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Metal Oxidation State and Imine Vibrational Frequencies of Reduced Copper and Nickel Tetraimine Macrocyclic Ligand Complexes

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Normal imine vibrational bands between 1500 and 1700 cm^{-1} are observed for copper(II) and nickel(II) tetraimine macrocyclic ligand complexes. Upon one-electron reduction these bands disappear for macrocycles with conjugated imine groups, and new bands appear at lower frequencies. Infrared spectroscopy of a ^{15}N-substituted macrocycle indicates these lower frequency bands involve imine vibrations. Formation of the nickel(I) or copper(I) carbonyl adducts results in return of the usual infrared imine bands. The oxidation state of the metal complexes is discussed in reference to the previously reported copper complex crystallographic and ESCA results and the nickel complex EPR data.

The four-coordinate copper(II) complex **1a** undergoes one-electron reduction to give a neutral diamagnetic product, **2a**. This presumed copper(I) complex, **2a**, reacts with carbon monoxide to yield the five-coordinate copper(I) carbonyl complex **3a**.[1] Complex **3a** is, formally, a 20-electron species and represents a previously undocumented coordination number for copper(I). In light of their unusual nature, complexes **2a** and **3a**, as well as related complexes, have been carefully examined to determine whether they are best regarded as containing copper(I) or some higher oxidation state of copper in a reduced macrocyclic ligand complex. The crystal structure[2] of **2a** shows no unusual bond distances that would indicate ligand reduction rather than copper reduction upon synthesis from the copper(II) complex, **1a**, and the macrocycle is slightly twisted toward tetrahedrality as might be expected for copper(I). The crystal structure[3] of **3a** shows a notable five-coordinate geometry with the copper atom 0.96 Å above the plane of the four nitrogen atoms and a 120° angle between the two α-diimine planes. A crystal structure determination of **6a** (as the tetraethylammonium salt) shows the copper atom displaced above the best plane of the four nitrogen atoms by 1.06 Å.[6] Examination of compounds **1a**, **2a**, and **3a** by ESCA[4] suggests that the copper atom in **1a** is in the copper(II) oxidation state while the copper atoms in **2a** and **3a** are in the copper(I) oxidation state. Related reduced copper macrocyclic ligand complexes have been found also to bind fifth ligands, including CO (see Scheme I, Table I, and ref 5). Generally, good π acids have been found to bind most strongly as fifth ligands in such species.[5]

Similarly, reduced nickel macrocyclic ligand complexes have been found to also bind carbon monoxide (see Scheme I, Table I, and ref 7 and 8). As reported by Busch et al., the reduced nickel complexes are paramagnetic and EPR spectroscopy provides an additional method of study.[9] The reduced complexes for macrocycles with α-diimine groups (for example, **2b** and **5b**) show *g* values typical of free radicals and no hyperfine splitting, indicating that reduction of the nickel(II) complexes give nickel(II) reduced ligand radical species.[7-9]

Scheme I

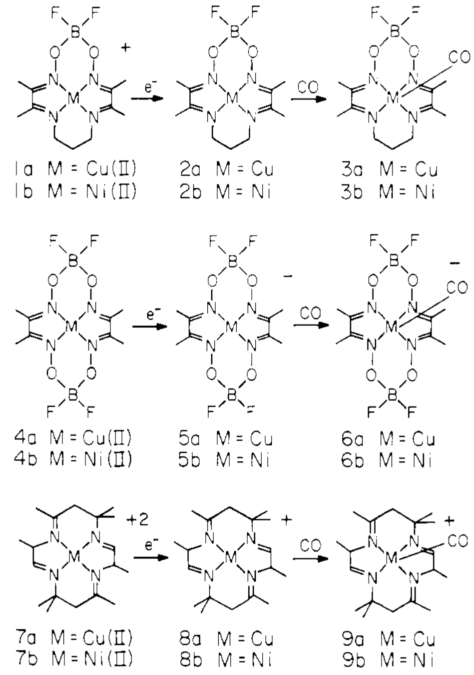

Table I. Equilibrium Binding Constants K_{CO} (M^{-1}) for the Reaction $ML^{n+} + CO \rightleftharpoons ML(CO)^{n+}$ [a]

	Cu	Ni
2	1.2×10^5	2.7×10^3
5	8.8×10^5	2.8×10^5
8	6.1×10^4	2.0×10^4

[a] K_{CO} for 2a and 5a from ref 5, for 2b and 5b from ref 8, and for 8a and 8b from ref 11.

The reduced complexes for nonconjugated imine groups (for example, **8b**) show *g* values typical of nickel(I) and nitrogen hyperfine splitting, indicating that the electron is added to the metal upon reduction.[7-9] Curiously, for all reduced nickel macrocyclic ligand CO adducts (for example, **3b**, **6b**, and **9b**) the EPR spectra indicate nickel(I) species[7,8] and that for the α-diimine macrocyclic complexes the unpaired spin density moves from the ligand to the metal upon CO adduct formation.

We report here an analysis of the infrared spectra of both copper and nickel tetraimine macrocyclic systems to link the similarities of the two more fully and to establish a better oxidation state description.

Infrared Spectral Results

The copper(II) complex **1a** has infrared bands assigned to the α-diimine unit at 1660 and 1590 cm^{-1} (Figure 1 and Table

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Table II. Infrared Spectra (KBr Pellets) in the Region Region 1300-2000 cm^{-1} [a]

1a	**2a**	**3a**	**1b**	**2b**
1660 w	1470 m	1640 w	1630 w	1465 w
1590 m	1320 s	1560 m	1575 m	1335 s
1440 w	(1430 w)	1430 m	1440 m	1440 w
1390 w	1380 w	1380 w	1390 w	1390 w
(1370 w)	1365 w	1360 w	1360 w	1360 w

4a	**5a**	**6a**	**4b**	**5b**	**6b**
1635 m	1330 m	1630 m	1635 m	1325 s	1610 m
					1510 w
1460 w	1470 m	(1440 w)	1430 w	1450 w	(1445 w)
1450 w	1420 m	1420 m		1420 m	1415 m
1385 w	1385 w	1380 w	1385 m	1380 m	1385 w
1370 w	1370 w	1370 w			1375 w
					1345 w

7a	**8a**	**7b**	**8b**
1680 m	1655 m	1670 m	1650 w
1660 s	1615 w	1650 s	1635 m
(1470 w)		(1470 w)	
1460 m	1450 w	1455 m	1455 w
1410 m		1410 m	1415 w
1390 s	1390 w	1390 s	1380 s
1375 s	1370 s	1375 s	1375 s
1335 w	1350 w	1330 w	

[a] Shoulders given in parentheses.

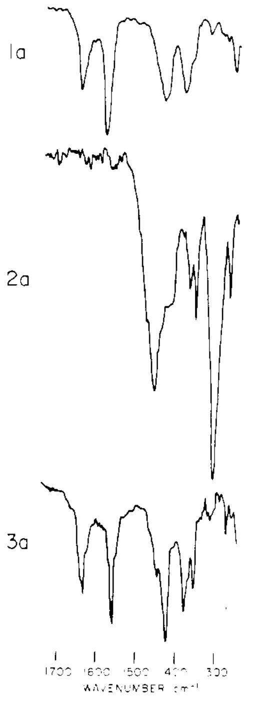

Figure 1. Infrared spectra (KBr pellets) in the region 1300–1700 cm^{-1}.

II), the typical region for imine absorptions. In the four-coordinate complex **2a** there are no bands in this region, but two new bands are found at 1470 and 1320 cm^{-1} (Figure 1 and Table II). Loss of the infrared imine bands upon one-electron reduction suggested ligand reduction in spite of the crystallographic and ESCA results.

In contrast, the CO complex, **3a**, has α-diimine bands in the region expected at 1640 and 1560 cm^{-1} (Figure 1 and Table II), consistent with no ligand reduction. The same loss of imine vibration at the normal frequency, but gain of a new vibration at 1330 cm^{-1}, is observed upon reduction of **4a** to **5a** (Table II). Upon CO adduct formation the normal vibration is again observed in **6a** (Table II). Nickel complexes of the α-diimine macrocycles **1b** and **4b** exhibit similar behavior, as listed in Table II. Note that a large shift in imine vibrational frequencies upon reduction is consistent with the ligand reduction observed in **2b** and **5b** by EPR.

The imine vibration identification was confirmed by synthesis of **4b** from $^{15}NH_2OH$, 2,3-butanedione and $BF_3{\cdot}Et_2O$. The 1650-cm^{-1} band shifts to 1615 cm^{-1}. Upon reduction to **5b** the 1325-cm^{-1} band moves to 1310 cm^{-1} and the 1450-cm^{-1} band shifts to 1440 cm^{-1}. Although the bands in the reduced complex, **5b**, are affected by the isotopic change, the shift is not as large as for **4b**. This is not unexpected since the imine vibration must be part of a larger vibration both decreasing the frequency and lessening the shift upon isotopic substitution.

For the nonconjugated tetraimine macrocyclic complexes **7a** and **7b**, normal imine vibrations are observed for both the M(II) and reduced species as shown in Table II. Both infrared and nickel EPR spectroscopy show no indication of ligand reduction.

Discussion

An accurate oxidation state description for the metal ions in the reduced complexes is more than a mere formalism or question of semantics. These complexes represent new structural and reactivity types of copper(I) and nickel(I) and merit a more precise description. Furthermore, the role of the macrocyclic ligand in promoting unusual complex structures and reactivities poses more general questions regarding other transition-metal complexes.

The similarity between the copper and nickel complex infrared spectra suggest similar oxidation-state behavior. EPR spectra indicate that the reduced, four-coordinate, nickel α-diimine species should be regarded as nickel(II) bound to a ligand radical anion. By analogy, the reduced copper complexes with α-diimine ligands would then have copper(II) or copper(III) bound to a ligand anion or dianion. Conversely, ESCA data requires the reduced copper complexes to be regarded as copper(I). The apparent disparity may reflect the fact that EPR spectroscopy monitors the unpaired electron *spin* density, while ESCA is more concerned with the electron *charge* density at the metal center.

If an analogy can be made to metal carbonyl chemistry, where increased electron density at the metal center may be transferred to the carbonyl via σ interactions and returned to the metal via π interactions, the increased electron density upon reduction of the α-diimine complexes may lead to similar π back-bonding. Electron density fed into the ligand π^* orbital might then be returned to the metal via σ interactions. The net effect would be infrared and EPR indications of increased electron density in the π^* orbital concurrent with the Cu(I) oxidation state observed by ESCA. Thus these highly covalent species might best be considered to be a hybrid between reduced-metal ligand complexes and metal reduced-ligand complexes, having properties attributable to both.

Experimental Section

Complexes **1a**,[3] **2a**,[3] **3a**,[3] **4a**,[6] **5a**,[6] **7a**,[10,11] **8a**,[10,11] **1b**,[8] **2b**,[8] **4b**,[12] **5b**,[8] **6b**,[8] **7b**,[11] and **8b**[11] were prepared by the methods given in the references listed.

Isotopically ^{15}N-substituted **4b** was prepared by stirring 2,3-butanedione (56 mg), ^{15}N-hydroxylamine hydrochloride (70 mg), and nickel(II) acetate dihydrate (240 mg) in 4 mL of ethanol at ambient temperature overnight. Subsequent syntheses were as previously described.[8]

Infrared spectra were obtained on a Beckman IR-4240 infrared spectrometer. Samples, contained in KBr pellets, were prepared under

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an inert atmosphere. Spectra of KBr pellet samples were comparable to the spectra of Nujol mull samples prepared under a helium atmosphere in a Vacuum Atmospheres Dri-Lab glovebox.

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Registry No. 1a, 64783-09-1; **1b**, 75400-06-5; **2a**, 61114-07-6; **2b**, 75399-94-9; **3a**, 61128-83-4; **4a**, 77321-01-8; **4b**, 35200-43-2; **5a**, 77321-02-9; **5b**, 75399-96-1; **6a**, 77321-03-0; **6b**, 73146-60-8; **7a**, 77321-04-1; **7b**, 69460-51-1; **8a**, 77321-05-2; **8b**, 77321-06-3.

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Resonance Raman Spectra, Excitation Profiles, and Infrared Spectra of [Co(salen)]$_2$O$_2$ in the Solid State

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Resonance Raman (RR) spectra of the dioxygen adduct of [*N,N'*-ethylenebis(salicylideniminato)]cobalt(II), [Co(salen)]$_2$O$_2$, have been measured in the crystalline state. The O_2 stretching and symmetric and antisymmetric CoO stretching vibrations have been located at 1011, 533, and ~370 cm^{-1}, respectively, on the basis of $^{16}O_2$–$^{18}O_2$ substitution experiments. The structure of the Co–O_2–Co bridge has been concluded to be approximately trans planar on the basis of the intensities of these vibrations in the IR and RR spectra. The Co–O_2 charge-transfer transition has been located at ca. 570 nm via the excitation profiles of the 1011- and 533-cm^{-1} bands.

Introduction

Since Tsumaki[1] discovered the reversible oxygenation of [*N,N'*-ethylenebis(salicylideniminato)]cobalt(II), Co(salen), in the solid state, extensive investigations have been carried out on molecular oxygen adducts of Schiff base complexes, metalloporphyrins, and N$_4$-macrocyclic complexes.[2] The techniques used in these investigations include X-ray analysis, MO treatments, and electronic, ESR, and vibrational spectroscopy together with kinetic, thermodynamic, and electrochemical measurements. As to vibrational spectroscopy, the O_2 stretching frequencies, $\nu(O_2)$, determined by infrared (IR) and resonance Raman (RR) studies have played a significant role in elucidating the nature of the metal–O_2 bonding.

In general, $\nu(O_2)$ of molecular oxygen adducts fall in two ranges: the superoxo (O_2^-) type which exhibits $\nu(O_2)$ in the 1200–1070-cm^{-1} regeion, and the peroxo (O_2^{2-}) type which exhibits $\nu(O_2)$ in the 930–740-cm^{-1} region[2] (see Figure 1). However, the cocondensation products of metal atoms such as Pd,[3] Ni,[3] and Fe[4] with O_2 in inert-gas matrices exhibit their $\nu(O_2)$ between these two regions. Recently, we have located the $\nu(O_2)$ of Co(TPP)(O_2) in an argon matrix at 1278 cm^{-1} that is substantially higher than the normal range for superoxo adducts.[5] Since the $\nu(O_2)$ of Co(TPP)(1-MeIm)O_2 is known to be 1142 cm^{-1},[6] we have attributed this large high-frequency shift of $\nu(O_2)$ (136 cm^{-1}) to the absence of the axial base ligand in Co(TPP)(O_2). That is, a base such as 1-MeIm increases the negative charge on the O_2 via σ and π donation, thus causing the low-frequency shift of $\nu(O_2)$.

The $\nu(O_2)$ frequency is moderately sensitive to the change in the base ligand. For example, the $\nu(O_2)$ of the [Co(salen)B]$_2$O$_2$-type complexes are at 910, 897, and 888 cm^{-1} for B = pyO, DMF, and py, respectively.[7] However, these frequencies are much higher than the $\nu(O_2)$ of the [(Co(NH$_3$)$_5$)$_2$O$_2$]$^{4+}$ ion (808 cm^{-1})[8] since both axial and equatorial ligands in the latter are more electron donating than those in the [Co(salen)B]$_2$O$_2$-type complexes. Several examples cited above clearly demonstrate that the $\nu(O_2)$ can be varied in a wide range depending upon the electron density on the Co atom which is governed by its surrounding groups.

As stated above, Co(salen) is the first synthetic reversible Co(II) oxygen carrier; 2 mol of crystalline Co(salen) bind 1 mol of molecular oxygen to form a unique 1:2 adduct, [Co(salen)]$_2$O$_2$, in the absence of a base ligand. Co(salen) exists in several crystalline modifications, some of which are oxygen active while others are not.[18] Different modifications are obtained depending upon the method of preparation, and the interconversion among them is caused by heating or grinding. According to X-ray analysis,[18] oxygen-inactive Co(salen) consists of discrete five-coordinate dimers without open structures (holes) which allow the passage of oxygen molecules in the crystal. Previously, Martell and Calvin[19] suggested the

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