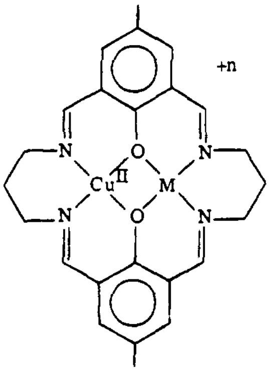
pyridine *N*-oxide photolysis has been reported by Jerina et al., though the oxidizing active species has not been clarified with certainty: Jerina, D. M.; Boyd, D. R.; Daly, J. W. *Tetrahedron Lett.* **1970**, 457-460.

Setsuo Takamuku,* Hiroyuki Matsumoto
Akira Hori, Hiroshi Sakurai
The Institute of Scientific and Industrial Research
Osaka University, Suita, Osaka 565, Japan

Received January 16, 1979

An Electrochemical Method for Measuring Electronic Delocalization in Mixed-Valent Species

Sir:



1 M = Cu(II), n = 2
2 M = Cu(I), n = 1
3 M = Mn(II), n = 2
4 M = Fe(II), n = 2
5 M = Co(II), n = 2
6 M = Ni(II), n = 2
7 M = Zn(II), n = 2

Binucleating macrocyclic ligands offer attractive opportunities to study electron-transfer processes and metal–metal interactions. For example, the mixed-valent complex, $\mathrm{Cu^{I}Cu^{II}L^{+}}$, **2**, apparently exhibits temperature-dependent intramolecular electron transfer ($\sim 10^{10}\ \mathrm{s^{-1}}$ at 25 °C).[1,2] The macrocyclic ligand in **2** also permits study of a series of complexes in which the ligand environment, including that of the bridging ligands, remains essentially constant while the metals are varied. Capitalizing on this feature we report here an electrochemical method for directly measuring the electronic delocalization energy in the mixed-valent complex, **2**, and in related materials.

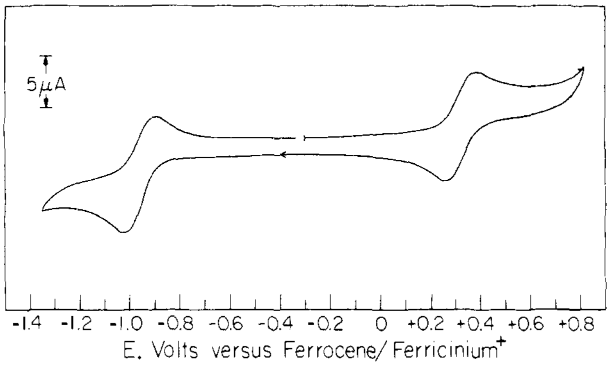


Figure 1. The cyclic voltammogram of $\mathrm{CuMnL^{+n}}$, **3**, in methanol. The wave at +0.3 V corresponds to the Mn(III/II) couple. At −1.0 V is the Cu(II/I) wave. The absence of shoulders on each wave indicates little contamination by homonuclear impurities.

The $\mathrm{Cu^{II}Cu^{II}L^{+2}}$ complex, **1**,[3] was prepared by the method of Robson.[4] All of the new heterobinuclear complexes, $\mathrm{Cu^{II}M^{II}L^{+2}}$, **3**–**7**, were prepared by a stepwise synthesis, under mild conditions, as follows. Condensation of 2 equiv of 2-hydroxy-5-methylisophthalaldehyde with 1 equiv each of 1,3-diaminopropane and Cu(II) led to isolation of a mononuclear copper(II) complex.[5] Further reaction with 1 equiv of the appropriate divalent metal ion gave a complex with Cu(II) presumably in an $\mathrm{N_2O_2}$ site and the second metal in an $\mathrm{O_4}$ site. Subsequent reaction with 1 more equiv of 1,3-diaminopropane gave the heterobinculear complexes, **3**–**7**.[6] All of the complexes gave satisfactory C, H, N, and M analyses and have been further characterized by X-ray fluorescence spectroscopy, electronic and infrared absorption spectroscopy, and variable-temperature magnetic susceptibility.[7] All complexes also exhibit cyclic voltammograms and differential pulse polarograms, which help to provide further evidence that the new complexes are uniformly heterobinuclear and not mixtures of homobinuclear species. For example, the $\mathrm{Cu^{II}Cu^{II}L^{+2}}$ complex, **1**, exhibits two one-electron redox processes at $E_1 = -0.94$ V and $E_2 = -1.31$ V:[3,8,9]

$$\mathrm{Cu^{II}Cu^{II}L^{+2} + e^- \overset{E_1}{\rightleftharpoons} Cu^{I}Cu^{II}L^{+}}$$

$$\mathrm{Cu^{I}Cu^{II}L^{+} + e^- \overset{E_2}{\rightleftharpoons} Cu^{I}Cu^{I}L} \qquad (1)$$

In contrast, only a single reduction of Cu(II) to Cu(I) is observed in the $\mathrm{CuM^{II}L^{+n}}$ series, **3**–**7**, as shown in Figure 1 for the complex $\mathrm{Cu^{II}Mn^{II}L^{+2}}$, **3**.

Mixed-valent ion stabilization energies can be extracted from the magnitude of the separation of the two one-electron redox processes, $E_1 - E_2$, observed for the homobinuclear complexes. The separation actually reflects several phenomena, which can be considered for any binuclear complex, in the absence of significant coordination geometry changes, as follows. (1) Noninteracting metal sites will have $E_1 - E_2 = 36$ mV, attributable to the simple statistical factor, $RT/F \ln 4$.[11] (2) Electrostatic interactions become important as the metals come closer together yielding $E_1 - E_2 > 36$ mV. If $E_1 - E_2$ is large enough ($\sim$100 mV), two one-electron waves can often be resolved.[12] (3) Superexchange interactions may occur in one or more oxidation states, which can either increase or decrease the magnitude of $E_1 - E_2$. (4) Electronic delocalization can stabilize mixed-valent species which will be reflected as an increased separation, $E_1 - E_2$.

The electrochemical behavior of the $\mathrm{Cu^{II}Cu^{II}L^{+2}}$ species, **1**, can be analyzed in this context. The measured separation $E_1 - E_2 = 370$ mV is corrected for the statistical factor, 36 mV, to give $E_1 - E_2 = 334$ mV. The measured superexchange stabilization in the $\mathrm{Cu^{II}Cu^{II}L^{+2}}$ species ($-3/4\,J = 217\ \mathrm{cm^{-1}} = 27$ mV)[13] is used to correct $E_1 - E_2$ to 361 mV. No correction need be applied due to the diamagnetic $\mathrm{Cu^{I}Cu^{I}L}$ species. The separation $E_1 - E_2 = 361$ mV then reflects electrostatic interactions and covalent stabilization of the mixed-valent $\mathrm{Cu^{I}Cu^{II}}$ species relative to the $\mathrm{Cu^{II}Cu^{II}}$ and $\mathrm{Cu^{I}Cu^{I}}$ species. Previous attempts to separate these contributions have relied on estimating the electrostatic component.[14] In the present case the heterobinuclear complexes, **3**–**6**, permit the covalent factor to be isolated since the electrostatic factor is constant.

Copper(II/I) reduction potentials as a function of the divalent metal ion in the second site

$$\mathrm{Cu^{II}M^{II}L^{+2} + e^- \rightleftharpoons Cu^{I}M^{II}L^{+}} \qquad (2)$$

$$\mathrm{M^{II} = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}}$$

are listed in Table I. Reduction potentials have been corrected for superexchange stabilization in the $\mathrm{Cu^{II}M^{II}L^{+2}}$ species as described above, and as estimated from magnetic susceptibility

0002-7863/80/1502-1443$01.00/0

Table I. Copper(II/I) Reduction Potentials as a Function of the Adjacent Metal.[a] Potentials Are Given vs. the Ferrocene/Ferricinium Ion[a]

complex	adjacent metal	E^f, measd	E^f, corr[b]
3	Mn(II)	−1.07 ± 0.01	−1.07 ± 0.01
4	Fe(II)	−1.07 ± 0.01	−1.06 ± 0.01
5	Co(II)	−1.08 ± 0.01	−1.07 ± 0.01
6	Ni(II)	−1.10 ± 0.01	−1.09 ± 0.01
1	Cu(II)	−0.94 ± 0 01	−0.93 ± 0.02[c]
7	Zn(II)	−1.06 ± 0.01	−1.06 ± 0.01

[a] Reference 9. [b] Corrected for estimated antiferromagnetic coupling as described in the text.[12,14] [c] The reduction potential, E^f, for the dicopper complex, **1**, has also been corrected for the statistical factor of 18 mV, as explained in the text.

measurements in the solid state.[15] These corrections increase in value to a maximum for the $Cu^{II}Cu^{II}L^{+2}$ species, **1**, but in all cases represent only a small perturbation on the overall reduction potentials. Notice that in all cases the observed Cu(II/I) reduction potentials are identical within error limits at −1.07 V, with the sole exception of the dicopper ion at −0.93 V. Since charges and ligand types are held constant in all complexes we propose that the observed 140-mV difference (3.2 ± 0.8 kcal/mol) can be ascribed to the stabilization of the mixed-valent $Cu^{I}Cu^{II}L^{+}$ ion, **2**, relative to the $Cu^{I}M^{II}L^{+}$, ions *owing to electronic delocalization.* That no significant electronic delocalization occurs in the mixed-valent heterobinuclear species, $Cu^{I}M^{II}L^{+}$, **3**-**7** ($M^{II} \neq Cu^{II}$), is suggested by the consistent Cu(II)/I) reduction potentials obtained for this series of complexes.

Acknowledgment. We thank T. J. Smith for providing a sample of $Cu^{II}Zn^{II}L(ClO_4)_2$ and for synthetic advice and the National Science Foundation (Grant No. CHE76-82124) for financial assistance.

References and Notes

(1) Gagné, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.

(2) Gagné, R. R.; Cimolino. M. C.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 4571.

(3) All complexes were studied as chloride salts, except for **7**, $Cu^{II}Zn^{II}L^{+2}$, which was prepared as a perchlorate salt. The anion does not appear to affect the redox behavior of copper, as digestion of the halides with silver perchlorate left the reduction potential invariant in all complexes.

(4) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 225.

(5) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759.

(6) Details of preparation and characterization will be reported in a subsequent paper. For $Cu^{II}Ni^{II}L^{+2}$, **6**, the mononuclear Ni(II) complex was made first, followed by complexation of Cu(II).

(7) Gagné, R. R.; Spiro, C. L.; Lambert, S. M.; Hendrickson, D. N., manuscript in preparation.

(8) Note that preliminary electrochemical measurements on the perchlorate salt of **1** gave $E_1 = -0.92$ V and $E_2 = -1.31$ V vs. the ferrocene/ferricinium couple, as reported in ref 1 and 2.

(9) All electrochemical measurements were made using *N,N*-dimethylformamide containing 0.1 M tetrabutylammonium perchlorate as solvent. Cyclic voltammetry and differential pulse polarography were performed using a platinum button electrode and a Ag/Ag^+ reference electrode with ferrocene as an internal standard, as described elsewhere.[2,10]

(10) Gagné, R. R.; Koval, C. A.; Lisenksy, G. A., manuscript in preparation.

(11) The statistical factor, $E_1 - E_2 = 36$ mV, holds for the case in which the two metal ions have identical inherent reduction potentials. This value rapidly decreases in magnitude as the inherent reduction potentials of the two metal centers differ: Flanagan, J. B. Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1978. In the present study the statistical factor correction need be applied only to the dicopper complex, **1**.

(12) (a) Ammar, F.; Savéant, J. M. *Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 115; **1973**; *47*, 215. (b) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370. (c) Myers, R. L.; Shain, I. *Ibid.* **1969**, *41*, 980. (d) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (e) Phelps, J.; Bard, A. J. *J. Electroanal. Chem.* **1976**, *68*, 313.

(13) Lambert, S. M.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683.

(14) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(15) Magnetic susceptibilities of $Cu^{II}M^{II}LCl_2$ were measured in the solid state,[7] but these should be reasonable estimates of solution values since solid-state intermolecular interactions are small and the macrocycle maintains the essential coordination features in both states. This conclusion is supported by susceptibility measurements of $(M^{II})_2LCl_2$ (five-coordinate metals) and $(M^{II})_2L(pyridine)_4Cl_2$ (six-coordinate metals) which give comparable results despite changes in the number and types of axial ligands.[7,16]

(16) Spiro, C.; Lambert, S.; Smith, T.; Gagné, R. R.; Hendrickson, D., manuscript in preparation.

Robert R. Gagné,* Clifford L. Spiro
Contribution No. 5917
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

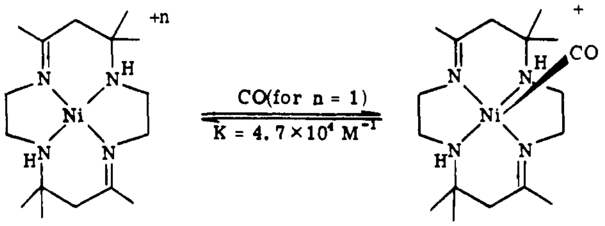
Received August 31, 1979

Intramolecular Electron Transfer and Valence Isomerization in Mononuclear Nickel-Macrocyclic Ligand Complexes: Formation of Paramagnetic Nickel(I)-Carbonyl Complexes

Sir:

Nickel(II) complexes of tetraaza macrocyclic ligands readily undergo one-electron reduction but various products are possible.[1-4] Ligands with at least one α-diimine moiety lead to formation of nickel(II)-ligand radical anion species, as indicated by EPR studies.[1] In contrast, nonconjugated systems are amenable to formation of nickel(I) complexes. We report here the design of a complex which exhibits an equilibrium between both extreme forms of the reduced species. In addition, we report that both classes of reduced complexes react with carbon monoxide to give paramagnetic, presumably five-coordinate, nickel(I) adducts.

Nickel(II) *trans*-diene, **1**,[5] as the perchlorate salt, was reduced electrochemically (−1.24 V vs. NHE in DMF solution) to give the presumably four-coordinate complex, **2**,[6] which was confirmed to be a nickel(I) complex by its EPR spectrum ($g_{\parallel} = 2.190$, $g_{\perp} = 2.056$).[1] Complex **2** binds carbon monoxide at ambient temperatures in DMF solution ($K = 4.7 \times 10^4$ M^{-1})[7] to give a bright green, air-sensitive complex, **3**, which was isolated under a CO atmosphere [ν_{CO} 1961 cm^{-1} (KBr)].[6] Complex **3** was found to be paramagnetic by magnetic susceptibility measurement of a solid sample (2.27 μ_B at 293 K) and by its EPR spectrum ($g_1 = 2.238$, $g_2 = 2.159$, $g_3 = 2.066$; frozen propylene carbonate solution at 100 K), which is distinct from that of complex **2**. Elemental analysis and the presence of only a single ν_{CO}, both in the solid state and in solution (acetonitrile or pyridine), suggest that complex **3** is a five-coordinate Ni(I) adduct similar to five-coordinate Cu(I)-macrocyclic ligand adducts recently reported.[9-11]



1, n = 2, Ni(II)

2, n = 1, Ni(I)

3, Ni(I)

Electrochemical reduction of bis(difluoroboroglyoximato)nickel(II), **4**[12] (−0.79 V vs. NHE in DMF solution), apparently leads to a Ni(II) complex containing a one-electron-reduced ligand, **5**, as demonstrated previously for analogous species.[1] Reduction with cobaltocene[13] permitted convenient isolation of the forest green complex, **5**.[6] The EPR spectrum of **5** in propylene carbonate glass (100 K) shows a