

Synthesis, Spectroscopy, and Redox Behavior of the Binuclear Complex Cation $[\text{Ni}_2(6,6'\text{-spirobi(cyclam)})]^{4+}$ (cyclam = 1,4,8,11-Tetraazacyclotetradecane): Characteristics of a Transient Ni(II)–Ni(III) Species

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The homobinuclear cation $[\text{Ni}_2(\text{L}_1)]^{4+}$ ($\text{L}_1 = 6,6'\text{-C-spirobi(cyclam)}$), in which the nitrogen donors adopt a *trans*-III configuration, has been synthesized, and its redox behavior has been investigated by electrochemical, spectroscopic, and kinetic methods. Cyclic voltammetry in aqueous media ($[\text{H}^+] = 0.1$ and 1.0 M in $\text{LiNO}_3/\text{LiClO}_4/\text{CF}_3\text{SO}_3\text{Li}$) shows a single wave ($\Delta E_p = 58$ mV). With the gradual addition of $\text{LiCl}/\text{Li}_2\text{SO}_4$, this wave is shifted cathodically. Simultaneously, the value of ΔE_p also gradually decreases from 58 to 37 mV in 1.0 M chloride and to 42 mV in 0.75 M sulfate media. Similar trends are also noticed in linear dc voltammograms. $[\text{Ni}_2(\text{L}_1)](\text{ClO}_4)_4$ in CH_3CN ($[\text{TEAP}] = 1.0$ M; $E_{1/2}^1 = 0.735$ V and $E_{1/2}^2 = 0.835$ V vs Fc/Fc^+) and $[\text{Ni}_2(\text{L}_1)]\text{Cl}_4$ in CH_2Cl_2 ($[\text{TEAC}] = 0.1$ M; $E_{1/2}^1 = 0.640$ V and $E_{1/2}^2 = 0.766$ V vs Fc/Fc^+) media show two overlapping waves. In nitromethane, the redox process is complicated by adsorption. Because of the very small difference in redox potentials, the selective oxidation of one of the Ni(II) centers to form a mixed-valent Ni(II)–Ni(III) species is not practical. However, during reductive decomposition of the bis-Ni(III) species, a mixed-valent species could be identified. In stopped flow kinetics experiments, the UV–visible spectrum of a transient Ni(II)–Ni(III) intermediate in acetonitrile has been elucidated by one-electron reduction of the bis-Ni(III) species with $[\text{Ni}^{\text{II}}(9\text{-aneN}_3)_2]^{2+}$ ($9\text{-aneN}_3 = 1,4,7\text{-triazacyclononane}$). The differences in the redox behavior in various media are explained in terms of electrostatic interactions between the adjacent nickel centers influenced by sterically controlled axial ligation of counterions and solvents. Evidence for changes in coordination geometry in Ni(II) and Ni(III) species obtained from UV–vis and ESR studies is also presented.

Introduction

One of the objectives of studying binuclear complexes is to understand the nature of interactions between the metal centers and how they affect redox processes.¹ In this regard, binuclear macrocyclic complexes represent an important class of compounds, since mixed-valent species with less common oxidation states can be stabilized.² Redox behavior in such complexes is controlled by the nature of donor atoms, the ability of the ligand to adapt to coordination geometry changes, and the distance between metal centers. Many binuclear macrocyclic complexes have been studied in which these parameters are varied systematically, and the influence of these parameters on electron transfer and electronic and magnetic properties has been demonstrated.³ The relative orientation of the metal centers in

binuclear complexes also plays a dominant role in determining magnetic⁴ and electron transfer properties.⁵ An important aspect is to distinguish between two successive $1e^-$ transfers and a simultaneous $2e^-$ transfer process, particularly when the redox active centers are identical and there is no through-bond interaction between the metal centers.³ Solvent molecules and counterions can play a significant role during such processes, particularly when the metal centers are coordinately unsaturated and are prone to undergo geometry changes.⁶ This is particularly true in the case of the Ni(II)/Ni(III) couple, where Ni(II) ions prefer to adopt a square planar geometry and the Ni(III) ion, an octahedral geometry. These geometric, electrochemical, and spectroscopic aspects of Ni(II)/Ni(III) macrocyclic complexes have been reviewed extensively.^{6a,7}

A series of multiloop crown ethers based on pentaerythritol, reported by Weber, were shown to complex alkali metal ions.⁸ Homotopic, azamacrocyclic ligands based on pentaerythritol were unknown until the first report appeared from this laboratory

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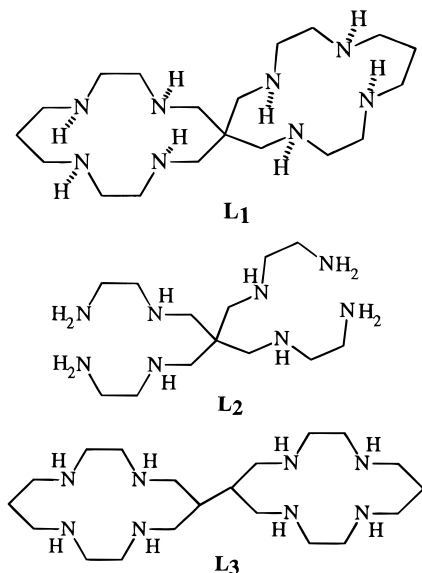
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on the crystal structure of the perchlorate salt of the binuclear Ni(II) complex of the ligand 6,6'-spirobi(cyclam), L_1 .⁹ Since then several papers on complexes of macrocyclic ligands based on pentaerythritol have appeared.¹⁰ In L_1 , the cyclam rings are large enough to bind a transition metal ion. However, they are not flexible enough to sandwich a single metal ion like the multiloop crown ethers.¹¹ Also, the ligand is capable of forming mononuclear complexes by complexation of one of the rings while the other remains protonated.¹² Since the two cyclam rings in L_1 are formed at the quaternary carbon of the pentaerythritol moiety, the planes containing the metal ions and the donors are "quasi-orthogonal" to each other, a rigid orientation that does not change significantly in solution. Such conformational rigidities are commonly experienced in *gem*-dialkyl-substituted compounds and more so in spiro-linked cyclic compounds. Indeed, this has been shown to enhance binding of Ni(II) ions significantly.¹³ Though somewhat sterically restricted, the two metal centers in the cyclam rings of L_1 can undergo a stepwise change in coordination geometry from bis-square planar to distorted bis-pseudooctahedral by successive axial ligation of the metal centers.

Following the synthesis of 6,6'-spirobi(cyclam),⁹ we report here the preparation, spectroscopy (UV-vis and ESR), and redox behavior of the homobinuclear cation $[\text{Ni}_2(L_1)]^{4+}$ with the N-donors in the *trans*-III configuration. Evidence that axial ligation induces a steric effect that affects the redox process is also presented.



Experimental Section

CAUTION! Perchlorate salts are potentially explosive when heated or dried on a filter paper. Sintered glass funnels should be used for filtration, and only small quantities of these complexes

should be air dried under suction. Extreme care should be taken to avoid contact with combustible organic matter and heat.

$[\text{H}_4L_1](\text{ClO}_4)_4$. The ligand L_1 was prepared as described previously¹⁴ and purified as follows. To 1.0 g (2.6 mmol) of the crude ligand dissolved in 50 mL of a mixture of 1:1 v/v ethanol and water was added 70% HClO_4 dropwise until the mixture was distinctly acidic. Colorless microcrystals of composition $[\text{H}_4L_1](\text{ClO}_4)_4$ were precipitated. The solution was further cooled or diluted with absolute ethanol to complete the precipitation. The crystalline salt was filtered under suction in a glass frit, washed successively with cold ethanol and ether, and dried under suction. Further, it was recrystallized from boiling water containing a trace of perchloric acid to yield analytically pure crystals. Yield: 1.50 g (1.9 mmol; 73%). Calcd for $\text{C}_{19}\text{H}_{48}\text{N}_8\text{Cl}_4\text{O}_{16}$: C, 28.99; H, 6.15; N, 14.25. Found: C, 28.88; H, 6.09; N, 14.12.

The pure ligand as a free base can be obtained by basifying a solution of the perchlorate salt with 5 M NaOH and extracting with chloroform.

$[\text{Ni}_2(L_1)]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. To a solution of 0.384 g (1.0 mmol) of ligand L_1 in 25 mL of aqueous ethanol (1:1 v/v) was added, with stirring, 0.475 g (2.0 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 10 mL of water, and the mixture was refluxed for 30 min. This solution was evaporated to dryness. The resultant moist yellow complex was dried in an oven at 100 °C for about 4 h, yielding pale violet $[\text{Ni}_2(L_1)]\text{Cl}_4$. The latter material was extracted with 3×50 mL of warm chloroform (large quantities can be extracted in a Soxhlet apparatus). Either the combined extracts were concentrated to yield the anhydrous tetrachloro complex as a pale lilac powder or the chloroform solution was left partially open to air to produce a pale lilac colored microcrystalline dihydrate species. Yield: 0.58 g (0.85 mmol). Calcd for $\text{C}_{19}\text{H}_{48}\text{N}_8\text{O}_2\text{Ni}_2\text{Cl}_4$: C, 33.55; H, 7.12; N, 16.48; Ni, 17.27; Cl, 20.88. Found: C, 33.56; H, 7.06; N, 16.35; Ni, 17.10; Cl, 20.70. FAB MS of the anhydrous species: Calcd for $[\text{C}_{19}\text{H}_{44}\text{N}_8\text{Ni}_2\text{Cl}_3]^+$, 608.1; obsd: for $[\text{C}_{19}\text{H}_{44}\text{N}_8\text{Ni}_2\text{Cl}_3]^+$, 607.8.

$[\text{Ni}_2(L_1)](\text{ClO}_4)_4$. To a solution of 0.384 g (1.0 mmol) of the ligand L_1 dissolved in 25 mL of ethanol was added 0.73 g (2.0 mmol) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10 mL of water, and the mixture was refluxed for about 30 min to form a pale violet solution of the bis-octahedral complex. This solution was filtered hot. Upon cooling, the pale yellow resultant solid (0.88 g, 0.97 mmol) was filtered, dried under suction, and recrystallized from 25–30 mL of boiling water containing a trace of perchloric acid to give orange yellow crystals. Yield: 0.8 g (0.9 mmol). Calcd for $\text{C}_{19}\text{H}_{44}\text{N}_8\text{Ni}_2\text{Cl}_4\text{O}_{16}$: C, 25.36; H, 4.93; N, 12.45; Ni, 13.05. Found: C, 25.49; H, 4.93; N, 12.34; Ni, 12.98. The electrospray mass spectrum in CH_3CN shows $[\text{M} - \text{HClO}_4]^+ = 799.0$ as the major fragment (mass calcd for $\text{C}_{19}\text{H}_{43}\text{N}_8\text{Ni}_2\text{Cl}_3\text{O}_{12}$, 799.1).

$[\text{Ni}_2(L_1)](\text{ClO}_4)_6$. A dried and freshly distilled solution of acetonitrile 1.0×10^{-3} M in $[\text{Ni}_2(L_1)](\text{ClO}_4)_4$ and 0.1 M in *n*-Bu₄NClO₄ was electrolyzed in an H-shaped cell with Pt electrodes as anode and cathode. A Hewlett-Packard power supply was used, and the electrolysis was conducted at a constant potential of 2.0 V. The completion of oxidation was monitored at 302 nm ($\epsilon = 1.72 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). A blanket of dry N₂ was provided to protect the cell from moisture. The resulting dark green solution of the complex ion remained stable for several days. The bis-Ni(III) salt precipitated on standing for about a week in a freezer. The dark green solids were collected by filtration under a N₂ atmosphere and dried under vacuum. This dark green solid appeared polymeric in nature and was insoluble in most solvents except (CH₃)₂SO. For the purpose of solution studies, a freshly prepared solution was diluted to 1×10^{-4} M and stored. The solution species was characterized by UV-visible and ESR spectroscopy.

Reagent quality chemicals (Aldrich Chemical Co.) were used as received. Lithium salts were prepared and purified by crystallization. Nonaqueous solvents and electrolytes were purified by standard methods.¹⁵ Tetra-*n*-butylammonium perchlorate (*n*-Bu₄NClO₄) purchased from GFS Chemicals was used as received. Ligand L_3 was prepared as described by Fabbrizzi et al.¹⁶ Microanalyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada.

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UV-visible spectra were recorded on either a Perkin-Elmer Lambda 4B or a Cary 17 dual-beam spectrophotometer. ESR spectra were recorded in an X-band Varian ES-6 spectrometer, in either aqueous or CH₃CN solutions at liquid N₂ temperatures or as indicated. Diphenylpicrylhydrazine (DPPH, $g = 2.0037$) was used as an external standard. Mass spectra were obtained on a Kratos Concept Model 2H mass spectrometer by FAB or electrospray techniques. In all cases, the theoretical isotopic distributions of relevant peaks were calculated and found to agree with the experimentally observed spectra.

A three-electrode cell configuration was used in electrochemical experiments. Platinum bead electrodes were used as working electrodes. Redox potentials in aqueous media were measured against a saturated calomel electrode (SCE) (0.244 V vs NHE), and an Ag/Ag⁺ electrode¹⁷ was used for measurements in nonaqueous media. The Fc/Fc⁺ couple was used as either 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 the data. Anion dependence of the redox potential was studied as follows: To a 10 mL aliquot of the bis-Ni(II) complex (1.92×10^{-3} M) in 1.0 M LiNO₃/LiClO₄ containing 0.1 M HNO₃/HClO₄ were made sequential additions, using a microsyringe, of 40 μ L of 2.5 M LiCl (for chloride ion) or a 66 μ L aliquot of 1.5 M Li₂SO₄ (for sulfate ion). The number of anions that axially coordinate upon oxidation was calculated from a plot of $\Delta E_{1/2}$ vs $\ln [X]$ ^{15,18} where $\Delta E_{1/2}$ is the redox potential measured at various concentrations of the anion. 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. Reversibility of cyclic voltammograms was confirmed as described elsewhere.¹⁸ Since a pulse width of 10 mV was used in nonaqueous electrochemical experiments, a working curve constructed from the data of Richardson and Taube¹⁹ was used directly to evaluate the individual redox potentials for the successive 1e⁻ processes in CH₃CN and CH₂-Cl₂. The accuracy of the measured potentials was within ± 5 mV. Linear scan voltammetric experiments were performed on a Metrohm Polarecord 626 instrument, and the DP-50 mode was used to record the differential pulse polarograms in aqueous media. Coulometric experiments were performed on a Princeton Applied Research potentiostat model 173 using the digital coulometer model 172. All electrochemical experiments were performed at 25 ± 0.3 °C.

A stopped-flow apparatus (Applied Photophysics) interfaced to an Acorn A5000 computer with RISC OS was used in conjunction with Spectrakinet software version 2.24. The Ni(III) species [Ni₂(L₁)]⁶⁺, [Ni(9)aneN₃]₂³⁺, and [Ni₂(L₃)]⁶⁺ (L₃ = 6,6-bis(cyclam)) were prepared by electrolysis. An acetonitrile solution of 1×10^{-3} M [Ni(9)aneN₃]₂³⁺ in 0.05 M *n*-Bu₄NClO₄ was used as a reference during the measurement of Ni(II)–Ni(III) transient spectra ($T = 20 \pm 0.1$ °C). A Haake D8 model thermostat was used to control temperature.

Results

Synthetic Aspects. L₁ was readily purified by precipitation as the perchlorate salt [H₄(L₁)](ClO₄)₄ with recrystallization from hot water. The Ni(II) complexes were prepared by directly reacting either the ligand or its salt with an appropriate Ni(II) salt in aqueous media. The perchlorate salt of the *trans*-III [Ni₂(L₁)]⁴⁺ cation is only sparingly soluble in distilled water and almost insoluble in dilute perchloric acid. This facilitates the isolation of the [Ni₂(L₁)]⁴⁺ cation as the perchlorate salt in quantitative and analytically pure form. [Ni₂(L₁)](ClO₄)₄ is highly soluble in acetonitrile, but only moderately so in CH₃-

Table 1. UV-Visible Spectroscopic Data of Binuclear Ni(II) and Ni(III) Cations in Various Solvents

complex	solvent	λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹)
[(Ni ^{II}) ₂ (L ₁)](ClO ₄) ₄	H ₂ O	449	75
		330	23
	CH ₃ CN	661	9
		471	24
		313	26
[(Ni ^{II}) ₂ (L ₁)]Cl ₄	CH ₃ NO ₂	455	137
	CH ₂ Cl ₂	640	15
		580	4
[(Ni ^{III}) ₂ (L ₁)](ClO ₄) ₆	1 M HClO ₄	218	1.8×10^4
		304	1.4×10^4
		353	1.0×10^4
[(Ni ^{III}) ₂ (L ₁)](ClO ₄) ₆	CH ₃ CN	302	1.7×10^4
		373	1.3×10^4

NO₂. In the absence of moisture, the chloro complex [Ni₂(L₁)Cl₄] is soluble in chlorinated solvents but insoluble in CH₃CN and CH₃NO₂.

UV-Visible Spectroscopy. The UV-visible spectroscopic data for the bis-Ni(II) and the bis-Ni(III) cations in various media are listed in Table 1. In aqueous media, the [(Ni₂(L₁)]⁴⁺ cation exists as an equilibrium mixture of the square planar and pseudooctahedral species. The thermodynamic parameters for the equilibrium in aqueous media ($[(\text{Ni})_2(\text{L}_1)]^{4+} = 9.65 \times 10^{-4}$ M; [NaClO₄] = 0.1 M; $\Delta H = 5.0 \pm 0.1$ kcal mol⁻¹; $\Delta S = 17.1 \pm 1$ eu) obtained from temperature dependence studies are almost identical to that for the [Ni(II)(cyclam)]²⁺ cation ($\Delta H = 5.4 \pm 0.4$ kcal mol⁻¹; $\Delta S = 20.0 \pm 2$ eu) under similar conditions.²⁰ These values and the molar absorptivities at 25 °C for the various absorption bands in water suggest that only about half (52%) of the Ni(II) centers exist in octahedral geometry. When the concentration of chloride is increased (from [LiCl] = 0.0 to 6.0 M), as a result of increased ionic strength, more of the square planar form is formed. Simultaneously, a bathochromic shift of the band at 450 nm by about 10 nm was observed. Temperature dependent studies in 1.0 M LiCl indicate that the equilibrium observed in this medium is not simply between the square planar and octahedral species alone. The bathochromic shift has been attributed to the formation of a five-coordinate species^{21a,c} which must be included in the overall equilibria. Five-coordinate species are capable of self-assembly into a cationic chloro-bridged polymer, particularly in the Ni(III) state. Formation of such species has been observed crystallographically in the bis-Cu(II) analogue, {[Cu₂(L₁)Cl]_n(ClO₄)_{3n}}^{21b}

The square planar–octahedral equilibrium is also observed in CH₃CN ($[(\text{Ni})_2(\text{L}_1)]^{4+} = 5.58 \times 10^{-4}$ M; [*n*-Bu₄NClO₄] = 0.1 M), and the bis-pseudooctahedral form is the predominant species (about 78%) in this medium. In CH₃NO₂ (0.1 M *n*-Bu₄NClO₄), both Ni(II) centers adopt square planar geometry and the neutral [Ni₂(L₁)Cl₄] species in CHCl₃ shows two distinct bands at 580 and 640 nm indicating the presence of two types of pseudooctahedral Ni(II) centers. The bis-square planar form found in CH₃NO₂ and the bis-pseudooctahedral form found in CHCl₃ are the sole species in these solvents, since they do not exhibit the square planar–octahedral equilibrium observed in aqueous (0.1 M NaClO₄) and acetonitrile (0.1 M Et₄NClO₄) media.

The bis-Ni(III) species was prepared by oxidation of [Ni₂L₁]⁴⁺ either with [Co(OH₂)₆]³⁺ in 3 M HClO₄ or with K₂S₂O₈ (in

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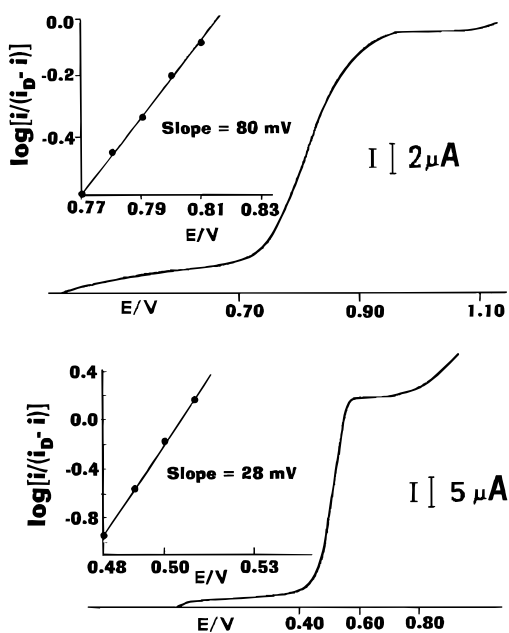


Figure 1. DC polarograms of $[\text{Ni}_2(\text{L}_1)]^{4+}$ in aqueous media: $[[\text{Ni}_2(\text{L}_1)]^{4+}] = 1.92 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 0.1 \text{ M}$. Top: $[\text{Cl}^-] = 0$. Bottom: $[\text{Cl}^-] = 0.01 \text{ M}$.

neutral aqueous media). In a spectrophotometric titration, the $[\text{Ni}_2(\text{L})]^{4+}$ cation in 1 M HClO_4 consumed exactly 2 equiv of $[\text{Co}(\text{OH}_2)_6]^{3+}$ (3 mL of $9.65 \times 10^{-5} \text{ M}$ $[(\text{Ni}_2(\text{L}_1)]^{4+}$ solution consumed $10 \times 3 \mu\text{L}$ of 0.0193 M $[\text{Co}(\text{OH}_2)_6]^{3+}$). The conversion of the Ni(II) to Ni(III) species occurred with an isobestic point at 250 nm (see Figure S1, Supporting Information). The bis-Ni(III) species shows three bands at 350, 303, and 220 nm characteristic of such complexes.⁷ The addition of various anions did not affect these optical features to any significant extent (cf. ESR spectra). The species $[\text{Ni}_2(\text{L}_1)(\text{CH}_3\text{CN})_4]^{6+}$ in acetonitrile was prepared either by electrolytic oxidation or by chemical oxidation with the NO^+ cation. Two prominent bands at 373 and 302 nm are observed.

Electrochemical Studies. (A) Studies in Aqueous Media. In acidic aqueous media ($[\text{H}^+] = 0.1$ and 1.0 M in LiClO_4 , LiNO_3 , or LiSO_3CF_3), the cyclic voltammogram of the cation $[\text{Ni}_2(\text{L}_1)]^{4+}$ shows only one wave ($\Delta E_p = E_{p,a} - E_{p,c} = 58 \text{ mV}$) in the temperature range $2\text{--}25^\circ\text{C}$. Though a value of 58 mV for ΔE_p was observed, the couple was not chemically reversible. Careful observation indicated that the reduction wave broadened and a small cathodic shoulder wave was noticeable owing to a homogeneous reaction involving the Ni(III) species (see discussions on ESR spectra). With increasing concentrations of chloride or sulfate ions, the reversibility characteristics of the wave improved dramatically and, also, a gradual cathodic shift of the wave (both peaks) was observed with the peaks becoming more sharp. Concurrently, a gradual decrease in the value of ΔE_p ($E_{p,c} - E_{p,a}$) also was observed. The ΔE_p values decreased from 58 mV in 1.0 M LiNO_3 or LiClO_4 or LiSO_3CF_3 media to 37 mV for chloride concentrations (from 0.0 to 0.1 M) and to 42 mV for an increase in sulfate concentrations (from 0.0 to 0.075 M). Further changes, if any, observed at higher concentrations of these anions were insignificant. The DC polarograms obtained under identical conditions also showed similar trends (Figure 1). The slopes for the $\log[i/(i_d - i)]$ vs E plots were found to be 80 mV in $[\text{LiNO}_3] = 1.0 \text{ M}$ and $[\text{H}^+] = 0.1 \text{ M}$. However, on increasing the concentrations of chloride and sulfate, this value decreased to 28 mV in $[\text{Cl}^-] = 0.1 \text{ M}$ and to 42 mV in $[\text{SO}_4^{2-}] = 0.075 \text{ M}$.

Coulometric studies under conditions employed for the above voltammetric experiments indicate that an overall two-electron

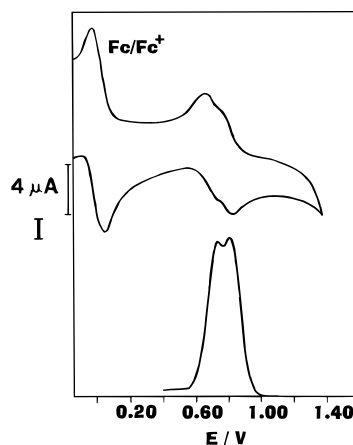


Figure 2. Cyclic voltammogram (top) and differential pulse polarogram (bottom) of $[\text{Ni}_2(\text{L}_1)]^{4+}$ in acetonitrile: $[[\text{Ni}_2(\text{L}_1)]^{4+}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{Et}_4\text{NClO}_4] = 0.1 \text{ M}$.

oxidation of $[\text{Ni}_2(\text{L}_1)]^{4+}$ was the sole process. The anion dependence of the $E_{1/2}$ potentials from cyclic voltammetric studies indicate that, per $[\text{Ni}_2(\text{L}_1)]^{6+}$ cation, either 3.9 chlorides or 3.3 sulfates are bound. This trend is consistent with the expected changes for the formation of a bis-Ni(III) ion. However, the number of ligands bound and ESR studies (vide infra) suggest that both of the Ni(III) centers may not adopt identical pseudooctahedral symmetries.

(B) Studies in Nonaqueous Media. Cyclic voltammetry of the cation $[\text{Ni}_2(\text{L})]^{4+}$ in acetonitrile media (0.1 M Et_4NClO_4 or 0.1 M $n\text{-Bu}_4\text{NClO}_4$) shows two overlapping reversible waves (Figure 2 (top)). Under identical conditions, two closely spaced but well-resolved peaks are observed in the differential pulse polarogram (Figure 2 (bottom)). The calculated redox potentials for the successive $1e^-$ transfers are 0.735 ($^{\text{AN}}E_{1/2}^{\text{AN}}$) and 0.835 ($^{\text{AN}}E_{2/2}^{\text{AN}}$) (vs Fc/Fc^+ ; $\text{AN} = \text{CH}_3\text{CN}$) respectively.¹⁹

In CH_3NO_2 , where only the square planar form is present, all of the electrochemical studies were complicated by adsorption of the electroactive species on the electrode. In CH_2Cl_2 , with only the pseudooctahedral species present, and in the presence of 0.1 M Et_4NCl , two waves corresponding to the successive $1e^-$ oxidations were observed. Again, the calculated redox potentials for the successive $1e^-$ steps are 0.640 ($^{\text{DCM}}E_{1/2}^{\text{DCM}}$) and 0.766 ($^{\text{DCM}}E_{2/2}^{\text{DCM}}$) (vs Fc/Fc^+ ; $\text{DCM} = \text{CH}_2\text{Cl}_2$) respectively.¹⁹

ESR Spectroscopy. ESR spectra of the Ni(III) species showed significant variations depending upon the oxidation procedure, the nature of solvents and counterions, and also the age of the sample.²² The ESR spectrum of the bis-Ni(III) species immediately after generation in chloride-free aqueous media (in 1 M H^+ ; oxidized with $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$) is shown in Figure 3a. An identical spectrum was also observed in neutral media when oxidation was carried out with $\text{K}_2\text{S}_2\text{O}_8$. Addition of chloride ($[\text{Cl}^-] = 0.1 \text{ M}$) to these species causes the feature at 2.005 to exhibit a septet hyperfine splitting pattern ($A_{\parallel} = 28.5 \text{ G}$) (see Figure 3b). This confirms that these features at $g = 2.181$ and 2.005 can be assigned to g_{\perp} and g_{\parallel} , respectively, of a pseudooctahedral Ni(III) center. Additional features at $g = 2.237$, 2.121 , and 2.037 (identified by arrows in Figure 3a) result from a Ni(III) center that appears to lack axial symmetry. Over a period of several minutes at room temperature, the latter features gradually diminished with the simultaneous growth of characteristics corresponding to the axially symmetric species. However, the latter features did not disappear completely. The

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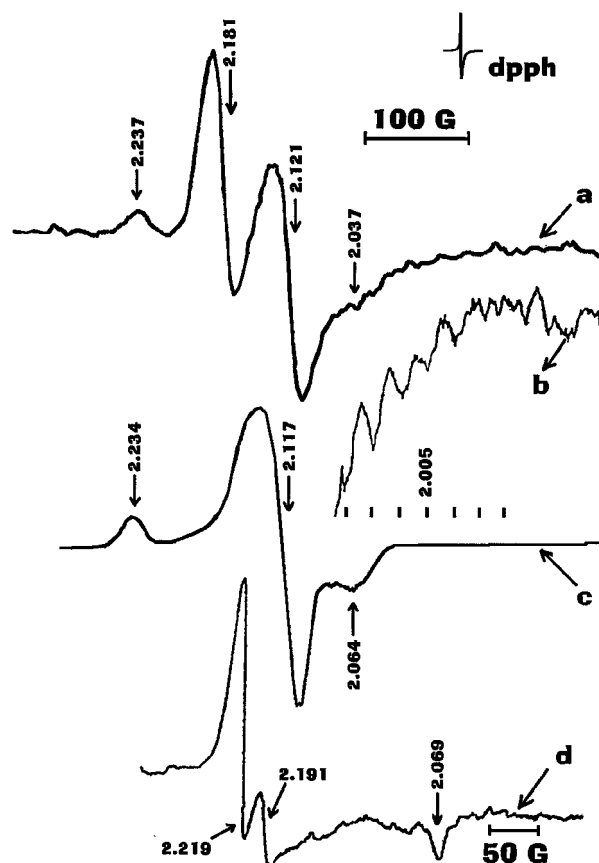


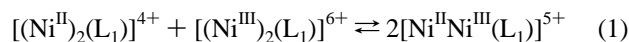
Figure 3. ESR spectrum of the Ni(III) species in various media: $[\text{Ni}_2(\text{L}_1)]^{4+} = 1.0 \times 10^{-3} \text{ M}$ (a) soon after oxidation ($[\text{Cl}^-] = 0$); (b) $[\text{Cl}^-] = 1.0 \text{ M}$; (c) $[\text{Cl}^-] = 6.0 \text{ M}$ (for a, b, and c, aqueous media; $\text{H}^+ = 1.0 \text{ M}$; oxidant = $[\text{Co}(\text{OH})_2]^{3+}$); (d) spectrum in CH_3NO_2 weeks after generation (oxidant = NOPF_6) (see text).

rapid modification and loss of the ESR signals in the absence of chloride (or any other coordinating anions) is due to decomposition of the bis-Ni(III) species to the bis-Ni(II) species via a mixed-valent Ni(II)–Ni(III) species. It is suspected that the small shoulder peak observed during the reduction scan in the cyclic voltammogram may be associated with this mixed-valent species. A detailed kinetic analysis of this process is underway.²³ The bis-Ni(III) species obtained by electrochemical oxidation in aqueous media ($[\text{LiClO}_4] = 0.1 \text{ M}$; $[\text{H}^+] = 0.1 \text{ M}$) showed very similar behavior.

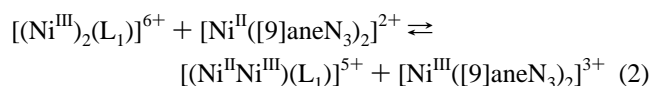
In contrast, the bis-Ni(III) species formed in 6 M HCl (see Figure 3c) showed all three features distinctly at $g = 2.234$, 2.117, and 2.064 devoid of the g_{\perp} and g_{\parallel} features observed in Figure 3a. It showed neither any significant decomposition over weeks nor any change in spectroscopic features. Long lived features similar to the latter were also derived in oxidations using NOBF_4 in both CH_3CN and CH_3NO_2 with $g = 2.259$, 2.139, and 2.064 for the former and in CH_3NO_2 , $g = 2.314$, 2.184, and 2.072. These features also essentially remain unchanged with dilution. After a long period of several weeks, changes were observed with the spectra in 6 M HCl and CH_3NO_2 to eventually form axially symmetric species. For example, the spectrum obtained in CH_3NO_2 is shown in Figure 3d.

UV–Visible Spectrum of the Ni(II)–Ni(III) Species. Electrochemical studies indicate that selective oxidation of one of the Ni(II) centers is not feasible in aqueous media. Only in CH_3CN and CH_2Cl_2 , are two reversible waves corresponding to a stepwise $1e^-$ oxidation observed. However, the difference

between the successive redox potentials in these solvents is not sufficiently great to generate the mixed-valent Ni(II)–Ni(III) ion on a preparative scale. Hence, the alternative method of *in situ* formation of the mixed-valent species in a stopped-flow cell was considered. Comproportionation of the isovalent bis-Ni(II) and bis-Ni(III) species (eq 1) in CH_3CN [isovalent species] = $1.0 \times 10^{-4} \text{ M}$; $[\text{n-Bu}_4\text{NClO}_4] = 0.05 \text{ M}$) was investigated. Though a very small spectroscopic change was



observed on the shoulders of the band at 370 nm of the bis-Ni(III) species, this change in absorbance was too weak to derive any reliable information. However, the kinetics of reduction of the bis-Ni(III) species in acetonitrile with $1e^-$ reductants were studied by stopped-flow techniques. Preliminary studies indicated that the outer sphere reductant $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$ with a redox potential²⁴ of 0.525 V vs Fc/Fc^+ in CH_3CN is a suitable candidate to reduce the bis-Ni(III) species as shown in eq 2.



When equimolar quantities of $[\text{Ni}(\text{[9]aneN}_3)_2]^{2+}$ and $[\text{Ni}_2(\text{L}_1)]^{6+}$ ($[\text{Ni}(\text{[9]aneN}_3)_2]^{2+} = [\text{Ni}_2(\text{L}_1)]^{6+} = 1.0 \times 10^{-4} \text{ M}$; $[\text{n-Bu}_4\text{NClO}_4] = 0.05 \text{ M}$) were mixed, a dramatic change in the UV–visible spectrum was observed. This reaction was monitored at various wavelengths in the range 350–420 nm. From such biphasic kinetic traces, a very fast formation step was observed followed by a slightly slower step.²⁵ A typical trace observed at 325 nm is shown in Figure S4 (Supporting Information), where a double-exponential function was used to calculate the rate constant. The rate constants for the formation of the mixed-valent species and its disproportionation were found to be $(40.7 \pm 3.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $(13.4 \pm 0.9) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively. For the purpose of comparison, the reduction of $[\text{Ni}_2(\text{L}_3)]^{6+}$ was also studied. In this case also, biphasic kinetics were observed. However, the high solubility of the $[\text{Ni}_2(\text{L}_3)](\text{ClO}_4)_6$ permitted this study to be conducted under pseudo-first-order conditions. The resulting second-order rate constants were found to be $(5.06 \pm 0.86) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $(0.75 \pm 0.20) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively. These studies indicate that, under the conditions employed, the rate of disproportionation of the mixed-valent $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}(\text{L}_1)]^{5+}$ species is about 3 times slower than its rate of formation, and for the species $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}(\text{L}_3)]^{5+}$ was at least 7 times slower. In separate kinetic scan experiments, the derivation of the time-resolved UV–visible spectra of the mixed-valent species was undertaken. Under the conditions employed, the formation of $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}(\text{L}_1)]^{5+}$ was complete within 120 ms, and the spectrum shows two features at 296 and 380 nm (Figure 4). This species disproportionated to the isovalent species within a second, showing an isobestic point at 280 nm. The UV–visible features are very similar to those observed for the bis-Ni(III) species except for their relative intensities. This spectrum of $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}(\text{L}_3)]^{5+}$ also showed two bands at 380 and 420 nm but no significant changes in the 275–340 nm range.

Discussion

Though in a number of respects the behavior of the cation $[\text{Ni}_2(\text{L}_1)]^{4+}$ is similar to that of $[\text{Ni}(\text{cyclam})]^{2+}$, there are also distinct differences.^{7,9,20,24} The proximity of two adjacent

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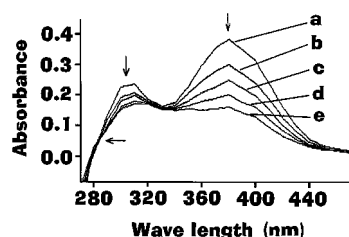
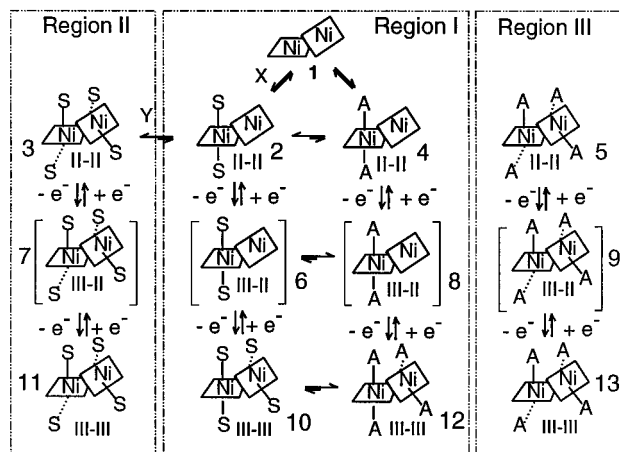


Figure 4. Time-resolved spectrum for the decomposition of the mixed-valent Ni(II)–Ni(III) species generated in CH₃CN ([*n*-Bu₄NClO₄] = 0.05 M) in a stopped-flow mixing chamber: (a) 0.012 s, (b) 0.062 s, (c) 0.125 s, (d) 0.250 s, (e) 0.500 s.

Scheme 1. Electrochemical Behavior in Aqueous (Region I), in CH₃CN (Region II), and in CHCl₃ (Region III) Media^a



^a A = anion; S = solvent. II–II, III–II, and III–III indicate oxidation states of metal ions. Structures in square brackets represent mixed-valent intermediates.

cyclam rings induces a subtle steric effect during axial ligation and, via the adjacent metal ion, an electrostatic effect which has a dramatic influence on the redox behavior. The overall behavior of the [Ni₂(L₁)]⁴⁺ cation in various media can be represented by the different regions as outlined in Scheme 1.

Region I. This region describes the behavior of [Ni₂(L₁)]⁴⁺ in aqueous media. On the basis of the molar absorptivities alone (0.1 M LiClO₄), it is reasonable to propose that equilibrium **X** dominates and **2** is the major species. Also, in aqueous media, there is no evidence for the existence of bis-octahedral species **3** and **5**. In aqueous 0.1 M LiClO₄ (or LiNO₃/CF₃SO₃Li) medium, the axial ligands in **2** are water molecules. Interconversion between species **2** and **1** occurs with an isobestic point. Hence, any intermediate mixed-ligand species of the type [Ni₂(L₁)(A)(H₂O)]ⁿ⁺ (A = ClO₄[−], NO₃[−], or CF₃SO₃[−]) need not be considered. Thus, in the presence of noncoordinating anions, the aqueous redox chemistry is controlled predominantly by the species **2**.

The 1e[−] oxidation of a Ni(II) center occurs with axial binding of either a solvent (S) or an anion (A). In aqueous media, the 1e[−] oxidation of [Ni₂(L₁)]⁴⁺ will result in the mixed-valent cation [(Ni^{III}(S)₂Ni^{II})(L₁)]⁵⁺, where S = H₂O, in which the electrostatic repulsion between the nickel centers is increased. This is expected to make the removal of a second electron from the neighbouring Ni(II) center even more difficult. Under such circumstances, ^WE_{1/2} > ^WE_{1/2} (W = water) and two 1e[−] waves should be observed. However, the observed cyclic voltammogram with ΔE_p = 58 mV has the characteristics described by Flanagan et al.²⁶ for multielectron transfer in complexes with

noninteracting metal centers. As has been shown by coulometric studies, though two electrons are transferred, the value of ΔE_p = E_p − E_{p/2} = 58 mV suggests that these potentials are separated only by a statistical value of ΔE_{1/2} = ^WE_{1/2} − ^WE_{1/2} = 35.6 mV. This difference is not sufficient (a minimum of 120 mV is required) to observe two distinct 1e[−] waves. Again, though ΔE_p = 58 mV suggests electrochemical reversibility (0.1 M H⁺; 1.0 M ClO₄[−]), the presence of a cathodic shoulder suggests chemical irreversibility due to a homogeneous reaction involving the transformation of the bis-Ni(III) species. This is evident in the time-dependent changes observed in the ESR spectra of the freshly generated bis-Ni(III) species as described earlier.

At low concentrations of chloride and sulfate (0.1 M), equilibrium **X** is not visibly disturbed to any significant extent. However, the redox behavior is significantly affected, suggesting the existence of species of type **4**. Since these anion-bound species **4** will have a much lower redox potential than **2**, ^AE_{1/2} < ^WE_{1/2}, (A = anion; W = water), their oxidation or reduction is much more facile, and in the resulting mixed-valent species (**8**) [(Ni^{III}(A₂Ni^{II})(L₁)]ⁿ⁺, the overall charge is reduced from +5 in **6** to +3 when A = Cl[−] and to +1 in when A = SO₄^{2−}. Hence, the electrostatic repulsion between the nickel centers is reduced significantly, resulting in a situation where ^AE_{1/2} < ^AE_{1/2}. Thus, the lowered second redox potential in species **8** led to a merging of the waves. As the concentrations of these coordinating anions is increased, the equilibrium concentration of **4** also increases. This is reflected in the gradual cathodic shift of the cyclic voltammogram wave, and the observed ΔE_p values decrease gradually from 58 mV and approach 28 mV when **4** is the predominant redox active species. Also, the broad reduction wave observed in the absence of Cl[−] media disappears in 0.1 M Cl[−] media. Under identical conditions, the nature of the linear dc voltammograms and the slopes obtained from the log[*i*/(*i*_d − *i*)] vs *E* plots are consistent with the above explanation. Since the redox active species exist as an equilibrium mixture, the E_{1/2} values derived from the single cyclic wave represent only the statistically averaged value corresponding to the equilibrium mixture. The changes observed in E_{1/2} and ΔE_p with increasing concentrations of chloride and sulfate ions reflect a gradual shift in the equilibrium between **2**, **6**, and **10** toward **4**, **8**, and **12**, respectively. As has been pointed out by Bond and Oldham,²⁷ the gradual reduction in ΔE_p alone is not to be interpreted to represent a gradual change in the values of E_{1/2}. However, in this case, evidence from kinetic and ESR studies also confirm that axial coordination plays an important role for this behavior.

Additionally, the behavior in the presence of Cl[−] ion needs special mention. In the presence of a large excess of chloride, the earlier described five-coordinate species become more relevant and particularly the formation of cationic polymers of the Ni(III) species is viable. Formations of such chloro-bridged structures not only reduce the redox potential for the successive 1e[−] processes but also enhance interaction between the Ni(III) centers of two different cations. The precipitation of electrolytically prepared [Ni₂(L₁)(ClO₄)₆] from CH₃CN solutions and its insolubility in most solvents also suggest that polymeric species are formed.

Region II. The behavior in acetonitrile can be interpreted in this region. In CH₃CN, equilibrium **Y** predominates and **3** is the major species both at room temperatures and even close to the boiling point of the solution (about 79%). In this less polar medium, the local variation of dielectric constant resulting from the first 1e[−] oxidation has a significant influence on the

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neighboring Ni(II) center in the mixed-valent species **7**. As a result, the successive $1e^-$ redox potentials ($^{\text{AN}}E^1_{1/2} = 735$ mV and $^{\text{AN}}E^2_{1/2} = 835$ mV vs Fc/Fc $^+$; AN = CH₃CN) are just far enough apart ($\Delta E_{1/2} = 100$ mV) to observe a distinguishable two $1e^-$ wave pattern (see Figure 2a).

Region III. This region describes the behavior of [Ni₂(L₁)]Cl₄ in CH₂Cl₂ media. In this medium, **5** (A = Cl $^-$) is the sole species. Though both Ni(II) centers are pseudooctahedral, their nonidentical geometry is reflected not only in the UV–visible spectrum but also in cyclic voltammetry by two distinguishable waves corresponding to the successive $1e^-$ oxidations of the Ni(II) centers. Despite the neutrality of [Ni₂(L₁)]Cl₄, **5**, the dielectric constant of this medium is sufficiently low that even an increase of +1 charge on the ion has a dramatic influence on the neighboring Ni(II) center. As a result, the cyclic voltammogram shows two ($E^1_{1/2} = 640$ mV and $E^2_{1/2} = 766$ mV vs Fc/Fc $^+$ couple) overlapping waves in CH₂Cl₂ (0.1 M Et₄NCl).

Steric Effects. There is hindrance experienced by both of the nickel centers in the bis-Ni(II) and bis-Ni(III) species in adopting pseudooctahedral symmetry (D_{4h}). Though the steric effects experienced in these cations are rather subtle, strong evidence for this effect is provided by UV–vis and ESR spectroscopic studies. As reflected in the UV–visible spectrum of [Ni₂(L₁)]Cl₄ in chlorinated solvents, in the macrocyclic complex steric constraints prohibit adoption of identical pseudooctahedral geometries by both Ni(II) centers. In the open chain complex, [Ni₂(L₂)]Cl₄, where both Ni(II) centers adopt identical pseudooctahedral geometries,²² the metal centers are displaced toward the open end of L₂ from the center of the rectangle described by the four nitrogen donors compared to that in the bis-square planar cation [Ni₂(L₂)] $^{4+}$. However, in the macrocyclic cation [Ni₂(L₁)] $^{4+}$, such a possibility is ruled out, and this induces a constraining effect.

The steric effect is even more dramatic in the bis-Ni(III) species where the Ni(III)–Cl distances are further shortened. Since formation of Ni(III) species from square planar macrocycles is invariably accompanied by axial ligation, the binding of two ligands per Ni(III) center is anticipated. However, anion dependence of redox potentials indicates that only 3.9 chlorides or 3.3 sulfates respectively are bound to the bis-Ni(III) cation, suggesting the influence of a steric factor. Evidence for this comes from the ESR spectrum in aqueous media. In the absence of Cl $^-$, upon quantitative oxidation of the [Ni₂(L₁)] $^{4+}$ cation in aqueous media, two types of Ni(III) centers are observed (see Figure 3a), one axially symmetrical and the other lacking D_{4h} symmetry (species similar to **10** or **12** in Scheme 1). Upon addition of Cl $^-$ [0.1 M], the symmetrical Ni(III) center exhibits a septet hyperfine structure of the g_{\parallel} feature resulting from the *trans*-axial chlorides (shown in Figure 3b). The second less symmetric Ni(III) center gives rise to the additional features in Figure 3a. Even in the presence of a large excess of Cl $^-$ (6000-fold), a complete conversion to the bispseudooctahedral Ni(III) species does not occur within a reasonable period of time. Instead, under such conditions, an ESR spectrum (see Figure 3c) consistent with both Ni(III) centers in similar, but totally anisotropic, environments (species **13** in Scheme 1) is observed. The room temperature solution spectrum of the latter species shows an isotropic signal at $g = 2.126$, and this can be related to the spectrum at 77 K by the expression $(1/3)(g_{xx} + g_{yy} + g_{zz}) = (1/3)(2.234 + 2.117 + 2.064) = 2.138$. Though the exact assignment of the g features is not known, the close agreement of the g values (2.126 and 2.138) suggests that both Ni(III) centers in this species adopt similar and less sterically demanding geometries. A similar explanation holds for the ESR spectra

of bis-Ni(III) species in both CH₃NO₂ and CH₃CN, and the similarity between the ESR spectra in these media suggests that the bis-Ni(III) species in these media must have the same coordination geometry as in 6 M HCl.

The observed hindrance to the formation of bispseudooctahedral Ni(III) (D_{4h}) species results in a compromise between various combinations of geometries the two Ni(III) centers can adopt. In the most stable form, both Ni(III) centers adopt either a five-coordinate geometry or a geometry intermediate between five- and six-coordinate. However, in the Cl $^-$ media, formation of a chloro-bridged polymer in which all of the Ni(III) centers are five-coordinate cannot be ruled out.^{21b} Alternatively, at low chloride concentrations, or in the absence of chloride, one of the Ni(III) centers can adopt an axially symmetric pseudooctahedral geometry and the other a five-coordinate geometry. As has been discussed earlier, a species of this type probably is formed when [Ni₂(L₁)] $^{2+}$ is oxidized in aqueous media (by [Co(OH₂)₆] $^{3+}$ in 1.0 M HClO₄ or by Na₂S₂O₈ in neutral media).

Formation of Ni(II)–Ni(III) Species. Redox behavior and stabilization of mixed-valent states in binuclear complexes have been studied extensively, and the various parameters that contribute to the stabilization of mixed-valent species in systems that show interaction between metal ions have been considered.²⁸ Though the redox behavior of cyclam and related macrocyclic complexes has been studied extensively, the study of mixed-valent species in noninteracting macrocyclic systems is very rare. In [Ni₂(L₁)] $^{4+}$, there is no evidence for through-bond interaction between the metal centers. The two factors that would stabilize a Ni(III) state are (1) the cyclam structure itself, which is known to stabilize this oxidation state, and (2) axial ligation by anions and solvent molecules, which further enhances kinetic inertness and reduces the rate of decomposition. Thus, the only factor that would inhibit the formation of Ni(II)–Ni(III) species is electrostatic repulsion, and in [Ni₂(L₁)] $^{4+}$, this is controlled by axial ligation since the intermetal distance is fixed.

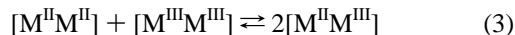
In nonaqueous media, the bis-Ni(III) is isolable as a solid and both the solid and solution species are very stable in the absence of moisture. Irrespective of the nature of the species formed, all undergo a slow change over a long time period to display eventually an axially symmetric spectrum. The reason for such a slow change can be attributed to geometric factors that considerably reduce the axial rates of substitution below those of [Ni(III)(cyclam)] $^{3+}$.

Steric effects under such circumstances can favor the formation of mixed-valent Ni(II)–Ni(III) species during a selective $1e^-$ reduction of the more susceptible Ni(III) center that lacks axial symmetry in the bis-Ni(III) species. The other Ni(III) center with its already oriented pseudooctahedral geometry during oxidation is stabilized by either selective anation or solvation. In general, the geometric preferences in tetraazamacrocyclic ligands for a Ni(II) ion are square planar and pseudooctahedral for a Ni(III) (d^7) ion.⁷ Hence, the formation of a square planar Ni(II) center during decomposition of any of the bis-Ni(III) species described above should relieve steric strain and facilitate the stabilization of an axially symmetric *trans*-[Ni(III)(X₂)] $^+$ center adjacent to a square planar Ni(II). Unlike the situation in CH₃CN, where a stable bis-Ni(III) is obtained, in aqueous media a reductive decomposition does occur that can lead to a mixed-valent species such as **6** or **8** (in Scheme 1). However, at present, there is only kinetic evidence available.²³

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Conclusion

A measure of the thermodynamic stability of the mixed-valent species, which parallels that of the electrostatic effect, is given by the difference $\Delta E_{1/2}$, where $\Delta E_{1/2} = E^1_{1/2} - E^2_{1/2}$. The comproportionation constant K_c for reaction 3 is related to $\Delta E_{1/2}$ by expression 5. Considering the electrochemical reversibility



$$K_c = [M^{II}M^{II}][M^{III}M^{III}]/[M^{II}M^{III}]^2 \quad (4)$$

$$K_c = \exp[\Delta E_{1/2} n_1 n_2 F/RT] \quad (5)$$

of the system studied here, one can use the method of Richardson and Taube¹⁹ to estimate $E^1_{1/2}$ and $E^2_{1/2}$ for the successive $1e^-$ oxidation of the nickel centers, at least, in CH_3CN and CH_2Cl_2 . However, in aqueous media, these potentials are separated only by a statistical value of 35.6 mV or less. Hence, the selective oxidation of only one of the Ni(II) centers in aqueous media is practicable neither electrochemically nor chemically. The fact that two electrons are involved in the overall oxidation of $[Ni_2(L_1)]^{4+}$ has been confirmed by both spectrophotometric titration with Co(III) and coulometric analysis. The absence of a mixed-valent intermediate within the time scale of the titration is confirmed by the observation of an isobestic point. Only in CH_3CN and CH_2Cl_2 media was $\Delta E_{1/2}$ large enough (about 100 mV) for observation of a mixed-valent intermediate. Though the $\Delta E_{1/2}$ value reflects a comproportionation

constant (K_c) of 49, the kinetic lability of the mixed-valent species in the cyclic voltammetric time scale is not known. The stopped flow kinetics studies in CH_3CN presented here confirm that it is possible to observe the mixed-valent intermediate in the millisecond time scale. However, it disproportionates at a fast enough rate to elude isolation. The only factor that may favor the isolation kinetically are either specific solvation or anation of one of the oxidation states, preferably the Ni(III) state. As described above, this is evident during the decomposition of the bis-Ni(III) species. Further evidence for configurational stability comes from the formation of the $[Cu^{II}-Ni^{III}X_2(L_1)]^{n+}$ cation, where the coordination geometry preferences for the Cu(II) (five coordinate) and Ni(III) (six-coordinate) are favorable.²⁹

Supporting Information Available: Figures for spectroscopic titration of $[Ni_2(L_1)]^{4+}$ with $[Co(OH_2)_6]^{3+}$, plot of absorbance vs time for the biphasic kinetics for formation and disproportionation of $[Ni^{II}-Ni^{III}(L_1)]^{5+}$ in CH_3CN and of cyclic voltammograms and tables of electrochemical data for chloride and sulfate complexation in aqueous media and rate data at various wavelengths for the kinetics (9 pages). Ordering information is given on any current masthead page.

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- (29) For $[Cu^{II}Ni^{III}X_2(L_1)]^{n+}$ species, a simple axial Cu(II) ESR spectrum is observed superimposed over an axial Ni(III) spectrum (1×10^{-3} M solution in 1 M $HClO_4$ at 77 K). Owing to the presence of a neighboring Ni^{III} ion, the observed $A_{||}$ values (95 G) were significantly smaller than the 195 G observed for $[Cu^{II}(cyclam)]^{2+}$ or for $[Cu^{II}-Ni^{III}(L_1)]^{4+}$ species under identical conditions. McAuley, A.; Subramanian, S. Unpublished results.