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.

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(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.

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(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]

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(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

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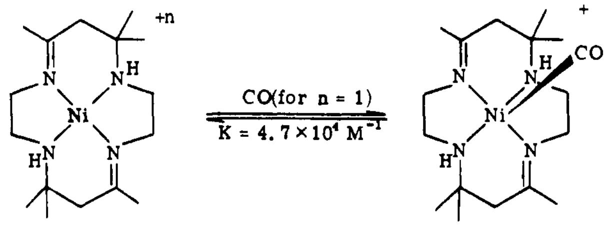
Intramolecular Electron Transfer and Valence Isomerization in Mononuclear Nickel-Macrocyclic Ligand Complexes: Formation of Paramagnetic Nickel(I)-Carbonyl Complexes

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

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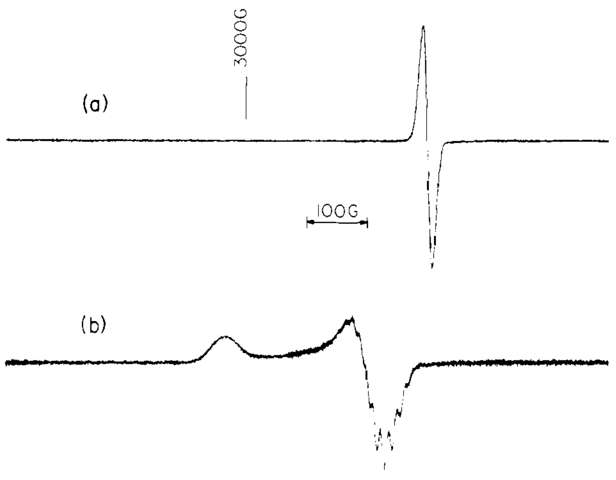
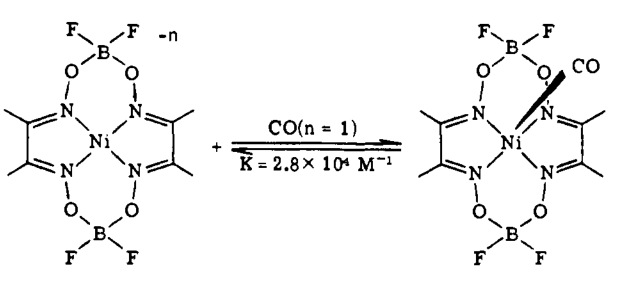


Figure 1. Frozen solution EPR spectra in propylene carbonate at 100 K: (a) **5** under He atmosphere; (b) **6** under CO atmosphere.

single isotropic line ($g = 2.002$), Figure 1, suggesting a metal-stabilized ligand radical.[1] At ambient temperatures **5** also binds CO [$K = 2.8 \times 10^5 \mathrm{M}^{-1}$;[7] ν_{CO} 2029 cm^{-1} (KBr)]. The magnetic susceptibility of the carbonyl adduct, **6** (1.96 μ_B at 293 K), and its EPR spectrum in propylene carbonate glass ($g_\parallel = 2.225$, $g_\perp = 2.065$ at 100 K), Figure 1, indicate that the adduct **6** is a paramagnetic, five-coordinate, Ni(I) complex, analogous to **3**. The conversion of the four-coordinate, nickel(II)-ligand radical anion, **5**, into a nickel(I)-CO adduct appears to be an example of ligand-to-metal intramolecular electron transfer.[14]

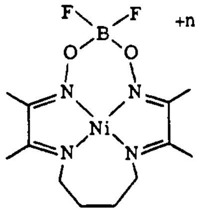


4, n = 0, Ni(II)

5, n = 1, Ni(II)

6, Ni(I)

That complexes **2** and **5** represent two extreme forms of reduced nickel species suggested the challenge of designing a single Ni(II)-macrocyclic ligand complex which upon reduction would exhibit both forms in equilibrium. Complex **7** was prepared as the perchlorate salt by condensing 2,3-butanedione monoxime with 1,4-diaminobutane, followed by reaction with $\mathrm{Ni^{II}(ClO_4)_2 \cdot nH_2O}$ and then $\mathrm{BF_3}$. Reduction with cobaltocene[13] gave the one-electron reduction product, NiL, **8**.[17] Solutions of **8** in propylene carbonate (295 K) give EPR spectra, Figure 2, having two signals, one attributable to Ni(I) at $g = 2.113$ and a second at $g = 2.048$ assignable to a Ni(II)-ligand radical anion species. We propose that complex **8** exists as two valence isomers in solution:



7, n = 1, Ni(II)

8, n = 0, Ni(II) and Ni(I)

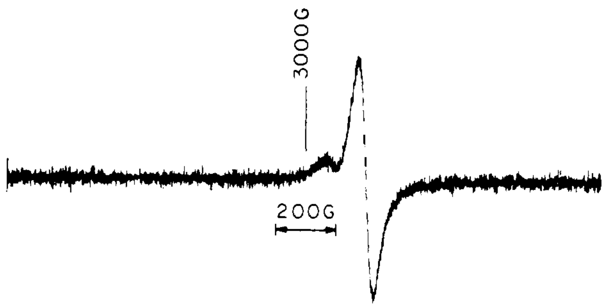


Figure 2. EPR spectrum of **8** in propylene carbonate at 295 K.

$$\mathrm{Ni^{II}(L^{-}\cdot)} \xrightleftharpoons{K = 0.27} \mathrm{Ni^{I}L} \qquad (1)$$

That the two EPR signals are indeed due to two interconvertible species is supported by two observations. Firstly, several preparations of complex **8** gave identical EPR spectra with a constant peak height ratio. Double integration of the first derivative EPR signals gave $K = 0.27 \pm 0.05$ ($\Delta G = 0.75 \pm 0.15$ kcal/mol), eq 1.[18] Secondly, the relative intensities of the two EPR signals varied as a function of temperature. After propylene carbonate solutions of **8** were cooled, the EPR signal at $g = 2.113$ decreased in intensity with concomitant increase in the signal at lower g values until, at ~233 K, only the lower g-value signal remained.[19] The $g = 2.113$ signal reappeared on warming.

Although apparent intramolecular electron transfer in a mononuclear complex has been reported previously,[14-16] the present complex, **8**, appears to be the first example of dynamic equilibrium between two valence isomers in a metal-macrocyclic ligand complex.[20] Further studies of the intramolecular electron-transfer rate and any ligand conformational considerations which influence such rates may prove generally useful in understanding electron-transfer processes.

Acknowledgment. We appreciate financial assistance from the National Science Foundation and a Sloan Fellowship to R.R.G.

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(18) Spectra in various solvents gave qualitatively similar results.
(19) Below 233 K the free-radical signal begins to decrease in intensity, presumably owing to dimerization giving diamagnetic nickel–nickel-bonded species, as has been demonstrated in similar species.[2] Dimerization does not appear to be significant in the temperature range of 295–233 K, since

the total integrated area of the two EPR signals remains constant.

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Robert R. Gagné,* D. Michael Ingle
Contribution No. 6104
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

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Heats of Formation of SO_2Cl^- and $(SO_2)_2Cl^-$

Sir:

Currently, ion-molecule reactions are the objects of intense investigations. Results from these studies have proven to be valuable in expanding the availability of gas-phase thermochemical values such as electron affinities and heats of formation. In particular, data from the study of ion-neutral association reactions provide a foundation for understanding subjects such as ion solvation, atmospheric ion chemistry, nucleation phenomena, and ion-molecule interactions.[1,2]

Recently, Robbiani and Franklin[3] have reported upper limits to the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ based on observations of the ion-molecule reactions

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \qquad (1)$$

$$SO_2Cl^- + SO_2Cl_2 \rightarrow S_2O_4Cl^- + Cl_2 \qquad (2)$$

From these reactions, they compute $\Delta H_f°(SO_2Cl^-) \leq -136$ kcal/mol and $\Delta H_f(S_2O_4Cl^-) \leq -220$ kcal/mol by postulating that the observed $S_2O_4Cl^-$ is formed by reaction 2. (The authors inadvertently use the upper limit for $\Delta H_f°(SO_2Cl^-)$ as a lower limit to conclude that this value must be *near* −135 kcal/mol.)

In our laboratory, a high pressure mass spectrometric technique has been employed[4] for determining the thermodynamic quantities of gas-phase reactions of the form

$$A^- \cdot B_n + B \rightleftharpoons A^- \cdot B_{n+1} \qquad (3)$$

Briefly, ions are formed in a high pressure region, typically 5 to 15 Torr, and focused into a thermally controlled reaction cell. The pressure is sufficiently high such that the ions reside in this cell for a time adequately long for clustering reactions to equilibrate. The ions leak through a small orifice (typically $75\text{-}\mu$ diameter) into a high vacuum region where they are mass analyzed and counted. From the ion intensities and known partial pressure of the clustering neutral, the equilibrium constant $K_{n,n+1}$ is determined.

Among the reactions which have been recently studied are the first four addition reactions (n = 0-3) of SO_2 onto Cl^- This work will be presented in greater detail in a future publication. From the enthalpy change $\Delta H°_{n,n+1}$ for the first two of these reactions (−21.8 for n = 0 and −12.3 kcal/mol for n = 1) and from the heat of formation of Cl^- and SO_2, the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ can be computed. These values are listed in Table I.

The heats of formation in the present study are well below the upper limit previously published by Robbiani and Franklin[3] and are, therefore, consistent with their results. The value of $-\Delta H°_{0,1}$ for reaction 3 is 21.8 kcal/mol and is equivalent to $D(SO_2\text{-}Cl^-)$. Robbiani and Franklin[3] concluded that this value was small (~5 kcal/mol) from their erroneous $\Delta H_f°(SO_2\text{-}Cl^-)$. Nonetheless, $D(SO_2\text{-}Cl^-)$ is still somewhat less than $D(Cl\text{-}Cl^-)$ which is 27 kcal/mol. Therefore, their expectation that some of their observed $SO_2Cl_3^-$ is formed by the reaction of SO_2Cl^- with SO_2Cl_2 may still be valid.

Table I. Heats of Formation

M	$\Delta H_f°(M)$, kcal/mol	ref
SO_2	−70.94	5
Cl^-	−58.8	5
SO_2Cl^-	−151.5	this work
$(SO_2)_2Cl^-$	−234.8	this work

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Robert G. Keesee, A. W. Castleman, Jr.*
Department of Chemistry and Chemical Physics Laboratory
CIRES, University of Colorado, Boulder, Colorado 80309

Received October 11, 1979

Formation of Porphyrin Ferryl (FeO^{2+}) Complexes through the Addition of Nitrogen Bases to Peroxo-Bridged Iron(III) Porphyrins

Sir:

The ferryl group $(Fe^{IV}{=}O)^{2+}$, or a protonated form thereof, has been frequently postulated as an intermediate in the mechanism of action of peroxidases, particularly in the identity of compound II of horseradish peroxidase, and in the autoxidation of Fe(II).[2] Complexes of Fe(IV) are rare[3] and no well-characterized, low molecular weight complexes containing the ferryl group are available for detailed study.[4] We recently reported on spectroscopic characterization of the Fe(III) peroxo-bridged complex, $PFeO_2FeP$ (P = a porphyrin dianion), which is formed by the addition of dioxygen to unligated PFe in toluene solution at low temperature.[5] We now report that nitrogeneous bases react with $PFeO_2FeP$ to yield new complexes which appear best described as ferryl complexes.

Addition of *N*-methylimidazole (Me-Im) to $TmTPFeO_2FeTmTP$ (TmTP = dianion of *meso*-tetra-*m*-tolylporphyrin) at −80 °C in toluene solution produces a new complex **1** $(Me\text{-}ImTmTPFeO)_x$, whose unique ^1H NMR and electronic spectra are shown in Figures 1 and 2, respectively. Titration of *N*-methylimidazole into a solution of $TmTPFeO_2FeTmTP$ reveals that 2 mol of base are required to consume all of the peroxide-bridged dimer originally present. Addition of further *N*-methylimidazole results in the growth of peaks characteristic of the free base, thus demonstrating that exchange between free *N*-methylimidazole and the newly formed iron complex is slow. The peaks due to coordinated Me-Im have not been resolved. **1** is indefinitely stable (>1 week) at −80 °C, while above −30 °C it decomposes to TmTPFeOFeTmTP at an appreciable rate.[6] The solution magnetic susceptibility of **1** measured at 360 MHz using the Evans technique[7] is 2.9 ± 0.1 μ_B/iron ion at −52 °C and is invariant down to −90 °C. Moreover the temperature dependence of the porphyrin paramagnetic shifts strictly follows the Curie law[7] over a larger temperature range (−85 to +15 °C) as is shown in the insert of Figure 1. Hence the iron ions exist in well-defined paramagnetic, noninteracting states.

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