidized species (Figure 3d). Control experiments ruled out oxygen playing any major role in this oxidation process. Even under an inert atmosphere, the slow formation of a Ni(III) species continued to occur in acidic perchlorate media, particularly in the presence of chloride or any coordinating anion.

Reduction of perchlorate ions is relatively difficult even by strong reducing agents such as Na/Hg. Kinetic studies have shown that Cr^{2+} and V^{2+} ions can reduce perchlorate ions relatively easily.[39] Fabbrizzi et al.[40] in their studies of $[Ni^{II}(HL_5)]^{3+}$ (L_5 = *N*-(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane) have identified structural features and conditions that promote reduction of perchlorate ions. In a subsequent study, we also showed that similar structural features in $[Ni^{II}(H_2L_6)]^{4+}$ enhanced reduction of perchlorate ions and the crystal structure of a *trans*-dichloronickel(III) complex obtained from such a process was reported.[41] In both these systems, the presence of one or more secondary ammonium centers facilitated through strong ion pairing the positioning of a perchlorate ion close to a Ni^{2+} ion (see line diagrams) so that the reduction process is enhanced.

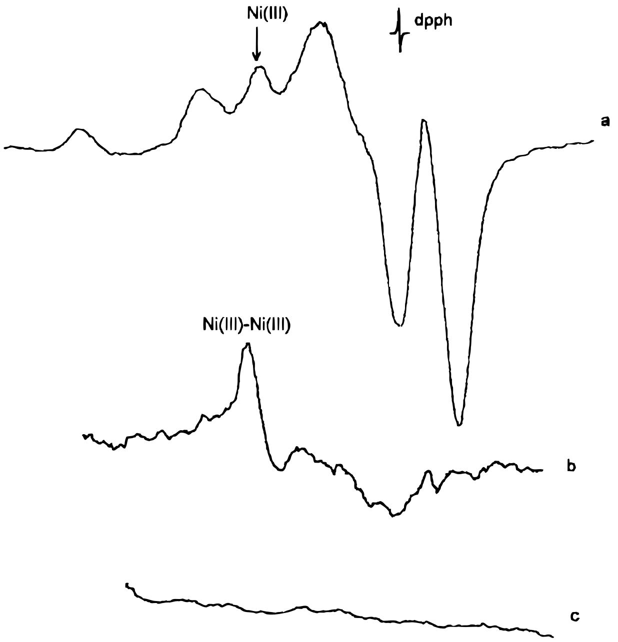
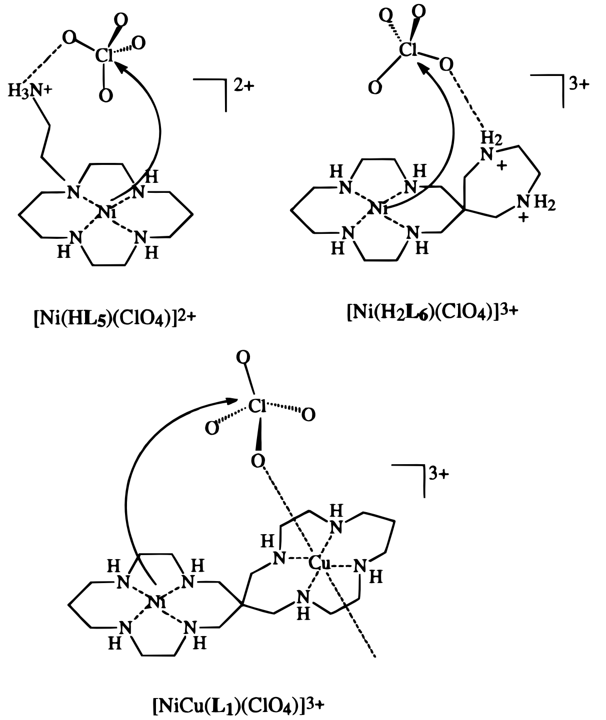


Figure 3. (a) Appearance of a Ni(III) feature in $[Cu^{II}Ni^{II}(L_1)]^{4+}$ in aqueous acidic perchlorate medium. (b) Slow appearance of a Ni(III) feature in $[Ni^{II}Ni^{II}(L_1)]^{4+}$ in CH_3NO_2. (c) Baseline for (b).

Chart 2



$[Ni(HL_5)(ClO_4)]^{2+}$

$[Ni(H_2L_6)(ClO_4)]^{3+}$

$[NiCu(L_1)(ClO_4)]^{3+}$

The binuclear complexes of L_1 have structural features that resemble those of $[Ni^{II}(HL_5)]^{3+}$ and $[Ni^{II}(H_2L_6)]^{4+}$. In the $[M_1M_2(L_1)]^{n+}$ type of cation, one of the metal ions can play

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(41) McAuley, A.; Subramanian, S. *Inorg. Chem.* **1991**, *30*, 371 and references therein.

the role of the ammonium centers as in $[Ni^{II}(HL_5)]^{3+}$ and $[Ni^{II}(H_2L_6)]^{4+}$ and bind a perchlorate ion. Compared to Ni^{2+} ion, Cu^{2+} exhibits more ionic character and is also a stronger oxidant. Thus, the Cu^{2+} ion in $[Cu^{II}Ni^{II}(L_1)]^{4+}$ essentially plays the role of binding a perchlorate ion and holding it in proximity to a Ni^{2+} ion which acts as the reducing agent. The product of reduction in many cases is a chloride ion. However, during the formation of $[Ni^{III}(HL_5)]^{4+}$ ion, the liberation of chlorine gas has been reported,[40] and in the case of $[Ni^{II}(H_2L_6)]^{4+}$, chlorine dioxide was detected as an intermediate, with chloride as the final product. In this regard, perchlorate reduction in the case of $[Ni(H_2L_1)]^{4+}$ ion might be expected. However, such an activity has not been observed to date. One of the reasons is the exceptionally low solubility of the complex, particularly in highly acidic perchlorate media. In the presence of other anions such as chloride, the solubility of this ion is enhanced. However, they stabilize pseudooctahedral structures (see discussion on UV−vis) which diminish their reducing power, and also, weakly coordinating perchlorate could not compete for access to the Ni(II) ion. As a result, the already slow reduction process may be either prevented or dramatically slowed.

In a weakly coordinating solvent such as CH_3NO_2, particularly, perchlorate ion is bound more strongly than in any polar solvents. The development of a faint EPR signal is also observed when a solution of $[Ni_2(L_1)](ClO_4)_4$ in CH_3NO_2 is stored over a very long period (6 months) (see Figure 3b). This observation suggests that even the bis-Ni(II) ion can facilitate in the reduction of perchlorate. The EPR signal described above is tentatively assigned to the $[Ni^{III}Ni^{III}(L_1)]^{6+}$ species since the mixed-valent $[Ni^{II}Ni^{III}(L_1)]^{5+}$ cation has been shown to be unstable.[14] However, a solution of $[Cu_2(L_1)](ClO_4)_4$ in CH_3NO_2 was observed to be quite stable over the same period of time. These observations further confirm not only the structural parameters essential for the binding of perchlorate but also the need for a reducing metal ion such as Ni^{2+} for the above-described process. A strong binding site near a reducing center is more favorable than two identical binding sites.

Summary

Electrostatic repulsion in $[H_4(L_1)]^{4+}$ favors isolation of the mononuclear species $[M^{II}(H_2L_1)]X_4$ (M = Ni and Cu; X = ClO_4^-) in a stepwise complexation process. Rates of substitution of H_2O in $[M^{II}(H_2O)]^{2+}$ and counterions are also an important factor. The utility of these mononuclear species in the selective formation of hetero-binuclear species is demonstrated with the preparation of $[CuNi(L_1)](ClO_4)_4$. Also, using electrochemical and spectroscopic studies, the effects of varying the nature and oxidation state of metal ions have been demonstrated.

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Supporting Information Available: Table giving unit cell data, figures showing spectrophotometric titration of $[Cu^{II}Ni^{II}(L_1)]^{4+}$ with $[Co(OH_2)_6]^{3+}$ and ESR spectra of complexes of L_2, and one X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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