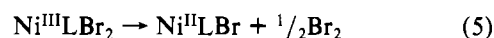
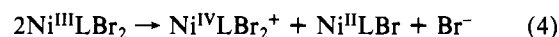


Figure 9. Proposed structure of a bridged transition state/intermediate in the exchange reaction between two nickel complexes.

9), in which the bridging Ni-halide bonds are strongly weakened by the single electron, which occupies essentially the σ -antibonding orbital d_{z^2} . In the Co(III) complexes this orbital is empty and the Co-X bond is therefore much stronger.

(2) The exchange reaction proceeds via a redox step. Two different possibilities exist:



In both cases an exchange can take place easily in the five-coordinate Ni(II) species, followed by reoxidation. A purely dissociative substitution reaction is very unlikely in these solvents. More detailed kinetic investigations are in progress.

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Complexes of Binucleating Ligands with Two Different Coordination Environments. 4. Electrochemical Properties and Molecular Structure of the Heterobinuclear Complex [5,5'-(1,2-Ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)(4-)]nickelcopper, NiCu(BAA)₂en

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The electrochemical properties of the heterobinuclear complex [5,5'-(1,2-ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)(4-)]nickelcopper, NiCu(BAA)₂en, have been investigated with cyclic voltammetry and controlled-potential electrolysis. The CV in dimethylformamide consists of one quasi-reversible wave in the 0- to -2.0-V region with an approximate $E_{1/2}$ of -0.90 V. Addition of an excess of Na⁺ as NaNO₃ causes a shift of +300 mV and greatly increases the cathodic peak current. The new wave, which is highly reversible in the scan rate range of 0.050-50.000 V/s, is due to two overlapping waves in which the potentials are very similar. The cathodic peak currents in the presence of Na⁺ were calculated by using a current function of 0.97, which is consistent with two reversible sequential, one-electron transfers with $E_2^\circ - E_1^\circ = -14$ mV. Agreement between experimental and calculated I_{pc} values was about 2% over the entire scan rate range on this basis when a small amount of weak reactant adsorption was included. The electrochemical properties of the binuclear complex were compared to those of related mononuclear Ni(II) and Cu(II) complexes in order to assess the significance of the presence of the two metal centers. As a means of understanding the electrochemistry in the context of structural properties, NiCu(BAA)₂en (C₂₆H₂₄N₂O₄CuNi) was crystallized from the electrochemical solvent, DMF, and examined by X-ray techniques. The structure consists of dimers of heterobinuclear molecules in which the copper is bound to four ketonic oxygens and the nickel is bound to two ketonic oxygens and two nitrogens from the ethylenediamine moiety. The intramolecular Ni-Cu distance is 2.925 Å. The distance between the mean planes of the molecules in the dimer is 3.21 Å. One of the methine carbons of the ligand backbone of one molecule lies 3.06 Å above the copper atom of the second molecule. The copper is displaced 0.11 Å out of the molecular plane toward this carbon in a typical square-pyramidal fashion. Crystal data: $P2_1/c$, $a = 13.052$ (2) Å, $b = 8.612$ (2) Å, $c = 20.295$ (4) Å, $\beta = 98.38$ (2)°, $Z = 4$, $R_1 = 0.050$, $R_2 = 0.051$.

Introduction

In previous papers in this series we have described a systematic synthetic approach to the preparation of heterobinuclear complexes based upon the selectivity of the different coordination sites in the Schiff-base diamine derivatives of 1,3,5-triketones.¹ In several instances, it has been possible to isolate and characterize both the mononuclear precursors and the heterobinuclear complexes that result from binding the two metal ions to the same ligand molecule.^{1a,2} With this approach and, by comparison to the mononuclear precursors, it is possible to determine the effect of two metal ions per

molecule on the chemical and physical properties.

The electrochemical properties of polynuclear transition-metal complexes have been of primary interest to use as a means of determining the chemical significance of having two or more metal ions per molecule that are close enough to have some reasonable interaction. Previously, we have described the unusual electrochemistry associated with the binuclear Cu(II) complexes of 1,3,5-triketones and their diamine Schiff bases.³⁻⁵ The results of these electrochemical studies in the presence of excess Na⁺ are consistent with two reversible, sequential, one-electron transfers at the same (or very nearly the same) potential. This interpretation is based upon the

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excellent agreement between the experimental results and the theory developed by Shain and co-workers^{6,7} for overlapping cyclic voltammetric waves. Surprisingly, identical electron-transfer properties are observed for the bis(1,3,5-triketono)dicopper(II) complexes in which the two Cu(II) ions are in the same coordination environments and in the diamine Schiff bases where they are in much different coordination environments, i.e. one is bound to two imido nitrogens and two enolic oxygens while the other is bound to four enolic oxygens.⁵ The major difference between the cyclic voltammograms of the two classes of binuclear Cu(II) complexes is simply a shift to more negative reduction potentials for the Schiff-base derivatives as compared to the triketonates. The overall symmetry and features of the CV waves for the two classes are very similar. Thus, it appears as if the acceptor orbitals are being averaged by the ligand and as if the two redox centers are behaving as one that is perturbed by ligand modifications.

Another conclusion from previous work⁵ is that the potentials for the reversible, sequential transfer of the two electrons are strongly affected by the presence of cations such as Li⁺ and Na⁺. It is apparent from this work that simple cations are strongly complexed by the reduced species since the potentials are about 300 mV more positive in their presence than in their absence. The presence of these cations enhances the reversibility of two-electron transfer and causes the two potentials to be virtually equal.

An electrochemical study of the heterobinuclear molecule NiCu(BAA)₂en and its mononuclear precursors Ni(HBAA)₂en-N₂O₂ and Cu(HBAA)₂en-O₂O₂ was undertaken to test the postulate that the acceptor orbitals in this class of complexes are significantly affected by the adjacent metal ion. Indeed, one of the long-range goals of this research is to determine whether the presence of two metal ions per molecule significantly alters the chemical reactivity when compared to related mononuclear complexes. The electrochemical study of NiCu(BAA)₂en, reported herein, yielded the surprising result that this heterobinuclear complex also exhibits electrochemical properties indicative of the transfer of two electrons at very nearly the same potential. As a means of determining whether the unusual electrochemical behavior is at all due to structural peculiarities in the electrochemical solvent, dimethylformamide, single crystals of NiCu(BAA)₂en were prepared from DMF and the structure was determined by X-ray techniques.

Experimental Section

Synthesis. The synthesis and characterization of NiCu(BAA)₂en,^{1a} Ni(HBAA)₂en-N₂O₂,^{1a} and Cu(HBAA)₂en-O₂O₂² have been reported.

Electrochemical Measurements. The electrochemical techniques and apparatus have been described.⁵ In addition, rapid-scan cyclic voltammograms were obtained with the assistance of a Nicolet Explorer III digital oscilloscope.

Structure Determination. The binuclear complex NiCu(BAA)₂en, C₂₆H₂₄N₂O₄CuNi (fw 550.8), crystallizes from dimethylformamide as small deep red needles. A primitive monoclinic system was suggested by oscillation photographs, and the space group $P2_1/c$ (C_{2h}^2) was confirmed by the structure analysis. Cell dimensions of $a = 13.052$ (2) Å, $b = 8.612$ (2) Å, $c = 20.295$ (4) Å, and $\beta = 98.38$ (2)° were obtained at a temperature of approximately 23 °C by least-squares analysis of the setting angles of 15 reflections with 2θ ranging from 20 to 35°. With four molecules per unit cell, the calculated density is 1.62 g/cm³. Intensity data were collected with a Syntex P₂ diffractometer, with Mo K α radiation selected by a graphite monochromator. Two crystals were used, one for data with 2θ less than 40° and a second for data with 2θ between 40 and 50°. The dimensions of the crystals were approximately 0.08 × 0.34 × 0.04 mm and 0.10 × 0.27 × 0.03 mm, respectively, and the needle axes, which were along

the crystallographic b axis, were each inclined about 20° to the φ axis. The θ - 2θ scan method was used, with a constant scan rate of 0.50°/min in 2θ on either side of the α_1 - α_2 doublet. Stationary-crystal stationary-counter background counts were made at each end of the scan range, for a total of half of the scan time. The intensities of the -2,2,2 and the 406 reflections were measured once every 5-6 h. A step correction was made for the random fluctuations of $\pm 3\%$, an average increase of 1-2% in intensity over the data collection period was observed. The data were reduced to F^2 and $\sigma(F^2)$ values by procedures previously described.⁸ Standard deviations were assigned as

$$\sigma(I) = [\sigma_c(I)^2 + (pI)^2]^{1/2}$$

where $\sigma_c = (I + K^2B)^{1/2}$, I = net intensity, B = background counts, $p = 0.05$, and $K = 2.0$ = ratio of scan time to background time. Corrections for absorption were made⁹ ($\mu = 18.2$ cm⁻¹), and they varied from 1.05 to 1.18. In all, the intensities of 4498 reflections in the quadrant $h, k, \pm l$ were measured, with 1865 independent reflections having $I > 2\sigma(I)$.

The structure was solved by heavy-atom methods in a straightforward manner. Least-squares refinement of isotropic parameters for C, N, and O atoms and of anisotropic parameters for Cu and Ni atoms converged with $R_1 = \sum \Delta / \sum |F_o| = 0.058$ and $R_2 = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2} = 0.071$, where $\Delta = \|F_o\| - |F_c|$. Scattering factors were taken from ref 10 with allowance made for anomalous scattering by the Cu and Ni atoms.¹¹ Upon refinement with the positions of the Cu and Ni atoms reversed, the R values rose to $R_1 = 0.060$ and $R_2 = 0.075$, confirming the assignment of Ni as the metal atom coordinating to the N atoms. Positions for the H atoms were now calculated, with assumed C-H distances of 0.95 Å, tetrahedral angles where appropriate, local C_{2v} symmetry at the C atoms, and a staggered conformation for the methyl groups. The B values for the thermal motion of the H atoms were fixed at 10% above the B values for the C atoms to which they were bonded. When these fixed H atoms were included in a least-squares refinement using all data, with separate scale factors varied for the low- and high-angle data, convergence was obtained at $R_1 = 0.053$ and $R_2 = 0.055$. In a final refinement, anisotropic temperature factors were assigned to all of the oxygen atoms, giving 168 variables refined. The R_1 and R_2 values were 0.050 and 0.051, and the "goodness of fit" was 1.17. The average value of $(w\Delta^2)$ varied by no more than $\pm 10\%$ for subsets of the data in various ranges of θ and of $|F_o|$. The highest peaks in a final difference Fourier map were near carbon atoms and were of height 0.6-0.7 e/Å³, the same as peaks representing H atoms in earlier maps. Alternative refinements were also tried, either with the methyl carbon atoms assigned anisotropic temperature factors or with the phenyl groups constrained to fixed geometry and other light atoms refined anisotropically. The R values were not significantly lowered, nor were the bond lengths changed significantly. Final positional and isotropic thermal parameters are presented in Table I. Interatomic distances and angles are listed in Tables II and III, respectively. The atom-numbering scheme is shown in Figure 1. Tables of structure factors, anisotropic thermal parameters, hydrogen atom parameters, and selected intermolecular distances have been deposited as supplementary material.

Results

Structural results show that NiCu(BAA)₂en consists of discrete binuclear molecules in which the Ni atom is coordinated to two nitrogens and two central enolate oxygens and the Cu atom is coordinated to four enolate oxygens (Figure 1). All of the atoms except for those in the phenyl groups and the methylene and methyl hydrogens are within about 0.1 Å of the mean molecular plane. Even the phenyl groups are tilted only 8° with respect to this plane. There is a fairly good molecular plane of symmetry normal to the molecular plane and passing through the Ni and Cu atoms as is seen in the tables of interatomic distances and angles (Tables II and III).

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Table I. Positional and Isotropic Thermal Parameters for NiCu(BAA)₂en

atom	x	y	z	B(iso) ^a
Cu	0.1580 (1)	0.1472 (1)	0.0573 (0)	
Ni	-0.0407 (1)	0.2968 (1)	0.0110 (1)	
O(1)	0.2448 (4)	0.0238 (6)	0.0139 (2)	
O(4)	0.0525 (4)	0.1617 (6)	-0.0186 (2)	
O(13)	0.0606 (4)	0.2922 (6)	0.0849 (3)	
O(16)	0.2543 (4)	0.1757 (6)	0.1338 (2)	
N(7)	-0.1339 (5)	0.2913 (8)	-0.0653 (3)	3.4 (1)
N(10)	-0.1257 (5)	0.4311 (7)	0.0470 (3)	3.2 (1)
C(2)	0.2201 (6)	-0.0367 (9)	-0.0460 (4)	2.7 (2)
C(3)	0.1294 (6)	-0.0116 (9)	-0.0872 (4)	2.9 (2)
C(4)	0.0459 (6)	0.0851 (9)	-0.0764 (4)	3.1 (2)
C(5)	-0.0423 (6)	0.1051 (9)	-0.1229 (4)	3.7 (2)
C(6)	-0.1253 (6)	0.2053 (10)	-0.1161 (4)	3.5 (2)
C(8)	-0.2256 (7)	0.3869 (10)	-0.0622 (4)	4.3 (2)
C(9)	-0.2169 (6)	0.4776 (10)	0.0010 (4)	4.1 (2)
C(11)	-0.1094 (6)	0.4877 (9)	0.1074 (4)	3.6 (2)
C(12)	-0.0221 (6)	0.4485 (9)	0.1545 (4)	3.5 (2)
C(13)	0.0603 (6)	0.3563 (10)	0.1441 (4)	3.5 (2)
C(14)	0.1486 (6)	0.3315 (9)	0.1932 (4)	3.3 (2)
C(15)	0.2333 (6)	0.2543 (9)	0.1867 (4)	2.9 (2)
C(6A)	-0.2110 (7)	0.2081 (11)	-0.1768 (5)	5.4 (2)
C(11A)	-0.1847 (7)	0.5984 (10)	0.1309 (4)	4.7 (2)
C(12A)	0.3053 (6)	-0.1315 (9)	-0.0659 (4)	3.1 (2)
C(2B)	0.2967 (6)	-0.2101 (10)	-0.1265 (4)	3.6 (2)
C(2C)	0.3795 (7)	-0.2938 (11)	-0.1433 (4)	4.5 (2)
C(2D)	0.4710 (7)	-0.3014 (10)	-0.1020 (4)	4.7 (2)
C(2E)	0.4811 (7)	-0.2271 (10)	-0.0410 (4)	4.3 (2)
C(2F)	0.3988 (6)	-0.1420 (10)	-0.0235 (4)	3.6 (2)
C(15A)	0.3261 (6)	0.2483 (8)	0.2402 (4)	2.7 (2)
C(15B)	0.4068 (6)	0.1464 (9)	0.2355 (4)	3.4 (2)
C(15C)	0.4916 (7)	0.1372 (10)	0.2854 (4)	4.4 (2)
C(15D)	0.4983 (7)	0.2330 (10)	0.3406 (4)	4.4 (2)
C(15E)	0.4203 (7)	0.3355 (10)	0.3446 (4)	4.5 (2)
C(15F)	0.3356 (6)	0.3453 (10)	0.2957 (4)	3.8 (2)

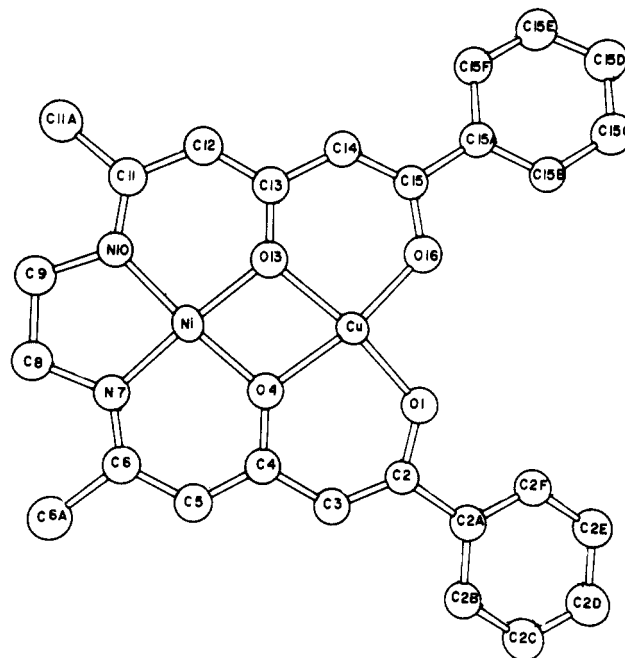
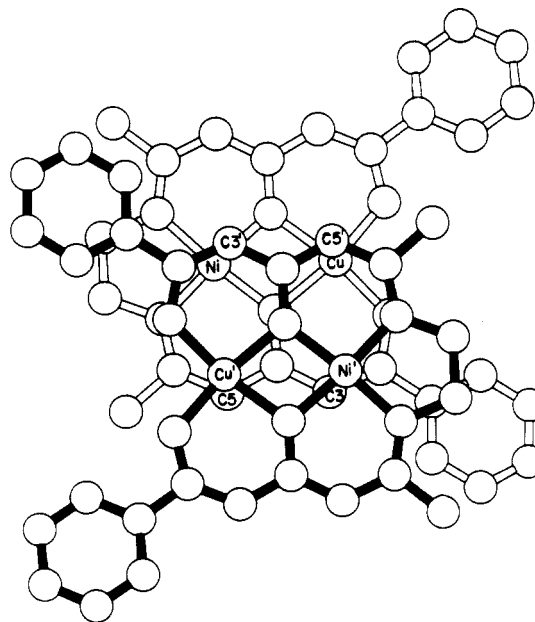
^a The form of the isotropic thermal parameter is $\exp[-B(\text{iso}) \cdot ((\sin^2 \theta)/\lambda^2)]$.

Table II. Interatomic Distances (Å)

Cu-Ni	2.925 (1)	C(11)-C(12)	1.42 (1)
Cu-O(1)	1.866 (5)	C(5)-C(4)	1.39 (1)
Cu-O(16)	1.866 (5)	C(12)-C(13)	1.38 (1)
Cu-O(4)	1.914 (5)	C(4)-C(3)	1.41 (1)
Cu-O(13)	1.923 (5)	C(13)-C(14)	1.43 (1)
Ni-O(4)	1.847 (5)	C(3)-C(2)	1.36 (1)
Ni-O(13)	1.849 (7)	C(14)-C(15)	1.37 (1)
Ni-N(7)	1.825 (7)	C(2)-C(2A)	1.48 (1)
Ni-N(10)	1.827 (6)	C(15)-C(15A)	1.46 (1)
O(1)-C(2)	1.32 (1)	C(2A)-C(2B)	1.40 (1)
O(16)-C(15)	1.31 (1)	C(2B)-C(2C)	1.38 (1)
O(4)-C(4)	1.34 (1)	C(2C)-C(2D)	1.36 (1)
O(13)-C(13)	1.32 (1)	C(2D)-C(2E)	1.38 (1)
N(7)-C(6)	1.29 (1)	C(2E)-C(2F)	1.39 (1)
N(10)-C(11)	1.31 (1)	C(2F)-C(2A)	1.39 (1)
N(7)-C(8)	1.46 (1)	C(15A)-C(15F)	1.39 (1)
N(10)-C(9)	1.46 (1)	C(15F)-C(15E)	1.38 (1)
C(8)-C(9)	1.49 (1)	C(15E)-C(15D)	1.37 (1)
C(6)-C(6A)	1.54 (1)	C(15D)-C(15C)	1.38 (1)
C(11)-C(11A)	1.50 (1)	C(15C)-C(15B)	1.39 (1)
C(6)-C(5)	1.41 (1)	C(15B)-C(15A)	1.38 (1)

Out-of-plane distortions from the mean molecular plane are consistent with this plane of symmetry. The planar molecules are arranged approximately in stacks along the *b* axis to which they are inclined by 39°. Neighboring molecules in the stack are related by inversion centers with the distances between mean molecular planes of 3.21 and 3.50 Å for neighbors related by inversion centers at (0, 0, 0) and (0, 1/2, 0), respectively.

The coordination of O(4), N(7), N(10), and O(13) around the Ni atoms is strictly planar while the Cu atom is displaced 0.11 Å from the plane through O(1), O(4), O(13), and O(16). The nearest-neighbor contacts to Ni and Cu across the in-

**Figure 1.** Numbering scheme for the atoms in NiCu(BAA)₂en.**Figure 2.** Orientation of the two NiCu(BAA)₂en molecules in the dimer showing important intermolecular interactions.

version center at (0, 0, 0) are Ni...C(3)(-x, -y, -z) = 3.21 Å and Cu...C(5)(-x, -y, -z) = 3.06 Å. The displacement of the Cu atom from its coordination plane is in the direction of this contact to C(5). There are fewer contacts on the other side of the molecule except that one of the methylene hydrogens from the ethylenediamine moiety approaches the Cu atom rather closely, Cu...H(9A)(-x, 1 -y, -z) = 2.63 Å. The orientation of two nearest neighbors (through $\bar{1}$ at 000) is shown in Figure 2.

The electron-transfer properties for the mononuclear complexes, Ni(HBAA)₂en-N₂O₂ and Cu(HBAA)₂en-O₂O₂, as determined by cyclic voltammetry are quite irreversible in DMF at a HMDE. The CV for Ni(HBAA)₂en-N₂O₂ is shown in Figure 3. There is a completely irreversible reduction between -1.8 and -1.9 V vs. saturated NaCl calomel, which presumably corresponds to reduction of Ni(II). There is no significant effect of adding Na⁺ to the solution. The CV of Cu(HBAA)₂en-O₂O₂ under the same conditions exhibits a

Table III. Interatomic Angles (deg)

O(4)-Cu-O(13)	76.3 (2)	Ni-N(10)-C(11)	125.8 (6)	O(1)-C(2)-C(3)	125.2 (6)
O(1)-Cu-O(4)	94.1 (2)	Ni-N(7)-C(8)	113.4 (5)	O(16)-C(15)-C(14)	124.8 (7)
O(13)-Cu-O(16)	93.8 (2)	Ni-N(10)-C(9)	113.9 (5)	O(1)-C(2)-C(2A)	112.1 (6)
O(16)-Cu-O(1)	94.9 (2)	C(6)-N(7)-C(8)	121.7 (7)	O(16)-C(15)-C(15A)	112.9 (7)
O(1)-Cu-O(13)	168.7 (2)	C(11)-N(10)-C(9)	120.3 (7)	C(2)-C(2A)-C(2B)	122.8 (7)
O(4)-Cu-O(16)	168.3 (2)	N(7)-C(8)-C(9)	111.8 (7)	C(2)-C(2A)-C(2F)	119.5 (7)
O(4)-Ni-O(13)	79.8 (2)	N(10)-C(9)-C(8)	111.1 (7)	C(2F)-C(2A)-C(2B)	117.7 (7)
O(4)-Ni-N(7)	95.3 (3)	N(7)-C(6)-C(6A)	119.6 (8)	C(2A)-C(2B)-C(2C)	120.4 (70)
O(13)-Ni-N(10)	95.4 (3)	N(10)-C(11)-C(11A)	120.8 (7)	C(2B)-C(2C)-C(2D)	121.5 (8)
N(7)-Ni-N(10)	89.3 (3)	C(5)-C(6)-C(6A)	114.3 (7)	C(2C)-C(2D)-C(2E)	119.4 (9)
O(4)-Ni-N(10)	175.2 (3)	C(12)-C(11)-C(11A)	115.9 (7)	C(2D)-C(2E)-C(2F)	119.8 (8)
O(13)-Ni-N(7)	175.4 (4)	N(7)-C(6)-C(5)	126.1 (8)	C(2E)-C(2F)-C(2A)	121.2 (7)
Cu-O(1)-C(2)	125.2 (5)	N(10)-C(11)-C(12)	123.3 (8)	C(15)-C(15A)-C(15F)	123.2 (7)
Cu-O(16)-C(15)	125.5 (5)	C(4)-C(5)-C(6)	125.7 (7)	C(15)-C(15A)-C(15B)	119.6 (7)
Cu-O(4)-Ni	102.1 (2)	C(11)-C(12)-C(13)	127.0 (7)	C(15B)-C(15A)-C(15F)	117.2 (7)
Cu-O(13)-Ni	101.7 (2)	O(4)-C(4)-C(5)	118.4 (7)	C(15A)-C(15F)-C(15E)	120.9 (8)
Cu-O(4)-C(4)	128.4 (5)	O(13)-C(13)-C(12)	119.0 (7)	C(15F)-C(15E)-C(15D)	121.7 (8)
Cu-O(13)-C(13)	128.7 (5)	O(4)-C(4)-C(3)	118.2 (7)	C(15B)-C(15D)-C(15C)	118.5 (8)
Ni-O(4)-C(4)	129.4 (5)	O(13)-C(13)-C(14)	117.6 (7)	C(15D)-C(15C)-C(15B)	120.3 (8)
Ni-O(13)-C(13)	129.1 (5)	C(2)-C(3)-C(4)	128.3 (7)	C(15C)-C(15B)-C(15A)	121.3 (8)
Ni-N(7)-C(6)	124.7 (6)	C(13)-C(14)-C(15)	128.3 (7)		

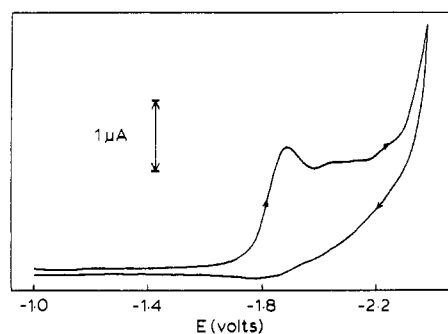


Figure 3. CV of 4.7×10^{-4} M Ni(HBAA)₂en-N₂O₂ in DMF with 0.1 M TEAP at 0.050 V/s with a HMDE.

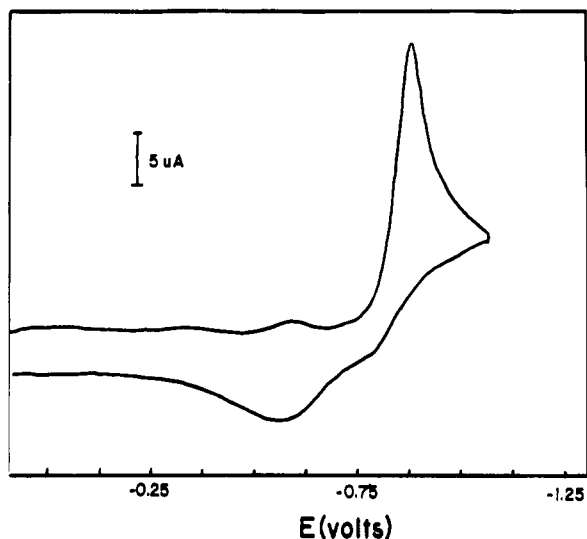


Figure 4. CV of 1.0×10^{-3} M Cu(HBAA)₂en-O₂O₂ in DMF with 0.1 M TEAP and 1.0×10^{-2} M NaNO₃ at 20 V/s with a HMDE.

reduction at about -1.2V followed by a strong adsorption and a positive current on the reverse sweep. Addition of a tenfold excess of Na⁺ as NaNO₃ shifts the reduction to about -0.85 V and helps the adsorption problem. The adsorption problem is further diminished at fast scans. The CV shown in Figure 4 represents the best results it was possible to achieve using a HMDE. Obviously, the process is irreversible. There is some improvement by using a Pt disk electrode, but the cathodic wave is still much larger than the anodic wave and, therefore, the process is still quite irreversible. The cyclic voltammetric results for Ni(acac)₂en,¹² in which the Ni environment is very

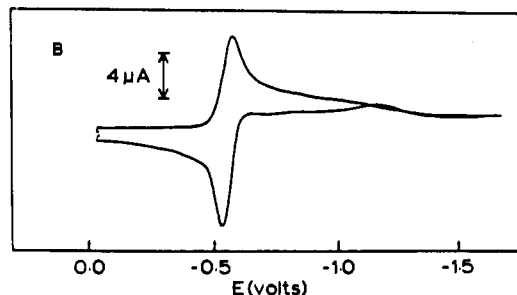
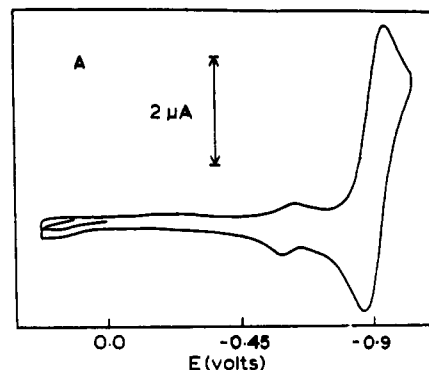


Figure 5. (A) CV of 1.0×10^{-3} M NiCu(BAA)₂en in DMF with 0.1 M TEAP at 0.050 V/s with a HMDE. (B) CV of 1.0×10^{-3} M NiCu(BAA)₂en in DMF with 0.1 M TEAP and 1.0×10^{-2} M NaNO₃ at 0.050 V/s with a HMDE.

similar to the Ni environment in NiCu(BAA)₂en, are consistent with a reversible one-electron transfer with $E_{1/2} = -2.09$ V vs. SSCE. In the scan rate range 0.500–50.00 V/s, the peak potential separation, ΔE_p , is 59 (± 5) mV, the peak current ratio, I_{pa}/I_{pc} , is 1.00 (± 0.10), the half-width of the cathodic wave, $E_{pc} - E_{pc/2}$, is 59 (± 4) mV, and $I_{pc}/\nu^{1/2}$ is reasonably constant.

The heterobinuclear NiCu(BAA)₂en in DMF with tetraethylammonium perchlorate (TEAP) as supporting electrolyte exhibits a quasi-reversible cyclic voltammetric wave with $E_{1/2}$ about -0.9 V vs. saturated SSCE (Figure 5A). The value of ΔE_p is scan rate dependent increasing from 101 mV at 0.050 V/s to 203 mV at 2.00 V/s. The value of $E_{pc} - E_{pc/2}$ increases from 64 to 122 mV in this range. The values I_{pa}/I_{pc} and $I_{pc}/\nu^{1/2}$ are, on the other hand, reasonably constant in this scan range. These results were obtained with a Pt-disk electrode

(12) The dianionic ligand (acac)₂en²⁻ is the ethylenediamine Schiff-base derivative of 2,4-pentanedione.

Table IV. Cyclic Voltammetric Data for NiCu(BAA)₂en in the Presence of Na⁺ Ions at Various Scan Rates^a

scan rate, V/s	E_{Pc} , V	E_{Pa} , V	ΔE_p , mV	$E_{1/2}$, V	I_{Pc} , μA	I_{Pa}/I_{Pc}	$E_{Pc} - E_{Pc/2}$, mV	$I_{Pc}/\nu^{1/2}$ ^b
0.050	-0.62	-0.59	35	-0.61	1.76	0.97	47	0.25
0.100	-0.62	-0.58	44	-0.60	2.48	0.94	47	0.25
0.500	-0.62	-0.56	51	-0.60	6.03	0.86	47	0.27
1.000	-0.62	-0.56	52	-0.59	8.76	0.82	49	0.28
2.000	-0.62	-0.56	54	-0.59	12.85	0.81	56	0.29
5.000	-0.62	-0.56	56	-0.59	23.34	0.76	61	0.33
10.000	-0.62	-0.56	55	-0.59	37.15	0.72	63	0.38
20.000	-0.62	-0.56	58	-0.59	62.15	0.65	68	0.44
50.000	-0.621	-0.55	67	-0.59	125.40	0.59	74	0.56

^a 2.32×10^{-4} M in DMF with 0.1 M TEAP and 2.3×10^{-3} M NaNO₃, HMDE. Potentials are vs. the saturated NaCl calomel electrode.
^b Units are $\mu A/(mV s^{-1})^{1/2}$.

Table V. Comparison between Experimental and Calculated Cathodic Peak Current Values for Ni(acac)₂en and NiCu(BAA)₂en

scan rate, V/s	exptl (calcd) I_{Pc} , μA		
	Ni(acac) ₂ en ^a	NiCu(BAA) ₂ en ^b	NiCu(BAA) ₂ en ^c
0.050	13.24 (10.9)	110.2 (108)	1.76 (1.83)
0.100	27.48 (24.4)	152.7 (152)	2.48 (2.62)
1.000	35.85 (34.6)	325.6 (340)	8.76 (9.18)
2.000	51.05 (48.9)	431.8 (481)	12.85 (13.74)
5.000	78.35 (77.3)		23.34 (24.12)
10.000	107.80 (109.0)		37.15 (37.92)
20.000	153.50 (155.0)		62.15 (61.24)
50.000	243.60 (244.0)		125.40 (120.70)

^a Current function, $\pi^{1/2}\chi(at) = 0.446$, $C_0 = 2.048 \times 10^{-3}$ M, $A = 2.22 \times 10^{-2}$ cm², and $D = 8.0 \times 10^{-6}$ cm²/s were used in the calculation. ^b Current function, $\pi^{1/2}\chi(at) = 0.446$, $C_0 = 7.74 \times 10^{-4}$ M, $A = 0.88$ cm² (Pt disk), and $D = 6.9 \times 10^{-6}$ cm²/s were used in the calculation. ^c Current function, $\pi^{1/2}\chi(at) = 0.970$, $C_0 = 2.315 \times 10^{-4}$ M, $A = 2.22 \times 10^{-2}$ cm², and $D = 6.9 \times 10^{-6}$ cm²/s were used in the calculation. The calculated values include the effect of weak reactant adsorption in which $a = 602AC_0D\pi^{1/2}\chi(at) = 7.88 \times 10^{-6}$ and $b = 1.30 \times 10^{-6}$. Experimental values are from Table IV in which the concentration of Na⁺ is 2.3×10^{-3} M (tenfold excess).

since severe adsorption was encountered with Hg at the faster scans. The original wave diminishes on addition of Na⁺, and a more reversible wave at about -0.6 V appears. When the ratio [Na⁺]:[NiCu(BAA)₂en] is 1.0 or greater, the initial, "more negative" wave is completely gone, leaving only the wave at -0.6 V in the region from 0 to -2.0 V. Increasing the ratio of [Na⁺]:[NiCu(BAA)₂en] from 1 to 10 causes the wave to sharpen, until at a ratio of 10 or greater the cathodic half-peak width, $E_{Pc} - E_{Pc/2}$, and peak separation, ΔE_p , attain a constant value (Figure 5B). The characteristics of the CV wave as a function of scan rate in the presence of a tenfold excess of Na⁺ are presented in Table IV. Under these conditions, excellent CV's could be obtained with a hanging-mercury-drop electrode. A typical CV is shown in Figure 5B.

In Table V, the experimental values of I_{Pc} for Ni(acac)₂en, NiCu(BAA)₂en without Na⁺, and NiCu(BAA)₂en with excess Na⁺ are compared with calculated I_{Pc} values. The general equation for the calculated values is

$$I_{Pc} = [602D_0^{1/2}AC_0^*\pi^{1/2}\chi(at)]\nu^{1/2}$$

Since D_0 , A , C_0^* , and ν are experimentally determined, the current function, $\pi^{1/2}\chi(at)$, can be calculated at one scan rate and used to calculate I_{Pc} throughout the scan rate range. The value of n , the number of electrons transferred, is incorporated into the current function in each case. For both Ni(acac)₂en and NiCu(BAA)₂en without Na⁺, the I_{Pc} values are quite well reproduced with $\pi^{1/2}\chi(at) = 0.446$, which is the value appropriate for a reversible one-electron transfer.¹³ For NiCu(BAA)₂en with a tenfold excess of Na⁺, calculation of

Table VI. Cycled Controlled-Potential Electrolysis of NiCu(BAA)₂en in the Presence and Absence of Na⁺

	potential, V	Q_T , C		no. of electrons/molecule ^c
		theoret	exptl	
A. No Na ⁺ Present				
1. redn	-1.00	3.40 ^a	3.38	1.99
2. oxidn	-0.40	3.40 ^a	2.90	1.71
3. redn	-1.00	3.40 ^a	2.93	1.72
B. 30-fold Excess Na ⁺ Present				
1. redn	-0.82	3.82 ^b	3.69	1.93
2. oxidn	-0.35	3.82 ^b	3.47	1.82
3. redn	-0.82	3.82 ^b	3.43	1.80

^a Total coulombs expected for a two-electron reduction or oxidation of 1.761×10^{-5} mol of NiCu(BAA)₂en. ^b Total coulombs expected for a two-electron reduction or oxidation of 1.976×10^{-5} mol of NiCu(BAA)₂en. ^c Each separate electrolysis step required approximately 2 h.

I_{Pc} values requires a much larger value of the current function, i.e. $\pi^{1/2}\chi(at) = 0.970$. This is indicative of two reversible, sequential one-electron transfers in which $E_2 - E_1 \cong -15$ mV.¹⁴ At the faster scan rates the experimentally observed I_{Pc} for NiCu(BAA)₂en with Na⁺ increases more rapidly than does $\nu^{1/2}$. Such behavior is characteristic of weak reactant adsorption and has been treated by Wopschall and Shain.¹⁵ Calculation of I_{Pc} including some weak reactant adsorption is possible with the equation

$$I_{Pc} = a\nu^{1/2} + b\nu$$

since the current due to the diffusing species is proportional to $\nu^{1/2}$ while that due to adsorbed species is proportional to ν . In these calculations, $a = 602AD_0^{1/2}C_0\pi^{1/2}\chi(at)$ and b is considered an adjustable parameter. With a current function equal to 0.970 and by including adsorption, the agreement between experimental and calculated I_{Pc} values is excellent.

Controlled-potential electrolysis (CPE) of NiCu(BAA)₂en in DMF with 0.1 M TEAP and a 30:1 molar ratio of NaNO₃ to complex at -0.82 V resulted in the transfer of 2.0 (± 0.1) electrons per molecule. Electrolysis in the absence of Na⁺ at -1.0 V also resulted in the transfer of 2.0 (± 0.1) electrons per molecule. Thus, by CPE both the "more negative" and the "more positive" waves correspond to two-electron-transfer processes. These results have been reproduced on samples from several different and independent preparations. Cycled CPE experiments were carried out by exhaustively reducing and reoxidizing and then reducing the same solution a second time. The results are given in Table VI. If the mercury was removed after the initial reduction and replaced with a fresh

(13) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706; *Anal. Chem.* **1965**, *37*, 178 and 191.

(14) We are grateful to Professor Dennis Evans for furnishing the program for calculating multi-electron-transfer current functions. See: Sokol, W. F.; Evans, D. H.; Niki, K.; Yagi, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *108*, 107.

(15) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

mercury pool, the subsequent reoxidation does not occur. Hence, during the long times associated with coulometry (ca. 2 h) the copper apparently is reduced to Cu^0 and amalgamated with the mercury causing decomposition of the complex.

Discussion

The heterobinuclear complex, $\text{NiCu}(\text{BAA})_2\text{en}$, is one member of a class of compounds whose synthesis depends upon the site selectivity for different metal ions offered by unsymmetric ligands such as $\text{H}_4(\text{BAA})_2\text{en}$.^{1,2} In the case of $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ with $\text{H}_4(\text{BAA})_2\text{en}$, the selectivity is, as far as we know, quantitative, and only one isomer is isolated, i.e. $\text{Ni}(\text{II})$ with N_2O_2 coordination and $\text{Cu}(\text{II})$ with O_2O_2 coordination. In a previous paper,^{1b} $\text{NiCu}(\text{BAA})_2\text{en}$ was characterized by analytical, spectral, and magnetic properties, which were all consistent with the isomer just described. Magnetic results were perhaps most instructive in this regard since the $\text{Ni}(\text{II})$ bound to the two nitrogens and two ketonic oxygens is square planar and diamagnetic, whereas when bound to the four ketonic oxygens it also binds two solvent molecules and is six-coordinate and paramagnetic.^{1c} The fact that $\text{NiCu}(\text{BAA})_2\text{en}$ has a magnetic moment of $1.89 \mu_B$ at 300 K and $1.85 \mu_B$ at 77 K^{1b} is proof that the $\text{Ni}(\text{II})$ is diamagnetic and that the $\text{Cu}(\text{II})$ is a normal paramagnetic species with no significant antiferromagnetic interactions.

An electrochemical investigation of $\text{NiCu}(\text{BAA})_2\text{en}$ was undertaken since it appeared that this molecule would be an excellent point of reference in our electrochemical studies of binuclear $\text{Cu}(\text{II})$ 1,3,5-triketones and their diamine Schiff bases.³⁻⁵ It would presumably furnish a compound in which one electroactive center in the binuclear $\text{Cu}(\text{II})$ complexes that reduces in the -0.5 to -0.9 -V region would be replaced by $\text{Ni}(\text{II})$ that could be expected to reduce at about -1.5 V vs. saturated NaCl calomel. In addition, the mononuclear complexes that represent each "half" of the heterobinuclear complex had been prepared and completely characterized in previous studies.^{1,2} In the case of $\text{Ni}(\text{HBAA})_2\text{en}-\text{N}_2\text{O}_2$, coordination of the $\text{Ni}(\text{II})$ to the two imido nitrogens and two enolic oxygens was confirmed by infrared and visible spectra and by the fact that the compound is rigorously diamagnetic. Even minute traces of the oxygen-bound isomer would be detectable by magnetic susceptibility measurements since under these conditions the $\text{Ni}(\text{II})$ also binds solvent molecules and is paramagnetic.^{1c} There is no evidence for any measurable concentration of the oxygen-bound isomer in any of the several samples prepared in our laboratory. For $\text{Cu}(\text{HBAA})_2\text{en}-\text{O}_2\text{O}_2$, coordination of the $\text{Cu}(\text{II})$ to the four enolic oxygens was confirmed by spectral and X-ray structural studies.² Thus, these two mononuclear complexes allow one to study the electrochemistry of each metal ion separately in very similar coordination environments and with identical ligands, as in $\text{NiCu}(\text{BAA})_2\text{en}$, but without the influence of the second metal ion. The electrochemical properties of these three compounds were investigated under as nearly identical conditions as possible.

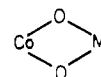
The mononuclear $\text{Ni}(\text{II})$ complex, $\text{Ni}(\text{HBAA})_2\text{en}$, exhibits irreversible redox behavior as shown in Figure 3. Reduction, presumably to $\text{Ni}(\text{I})$, takes place at about -1.85 V, and there is virtually no anodic wave. Another compound, $\text{Ni}(\text{acac})_2\text{en}$, which is structurally and electronically similar to the $\text{Ni}(\text{II})$ compounds of interest to this study, has been investigated under the same experimental conditions. The CV of $\text{Ni}(\text{acac})_2\text{en}$ shows a reversible redox process consistent with the transfer of one electron. This is confirmed by the fact that ΔE_p and $E_{pc} - E_{pc/2}$ at scan rates from 0.10 to 50.00 V/s are close to the expected value of 59 mV, and the I_{pc} values are very well reproduced by the current function equal to 0.446. The reduction potential is -2.1 V vs. saturated NaCl calomel. Busch and co-workers¹⁶ have examined a number of nitrogen

macrocyclic $\text{Ni}(\text{II})$ complexes in acetonitrile vs. $\text{Ag}/\text{AgNO}_3(0.1 \text{ M})$ and have found that for complexes with dianionic ligands (neutral complexes) the reduction potentials are more negative than -2.0 V under these conditions. Each of these results suggests that $\text{Ni}(\text{II})$ in a N_2O_2 environment with anionic ligands should reduce at quite negative potentials.

Mononuclear $\text{Cu}(\text{II})$ complexes structurally and electronically related to $\text{NiCu}(\text{BAA})_2\text{en}$, in general, exhibit irreversible CV waves. Under the same conditions employed for $\text{NiCu}(\text{BAA})_2\text{en}$, $\text{Cu}(\text{HBAA})_2\text{en}$ has a relatively irreversible CV wave with a reduction potential of about -0.85 V. Three bis(1,3-diketono)copper(II) complexes, $\text{Cu}(\text{acac})_2$, $\text{Cu}(\text{DBM})_2$, and $\text{Cu}(\text{BA})_2$,¹⁷ under these conditions described for $\text{NiCu}(\text{BAA})_2\text{en}$ reduce at potentials of about -0.85 , -0.67 , and -0.58 V, respectively.¹⁸ The CV for $\text{Cu}(\text{acac})_2$ is irreversible in that no anodic wave is observed while $\text{Cu}(\text{DBM})_2$ and $\text{Cu}(\text{BA})_2$ are quasi-reversible in that anodic waves are observed, but there is a strong scan rate dependence. Controlled-potential electrolysis proved that in each case 2.0 electrons per molecule were transferred during exhaustive electrolysis, thereby forming the Cu/Hg amalgam. On CPE, therefore, reduction results in total decomposition of the complex.

The electrochemical properties of the mononuclear complexes do not give any strong clues to aid in understanding the redox properties of $\text{NiCu}(\text{BAA})_2\text{en}$. It is, however, very clear that the introduction of a second metal ion has a profound effect on the redox properties. The effects are multiple and include substantial changes in the redox potentials, reversibility, stability of the reduced product, and the number of electrons transferred. The cyclic voltammetric results for $\text{NiCu}(\text{BAA})_2\text{en}$ in the absence of Na^+ using the values of ΔE_p , I_{pa}/I_{pc} , $E_{pc} - E_{pc/2}$, and $I_{pc}/\nu^{1/2}$ as measures of reversibility show that the process is quasi-reversible and that it becomes more irreversible at faster scan rates. At scan rates faster than 1.0 V/s, the wave is distorted and poorly defined. The CV process appears to be due to a one-electron transfer since the cathodic peak currents are well reproduced by using a one-electron current function (Table V).

In the presence of an excess of Na^+ , the CV wave for $\text{NiCu}(\text{BAA})_2\text{en}$ shifts about +300 mV (Figure 5). This is the same behavior that is observed for the binuclear $\text{Cu}(\text{II})$ triketones and their diamine Schiff bases.⁵ The shift in potentials for these compounds has been explained on the basis of complexation of the Na^+ by the binuclear compounds with particularly strong association between Na^+ and the anionic reduction products.⁵ In the current study, these would be $[\text{NiCu}(\text{BAA})_2\text{en}]^-$ and $[\text{NiCu}(\text{BAA})_2\text{en}]^{2-}$. Presumably the Na^+ would be bound to the two terminal oxygens that are also bound to the $\text{Cu}(\text{II})$. There is precedent for this kind of interaction including X-ray structure determinations of $\text{Co}(\text{I})$ Schiff-base complexes of Na^+ and Li^+ of the type $[\text{Co}(\text{salen})\text{Na}(\text{THF})]_n$ and $\text{Co}(\text{salen})\text{Li}(\text{THF})_2$.¹⁹ In these cases the Na^+ and Li^+ ions are coordinated to the ligand oxygens forming a four-membered



ring. The Na^+ and Li^+ coordination appears to stabilize $\text{Co}(\text{I})$, and judging from the +300-mV shift in potentials, they also

- (16) Busch, D. H.; Pillsbury, D. G.; Lovecchio, F. V.; Tait, A. M.; Ung, Y.; Jackels, S.; Rakowski, M. C.; Shammel, W. P.; Martin, L. Y. *ACS Symp. Ser.* 1977, 38, 32.
 (17) acac^- is 2,4-pentanedionato, DBM^- is 1,3-diphenyl-1,3-propanedionato, and BA^- is 1-phenyl-1,3-butanedionato.
 (18) Fenton, D. E. Ph.D. Thesis, Wayne State University, 1978.
 (19) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zansori, A. R. *Inorg. Chem.* 1979, 18, 3469.

stabilize the low oxidation states of the binuclear Cu(II) and the Ni₂Cu complexes.

In addition to the +300-mV shift in potential, the presence of Na⁺ results in a significant increase in the peak currents. There are two possible reasons for this: (1) more electrons are being transferred and/or (2) the reactant is weakly adsorbed on the electrode surface. The two effects are easily distinguished on the basis of scan rate data since the cathodic current due to weakly adsorbed reactant increases directly with scan rate rather than with the square of the scan rate.¹⁵ Thus, at slow scans, the effect of reactant adsorption is relatively small. As seen from the calculations in Table V, both factors are contributing to the large value of I_{pc} . The calculated values of I_{pc} (with a current function of 0.970) at slow scans where the effect of adsorption is minimal agree very well with experimental results. Indeed, throughout the entire scan rate range a current function of 0.970 and the inclusion of weak reactant adsorption resulted in excellent agreement between calculated and experimental results of I_{pc} for NiCu(BAA)₂en with an excess of Na⁺ present. Confirmation of the basic correctness of the current function may be obtained independently from values of ΔE_p and $E_{pc} - E_{pc/2}$ since these are related to $E_2 - E_1$ and, therefore, to $\pi^{1/2}\chi(at)$ for the sequential transfer of two electrons.^{6,7} Concentrating on the slower scans the values of ΔE_p and $E_{pc} - E_{pc/2}$ are clearly less than 59 mV. The values at 1.000 V/s are 52 and 49 mV, respectively. The current function of 0.950, which is calculated with these parameters, corresponds to a potential separation, $E_2 - E_1$, of -20 mV.¹⁴ On the other hand, the current function of 0.970 that reproduces the I_{pc} values so well corresponds to $E_2 - E_1 = -14$ mV and $\Delta E_p = E_{pc} - E_{pc/2} = 46$ mV. Hence, the values 0.970 and 0.950 bracket a reasonable range for $E_2 - E_1$ of -17 ± 3 mV. Inasmuch as the current function is more than twice the 0.4463 value for a simple one-electron transfer, there can be little doubt that the cyclic voltammograms observed are due to the transfer of two electrons. In this case the I_{pc} current values are consistent with two reversible, sequential, one-electron transfers with very similar potentials. On the basis of these results, the addition of Na⁺ not only shifts the potential +300 mV but also changes the redox process from one-electron transfer to two-electron transfer and greatly increases the reversibility. This is also true for the binuclear Cu(II) complexes.⁵

At faster scans it is obvious that the cathodic peak current for the NiCu(BAA)₂en wave, in the presence of Na⁺, increases more rapidly than $\nu^{1/2}$. However, the anodic peak current, I_{pa} , does not increase at the same rate. As a result, the ratio I_{pa}/I_{pc} decreases markedly as the scan rate increases. Such behavior is characteristic of weak reactant adsorption.¹⁵ In this case, the adsorption is weak enough so as not to significantly distort the wave. The major effect is to decrease the dependence on diffusion with the resultant increase in the current. The excellent agreement between the experimental and calculated I_{pc} shown in Table V supports the conclusion that the CV is the result of a basically reversible two-electron transfer in which $E_2^\circ - E_1^\circ \cong -17$ mV with a few percent of the reactant weakly adsorbed. The interpretation involving both two-electron transfer and weak reactant adsorption explains essentially all of the data in Table IV. It should be emphasized that the role of Na⁺ (or other simple cations) is critical in this process.

There is no indication on the basis of the present data that the ligand is actively involved in the electrochemistry since the ligand reduction potentials observed⁴ are quite negative and no analogous electrochemistry is observed in the mononuclear Ni(HBAA)₂en and Cu(HBAA)₂en complexes. In addition, the CV of such organic molecules is normally totally irreversible in nonprotic media. These facts would seem to

preclude any normal ligand redox processes taking place in the 0.0- to -1.5-V region in DMF. Thus, it appears that the redox is metal based. Presuming that this interpretation is correct, there is a profound chemical effect of having two metal ions held in a particular juxtaposition by the ligand(s) since the entire electrochemical character is altered compared to mononuclear precursors. Considering for the moment just the reduction potentials, under similar conditions the reduction potential of NiCu(BAA)₂en is -0.59 V, while for Ni(acac)₂en is -2.09 V, for Ni(HBAA)₂en-N₂O₂ is about -1.8 V, and for Cu(HBAA)₂en-O₂O₂ is about -0.85 V. The considerable positive shift in the reduction potential of NiCu(BAA)₂en must be caused by the presence of the two metal ions. In addition, with the exception of Ni(acac)₂en, the mononuclear complexes exhibit irreversible CV's while the process for NiCu(BAA)₂en is quite reversible. This also must be due to the presence of two metal ions.

The controlled-potential electrolysis results support the conclusion that the CV wave observed for NiCu(BAA)₂en with Na⁺ present is a two-electron transfer process. However, on the long time scale of CPE there is decomposition that results in Cu⁰. This is apparent from the experiment in which, after reduction, the Hg pool was replaced with fresh Hg. There was no reoxidation with fresh Hg implying that the copper had been removed as Cu/Hg amalgam. In addition, electrolysis using a Pt electrode resulted in Cu⁰ deposition on the electrode. These results are consistent with a slow disproportionation-type reaction proceeding on the time scale of CPE.

The difficulty in accepting the logical conclusion of the cyclic voltammogram results, i.e. that the Cu(II) and the Ni(II) are reducing at virtually the same potentials, led us to search for a possible explanation for this behavior in structural factors. For this reason crystals were grown from the electrochemical solvent, DMF, and the structure was determined by X-ray techniques. Of course, extrapolating from the solid structure to the solution electrochemical behavior may not be a fruitful exercise. However, significant structural peculiarities may furnish valuable clues to the molecular source of the electrochemical properties. For this reason, discussion of the structure will be centered on the characteristics that are somewhat unusual as compared to related compounds.^{1,2}

One distinctive feature of these NiM(BAA)₂en complexes is the planarity of the ligand atoms including the carbons of the ethylenediamine moiety, which results in eclipsed hydrogens on these methylene carbons. This phenomenon has been discussed in previous papers.^{1b,c} Perhaps the most distinctive structural feature of NiCu(BAA)₂en is the axial interaction of the copper that gives rise to dimers. The atom from a second molecule that approaches the Cu atom most closely is the C(5). Although the distance is long (Cu-C(5) = 3.06 Å), there is little question that there is an interaction since the Cu atom is drawn 0.11 Å out of the molecular plane toward C(5) indicating a reasonably strong axial interaction.²⁰ To our knowledge, the Cu(II)-C axial interaction observed for NiCu(BAA)₂en is quite rare. It is interesting to note in this regard that a Cu(I) environment described by Gagne and co-workers²¹ in a mixed-valent Cu(II)-Cu(I) macrocyclic ligand complex is very similar to the Cu(II) environment in NiCu(BAA)₂en. The Cu(I) in the macrocyclic complex is disordered with 65% of them displaced 0.15 Å from the best plane of the N₂O₂ donor atoms toward an aromatic ring carbon of an adjacent molecule. The Cu(I)-C distance is 3.04 Å. In addition to the similar Cu(II)-C and Cu(I)-C distances and copper atom displacements, the carbon atoms involved in both

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axial interactions are similar with respect to their type and position in the two different ligands.

One might have expected that dimer formation in NiCu(BAA)₂en would have been the result of a Cu(II) axial interaction with an oxygen from the other molecular pair. Indeed, this is common and has even been observed in the mononuclear precursor, Cu(HBAA)₂en-O₂,² and in a binuclear Cu(II) triketonate.² Judging from the fact that the axial Cu(II)-O distance in Cu(HBAA)₂en is 2.27 Å and the Cu(II)-C distance in NiCu(BAA)₂en is 3.06 Å, a Cu(II)-O interaction would have afforded the possibility of a much stronger interaction. For some reason, addition of the Ni(II) has lengthened the axial Cu-L distance from 2.27 to 3.06 Å and changed the nature of L from oxygen to carbon (or the π system). Perhaps associated with this change is the fact that the Cu-bridging oxygen bond distance of 1.918 Å is the shortest yet observed for this general class of compounds.²⁰ While it is not clear whether the axial change has a large effect on the electrochemical properties, it does suggest that the addition of Ni(II) has changed the electronic nature of the axial Cu(II) orbitals and subsequently changed the Lewis acidity of the copper. It is logical to assume that these orbitals are the same ones most strongly affected by the electrode as the molecule diffuses toward the electrode.

If the presumption that the Ni(II) is reduced to Ni(I) in the CV and in the CPE is correct, then the reduction potential for Ni(II) → Ni(I) has been shifted about +0.9 V upon the introduction of Cu(II) into Ni(HBAA)₂en. Conceptually a shift of this magnitude is possible, since ligand modifications including changes in remote substituents often cause shifts considerably larger.^{16,22-24} Concentrating on just the coordination environment about the Ni(II) may give some clues as to the origin of a potential shift. The bond lengths and angles appear quite normal, but somewhat different from analogous values in Ni(acac)₂en.²⁵ The most significant difference between the Ni(II) environments in Ni(acac)₂en and NiCu(BAA)₂en seems to be that the average Ni-O bond length in NiCu(BAA)₂en is 0.014 Å shorter than in Ni(acac)₂en and the average Ni-N distance is 0.024 Å shorter

in NiCu(BAA)₂en than in Ni(acac)₂en. Hence, there appears to be a systematic shortening of the Ni-donor bonds in NiCu(BAA)₂en as compared to Ni(acac)₂en. The other significant difference is the size of the O-Ni-O angle, which is 79.8° in NiCu(BAA)₂en and 82.8° in Ni(acac)₂en. Since both Ni atoms are rigorously planar, the smaller angle in NiCu(BAA)₂en is compensated by an increase of about 1° in the other three angles.

Another structural parameter of this molecule that distinguishes it somewhat from all the other homo- and heterobinuclear complexes of this class studied to date is the metal-metal distance. The Ni-Cu distance of 2.925 Å is the shortest yet observed by about 0.1 Å. Presumably this is due to the relatively short bonds to the bridging oxygen and the high degree of coplanarity for the metals and donor atoms.

At this point, it is not clear whether or not the structural parameters discussed above have any significant role in establishing the unusual electrochemical properties observed. However, they do draw attention to features that may be important and that form some basis for the design and study of future systems. While we have no satisfactory physical explanation for the observed behavior, phenomenologically it is similar to the binuclear Cu(II) complexes.³⁻⁵ In many respects, these compounds behave electrochemically as if they had only one electroactive center that is capable of undergoing two-electron redox rather than two centers each capable of one-electron redox. We have not yet observed two separated CV waves for any of the binuclear Cu(II) complexes no matter whether the Cu(II) ions are in equivalent environments (as in symmetric triketonates) or in nonequivalent environments (as in the diamine Schiff bases). The effect of such ligand changes is to perturb the redox center(s) and shift the potential, but they do not bring about two separated Cu(II) → Cu(I) waves. Curiously, the same observation has now been extended to the heterobinuclear complex NiCu(BAA)₂en.

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Registry No. NiCu(BAA)₂en, 55998-68-0; Ni(HBAA)₂en, 55998-67-9; Cu(HBAA)₂en, 56550-32-4; Ni(acac)₂en, 42948-35-6; NaNO₃, 7631-99-4; Na, 7440-23-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, intermolecular distances, hydrogen positions, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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A Bond-Order Function for Metal-Metal Bonds

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For computational purposes multiple bonds are considered as single bonds intensified by screening of the internuclear repulsion. A linear relationship between bond order and screening allows the calculation of multiple-bond properties from single-bond potential energy Morse curves. The scheme is successfully applied for the calculation of bond length and dissociation energy of the homonuclear double, triple, and quadruple bonds of Cr, Mo, W, and Re.

A general relationship between bonds that differ in order only was recently described¹ for bonds between atoms of the p-block elements. The method assumes that bond order derives

essentially from changes in the repulsive part of covalent interactions and more specifically from a modification of the internuclear repulsion due to electronic screening. In practice, a single-bond potential energy curve is modified by allowing for reduced internuclear repulsion to produce potential energy curves for bonds of higher order. The modification consists

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