to convert to the trans(imidazole) isomer in solution. The reported electronic spectral data are also consistent with a sample which had undergone substantial isomerization.

One-Electron-Reduced Nickel(II)–Macrocyclic Ligand Complexes. Four-Coordinate Nickel(I) Species and Nickel(II)–Ligand Radical Species Which Form Paramagnetic, Five-Coordinate Nickel(I) Adducts

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Mononuclear nickel(II) complexes of tetraaza macrocyclic ligands undergo one-electron reduction to give either nickel(I) species or species containing nickel(II) complexed to a ligand radical. Both reduced species react with carbon monoxidde to give paramagnetic, five-coordinate, nickel(I) carbonyl adducts. The nature of the reduced nickel species and of their carbonyl adducts was examined by EPR and by electronic absorption spectroscopy, which confirm the descriptions as Ni(I) or Ni(II)–ligand radicals. Condensation of 1,4-diaminobutane with 2,3-butanedionemonoxime, followed by reaction with nickel(II) and then BF$_3$ and, finally, one-electron reduction, gave a complex exhibiting dynamic valence isomerism. At 298 K its EPR spectrum shows signals attributable both to Ni(I) and to a Ni(II)–ligand radical species. On cooling of the solution, the Ni(I) signal disappears with concomitant increase in the Ni(II)–ligand radical signal. Carbon monoxide equilibrium binding constants, measured electrochemically for 11 complexes, ranged from zero to 10^5 M^{-1}. Carbonyl stretching frequencies for seven five-coordinate complexes in pyridine solution and for two isolated adducts ranged from 1949 to 2020 cm^{-1}. Similarities are suggested between the new nickel complexes and related copper systems.

Introduction

Metal complexes of synthetic tetraaza macrocycles have received a great deal of attention. The kinetic stability toward dissociation that they impose on their complexes apparently contributes to their unusual chemical and electrochemical properties.[1,2] In addition to kinetic stability, certain macrocycles such as some of those employed here lend thermodynamic stability to their metal complexes. Often these macrocyclic ligands stabilize metals in formal oxidation states that normally are not subject to isolation or study in other types of coordination compounds. This affords the opportunity to study the chemical reactivity of uncommon oxidation states in a homeostructural ligand environment and to study the effect of ligand modifications on these chemical properties.

The 14-membered cyclic tetraaza ligands present an excellent opportunity to study the effect of the degree of ligand unsaturation on the chemical reactivity of metal coomplexes.[3,4] Recently, reduced copper complexes, considered as copper(I) species, have been isolated in a macrocyclic ligand environment.[5–8] These complexes show varying affinities for binding π acids as fifth ligands, creating what are best described as "20-electron" Cu(I) complexes.[6,7] These diamagnetic complexes have been regarded as copper(I) compounds for both the four-coordinate and the five-coordinate species.[6–9] In an

effort to better understand the bonding in these unusual d^{10} copper complexes, we have examined the analogous four-coordinate, paramagnetic d^9 nickel complexes, which have been previously studied by Busch et al.[3] In addition, we report here the synthesis and some of the chemical properties of several paramagnetic, presumably five-coordinate, nickel(I) carbonyl complexes,[10] which constitute a new class of coordination compounds.

Results and Discussion

Synthesis, EPR, and Electronic Absorption Spectra. Reduction of cyclic tetraaza–nickel(II) complexes has been shown to give either nickel(I) complexes or metal-stabilized ligand

Table I. EPR Data for Reduced Nickel Complexes in Propylene Carbonate Glass at 100 K

Ni complex	Ar^d	CO^e
1^a	2.002 (20)^b	$g_\parallel = 2.227, g_\perp = 2.063$ (10)^c
2	2.007 (25)^b	$g_\parallel = 2.226, g_\perp = 2.065$ (12)^c
3	2.002 (16)^b	$g_\parallel = 2.225, g_\perp = 2.065$ (12)^c
5^a	2.000 (23)^b	$g_\parallel = 2.230, g_\perp = 2.066$
6^a	2.008 (35)^b	$g_\parallel = 2.235, g_\perp = 2.069$ (12)^c
7	$g_\parallel = 2.253, g_\perp = 2.054$	$g_1 = 2.198, g_2 = 2.123, g_3 = 2.012$
8	$g_\parallel = 2.235, g_\perp = 2.086$	$g_1 = 2.305, g_2 = 2.151, g_3 = 2.056$
9	$g_\parallel = 2.220, g_\perp = 2.063$	$g_1 = 2.201, g_2 = 2.123, g_3 = 2.018$
10^a	$g_\parallel = 2.190, g_\perp = 2.056$	$g_1 = 2.238, g_2 = 2.159, g_3 = 2.066$
11	2.020 (40)^b	$g_\parallel = 2.242, g_\perp = 2.068$ (12)^c

^{a} Generated chemically or electrochemically in situ. ^{b} Peak-to-peak width (in gauss) of first derivative spectra. ^{c} Nitrogen superhyperfine (in gauss), where resolvable. ^{d} Spectra taken in argon-saturated propylene carbonate. ^{e} Spectra taken in carbon monoxide saturated propylene carbonate.

(1) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.
(2) Rillema, D. P.; Endicott, J. F.; Papaconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.
(3) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.
(4) Millar, M.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 6052.
(5) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1971**, *10*, 463.
(6) Gagné, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 6709.
(7) Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170.
(8) Gagné, R. R.; Allison, J. L.; Lisensky, G. C. *Inorg. Chem.* **1978**, *17*, 3563.

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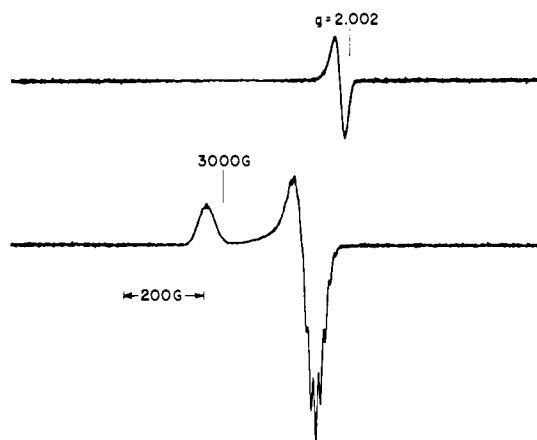(10) Gagné, R. R.; Ingle, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 1444.

Figure 1. EPR spectra in propylene carbonate glasses at 100 K of **2** under 1 atm of helium (top) and carbon monoxide (bottom).[12]

radicals, depending on the nature of the ligand.[3] With use of electrochemical methods, 11 such complexes, **1–11**, have been examined; several reduced species have been isolated by using chemical reducing agents.

Nickel(II) complexes with conjugated α-diimine moieties, undergo one-electron reduction to give nickel-stabilized ligand radicals, $Ni^{II}(mac^-)$, **1–6**. Upon exposure to carbon monoxide
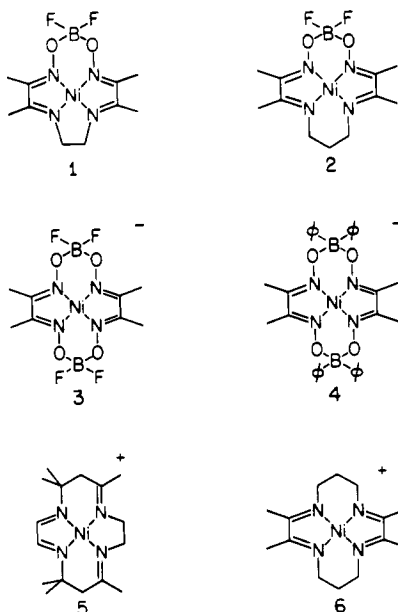
in solution, these complexes form presumably five-coordinate nickel(I) carbonyl complexes (eq 1). These conclusions are

$$Ni^{II}(mac^-) + CO \xrightleftharpoons{K^{CO}} Ni^I mac(CO) \qquad (1)$$
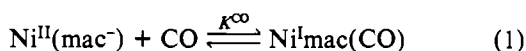
supported by electron paramagnetic resonance spectra of the reduced nickel complexes, obtained in propylene carbonate glasses at 100 K. The results are shown in Table I. The four-coordinate, reduced complexes **1–6** gave isotropic spectra (Table I) indicative of the presence of ligand radicals, as shown for **2** in Figure 1. Upon addition of carbon monoxide (Figure 1) the isotropic spectra are converted to anisotropic spectra of a d^9 metal with axial symmetry (Table I).[11] The EPR spectra strongly suggest square-pyramidal geometries for the carbonyl adducts $Ni^I mac(CO)$, derived from **1–6**. This process, by which the odd electron is induced to migrate to a largely metal orbital from a predominantly ligand orbital, may be considered an intramolecular electron transfer.[10,12]

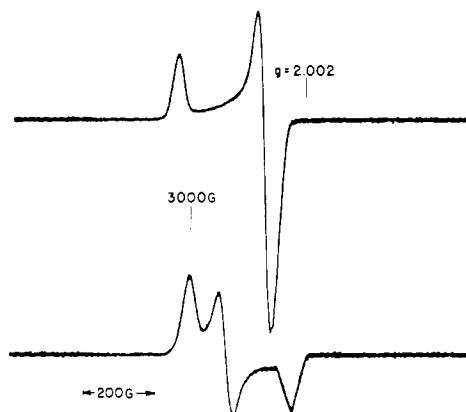(11) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, 5, 143.

Figure 2. EPR spectra in propylene carbonate glasses at 100 K of **9** under 1 atm of helium (top) and carbon monoxide (bottom).

Table II. Equilibrium Binding Constants of Various Reduced Nickel Complexes with Carbon Monoxide in DMF Containing 0.100 M TBAP

Ni complex	$E_{1/2}[Ar], V^a$	$K^{CO}, M^{-1\ b}$
1	−0.478	0^c
2	−0.617	2.7 (3) × 10³
3	−0.786	2.8 (3) × 10⁵
4	−0.979	5.1 (5) × 10⁴
5	−0.456	0^c
6	−0.527	1.7 (4) × 10²
7	$−1.295^d$	7.8 × 10⁴
8	−1.249	1.8 (2) × 10⁴
9	−1.241	4.7 (5) × 10⁴
10	−1.081	4.5 (5) × 10⁴
11	−0.798	1.3 (1) × 10⁴

^{a} Vs. NHE. ^{b} Errors are based on ΔE error of ±0.0025 V (i.e., a total error of ±5 mV). ^{c} $K_f^{CO} \leq 10\ M^{-1}$ are reported as zero. ^{d} Estimated by cyclic voltammetry.

In contrast, Ni(II) complexes without conjugated α-diimines undergo one-electron reduction to give Ni(I) complexes $Ni^I mac$, **7–10**, which also coordinate CO to give presumably
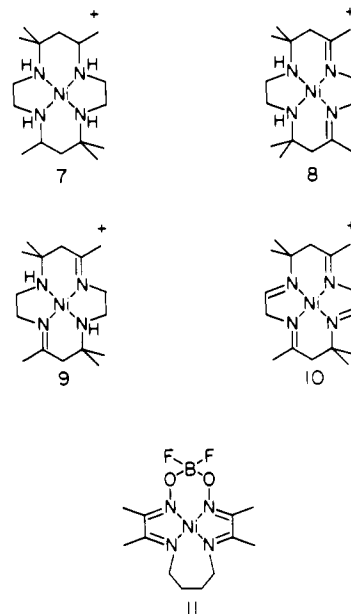
(12) Certain paramagnetic reduced nickel complexes have a tendency to dimerize to some extent in solution forming diamagnetic adducts. This equilibrium situation has been discussed previously: see ref 10 and Penz et al. [Penz, S.-M.; Ibers, J. A.; Millar, M.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 8037]. The contrasting EPR signal intensities of **2**, in Figure 1, under CO vs. He atmospheres may suggest such dimerization. Under CO the principal species is probably the monomeric carbonyl, whereas under He significant dimerization is present.

five-coordinate nickel(I) carbonyl complexes (eq 2). Again,

$$Ni^I mac + CO \overset{K^{CO}}{\rightleftharpoons} Ni^I mac(CO) \qquad (2)$$
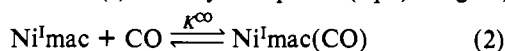
EPR spectra support these conclusions. The reduced, four-coordinate complexes 7–10 give anisotropic, axial EPR spectra, (Table I and Figure 2) as expected for square-planar, d⁹, metal complexes. Upon exposure to carbon monoxide complexes 7–10, as $Ni^I mas(CO)$, give rhombic spectra[11] (Figure 2).

The oxidized forms of complexes 1–6 exhibit a rather large range of reduction potentials (vide infra; Table II). This observation suggested that in the reduced species 1–6 the Ni(II) ion plays a significant role in stabilizing the ligand-radical anion. In an attempt to minimize the stabilizing influence of the metal, by minimizing the favorable metal–ligand interaction, a macrocyclic ligand with a hole size larger than in species 1–6 was sought. Condensation of 1,4-diaminobutane with 2,3-butanedione oxime, followed by treatment with Ni(II) and then BF_3 and, finally, reduction, gave complex 11.[10] The four-coordinate complex 11 gave an EPR spectrum which, under ambient conditions, is a hybrid of those obtained for $Ni^{II}(mac^-)$, 1–6, and $Ni^I mac$, 7–10.[10] In acetonitrile and other aprotic solvents the EPR spectrum of complex 11 shows two g values (g = 2.113 and 2.048) at 298 K (Figure 3). As the temperature is lowered, the signal at g = 2.113 decreases in intensity while the g = 2.048 signal grows stronger until, at 233 K, the g = 2.113 signal cannot be seen. The phenomenon is reversible with both signals returning to their original intensities on rewarming to 298 K. We assign the g = 2.048 signal to a nickel(II)–ligand radical species, $Ni^{II}(mac^-)$, analogous to 1–6. The g = 2.113 signal is assigned to a nickel(I) species $Ni^I mac$, analogous to 7–10. We propose that these two signals reflect a thermal equilibrium between two distinct species, i.e., a case of thermally dependent valence isomerism (eq 3). To our knowledge, this is the first case of

$$Ni^{II}(mac^-) \overset{K}{\rightleftharpoons} Ni^I mac \qquad (3)$$
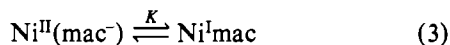
dynamic equilibrium between two valence isomers in a metal–macrocyclic ligand complex.[13] Double integration of the EPR signals for 11 at 298 K gave an equilibrium constant of K = 0.27 ± 0.05. This corresponds to an estimated energy difference between the nickel(I) and nickel(II)-stabilized ligand radical forms of 0.75 ± 0.15 kcal/mol.

It is to be emphasized that all of the five-coordinate carbonyl adducts $Ni^I mac(CO)$, derived from 1–11, appear to be best described as containing nickel(I). The EPR spectra, as expected, are consistent with the $d_{x^2-y^2}$ orbital being the highest occupied metal orbital in the carbonyl adducts.[11]

Electronic absorption spectra are not very informative as to the nature of complexes 1–11 and their carbonyl adducts. The reduced nickel species are all deeply colored, and their electronic absorption spectra consist of moderately intense charge-transfer bands. Nickel(II)–ligand radical complexes, 1–6, are all green and exhibit qualitatively similar spectra; upon formation of the carbonyl adduct, brownish-red solutions are formed. The spectra of 3 and its isolated carbonyl adduct 12, taken in propylene carbonate solution (Figure 4), are representative. While these charge-transfer bands are not assigned, they are felt to arise from low-energy ligand π* to nickel $d_{x^2-y^2}$ transitions.

The nickel(I) complexes, 7–10, are all deep brown. Their carbonyl complexes are bright green. Sample solution spectra
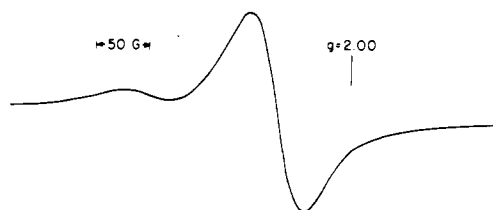
(13) For examples of phase change dependent valence isomerization in nickel(III) porphyrins see ref 14 and 15. For an example of valence isomerization between bent and linear cobalt nitrosyl complexes see ref 16.
(14) Johnson, E. C.; Niem, T.; Dolphin, D. *Can. J. Chem.* **1978**, *56*, 1382.
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(16) Collman, J. P.; Farnham, P.; Dolcetti, G. *J. Am. Chem. Soc.* **1971**, *93*, 1788.

Figure 3. EPR spectrum of 11 in acetonitrile at 298 K.

Figure 4. Electronic absorption spectrum of 3 under H (solid line) and of its carbonyl adduct 12 under CO (dashed line) in propylene carbonate solution at 298 K.
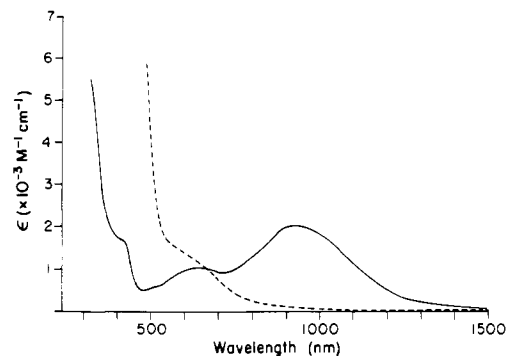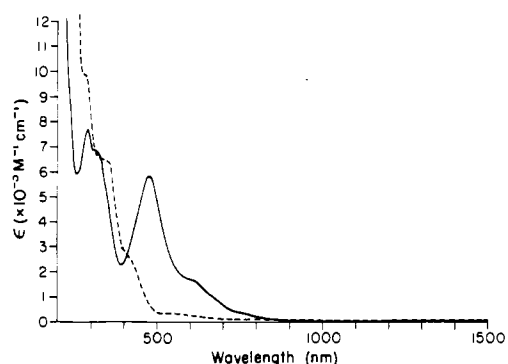

Figure 5. Electronic absorption spectra of 9 under He (solid line) and of its carbonyl adduct 13 under CO (dashed line) in propylene carbonate solution at 298 K.

obtained for 9 and its isolated carbonyl adduct 13, in propylene carbonate solution, are shown in Figure 5. Charge-transfer bands for complexes 7–10 may arise from nickel $d_{x^2-y^2}$ to ligand π* transitions.

Complex 11 exhibits temperature-dependent electronic absorption spectra in acetonitrile or propylene carbonate solutions, which are ascribed to the $Ni^{II}(mac^-)$ to $Ni^I mac$ dynamic equilibrium described earlier (eq 3) (Figure 6). At 299 K, the two bands centered at 560 and 860 nm are assigned to the nickel(II)-stabilized ligand-radical form; the less intense bands at 790 and 1080 nm are assigned to the nickel(I) form. At reduced temperature (233 K), the bands associated with the nickel(I) form decrease in intensity. Upon rewarming to 299 K, the original spectrum is obtained.

Equilibrium Binding Constants. Equilibrium constants for CO binding, eq 1 and 2, for complexes 1–11, were determined. The binding constants for these complexes measured in *N,N*-dimethylformamide (DMF) are given in Table II. The technique for measuring these binding constants has been described elsewhere.[9]

This electrochemical technique allows for the measuring of the binding constants of CO to the reduced nickel complex by using the readily available nickel(II) compounds as starting materials. On the assumption that coordination of CO to the reduced nickel complex is the only equilibrium occurring in
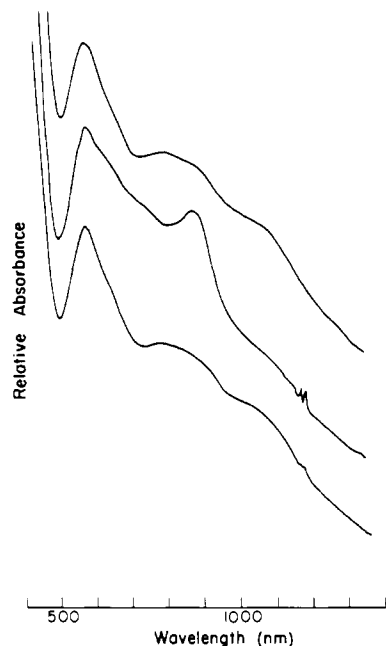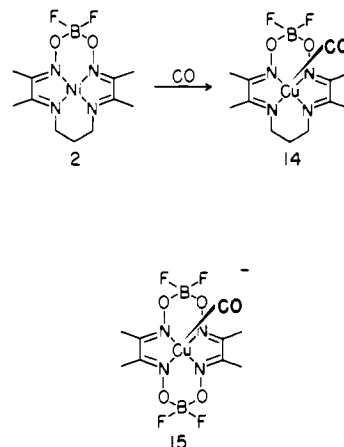
Figure 6. Electronic absorption spectra of 11 in propylene carbonate solution at 299 K (top), at 233 K (middle), and upon rewarming to 299 K (bottom).

solution, application of the Nernst equation yields the electrochemical relationship (eq 4) between the binding constant,

$$K^{CO} = [\exp(\Delta E(F/RT)) - 1]/[CO] \qquad (4)$$

K^{CO}, the concentration of carbon monoxide, [CO], and the observed difference in the experimentally obtained reduction potentials under argon and CO, ΔE.[17] Reduction potentials were obtained by dc polarography. All nickel complexes reported here undergo reversible or quasi-reversible reductions in DMF. Slopes obtained from the dc polarography indicated one-electron reduction in all cases except for 1 and 2, which show evidence for dimerization as the reduced complex.[18] Constant potential electrolysis indicated that all reductions were one-electron reductions.

Binding constants for CO vary substantially from complex to complex. Compounds 7–10, which do not contain conjugated α-diimine moieties, form four-coordinate nickel(I) complexes upon reduction. These four complexes have similar CO binding constants (Table II). Variations in binding constants may reflect differences in the flexibility of the macrocycle, as the complexes are expected to be square pyramidal with the metal atom displaced some distance out of the plane of the four nitrogen ligands. Crystal structures for the copper(I) analogue complexes 14[7] and 15[19] show the metals to be displaced out of the plane of the four nitrogens by 0.96 and 1.02 Å, respectively; as a result, the macrocycle must distort to accommodate the large out of plane displacement. For the carbonyl adducts of 7–10 the actual displacements of the nickel atoms out of the ligand planes are not known, but some metal displacement accompanied by ligand distortion is anticipated.

(17) James, B. R. Ph.D. Thesis, Oxford University, Oxford, U.K., 1960.
(18) Calculating equilibrium constants by the use of shifts in $E_{1/2}$ requires the processes to be chemically and electrochemically reversible. The data reported here were obtained by using sampled dc polarography, except for 7 which was done by using cyclic voltammetry; reversibility was determined by the requirement that plots of E vs. ln $[i/(d_d - i)]$ have slopes of $-RT/nF$, i.e., 58.6 mV at 22 °C for a one-electron process. All complexes studied here gave slopes close to 58.6 mV, except 1, which was 41.5 mV, and 2, which was 45.4 mV. Concentration-dependent electronic spectral changes confirm the proposal that dimerization of 2 occurs in solution. Similar dimerization of reduced conjugated macrocyclic nickel complexes have been investigated previously.[12]
(19) Gagné, R. R.; Ingle, D. M.; McCool, M.; Marsh, R. E., manuscript in preparation.

For example, complexes 7, 9, and 10 differ only by the degree of unsaturation in the macrocycle; although the three compounds exhibit a marked change in their reduction potentials, the CO binding constants are similar, with the saturated complex 7 having the lowest K^{CO}. With all four nitrogens of 7 being saturated, it can be expected that the ligand may be slightly more rigid than the others, possibly accounting for the lowered K^{CO}. In addition, the similarity of CO binding constants suggests that the σ basicity of the macrocyclic ligand may not make a large contribution to the stability of the five-coordinate complex, although they do affect the stability of the four-coordinate Ni(I) complex.

Complexes which do possess conjugated α-diimine functions show a much wider variation in CO binding constants. Compounds 1 and 5 show no carbonyl adduct formation measurable by the electrochemical method; EPR spectra, vide supra, suggest, however, that there is a small extent of carbonyl formation at low temperatures for those two complexes.

Complexes 1, 2, and 11 represent a series in which the ring size becomes larger, permitting both longer Ni–N bonds and a greater deviation from rigid planarity in the four-coordinate complex. The smallest macrocyclic compound, 1, has the least negative reduction potential of the three compounds. As the macrocycle size in increased, the reduction potential becomes more negative; the smaller ligand apparently encourages greater stabilization of the ligand radical by better orbital overlap, increasing the metal–ligand interaction. Complex 1 also has the smallest CO binding constant of the three complexes, with the larger macrocycles having larger values for K^{CO}. The variation in K^{CO} in these complexes may be attributable primarily to the extent to which the ligand-radical orbital is stabilized, via the difference in energy between the ligand π^* and the metal $d_{x^2-y^2}$. In fact, the magnitude of this separation between the π^* orbital of the ligand and the metal $d_{x^2-y^2}$ orbital may account for many of the observed trends in carbon monoxide binding constants. An additional factor which may influence the magnitude of K^{CO} is geometric. As discussed earlier, smaller macrocyclic ligands such as in 1 in the series 1, 2, and 11 should be more difficult to distort to give the square-pyramidal nickel(I) carbonyl adducts.

Complexes 2, 3, and 6 show a series in which the trimethylene groups bridging the two α-diimines are replaced successively with difluoroborate groups. Again the reduction potentials, as well as their affinity for CO, varies monotonically over the short series; the more positive reduction potential also corresponds to the smallest K^{CO}. For the analogous copper(I) carbonyl complexes, where X-ray crystallographic results show possible copper–fluorine interactions for compound 14[7] and 15,[19] the suggestion was offered that the higher CO binding constants also observed for copper(I) complexes containing difluoroborate groups were due to a favorable metal–fluorine interaction in the five-coordinate complex.[9] Compound 4, in

Table III. Carbonyl Stretching Frequencies of Nickel(I) Carbonyl Complexes Measured in Pyridine Solution

Ni complex	ν_{CO}, cm^{-1}	Ni complex	ν_{CO}, cm^{-1}
2(CO)[a]	2015	8(CO)[a]	1957
3(CO)[b]	2020 (2029)[c]	9(CO)[b]	1962 (1961)[c]
6(CO)[a]	2020	10(CO)[a]	2020
7(CO)[a]	1949		

[a] Carbonyl complexes were generated in situ. [b] Carbonyl complexes were both generated in situ and isolated as crystalline products. [c] IR taken in solid state (KBr pellet).

which the fluorines have been replaced with phenyl groups, exhibits a CO binding constant not significantly smaller than that of **3**; this indicates the probable lack of strong metal–fluorine interactions.

Infrared Carbonyl Stretching Frequencies. Infrared stretching frequencies of the carbonyl group for several of these reduced nickel complexes measured in CO-saturated pyridine solution are listed in Table III. These complexes fall into three groups. Complexes with four imine nitrogens (conjugated or not) have ν_{CO} near 2020 cm^{-1}; complexes with two imines are near 1960 cm^{-1}; the carbonyl adduct of complex **7** which has a totally saturated ligand, i.e., no imine nitrogens, has the lowest carbon monoxide stretching frequency, 1949 cm^{-1}. These carbonyl stretching frequencies show no correlation to binding constant. The lack of dependence of carbonyl stretching frequency on K^{CO} suggests that a major contribution to the metal–carbon bond does not involve the metal d orbitals. This is consistent with the expectation that the binding of late transition series metals to π-acids like CO is primarily through their 4s and 4p orbitals, rather than their d orbitals. However, minor contributions from the d_{xy} and d_{yz} orbitals to π back-donation are expected to have some contribution in the nickel–carbon bond and thus influence the carbonyl stretching frequencies. In the expected square-pyramidal environment, the metal d_{xz} and d_{yz} orbitals should interact directly with the ligand nitrogen lone pair as well as the carbon monoxide π-antibonding orbitals. Through a symbiotic effect, the harder saturated nitrogens appear to cause a greater delocalization of electron density into the CO π* orbital by way of the metal d orbitals than unsaturated nitrogen donors, thus leading to lower carbonyl stretching frequencies for the saturated complex.

Summary

Although five-coordinate Ni(I) species are known,[20] carbonyl complexes of metals with a valence electron count greater than 18 are rare. While the four-coordinate complexes exhibit unusual redox properties, undergoing either metal or ligand reduction depending on the macrocyclic ligand structure, the five-coordinate carbonyl adducts are all found to be paramagnetic, "19-electron" nickel(I) complexes. It is felt the the metal d orbitals play a minor role in CO binding and that the predominant interaction is through σ interactions with the metal 4s and 4p orbitals.

Comparisons of compound **11**, which appears to be in equilibrium between two reduced forms, and compounds **1** and **2**, which appear to be relatively trapped into the nickel(II)–ligand radical form, show that the macrocycle size is an important factor in determining the extent to which the nickel ion can stabilize the ligand radical.

These nickel complexes were studied to aid in the understanding of the bonding in the diamagnetic copper(I) complexes studied earlier.[6–9] The paramagnetic nickel analogues to the reduced copper systems have given complementary data to help formulate bonding schemes for the carbonyl adducts.

In light of a number of similarities between those copper compounds and the nickel(II)–ligand radical and nickel(I) carbonyl compounds, we are presently reexamining the copper(I) designation for the metal in the reduced four-coordinate copper complexes.

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. Reagent grade *N,N*-dimethylformamide (DMF) was dried first over MgSO$_4$, followed by distillation from 4-Å molecular sieves. Argon, for electrochemical measurements, was purified by passing it over hot copper turnings and then through 4-Å molecular sieves. Carbon monoxide was passed over activated Ridox and then 4-Å molecular sieves. Tetrabutylammonium perchlorate, TBAP (Southwester Analytical Chemicals), was dried exhaustively in vacuo before use. Nickel(II) compounds, precursors to complexes **3**,[21] **5**,[22] **6**,[23,24] **7**,[24] **8**,[25,26] **9**,[27] and **10**[25,26] were prepared by the methods given in the references listed. All nickel(II) salts were used as the perchlorate salt, except for the precursor to complex **7**, which was used as the tetrafluoroborate salt. *Caution*: Perchlorate salts may be explosive. All compounds gave acceptable elemental analysis.

Physical Measurements. Manipulation of samples of air-sensitive materials for physical studies were accomplished in a Vacuum Atmospheres Dri-lab glovebox with a helium atmosphere. Solvents were thoroughly deaerated prior to use.

X-Band EPR spectra were recorded on a Varian E-line spectrometer. Temperatures of 100 K were maintained by using an Air Products Heli-Tran liquid-transfer refrigerator. Temperatures near the ambient temperature were maintained by using a Varian V-4540 variable-temperature controller. Samples were contained in cylindrical quartz tubes (2-mm diameter) equipped with 2-mm oblique-bore vacuum stopcocks and $\bar{\intercal}$ 14/20 joints. Solutions of the carbonyl adducts were made by evacuating the helium atmosphere in the tube on a vacuum line and then introducing carbon monoxide gas.

Infrared spectra were obtained by using sodium chloride cells (1 mm). Carbon monoxide was introduced into the cell by the insertion of a syringe needle, attached to a Tygon tube with a flow of CO passing into serum caps on the solution IR cells until the carbonyl adduct was generated.

Electronic absorption spectra were recorded on a Cary-14 spectrometer. Solution spectra were recorded by using quartz cells (0.1 cm or 1 cm) equipped with Kontes Teflon stopcocks to allow for addition of carbon monoxide as described above under the EPR procedure. Temperature control was maintained by using a quartz vacuum Dewar and a regulated flow of liquid-nitrogen-cooled nitrogen gas; temperatures were recorded by using an iron–constantine thermocouple. NMR spectra were obtained on a Varian EM-390. Chemical shifts are reported relative to internal Me$_4$Si.

Electrochemistry. The methods and equipment used for polarographic analysis have been described elsewhere.[9]

Syntheses. (3,6,10,13-Tetraaza-1-bora-1,1-difluoro-4,5,11,12-tetramethyl-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato)nickel(II) Perchlorate (16, Precursor to 2). Excess boron trifluoride etherate (7 mL) was added to a slurry of [(3,3'-trimethylenendinitrilo)bis(2-butanone oximato)]nickel(II) perchlorate[21] (5 g) in dioxane (30 mL). The reaction was heated at reflux for 1 h. After cooling to the ambient temperature, the reaction mixture was filtered. The yellow-orange solid was washed successively with ethanol and ether. Recrystallization from aqueous acetone gave the yellow-orange microcrystalline solid. Anal. Calcd for C$_{11}$C$_{18}$BClF$_2$N$_4$NiO$_6$: C, 29.67; H, 4.07; N, 12.58. Found: C, 30.0; H, 4.3; N, 12.6.

(3,6,10,13-Tetraaza-1-bora-1,1-difluoro-4,5,11,12-tetramethyl-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato)nickel (2).[29] In a He atmosphere chamber, **16** (2.3 g) was slurried in acetone (35 mL). Cobaltocene[28] (0.97 g) was added. The reaction was stirred 8 min.

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The product was then isolated by vacuum filtration. The forest green crystals were then washed with acetone and dried under a stream of He. Anal. Calcd for $C_{11}H_{18}BF_2N_4NiO_2$: C, 38.21; H, 5.25; N, 16.20. Found: C, 38.3; H, 5.1; N, 16.2.

Cobaltocenium Bis(difluoroboroglyoximato)nickelate (3). Under a He atmosphere, nickel(II) bis(difluoroboroglyoximate)[26] (0.40 g) was slurried in acetone (20 mL). Cobaltocene (0.24 g) was added. The reaction was stirred vigorously for 8 min. The product was then isolated by vacuum filtration. The dark green microcrystalline product was then washed with acetone and dried in vacuo. Anal. Calcd for $C_{18}H_{22}B_2CoF_4N_4NiO_4$: C, 37.68; H, 3.87; N, 9.77; Ni, 10.23. Found: C, 38.1; H, 3.9; N, 10.0; Ni, 10.3.

Cobaltocenium Carbonylbis(difluoroboroglyoximato)nickelato (12). Under a carbon monoxide atmosphere in a Schlenk apparatus, cobaltocene (0.20 g) was dissolved in CO-saturated acetone (5 mL). Nickel(II) bis(difluoroboroglyoxime) (0.33 g) was dissolved in CO-saturated acetone (35 mL). The two solutions were combined with stirring under a stream of CO. After 10 min, the reaction was filtered, and the brown microcrystalline product was dried under a stream of CO. Anal. Calcd for $C_{19}H_{22}B_2CoF_4N_4NiO_5$: C, 37.93; H, 3.69; N, 9.31; Ni, 9.76. Found: C, 37.8; H, 3.5; N, 9.5; Ni, 9.7.

Carbonyl(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) Perchlorate (13). To sodium amalgam (0.25%, 100 g) under an inert nitrogen atmosphere in a Schlenk apparatus was added a degassed solution of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) diperchlorate (1.0 g) in a acetonitrile (50 mL). The reaction mixture was stirred for 6 h. The dark brown solution was filtered under a nitrogen atmosphere.[1] The filtrate was then stirred under a carbon monoxide atmosphere. The solution became bright green. The solvent was slowly evaporated under a stream of carbon monoxide. The remaining solid was washed under a nitrogen atmosphere with oxygen-free water (50 mL). The mixture was rapidly filtered. The dark green solid was dried in vacuo. Anal. Calcd for $C_{17}H_{24}ClN_4NiO_5$: C, 43.75; H, 6.91; N, 12.01; Ni, 12.58. Found: C, 43.6; H, 6.6; N, 11.9; Ni, 12.5.

(3,6,9,12-Tetraaza-1-bora-1,1-difluoro-4,5,10,11-tetramethyl-2,13-dioxacyclotrideca-3,5,9,11-tetraenato)nickel(II) Perchlorate–Ethanol (17, Precursor to 1). Excess boron trifluoride etherate (7 mL) was added to a slurry of [(3,3′-ethylenedinitrilo)bis(2-butanone oximato)]nickel(II) perchlorate[21] (5 g) in dioxane (30 mL). The reaction was heated at reflux for 1 h. After cooling to the ambient temperature, the reaction mixture was filtered. The yellow solid was washed successively with ethanol and ether. Recrystallization from aqueous ethanol gave a red-orange microcrystalline solid. Anal. Calcd for **17**, $0.25C_2H_5OH \cdot C_{42}H_{70}N_{16}O_{25}Cl_4B_4F_8Ni_4$: C, 28.43; H, 3.95; N, 12.63. Found: C, 28.9; H, 4.1; N, 13.2.

[(3,3-Tetramethylenedinitrilo)bis(2-butanone oximato)]nickel(II) Perchlorate (18). 4,9-Diaza-3,10-dimethyldodeca-3,9-diene-2,11-dione

dioxime (10.0 g) was dissolved in hot ethanol (75 mL). A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (7.6 g) in ethanol (20 mL) was added to the hot solution of ligand. The reaction was refluxed 1 h with stirring. Upon cooling to 2 °C, the mixture was filtered. The orange solid was vacuum-dried. Anal. Calcd for $C_{12}H_{21}ClN_4NiO_6$: C, 35.20; H, 5.17; N, 13.68. Found: C, 35.0; H, 5.1; N, 13.7.

(3,6,11,14-Tetraaza-1-bora-1,1-difluoro-4,5,12,13-tetramethyl-2,15-dioxacyclopentadeca-3,5,11-13-tetraenato)nickel(II) Perchlorate Hydrate (19, Precursor to 11). A slurry of **18** (1.0 g) in dioxane (15 mL) was treated with boron trifluoride etherate (5 mL) and refluxed 4 h. The reaction mixture was cooled to the ambient temperature. A white crystalline solid was separated off by filtration. The filtrate was taken to dryness on a rotary evaporator. The residue was recrystallized from water with concentrated sodium perchlorate. The bright green crystalline product was collected by filtration. Upon drying in vacuo, the green crystals gave an orange powder. Anal. Calcd for $C_{12}H_{22}BClF_2N_4NiO_7$: C, 30.19; H, 4.65; N, 11.74. Found: C, 30.4; H, 4.5; N, 11.8.

Synthesis of (3,6,10,13-Tetraaza-1,8-dibora-4,5,11,12-tetramethyl-1,7,9,14-tetraoxa-1,1,8,8-tetraphenylcyclotetradeca-3,5,10,12-tetraenato)nickel(II) (20, Precursor to 4). Nickel(II) dimethylglyoxime (2.0 g) was refluxed with (aminoethoxy)diphenylborane (2.5 g) in dioxane (25 mL) for 2 days under a nitrogen atmosphere. The hot reaction mixture was filtered. Upon cooling to the ambient temperature, yellow crystals formed. The product was collected by vacuum filtration. NMR (Me_2SO-d_6): δ 2.07 (s, 3), 7.00 (s, 5). Anal. Calcd for $C_{32}H_{32}B_2N_4NiO_4$: C, 62.29; H, 5.23; N, 9.08. Found: C, 61.8; H, 5.0; N, 9.1.

Synthesis of (3,6,11,14-Tetraaza-1-bora-1,1-difluoro-4,5,12,13-tetramethyl-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)nickel (11). Under an inert atmosphere, a solution of cobaltocene (0.060 g) in acetonitrile (2 mL) was combined with **19** (0.200 g). The reaction mixture was stirred 8 min. The product was isolated by vacuum filtration. The blue-green microcrystalline product was dried in vacuo. Anal. Calcd for $C_{12}H_{20}BF_2N_4NiO_2$: C, 40.05; H, 5.6; N, 15.57. Found: C, 39.9; H, 5.3; N, 15.1.

Registry No. **1**, 75399-93-8; **2**, 75399-94-9; **2**(CO), 75399-95-0; **3**, 75399-97-2; **4**, 75399-98-3; **5**, 75399-99-4; **6**, 75400-00-9; **6**(CO), 75420-56-3; **7**, 47105-34-0; **7**(CO), 75400-01-0; **8**, 75400-02-1; **8**(CO), 75400-03-2; **9**, 57719-35-4; **10**, 75400-04-3; **10**(CO), 75400-05-4; **11**, 73133-14-9; **12**, 75443-47-9; **13**, 73469-50-8; **16**, 75400-07-6; **17**, 75400-09-8; **18**, 75400-11-2; **19**, 73133-13-8; **20**, 75400-12-3; [(3,3′-trimethylenedinitrilo)-bis(2-butanone oximato)]nickel(II) perchlorate, 15137-49-2; nickel(II) bis(difluoroboroglyoximate), 35200-43-2; (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) diperchlorate, 36539-75-0; [(3,3′-ethylenedinitrilo)-bis(2-butanone oximato)]nickel(II) perchlorate, 15283-07-5; nickel(II) dimethylglyoxime, 13478-93-8; BF_3, 7637-07-2; (aminoethoxy)diphenylborane, 524-95-8; CO, 630-08-0.

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(29) All reduced nickel complexes are air sensitive and must be handled routinely under an inert atmosphere.