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Comparison of the Electrochemical Reduction of Pentadentate Binucleated Nickel(II) and Copper(II) Compounds in Dimethylformamide

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A series of binuclear complexes of nickel(II) (Ni_2L) and copper(II) (Cu_2L) (L consists of a deprotonated pentadentate ligand derived from the condensation of acetylacetone or salicylaldehyde with 1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol and an exogenous two-atom bridge between the two metal centers consisting of deprotonated pyrazole and related species) have been prepared and the redox processes in dimethylformamide examined at the mercury and platinum electrodes. For the Ni_2L series, two nearly reversible electrode processes are observed at very negative potentials.

$$Ni_2L + e^- \underset{}{\overset{E^\circ_1}{\rightleftharpoons}} [Ni_2L]^- \quad (1)$$

$$[Ni_2L]^- + e^- \overset{E^\circ_2}{\rightleftharpoons} [Ni_2L]^{2-} \quad (2)$$

Evidence for structurally different forms of the complexes is provided. At low temperatures, in the absence of light and oxygen, controlled-potential electrolysis experiments can generate a nickel(I) species (as indicated by ESR) by a one-electron-reduction step, although more than one species is formed in this experiment. E° values for the two reduction processes, described in eq 1 and 2, are well-separated. By contrast, the Cu_2L complexes are kinetically labile and both $[Cu_2L]^-$ and $[Cu_2L]^{2-}$ are very unstable. Two one-electron-reduction steps are observed at considerably less negative potentials than for Ni_2L. The data obtained do not fit the model for simple electron transfer and rapid structural rearrangement; the redox cross-reaction

$$[Cu_2L]^{2-} + Cu_2L \rightleftharpoons 2[Cu_2L]^- \quad (3)$$

and the nature of the bridging groups appear to be important.

Introduction

Electrochemical studies have been reported for a range of binuclear copper(II) complexes with some attention also being given to the nickel(II) analogues.[2-6] In particular, redox properties associated with multinuclear metal sites in metalloproteins,[7] especially the binuclear *type 3* copper proteins, have stimulated activity in this area.[8,9] Of particular interest with respect to the Cu_2L type complexes has been the nature of the reduction processes and the question as to whether they occur by two one-electron steps or a single two-electron transfer when a change from a formally copper(II) species to copper(I) occurs and indeed as to whether the two metal centers are interacting or not during the redox processes.[10]

We have shown that for a range of binucleated Cu(II) complexes the solid-state structures and physical properties of such species are strongly dependent on the exogenous and endogenous bridging atoms.[11] For example, minor changes in the pentadentate ligands can have major effects on the magnetic exchange interactions of the two coupled, $S = {}^1/_2$, Cu(II) centers. The exchange interactions are also strongly dependent on the nature of the exogenous bridging atoms.[11a,c] Examples of both net antiferromagnetism and ferromagnetism have been observed, and in one case, structural isomers of one of these compounds show both types of interaction.[11b]

During the electron-transfer processes of such binucleated species the possibility of structural change(s) or chemical reaction(s) is likely to be important. For example, we have recently shown that a binucleated copper(II) complex having an endogenous phenoxo bridge and a pyrazolato exogenous bridge undergoes substantial modifications during reduction and gives rise to some unusual and unique electrochemistry.[12] The effect of both endogenous and exogenous bridging groups may be reflected in the nature of electrochemical responses, and simple designation of such redox processes as reversible or irreversible (as has usually been done[2-6,13,14]) could omit recognition of this important aspect.

While copper(II) binuclear complexes tend to be relatively kinetically labile, nickel(II) analogues may be more inert and deductions concerning their redox behavior, therefore, more simple. To date, the electrochemistry of a binuclear nickel(II) complex containing a phenoxo-bridged macrocyclic ligand has been reported in acetonitrile with a reversible one-electron-reduction process being observed.[2a] More recently two phenoxo-bridged binuclear nickel(II) complexes have been examined and have shown non-Nernstian behavior in both DMF and CH_2Cl_2.[5] The present work represents a detailed investigation of a range of binuclear nickel(II) complexes. Studies are aimed at understanding the influence of the bridging groups on the redox processes of binuclear complexes. The effect of stereochemistry on the redox potential of the coordinated mononuclear nickel ion has been examined previously,[15,16] but the significance of those studies is confined to the structurally rigid macrocyclic complexes, whereas other factors apply to the bridging ligands of the present compounds. The newly synthesised binuclear nickel(II) compounds **1**, **2a**, **3a**, **4**, **5**, and **6** (Chart I) have been characterized, and their detailed electro-

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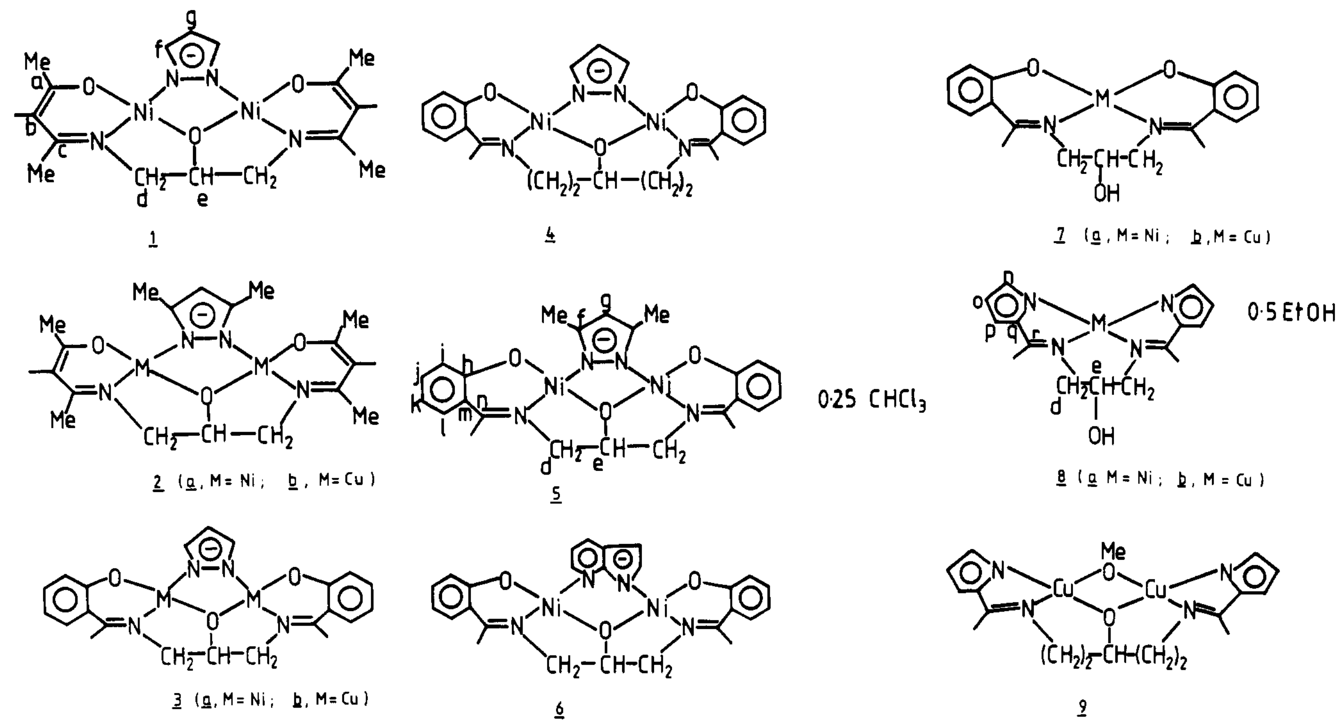
Chart I. Structures for Compounds 1–9



chemistry in DMF has been investigated. Several binucleated copper(II) species, **2b**, **3b**, and **9**, and some mononuclear nickel(II), **7a** and **8a**, and copper(II), **7b** and **8b**, complexes have also been studied for comparison.

Experimental Section

Ligand Synthesis. The Schiff base ligands were formed by condensation of 2 equiv of pyrrole-2-carboxaldehyde, salicylaldehyde, or acetylacetone with 1 equiv of 1,3-diaminopropan-2-ol (Aldrich Chemical Co. Ltd.) or with 1,5-diaminopentan-3-ol dihydrochloride. The ligands 1,3-bis(salicylideneamino)propan-2-ol and 1,5-bis(salicylideneamino)pentan-3-ol were isolated as solids while the others were prepared in situ and not isolated.[11a]

Preparation of Complexes. Compound 1. Acetylacetone (10 g, 0.1 mol) and 1,3-diaminopropan-2-ol (4.5 g, 0.05 mol) were mixed at room temperature and diluted to 100 cm^3 with ethanol/methanol. This was used as a stock solution for the preparation of compounds **1**, **2a**, and **3a**.

The ligand solution (10 cm^3, 0.005 mol) was added to nickel(II) perchlorate hexahydrate (3.65 g, 0.01 mol) in methanol (25 cm^3). Addition of pyrazole (0.35 g, 0.0051 mol) in methanol (5 cm^3) and potassium hydroxide (0.84 g, 0.015 mol) in methanol (20 cm^3) gave a yellow-brown precipitate. After 0.3 h the precipitate was collected by filtration, washed with methanol, and dried under suction. The product was dissolved in a mixture of dichloromethane (70 cm^3) and methanol (20 cm^3). The resulting solution was allowed to evaporate at room temperature to give 1.0 g of product. Anal. Calcd for $C_{16}H_{22}N_4O_3Ni_2$:C, 44.10; H, 5.10; N, 12.86; Ni, 26.94. Found: C, 44.14; H, 5.02; N, 12.92; Ni, 27.1.

Compound 2a. A mixture of the above ligand solution (10 cm^3, 0.005 mol) and 3,5-dimethylpyrazole (0.5 g, 0.0052 mol) in methanol (15 cm^3) was added to nickel(II) perchlorate hexahydrate (3.65 g, 0.01 mol) in methanol (10 cm^3). The addition of potassium hydroxide (0.84 g, 0.015 mol) in methanol (50 cm^3) gave a dark brown precipitate, which was filtered after 0.2 h, washed with methanol, and dried under suction. The brown crystals that had formed in the filtrate were collected, combined with the original residue, and dissolved in dichloromethane (30 cm^3). After methanol (15 cm^3) was added to the solution, it was allowed to evaporate at room temperature overnight to give a brown crystalline solid. This product was collected, washed with methanol and ethanol, and dried under suction. Yield: 0.6 g. Anal. Calcd for $C_{18}H_{26}N_4O_3Ni_2$: C, 46.61; H, 5.65; N, 12.08; Ni, 25.31. Found: C, 46.58; H, 5.60; N, 11.91; Ni, 25.5.

Compound 3a. A mixture of 1,3-bis(salicylideneamino)propan-2-ol (1.5 g, 0.005 mol), pyrazole (0.4 g, 0.0059 mol), and potassium hydroxide (0.3 g, 0.0053 mol) in methanol (40 cm^3) was added to nickel(II) nitrate hexahydrate (2.9 g, 0.01 mol) in methanol (60 cm^3). The mixture was allowed to stand overnight, and the resulting product was collected, washed with methanol, and air-dried. Yield: 0.8 g. This product was extracted with chloroform (250 cm^3) continuously in a Soxhlet extractor for 3 days. The red-brown crystalline solid that formed in the extract was collected by filtration, washed with chloroform, and air-dried. Yield; 0.23 g. Anal. Calcd for $C_{20}H_{18}N_4O_3Ni_2$: C, 50.07; H, 3.78; N, 11.68; Ni, 24.47. Found: C, 50.05; H, 3.82; N, 11.72; Ni, 24.2

Compound 4. A mixture of 1,5-bis(salicylideneamino)pentan-3-ol (0.32 g, 0.001 mol) and pyrazole (0.1 g, 0.0015 mol) in methanol (15 cm^3) was added to a stirred solution of nickel(II) perchlorate hexahydrate (0.73 g, 0.002 mol) in methanol (10 cm^3) to give a green solution, which on the addition of potassium hydroxide (0.23 g, 0.0041 mol) gave a yellow-green precipitate. The solvent was removed with a rotary evaporator to give a thick slurry. This material was extracted with chloroform (25 cm^3), and the extract was washed with water (3 × 5 cm^3) and dried over anhydrous magnesium sulfate. The mixture was filtered, and the residue was washed with dichloromethane (50 cm^3). The filtrate and washings were combined, and a microcrystalline solid formed on slow evaporation of the solvent. The product was collected, washed with chloroform, and dried in air. Further evaporation of the filtrate at room temperature gave an additional 0.13 g of material. Total yield: 0.27 g. Anal. Calcd for $C_{22}H_{22}N_4O_3Ni_2$: C, 52.03; H, 4.37; N, 11.03; Ni, 23.11. Found: C, 51.87; H, 4.28; N, 11.06; Ni, 22.8.

Compound 5. 1,3-Bis(salicylideneamino)propan-2-ol (1.5 g, 0.005 mol) and 3,5-dimethylpyrazole (0.5 g, 0.0052 mol) in methanol (20 cm^3) were added to a stirred solution of nickel(II) perchlorate hexahydrate (3.7 g, 0.01 mol) in methanol (15 cm^3). When potassium hydroxide (1.12 g, 0.02 mol) in methanol (20 cm^3) was added, a yellow-brown precipitate formed. After 0.3 h the mixture was filtered and the precipitate (4.2 g) and a further 0.23 g of product from the filtrate were obtained. The product was extracted with chloroform (250 cm^3) for 16 h in a Soxhlet extractor. The extract was reduced to 60 cm^3 on a rotary evaporator and ethanol (17 cm^3) was added to the hot solution. The yellow-brown precipitate, which formed when the solution was cooled, was collected by filtration. This material and an additional amount of product obtained by evaporation of the filtrate at room temperature represented a yield of 1.51 g. The compound contains 0.25 mol of $CHCl_3$. Anal. Calcd for $C_{22.25}H_{22.25}N_4O_3Cl_{0.75}Ni_2$: C, 49.70; H, 4.17; N, 10.42; Ni, 21.83. Found: C, 49.57; H, 4.14; N, 10.42; Ni, 20.2.

Compound 6. A mixture of 1,3-bis(salicylideneamino)propan-2-ol (0.75 g, 0.0025 mol) and 7-azaindole (0.3 g, 0.0025 mol) in methanol (15 cm^3) was added to a stirred solution of nickel(II) perchlorate hexahydrate (1.83 g, 0.005 mol) in methanol (15 cm^3). The brown precipitate that formed on the addition of potassium hydroxide (0.56 g, 0.01 mol) was collected after 1.5 h, washed with methanol, and dried in air. This material was extracted with chloroform (300 cm^3) in a Soxhlet extractor for 24 h. The extract was filtered to give 0.05 g of brown microcrystalline solid. A further extraction of the residue (48 h) yielded additional product (0.43 g). Anal. Calcd for $C_{24}H_{20}N_4O_3Ni_2$: C, 54.41; H, 3.80; N, 10.57; Ni, 22.15. Found: C, 54.19; H, 3.76; N, 10.56; Ni, 21.6.

Compound 7a. A solution of 1,3-bis(salicylideneamino)propan-2-ol (0.6 g, 0.002 mol) in methanol (15 cm^3) was added to nickel(II) perchlorate hexahydrate (0.73 g, 0.002 mol) in methanol (10 cm^3). The solution became yellow-brown in color when potassium hydroxide (0.32 g, 0.0057 mol) in methanol (15 cm^3) was added to give an apparent of pH of 7. After 0.5 h a brown crystalline solid began to form. The mixture was allowed to stand overnight at room temperature. The product was collected by filtration, washed with methanol, dried under suction, and finally recrystallized from boiling ethanol. Yield: 0.11 g. Anal. Calcd for $C_{17}H_{16}N_2O_3Ni$: C, 57.52; H, 4.54; N, 7.89; Ni, 16.53. Found: C, 57.56; H, 4.54; N, 7.87; Ni, 16.3.

Compound 8a. A solution of pyrrole-2-carboxaldehyde (1.9 g, 0.02 mol) and 1,3-diaminopropan-2-ol (0.9 g, 0.01 mol) in ethanol (25 cm^3) was heated at 60 °C for 1 h. The solution was cooled and added to nickel(II) acetate tetrahydrate (2.5 g, 0.01 mol) in ethanol (250 cm^3). After 0.3 h, crystals began to form in the deep red solution. After a further 16 h the product was collected, washed with ethanol, and dried in air. Yield: 2.35 g. Anal. Calcd for $C_{14}H_{17}N_4O_{1.5}Ni$: C, 51.90; H, 5.29; N, 17.29; Ni, 18.11. Found: C, 51.79; H, 5.23; N, 17.66; Ni, 17.8.

Compound 11. (All manipulations were done under an oxygen-free atmosphere with Schlenk techniques.) Tetrakis(acetonitrile)copper(I) hexafluorophosphate (2.35 g, 0.006 mol) and tetraethylammonium hexafluorophosphate (1.65 g, 0.006 mol) were dissolved in warm, dry methanol (30 cm^3). A mixture of 1,3-bis(salicylideneamino)propan-2-ol (0.9 g, 0.003 mol) and sodium acetate (0.25 g, 0.003 mol) in methanol (25 cm^3) was then added to give a dark brown solution. After about 5 min, a crystalline solid formed. The mixture was filtered, and the green product was recrystallized from hot methanol. Yield: 0.1 g. Anal. Calcd for $C_{19}H_{20}N_3O_3F_6PCu_2$: C, 37.38; H, 3.30; N, 6.88; Cu, 20.82. Found: C, 37.41; H, 3.36; N, 6.74; Cu, 20.8. Infrared (KBr disk): 3600 cm^{-1} (m), ν_{OH}; 2280 cm^{-1} (w), $\nu_{C\equiv N}$; 1615 cm^{-1} (s), ν(C=N).

Compounds 2b, 3b, 7b, 8b, 9, and 10 have been described elsewhere.[11a,11c,12]

Measurements. Infrared spectra were measured with a Perkin-Elmer Model 457 spectrometer. Absorption spectra (visible and ultraviolet) were recorded on a Cary Model 17 spectrophotometer. Proton NMR spectra were obtained with a Perkin-Elmer Model R32 spectrometer while ^{13}C, proton noise decoupled NMR spectra were obtained at 50.1 MHz on a JEOL FX 200 spectrometer. The electrochemical measurements (cyclic voltammetry and polarography) were carried out by using a Princeton Applied Research (PAR) Model 170 electrochemical system. A three-electrode configuration was used. The working electrodes were a PAR hanging mercury drop electrode, a dropping mercury electrode, and a platinum-wire electrode. A 10-cm^3 PAR electrochemical cell, which was continuously purged with argon, was used. Tetraethylammonium perchlorate (Fluka) was the supporting electrolyte, unless otherwise stated. Before use, it was twice recrystallized from water, dried in vacuo at 60 °C, and stored under oxygen-free nitrogen. The solvent, dimethylformamide (Analytical Reagent or spectroscopic grade) was dried over molecular sieves (3A) for 48 h, decanted, and allowed to stand over barium oxide for 24 h and then transferred into a 3-necked flask fitted with a Vigreux fractionating column. The solvent was degassed and distilled under a vacuum in subdued light. The distilled solvent was stored under oxygen-free nitrogen at 5 °C in darkness in a solvent vessel designed for anaerobic solvent transfer. The concentration of supporting electrolyte used in all experiments was 0.1 M, and the concentration of the compounds examined was 2×10^{-3} M unless otherwise stated. Controlled-potential electrolysis was carried out at a platinum-gauze electrode at low temperature, in the darkness and at concentrations in the range $(1-2) \times 10^{-3}$ M, using a 3-electrode configuration with the counter platinum electrode separated from the solution to be electrolyzed by a compartment containing a glass frit. All potentials are given with respect to a saturated calomel electrode (SCE).

ESR measurements were made on a Varian E-9 X-band spectrometer equipped with a liquid-nitrogen Dewar. The magnetic field was calibrated with diphenylpicrylhydrazyl (DPPH).

Results and Discussion

Characterization of the Nickel(II) and Copper(II) Complexes. Our previous studies have shown that the potentially pentadentate 1,3-bis(salicylideneamino)propan-2-ol and 1,5-bis(salicylideneamino)pentan-3-ol act as binucleating ligands in a series of compounds having two copper(II) ions bridged by a secondary alkoxo moiety and by an endogenous single-atom (OH, OR, Cl, Br) or two-atom (acetate, pyrazolate) bridging ligand.[11a,c]

The chemical analysis and spectral properties (vide infra) of the nickel(II) complexes **1**, **2a**, **3a**, **4**, **5**, and **6** and previous studies[11c,12] of the copper(II) complexes **2b**, **3b**, and **10** suggest they also are binucleated species having the secondary alkoxo or phenoxo bridging unit and an exogenous two-atom (nitrogen) bridging deprotonated pyrazolate (or its analog) group. Indeed, the crystal and molecular structure of **3b** substantiates such a situation.[11c] Although we have been unable to grow crystals of the nickel(II) complex **3a** that are suitable for single-crystal X-ray diffraction studies, it is interesting to note that X-ray diffraction patterns of powdered samples of **3a** and **3b** are almost identical. The structures of the two compounds are likely to be quite similar. Compounds **7a** and **8a** appear to be mononuclear and have square-planar coordination of the nickel(II) ions wherein the uncoordinated hydroxyl group gives rise to a broad absorption at ca. 3400 cm^{-1}, which has previously been assigned[11a] as ν_{O-H} in the corresponding copper(II) complexes **7b** and **8b**. The occurrence of a doublet at 4.43 ppm in the ^1H NMR spectrum of **8a** in acetone-d_6 is due to this hydroxyl group. Other important absorption bands observed in the infrared spectra for the salicylideneamino compounds occur in the region 1610–1630 cm^{-1} ($\nu_{C=N}$)[3,17] and for the acetylacetone imine complexes at 1505–1510 ($\nu_{C=N}$)[18] and 1580–1590 cm^{-1} ($\nu_{C=C}$).[18]

The nickel(II) complexes are yellow-brown or red solids. Electronic spectral data for the compounds in the solid state and in chloroform are recorded in Table SI.[36] All compounds except **8a** have an absorption in the region 540–615 nm, which is characteristic for nickel(II) ions in square-planar coordination.[19] The compounds retain their color in chloroform solution, and the failure to observe this band in the 500–600-nm region may be due to considerable overlap with the transitions at higher energies, which have very high molar absorptivities.

The diamagnetic nature of the nickel(II) compounds is illustrated by the fact that well-resolved, sharp proton-decoupled ^{13}C spectra are obtained for compounds having sufficient solubility in solvents suitable for the measurements. Assignment of individual carbon atoms is straightforward when the various effects of chemical shifts shown in Table SII[36] are correlated with methyl substitution in the ligands, the relative intensities of signals, and replacement of acetylacetone imine functions by salicylideneamine moieties and the chemical shifts of carbon atoms in the pyrazolate ion and related diamagnetic nickel(II) complexes are considered.[20-22]

Structural characterization of the copper(II) compounds has been described elsewhere.[11a,c]

Electrochemistry. Dc Polarography of the Nickel(II) Compounds. The reduction of the binuclear complex **1** at the dropping mercury electrode (DME) at 21 °C in DMF over the potential range 0 to −3.0 V (vs. SCE) consists of two well-defined reduction waves (processes 1 and 2) with similar limiting currents per unit concentration (Figure 1a). The limiting currents (i_l) are diffusion controlled. Similar behavior is observed for the binuclear compounds **2a**, **3a**, **4**, **5**, and **6**, apart from the appearance of two additional minor waves that are clearly evident, particularly in **5** (Figure 1b). These two additional waves have similar separations in $E_{1/2}$ values to the primary processes and appear to be closely related. The additional processes in Figure 1b are referred to as processes 3 and 4. The ratio of the limiting currents of these minor waves to the major ones is independent of concentration and drop time for a given sample. In general the $E_{1/2}(1)$ and $E_{1/2}(2)$ values for the two main (primary) electrode processes are independent of the drop time. Data at a drop time of 0.5 s are summarized in Table I. The $E_{3/4} - E_{1/4}$ values and the slopes of log $(i/(i_l$

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(20) The resonance in **8a** at 6.8 ppm is presently unassigned but may be the result of a condensation reaction between the ligand and the solvent acetone (see, for example: House, D. A.; Curtis, N. F. *J. Am. Chem. Soc.* **1964**, *86*, 223). The very low solubility of the compound in other solvents suitable for ^{13}C NMR has precluded confirmation.

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Table I. Dc Polarographic Data for the Reduction of Nickel(II) Complexes[a]

	process 1				process 2			
compd	$E_{1/2}(1)$, V vs. SCE	$E_{3/4}(1) - E_{1/4}(1)$, mV	slope (1),[b] mV	$i_l(1)$, μA	$E_{1/2}(2)$, V vs. SCE	$E_{3/4}(2) - E_{1/4}(2)$, mV	slope (2),[b] mV	$i_l(2)$, μA
1	−1.775	54	58	5.9	−2.300	54	57	5.8
2a	−1.699	52	58	5.0	−2.259	54	63	4.6
3a	−1.575	60	64	6.4	−2.018	62	85, 64	5.7
4	−1.445	52	55	4.2	−1.955	62	72	6.4
5	−1.463	51	57	5.0	−1.955	62	68	5.8
6	−1.375	57	58	5.7	−1.935	56	60	6.2
7a	−1.434	53	58	5.5	−2.178	43	50, 38[c]	4.9
8a	−1.667	58	64	7.4				

[a] In DMF, supporting electrolyte 0.1 M Et_4NClO_4; temperature 21 ± 2 °C; drop time 0.5 s; $E_{1/2}$ = half-wave potential; $E_{1/4}$ and $E_{3/4}$ potentials at values of $i_l/4$ and $3i_l/4$, respectively, where i_l is the limiting current. [b] Reciprocal slope of $\log(i/(i_l - i))$ vs. E. [c] Log plot best fitted with two straight lines.

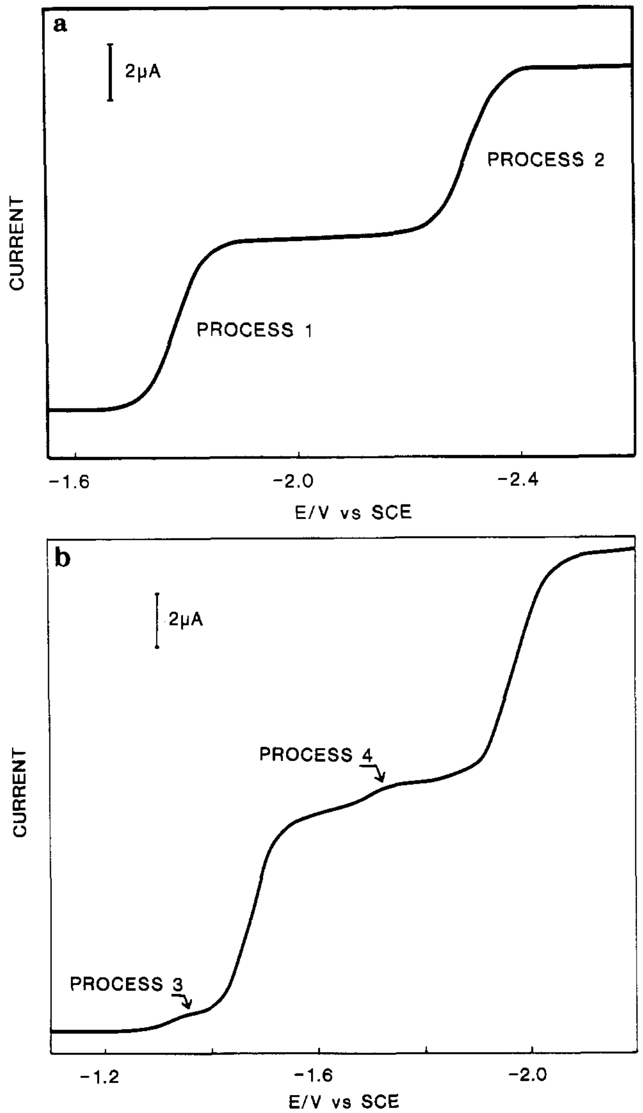

Figure 1. (a) Dc polarographic reduction of compound **1**: 21 °C, 0.5-s drop time. (b) Dc polarographic reduction of compound **5**: 21 °C, 1.0-s drop time.

− *i*)) vs. *E* plots lie within the ranges (55 ± 5) mV and (59 ± 5) mV, respectively, for the first reduction step. Both values are consistent with Nernstian charge-transfer behavior for a process involving a one-electron transfer. The second reduction is essentially a one-electron process but typically has larger ($E_{3/4} - E_{1/4}$) values and larger slopes of the plot or a nonlinear plot of $\log(i/(i_l - i))$ vs. *E*. The more complex behavior for the second reduction step may be due to chemical reactions associated with electron transfer or adsorption of electroactive species on the electrode. In summary, for these binuclear nickel(II) species, two

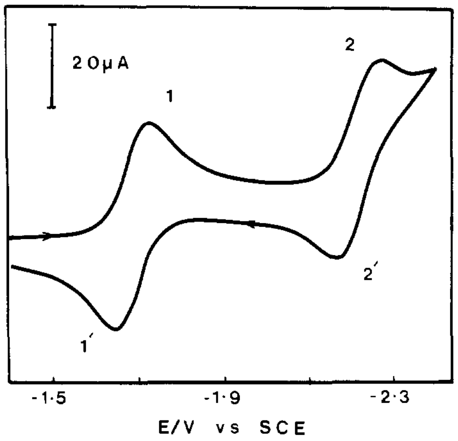

Figure 2. Cyclic voltammetric reduction of compound **1** at a platinum electrode: 21 °C, 100 mV s^{-1} scan rate.

one-electron-reduction steps are involved (L = pentadentate ligand and the exogenous ligand):

$$Ni_2L + e^- \xrightleftharpoons{E_{1/2}(1),\ k_s(1)} [Ni_2L]^- \qquad (4)$$

$$[Ni_2L]^- + e^- \xrightleftharpoons{E_{1/2}(2),\ k_s(2)} [Ni_2L]^{2-} \qquad (5)$$

where k_s is the heterogeneous charge-transfer rate constant. For these compounds $k_s > 10^{-2}$ cm s^{-1} in DMF so that $E_{1/2}$ is approximately equal to the standard redox potential $E°$ under the conditions of dc polarography.

Cyclic Voltammetry of the Nickel(II) Compounds. The data for the primary reduction processes in the nickel(II) complexes that occur at a platinum electrode and a hanging mercury drop electrode (HMDE) are collected in Tables II–IV. Table IV shows the detailed scan and temperature dependence for compound **1**. The binuclear nickel(II) compounds display a two-step reduction consisting of a one-electron transfer at each step as indicated by the separation in reduction and oxidation potentials (ΔE_p values). The cyclic voltammetry of **1** at a platinum electrode is shown in Figure 2. A similar result was obtained at the HMDE. The first of these primary reduction processes has the characteristics of an electrochemically reversible couple under the conditions of Tables II and III. The second process is close to chemically reversible under the conditions of cyclic voltammetry although in some instances there is evidence for chemical reactions associated with electron transfer. The two additional (minor) processes observed under polarographic conditions (e.g. compound **5**) are also present in the cyclic voltammetry at both mercury and platinum electrodes, and hence they are inherent in the chemistry of these complexes. These additional electrode processes will be described here as secondary processes. For example, in the cyclic voltammogram of compound **3a** at a platinum electrode (Figure 3) in addition to peaks 1 and 2, which represent the primary reduction processes, peak 3′ is observed. The latter peak is unaffected by supporting electrolyte (Et_4NClO_4 or Et_4NPF_6). However, at low temperature

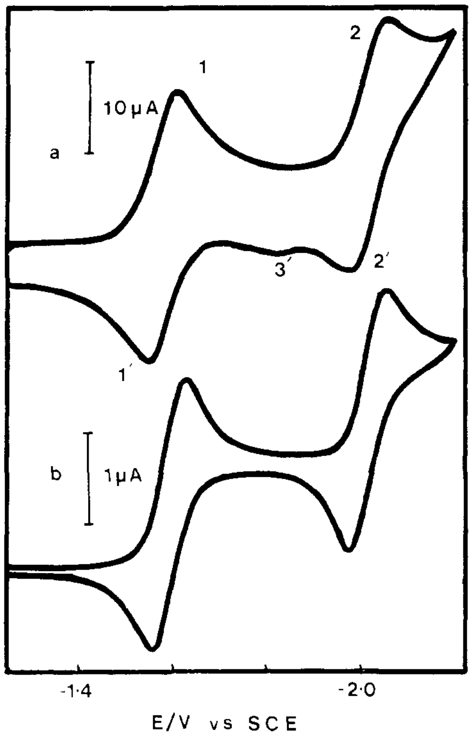

Figure 3. Cyclic voltammetric reduction of compound **3a** at a platinum electrode: (a) 20 °C, 100 mV s^{-1} scan rate; (b) −60 °C, 10 mV s^{-1} scan rate.

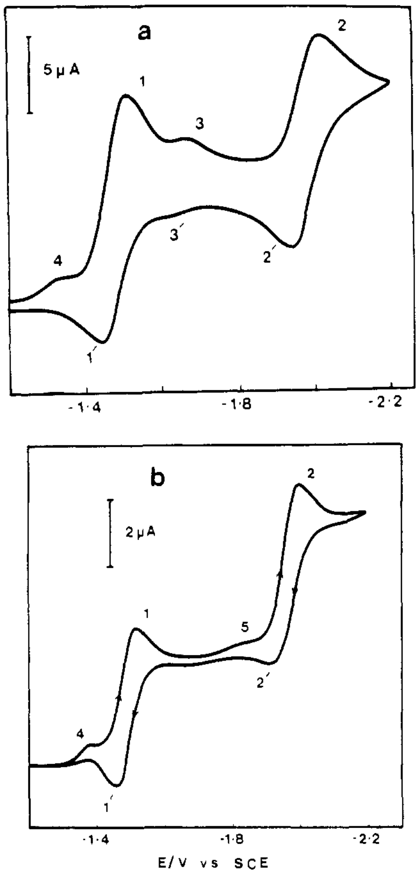

Figure 4. Cyclic voltammetric reduction of compound **5** at a platinum electrode: (a) 21 °C, 20 mV s^{-1} scan rate; (b) −47 °C, 20 mV s^{-1} scan rate.

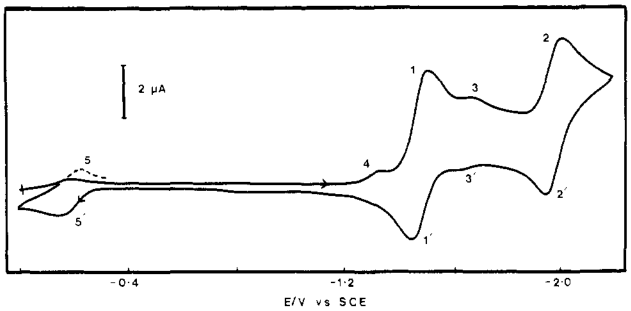

Figure 5. Cyclic voltammetric reduction of compound **5** at the HMDE: 21 °C, 50 mV s^{-1} scan rate.

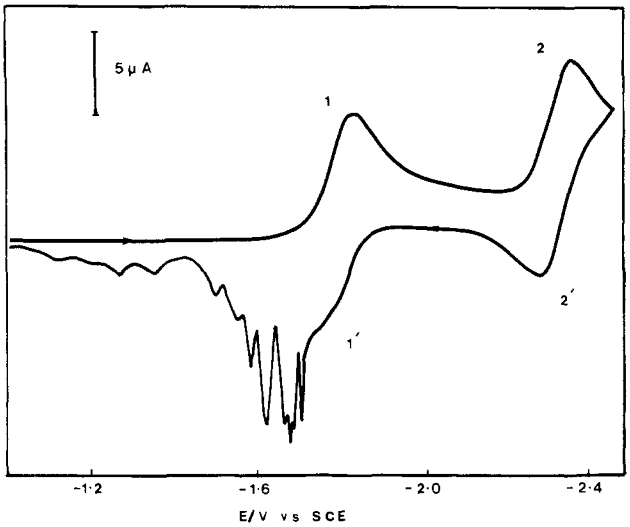

Figure 6. Cyclic voltammetric reduction of compound **1** at the HMDE: 21 °C, 100 mV s^{-1} scan rate.

(−60 °C) and slow scan rate (10 mV s^{-1}), the voltammogram simplifies to two clearly defined couples, which correspond to the primary processes. It is pertinent to point out here that measurements at low temperatures were useful in that secondary processes were often not observed and much simpler voltammograms were thus obtained. A particularly striking example of the temperature dependence is shown in Figure 4 for compound **5** at 21 °C and −47 °C. The two primary reduction processes (peaks 1 and 2) are observed but in addition, two secondary reduction processes (peaks 3 and 3′) and a chemically irreversible process (peak 4) are seen at 21 °C. At −47 °C peaks 3 and 3′ are no longer evident but a small peak, 5, corresponding to a chemically irreversible process, occurs immediately before the second couple. Peak 4 is also present in compound **6**. That this peak is not a prewave is indicated by the fact that its height, relative to peak 1, is not affected by the concentration of **5** in the range 2×10^{-4} to 1×10^{-2} M. The process responsible for the peak is independent of temperature over the range −47 to +80 °C. When samples of **5** obtained from different preparations were examined, variable heights for peak 4 were evident, indicating that this electrode process arises from distinct species within the samples. Such species must be closely related structurally to **5** because of its similar reduction potential, its failure to affect the elemental analysis results, and the fact that it could be separated from the main component by thin-layer chromatography or HPLC. The ^{13}C NMR spectrum also shows no evidence of disparate species. The cyclic voltammograms for the binuclear nickel(II) complexes are similar at both the HMDE and platinum electrodes. In addition to the secondary processes, however, another couple is observed at the HMDE at less negative potentials (peaks 5 and 5′) for compounds **5** (Figure 5) and **6**. This may be the result of a specific chemical interaction with the mercury electrode. In one extreme case (compound **1**) oscillations occur on reduction at the mercury surface (Figure 6), and surface reactions are indicated.

Coulometry of the Nickel(II) Compounds. Initial experiments on the controlled-potential electrolysis of **3a** in 0.1 M Et_4NClO_4 in DMF were found to be affected by temperature and light at a platinum-gauze electrode maintained at −1.8 V vs. SCE. At

Table II. Cyclic Voltammetric Data for the Primary Reduction Processes at a Platinum Electrode[a]

		process 1				process 2			
compd	temp, °C	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f[b]	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f[b]
				Nickel(II) Compounds					
1	21	−1.832	−1.752	70	1.10	−2.354	−2.265	89	0.93
2a	21	−1.744	−1.668	76	0.99	−2.300	−2.223	80	1.08
3a	20	−1.600	−1.533	67	1.01	−2.050	−1.972	78	1.13
4	20	−1.455	−1.418	74	1.00	−1.996	−1.915	81	0.95
	−47	−1.516	−1.440	76	1.02	−2.002	−1.915	87	0.87
5	21	−1.520	−1.438	82	0.95	−2.018	−1.940	78	1.10
	21	−1.510[c]	−1.440[c]	70[c]	0.73	−2.010	−1.942[c]	68[c]	1.01
	−47	−1.535	−1.446	89	1.29	−2.013	−1.935	78	0.72
	−47	−1.518[c]	−1.455[c]	63[c]	0.98	−2.002[c]	−1.927[c]	75[c]	0.61
6	21	−1.420	−1.350	70	0.88	−1.975	−1.898	77	0.89
7a	20	−1.486	−1.412	74	1.00				
	−47	−1.511	−1.413	98	1.01				
8a	20	−1.725	−1.642	83	1.07				
				Copper(II) Compounds					
2b	21.5	−1.280	−0.923	357	0.85	−1.580[d]			
3b	21	−1.155	−0.898	257	0.79	−1.600[d]			
10	20	−0.850	−0.740	110	1.00	−1.230[d]			
	−23	−0.906	−0.727	179	1.06	−1.360[d]			

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; scan rate 100 mV s^{-1}; E_p = peak potential; i_p = peak height; ΔE_p = peak to peak separation. [b] Determined according to: Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1046. Symbols f and r denote forward (reductive) and reverse (oxidative) scan directions, respectively. [c] Scan rate 20 mV s^{-1}. [d] No peak seen on reverse scan.

Table III. Cyclic Voltammetric Data for the Primary Reduction Processes at the HMDE[a]

		process 1				process 2			
compd	temp, °C	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f[b]	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f[b]
				Nickel(II) Compounds					
1	21	−1.818	−1.748	70	0.90	−2.353	−2.277	76	0.83
	−23	−1.829	−1.765	64	0.90	−2.331	−2.265	66	1.06
2a	21	−1.745	−1.670	75	0.83	−2.300	−2.230	70	0.90
3a[c]	20	−1.610	−1.532	78	0.94	−2.048	−1.975	73	1.00
4	20	−1.492	−1.415	77	0.95	−1.995	−1.910	85	0.81
5	21	−1.509	−1.433	76	0.82	−2.003	−1.933	70	1.17
6	21	−1.407	−1.337	70	1.16	−1.976	−1.895	81	0.94
7a	20	−1.487	−1.415	72	0.83				
	−23	−1.497	−1.422	75	0.88				
				Copper(II) Compounds					
3b	20	−1.043	−0.962	81	0.83	−1.580[d]			
10	20	−0.825	−0.760	65	1.20	−1.087	−0.973	114	1.26
	−23	−0.847	−0.775	72	1.05	−1.070	−0.975	95	1.19

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; scan rate 100 mV s^{-1}. Symbols are defined in Table II. [b] Determined according to: Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1046. [c] Supporting electrolyte 0.1 M Et_4NPF_6. [d] Irreversible process.

20 °C in diffuse sunlight there was no appreciable decay in the working electrode current. However, when light was excluded, current decay with electrolysis was observed but a plot of log $i(t)$ [i = working electrode current] vs. t produced a concave curve. When electrolysis was terminated, the green solution reverted to the yellow color of the starting material. Reapplication of the potential restored the green color. These observations are consistent with a catalytic reaction where reduced species reacts with the solvent, impurities, supporting electrolyte, and/or light.[23,24]

When the temperature was lowered to −70 °C controlled-potential electrolysis of **3a** gave a linear log $i(t)$ vs. t plot with n = 1.08. The product could be oxidized back to the starting material, which indicated chemical reversibility. The values for n for the first primary reduction process of the nickel(II) species were all determined in this manner and are given in Table V. Values of $n > 1$ were generally obtained for the compounds. The log $i(t)$ vs. t plot for **1** was not linear, and **2a** also showed departure from ideal behavior to give an overall value of n = 1.99. Clearly, the product of electrolysis is not completely stable (even under these conditions) on the time scale of controlled-potential electrolysis for all complexes, and a regenerative mechanism is involved as noted above although the low temperature does slow down the rate of reaction.

The species obtained from the first primary reduction process were subject to ESR measurements as solid glasses at 77 K. The existence of paramagnetic nickel species was established, and while the reduced mononuclear compound **7a** showed a spectrum with g = 2.29 and g = 2.07, values that correspond to square-planar[15,25] and square-pyramidal nickel(I) compounds,[16,26] the reduced binuclear species gave rise to more than one ESR-active compound as indicated by the complex ESR spectra. One of the simpler spectra, that for compound **3a**, is shown in Figure 7. Although it is not possible to completely assign the signals to individual species, it is however clear that the first primary reduction process in these complexes occurs at the metal ion rather than at the ligand as indicated by the absence of an intense signal at $g \simeq 2.0$ corresponding to a radical anion.

Summary of the Electrochemistry of the Nickel(II) Compounds. To a first-order approximation, the binuclear nickel(II) complexes

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(25) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. *Inorg. Chem.* **1982**, *21*, 2403.
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Table IV. Cyclic Voltammetric Data for the Reduction of Compound **1** at the HMDE[a]

scan rate, mV s^{-1}	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f [b]	i_p^f, μA	$i_p^f v^{-1/2}$, μA s$^{-1/2}$
		Process 1, 21 °C				
500	-1.838	-1.758	70	0.96	12.5	0.56
200	-1.830	-1.754	66	0.94	8.5	0.60
100	-1.818	-1.748	70	0.90	6.3	0.63
50	-1.820	-1.750	70	0.96	4.3	0.61
20	-1.818	-1.749	69	0.99	2.9	0.65
10[c]	-1.820	-1.740	80	1.11	2.1	0.66
		Process 2				
500	-2.369	-2.283	86	1.06	10.3	0.46
200	-2.352	-2.275	77	0.97	6.6	0.46
100	-2.353	-2.277	76	0.83	5.8	0.58
50	-2.347	-2.278	69	0.78	4.3	0.61
20	-2.340	-2.272	68	0.78	2.6	0.58
10[c]	-2.340	-2.266	74	0.73	1.9	0.60
		Process 1, -23 °C				
500	-1.843	-1.765	78	0.97	9.0	0.40
200	-1.832	-1.766	66	0.94	6.3	0.45
100	-1.829	-1.765	64	0.90	4.6	0.46
50	-1.825	-1.770	55	0.91	3.2	0.45
20	-1.823	-1.770	53	0.94	2.0	0.45
10[c]	-1.822	-1.765	57	1.11	1.6	0.51
		Process 2				
500	-2.346	-2.267	79	1.00	9.0	0.40
200	-2.332	-2.265	67	1.02	6.0	0.42
100	-2.331	-2.265	66	1.06	4.2	0.42
50	-2.328	-2.268	60	1.09	3.1	0.44
20	-2.325	-2.271	54	1.09	2.0	0.45
10[c]	-2.323	-2.267	56	1.09	1.4	0.44

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4. v = scan rate; other symbols defined in Table II. [b] Determined according to: Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406. [c] Data obtained at this scan rate are subject to depletion effects.

Table V. Net Electron Transfer for the First Primary Reduction Process of the Nickel(II) Compounds[a,b]

compd	n, no. of e/molecule[c]	color of reduced species
1	0.7[d] (-2.05 V)	brown
2a	1.99[e] (-2.00 V)	brown
3a	1.08 (-1.80 V)	green
5	1.37 (-1.75 V)	brown
6	1.11 (-1.70 V)	brown
7a	0.93 (-1.80 V)	green

[a] Supporting electrolyte 0.1 M Et_4NClO_4 in DMF. [b] Carried out at -70 °C, under argon at a platinum-gauze electrode in darkness. [c] Electrolysis potential in parentheses. [d] Average of two limiting gradients for the nonlinear log $i(t)$ vs. t plot. [e] Measured at -52 °C.

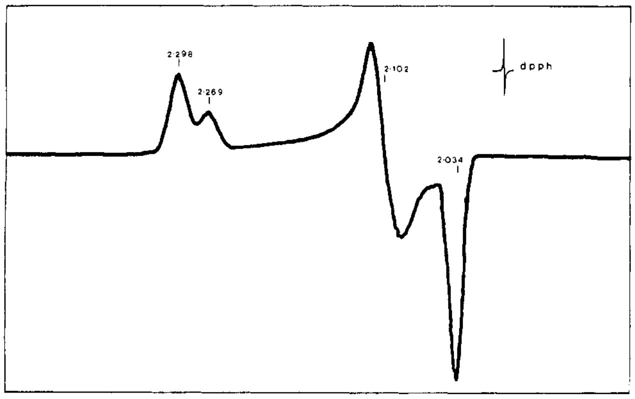

Figure 7. ESR spectrum of an electrolyzed solution of compound **3a** in DMF at 77 K (g values are indicated on the spectrum).

give rise to two one-electron processes described by eq 1 and 2. However, the chemistry clearly includes some complexities. The results of the cyclic voltammetry and ESR spectra of the reduced species may be explained by the existence of at least two binuclear species, in each sample, which are very closely related structurally. Compound **5** illustrates this most clearly. Although other investigators have observed these secondary processes in the voltammogram[4] they have hitherto remained unconsidered.

For the sake of simplicity, two closely related binuclear nickel(II) species α-[Ni_2L) and β-[Ni_2L] are considered. The following electrode processes responsible for the primary reductions can be postulated:

$$\alpha\text{-}[Ni_2L] + e^- \xrightleftharpoons{E^\circ(1\alpha),\ k_s(1\alpha)} \alpha\text{-}[Ni_2L]^- \quad (6)$$

$$\alpha\text{-}[Ni_2L]^- + e^- \xrightleftharpoons{E^\circ(2\alpha),\ k_s(2\alpha)} \alpha\text{-}[Ni_2L]^{2-} \quad (7)$$

$$\beta\text{-}[Ni_2L] + e^- \xrightleftharpoons{E^\circ(1\beta),\ k_s(1\beta)} \beta\text{-}[Ni_2L]^- \quad (8)$$

$$\beta\text{-}[Ni_2L]^- + e^- \xrightleftharpoons{E^\circ(2\beta),\ k_s(2\beta)} \beta\text{-}[Ni_2L]^{2-} \quad (9)$$

Interconversion of the α and β forms can occur:

$$\alpha\text{-}[Ni_2L]^- \xrightleftharpoons[k_{-1}]{k_1} \beta\text{-}[Ni_2L]^- \quad (10)$$

$$\alpha\text{-}[Ni_2L]^{2-} \xrightleftharpoons[k_{-2}]{k_2} \beta\text{-}[Ni_2L]^{2-} \quad (11)$$

The existence of all these species leads to the reactions

$$\beta\text{-}[Ni_2L]^{2-} + \alpha\text{-}[Ni_2L]^- \xrightleftharpoons[k_{-3}]{k_3} \beta\text{-}[Ni_2L]^- + \alpha\text{-}[Ni_2L]^{2-} \quad (12)$$

$$\beta\text{-}[Ni_2L]^- + \alpha\text{-}[Ni_2L]^{2-} \xrightleftharpoons[k_{-4}]{k_4} \beta\text{-}[Ni_2L]^{2-} + \alpha\text{-}[Ni_2L]^- \quad (13)$$

which must be thermodynamically favorable. The cyclic voltammetric data at low temperatures at the platinum electrode may be explained by the existence of the α and β species. At higher temperatures and in longer time scale experiments, the highly reactive anions have alternate reaction pathways (e.g. reactions with light, oxygen, or mercury at the HMDE). A theoretical treatment of such processes that are pertinent to the present study has recently[27] been made. Data are consistent with this theoretical study, although unfortunately in the present instance no knowledge of the structure of the complexes is available.

The cyclic voltammogram of the mononuclear **7a** shows a single reduction process when scanned to -1.7 V (Figure 8a). When the scan range is extended to -2.5 V (Figure 8b) an additional reduction process (peak 2) appears near the solvent limit. This chemically irreversible process gives rise to three additional peaks (3, 4, and 5) on the reverse scan. Two one-electron-reduction processes were also evident in the dc polarography at the DME ($E_{1/2}$ = -1.434 and -2.178 V at a drop time of 0.5 s), and it is likely that decomposition of the dianion is being observed since the nickel would have been converted to the zero oxidation state. While it is well-known that ligands which are strong π acceptors stabilize this oxidation state,[28] this is unlikely to occur here.

Dc Polarography of the Copper(II) Compounds. The three binuclear copper(II) compounds, **2b**, **3b**, and **10**, also show two primary reduction processes. Polarographic data are summarized in Table VI. In the case of **10**, two well-separated waves of equal

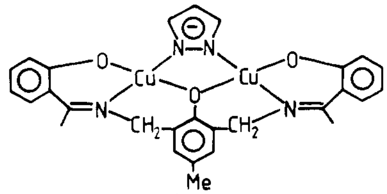

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Table VI. Dc Polarographic Data for the Reduction of Copper Complexes[a]

		process 1				process 2			
compd	drop time, s	$E_{1/2}(1)$, V vs. SCE	$E_{3/4}(1) - E_{1/4}(1)$, mV	slope (1),[b] mV	$i_l(1)$, μA	$E_{1/2}(2)$, V vs. SCE	$E_{3/4}(2) - E_{1/4}(2)$, mV	slope (2),[b] mV	$i_l(2)$, μA
2b	0.5	−1.098	53	59	3.5	−1.338	65	56, 76[c]	2.9
	1.0	−1.098	50	49	4.2	−1.327	62	68	3.8
3b	0.5	−0.999	56	58	5.8	−1.215	55	40, 74[c]	4.8
	1.0	−0.994	48	54	6.5	−1.185	44	58	6.0
10	0.5	−0.783	53	59	5.8	−1.046	53	59	5.6
	1.0	−0.783	57	62	6.8	−1.046	53	57	6.8
	2.0	−0.790	57	65	8.2	−1.018	47	51	7.5
9	0.5	−1.113	48	53					
7b	0.5	−1.018	42	45					

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; temperature 21 ± 2 °C. Symbols are defined in Table I. [b] Reciprocal slope of log $(i/(i_l - i))$ vs. E. [c] Plot fitted to two straight lines.

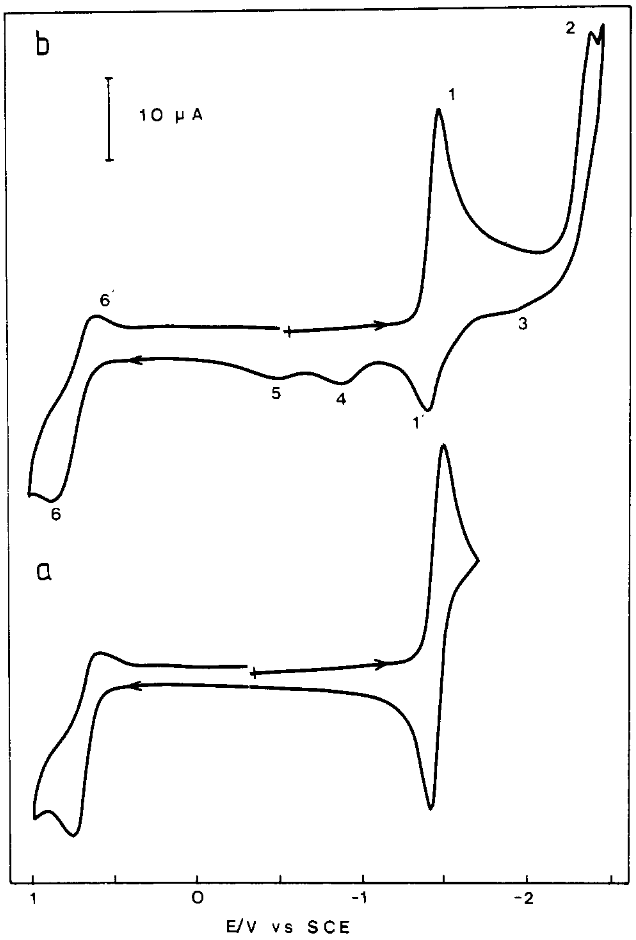

Figure 8. Cyclic voltammograms of compound **7a** at a platinum electrode: 20 °C, 100 mV s^{-1} scan rate. Range: (a) +1.0 to −1.7 V; (b) +1.0 to −2.5 V.

limiting current per unit concentration are observed, each corresponding to a one-electron reduction as indicated by comparisons with the limiting current from the reaction $Na^+ + e^- \rightleftharpoons Na(Hg)$ to the transfer step. Structural changes are believed to be associated with each of these steps[12] and the reaction

$$[Cu_2L]^{2-} + Cu_2L \rightleftharpoons 2[Cu_2L]^- \qquad (14)$$

is considered to play a significant role in the observed electrochemistry.[12] Complex electrode reactions are observed for **2b** and **3b** and the two reduction processes are not well separated. Figure 9 shows a dc polarogram of **3b**. A time dependence, which is not present in the Ni_2L data in the response, is indicated for the copper compounds. In particular the distinction between the two processes in **3b** is such that quantitative parameters for the second wave could not be determined unequivocally by dc polarographic techniques. However, differential-pulse polarography yields peak potentials that are in agreement with those calculated from dc polarography. In addition, a third process at a more negative potential was also detected with a peak potential of −1.32 V vs. SCE.

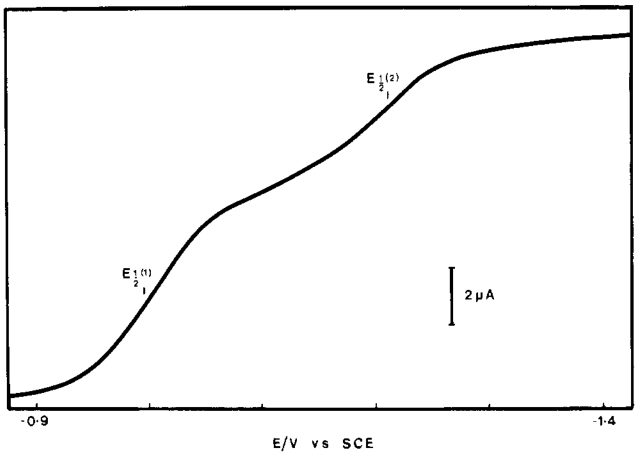

Figure 9. Dc polarographic reduction of compound **3b**: 21 °C, 0.5-s drop time.

Table VII. Cyclic Voltammetric Data for the Reduction of Compound **3b** at a Platinum Electrode[a]

scan rate, mV s^{-1}	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f	i_p^f, μA	$i_p^f v^{-1/2}$, μA s$^{-1/2}$
		Process 1				
200	−1.222	−0.845	377	0.78	22.5	1.59
100	−1.155	−0.898	257	0.79	16.0	1.60
50	−1.150	−0.914	236	0.78	12.3	1.73
20	−1.108	−0.938	170	0.76	8.0	1.79
10[b]	−1.090	−0.940	150	0.75	5.6	2.06
		Process 2[c]				
100	−1.600				15.5	1.55
50	−1.592				8	1.13
20	−1.583				5	1.11
10[b]	−1.592				3.3	1.04

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; T = 21 °C. Symbols as defined in Tables II and IV. [b] Data obtained at this scan rate are subject to depletion effects. [c] Irreversible; measurements taken from an −0.6 to −2.0 V scan.

Cyclic Voltammetry of the Copper(II) Compounds. Data for compound **3b** are summarized in Tables VII and VIII. Details of the results of cyclic voltammetry of **10** in DMF at the platinum electrode and at the HMDE have been presented previously[12] and include the processes

$$Cu_2L + e^- \xrightleftharpoons{E^\circ(1),\ k_s(1)} [Cu_2L]^- \qquad (15)$$

$$[Cu_2L]^- + e^- \xrightleftharpoons{E^\circ(2),\ k_s(2)} [Cu_2L]^{2-} \qquad (16)$$

$$[Cu_2L]^{2-} + [Cu_2L] \rightleftharpoons 2[Cu_2L]^- \qquad (17)$$

Table VIII. Cyclic Voltammetric Data for the Reduction of Compound **3b** at the HMDE[a]

scan rate, mV s^{-1}	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f	i_p^f, μA	$i_p^f v^{-1/2}$, μA $s^{-1/2}$
		Process 1				
500	-1.055	-0.967	88	0.94	10.5	0.47
200	-1.042	-0.960	82	0.85	6.8	0.48
100	-1.043	-0.962	81	0.83	4.8	0.48
50	-1.044	-0.962	82	0.88	3.5	0.49
20	-1.043	-0.958	85	0.89	2.4	0.54
10[b]	-1.040	-0.958	82	0.85	1.8	0.57
		Process 2[c]				
200	-1.620				3.6	0.25
100	-1.580				2.3	0.23
50	-1.595				1.7	0.24
20	-1.583				1.0	0.22

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; T = 20 °C. Symbols as defined in Table II and IV. [b] Data obtained at this scan rate are subject to depletion effects. [c] Irreversible, drop size smaller than for process 1.

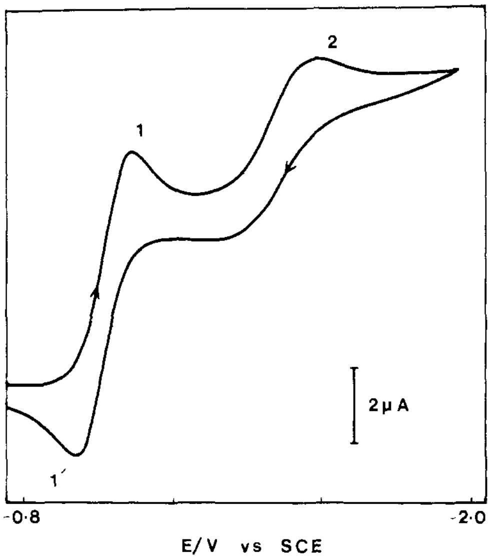

Figure 10. Cyclic voltammetric reduction of compound **3b** at a platinum electrode: 20 °C, 10 mV s^{-1} scan rate.

and structural rearrangements between the α and β forms of the electroactive species. The striking difference between the cyclic voltammetry of the other binuclear copper(II) species at the two different electrodes is clearly shown in Figure 10 (platinum electrode) and Figure 11 (HMDE) for compound **3b**. Peaks 3′, 4′, and 5′ are attributed to complex formation with the mercury electrode. Similar results are obtained for **2b**. The larger ΔE_p values for both compounds at the platinum electrode suggest a slower rate of electron transfer at that electrode compared to that at the HMDE. Some data as a function of scan rate are presented in Table VII and VIII. In contrast to **10**, the dianions of **2b** and **3b** appear to very unstable.

In the case of Ni_2L complexes, the $E°$ values of the different forms (α and β) are well separated. With copper, far greater interaction of the structurally related forms of the complexes occurs. The existence of at least two binuclear copper(II) species, α-[Cu_2L] and β-[Cu_2L] is again likely, as discussed previously for compound **10** and the nickel analogues. Structural rearragnement of α-$[Cu_2L]^-$ to β-$[Cu_2L]^-$ after reduction is supported by the time and temperature dependence of the electrode reactions in these compounds, as has been described in detail for **10**.[12]

Comparison of Data for Reduction of the Nickel(II) and Copper(II) Compounds. The reduction processes of the binuclear nickel(II) compounds occur at very negative potentials, particularly for the acetylacetone iminato derivatives, which are also less easily reduced than either of the two mononuclear compounds. The salicylideneamine derivatives **3a** and **5** are more stable to reduction than the mononuclear **7a**. However **4** is more easily reduced than its shorter carbon chain bridged analogue **3a**, which suggests that the chelate ring size of the endogenous ligand is important. Changes in the ligand "bite" of the exogenous ligand also affect the ease of reduction of the nickel sites, as indicated by the observation that **6** is easier to reduce than **3a**. Despite the very negative reduction potentials for the nickel complexes, $[Ni_2L]^-$ and $[Ni_2L]^{2-}$ have appreciable stability on the cyclic voltammetry time scale. In the few direct comparisons that are possible in the present study, it appears that the copper(II) species are easier to reduce than their corresponding nickel(II) analogues. In addition, they appear to be far more kinetically labile and $E°$ values between structurally related complexes and between the $[M_2L]^{0/-}$ and $[M_2L]^{-/2-}$ (M = Ni, Cu) couples are closer together with the copper complexes.

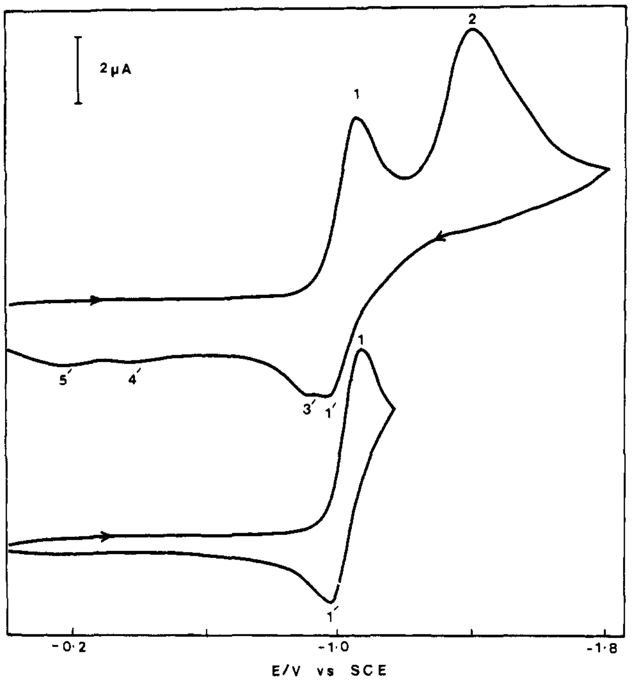

Figure 11. Cyclic voltammetric reduction of compound **3b** at the HMDE: 20 °C, 100 mV s^{-1} scan rate.

Single-crystal X-ray studies of an isolated one-electron-reduced binuclear copper(II) macrocyclic species[29] and solution studies by ESR[30] and XPES[31] measures have been reported. The contribution from the super-exchange coupling between the copper(II) ions to the stability of the mixed oxidation state intermediate was estimated to be small.[32] In the present study, compounds **2b**, **3b**, and **10** show antiferromagnetic exchange coupling of the two Cu(II), $S = {}^1/_2$, centers. For this very limited number of complexes there is a reasonable linear relationship between $\Delta E_{1/2}$ and $2J$ (the singlet–triplet separation). This does not imply that the relationship is direct in origin. The exchange coupling is a function of the coordination geometry around the metal ions, which may in turn influence various structural rearrangements incuding isomerization and solvent coordination. A more detailed study that involves a range of binuclear copper(II) species must be carried out before further generalizations can be made.

The chemical instability of the reduced copper compounds in this series is illustrated in the attempted preparation of a binuclear copper(I) compound having an exogenous acetate bridge. The compound isolated appears to have the structure shown sche-

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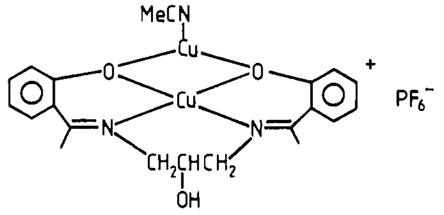
Table IX. Cyclic Voltammetric Data for the Oxidation of Nickel(II) Compounds at the Platinum Electrode[a]

compd	temp, °C	E_p^f, V vs. SCE	E_p^r, V vs. SCE	ΔE_p, mV	i_p^r/i_p^f
3a	20	0.950	0.727	223	0.8
5	−47	1.01	0.47	540	0.9
7a	20	0.745	0.630	115	0.68
7a	−47	0.840	0.450	390	1.19

[a] In DMF; supporting electrolyte 0.1 M Et_4NClO_4; scan rate 100 mV s^{-1}. In the case of an oxidation process the superscripts f and r now denote forward (oxidative) and reverse (reductive) scan directions, respectively.

matically as **11**. This species is similar to that proposed by Okawa and Kida[33] for a related compound.



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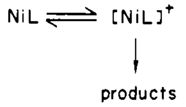
Oxidation Processes at the Platinum Electrode. The oxidation of the mononuclear nickel(II) complex **7a** is well-defined (Figure 8). The variation of the oxidation to reduction peak current ratio, with scan rate, for **7a** implies that the product is unstable and that the reaction can be represented by



$$\begin{array}{l}\mathrm{NiL} \rightleftharpoons [\mathrm{NiL}]^+ + e^- \\ \qquad\qquad \downarrow \\ \qquad\quad \text{products}\end{array} \qquad (18)$$

However, the small oxidation current, relative to the one-electron-reduction current, suggests considerable complexity and mechanistic details are unknown. Two oxidation processes are evident for **3a** at room temperature. The data for the first oxidative step are given in Table IX. However, the second oxidation, which occurs at more positive potential, was difficult to reproduce, a factor that may be due to precipitation of products on the electrode surface, as the current rapidly decays to zero in repetitive scanning under conditions of cyclic voltammetry. Two irreversible oxidation steps (0.8 and 1.1 V vs. SCE) are observed for **6** at room temperature while corresponding values of 0.82, 1.04 (**4**) and 1.0, and 1.2 V (**1**) are found at a scan rate of 100 mV s^{-1} for other compounds. In all cases chemical reactions and electrode surface reactions are competing with slow electron-transfer processes. Electrochemically reversible or quasi-reversible oxidations have been reported for a number of mononuclear nickel(II) compounds in acetonitrile.[15,34,35] This solvent may stabilize nickel in oxidation state III but it is not possible to carry out similar experiments in the present case because of the very limited solubility of most compounds in acetonitrile.

Irreversible oxidation of the copper(II) compounds occurs at about 1 V (vs. SCE) at the platinum electrode. Only one oxidation process is observed, and coating of the electrode with electrode-inactive material occurs as in the case of the nickel complexes. The electrochemical oxidation reactions are also irreversible at low temperatures (−60 °C).

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Registry No. **1**, 100230-53-3; **2a**, 100230-54-4; **2b**, 97703-60-1; **3a**, 100230-55-5; **3b**, 97703-56-5; **4**, 100230-56-6; **5**, 100230-57-7; **6**, 100230-58-8; **7a**, 100230-59-9; **7b**, 100230-60-2; **8a**, 100230-61-3; **9**, 100230-62-4; **10**, 100243-61-6; **11**, 100230-64-6; tetrakis(acetonitrile)-copper(I) hexafluorophosphate, 64443-05-6.

Supplementary Material Available: Tables SI and SII, listing electronic absorption spectra and ^{13}C NMR data, respectively, for nickel(II) compounds (2 pages). Ordering information is given on any current masthead page.

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(36) See paragraph regarding supplementary material at the end of the paper.

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Acid Decomposition Reactions of Diperoxo(amine)chromium(IV) Complexes

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The acid decomposition reactions of two diperoxo amine complexes of Cr(IV), viz. diperoxoaquo(ethylenediamine)chromium(IV), $Cr(O_2)_2(en)(H_2O)$, and diperoxo(diethylenetriamine)chromium(IV), $Cr(O_2)_2(dien)$, have been investigated at various H^+ concentrations. Three products have been obtained from the acid decomposition at 25–30 °C, and their relative proportions vary as a function of $[H^+]$. The products have been identified to be Cr(VI) (as $H_2Cr_2O_7$), $Cr(H_2O)_6^{3+}$, and $Cr(en)(H_2O)_4^{3+}$ in the case of $Cr(O_2)_2(en)(H_2O)$. The dien derivative gives minor amounts of Cr(VI) as well as $Cr(H_2O)_6^{3+}$ and substantial amounts of $Cr(dienH)(H_2O)_4^{4+}$. Kinetic as well as product analysis data have been rationalized in terms of a reaction scheme involving monoperoxochromium(VI), 6-coordinate chromium(IV), and hydroperoxo radical intermediates. The formation of the hydroperoxo radical intermediate has also been detected by means of scavenging experiments with tetranitromethane. The data have been discussed in terms of a model in which the nuclear reorganizations needed for the conversion of Cr(VI) to octahedral Cr(III) derivatives are important.

Introduction

There has been much current interest in the study of transition-metal complexes in unusual oxidation states,[2–4] particularly in view of their possible roles in biochemical and chemical catalysis.[5,6] Since clinical use of Cr(III) in the control of diabetes

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