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Contribution from the Division of Chemical and Physical Sciences,
Deakin University, Waurn Ponds 3217, Victoria, Australia

Investigation of Factors Stabilizing Formally Zerovalent Copper Macrocyclic Complexes

Alan M. Bond* and Mohamed A. Khalifa[1]

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Electrochemical reduction of $[\mathrm{Cu(Me_4[14]1,4,8,11\text{-}tetraeneN_4)}(N\text{-}\mathrm{Me\text{-}imidazole})](\mathrm{PF_6})_2$, $[\mathrm{Cu(N_4)MeIm}]^{2+}$, has been studied in detail to ascertain the factors favoring stabilization of formally zerovalent copper complexes. At platinum, gold, glassy-carbon, and mercury electrodes, two chemically reversible one-electron-reduction processes are observed in dichloromethane or acetone. In dichloromethane, the reversible half-wave potential for the first reduction process is dependent on the concentration of MeIm, implying that this process corresponds to the reaction $[\mathrm{Cu(N_4)MeIm}]^{2+} + e^- \rightleftharpoons [\mathrm{Cu(N_4)}]^+ + \mathrm{MeIm}$. The second one-electron-reduction step is independent of MeIm concentration and is assumed to correspond to the process $[\mathrm{Cu(N_4)}]^+ + e^- \rightleftharpoons [\mathrm{Cu(N_4)}]^0$. The oxygen-sensitive copper(I) complex $[\mathrm{Cu(N_4)}]^+$ can be identified as the product of either a one-electron controlled-potential reductive electrolysis in dichloromethane or acetone or chemical reduction with cobaltocene. The extremely air- and moisture-sensitive formally copper(0) complex $[\mathrm{Cu(N_4)}]^0$ can be identified after a two-electron controlled-potential reductive electrolysis of $[\mathrm{Cu(N_4)MeIm}]^{2+}$ or a one-electron reduction of $[\mathrm{Cu(N_4)}]^+$ at −70 °C in acetone. The rate of decomposition of the zerovalent complex to elemental copper is enhanced by acetonitrile, platinum electrodes, and water. Reaction with oxygen is very rapid, but does not regenerate the starting material. The stabilization of a formally zerovalent copper complex is considered to be favored by factors such as appropriate charge, geometry, nature of the macrocyclic ligand, and correct choice of solvent and electrodes. A reversible one-electron-oxidation process observed at mercury but not at other electrodes is attributed to interaction of MeIm with mercury following dissociation of the macrocyclic complex: $2[\mathrm{Cu(N_4)MeIm}]^{2+} \rightleftharpoons 2[\mathrm{Cu(N_4)}]^{2+} + 2\mathrm{MeIm}$; $2\mathrm{MeIm} + \mathrm{Hg} \rightleftharpoons [\mathrm{Hg(MeIm)_2}]^{2+} + 2e^-$. At platinum, gold, and glassy-carbon electrodes a chemically irreversible oxidation process is observed at different potentials to the oxidation process at mercury electrodes. However, unlike copper macrocyclic systems such as $[\mathrm{Cu[14]aneN_4}]^{2+}$ ($[\mathrm{Cu(cyclam)}]^{2+}$), no stable copper(III) complex could be detected under conditions of cyclic voltammetry even with scan rates of 500 mV s^{-1}. That is, factors that stabilize formally zerovalent complexes appear to destabilize copper(III) complexes.

Introduction

The chemistry of transition-metal macrocycles is now extensive.[2] Redox properties of this class of complex have been of considerable interest because of the close relationship to molecules of biological significance. In the case of copper, the predominant interest has been in oxidation. For example, Olson and Vasilevskis electrochemically oxidized copper macrocyclic tetraamine complexes in acetonitrile to give moderately stable Cu(III) complexes.[3] Similarly, Fabbrizzi and Poggi[4] have reported the synthesis of a copper(III) complex of the 1,4,8,11-tetraazacyclotetradecane-4,8-diamido macrocycle by the electrochemical oxidation of the corresponding copper(II) complex at a platinum electrode. Copper(III) amine, amino acid, and peptide complexes have also been reported in pulse radiolysis, chemical, and electrochemical oxidation studies.[5-7]

Reduction of copper(II) macrocyclic complexes to the copper(I) state has also been examined in some detail. The relationship of the chemistry of the Cu(II)/Cu(I) redox couple to copper biochemistry has also been discussed.[8,9] The geometry and nature of the ligand appear to be important factors determining the stability of copper(I) complexes since many copper(I) complexes, including macrocycles,[10] disproportionate to copper(II) and metallic copper[11] or else decompose via other pathways.[10] Ligand environments having square-planar structures such as copper(II) dithiocarbamate, $\mathrm{Cu(dtc)_2}$, can be reduced in solution to monomeric four-coordinate copper(I) complexes

$$\mathrm{Cu(dtc)_2} + e^- \rightleftharpoons \mathrm{Cu(dtc)_2}^- \qquad (1)$$

with the isolated copper(I) complex being the tetramer $\mathrm{Cu_4(dtc)_4}$.[12] Chelate ligand systems such as the sulfur-based dithiocarbamate seem to inhibit disproportionation, particularly when structural stability is gained via rearrangement. Similarly, some tetradentate macrocyclic ligands (hereafter referred to as $\mathrm{N_4}$) such as i[9] and others[13,14] also give well-defined copper(I) complexes. Interestingly, Meyerstein et al[13] note that methylation of $\mathrm{Cu^{II}(N_4)}$, ($\mathrm{N_4}$ = ii, R = H) leads to formation of the remarkably stable $[\mathrm{Cu^I(N_4)}]^+$ ($\mathrm{N_4}$ = ii, R = $\mathrm{CH_3}$) complex. Surprisingly, this complex is not oxidized chemically[4] to produce a stable $\mathrm{Cu^{II}(N_4)}$ moiety. π and σ effects on the Cu(II)/Cu(I) redox couple for macrocyclic ligand systems also have been investigated[15] and are reasonably well understood. Addition of carbon monoxide and other ligands produces very stable five-coordinate copper(I) macrocyclic complexes.[8,9,16-19] Tetradentate macrocyclic ligands that enforce a nearly square-planar yet flexible ligand geometry for Cu(I) seem to promote five coordination,[16] and this square-pyramidal structure is suggested to be significant in biologically important molecules.[9]

Thus, stimulated by possible relationships to copper biochemistry, oxidation states of copper macrocyclic complexes from i–iii

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(1) On leave from Department of Chemistry, Alexandria University, Alexandria, Egypt.

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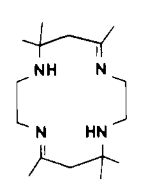

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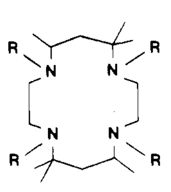

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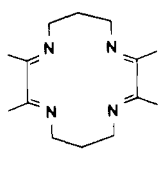

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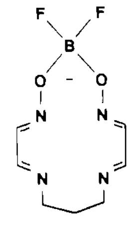

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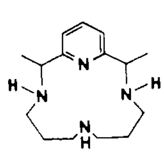

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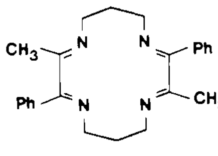

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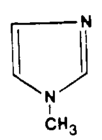

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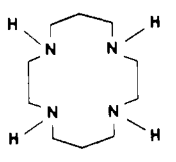

(viii)

have been examined in detail, particularly via electrochemical methods.[8,9,16,17,20,21] The majority of these electrochemical reduction studies have been undertaken in potentially coordinating solvents such as acetonitrile[8,9,17,20] or dimethylformamide.[13,19,20] In view of possible reactions of the kind

$$\mathrm{Cu^{II}(N_4)} + \mathrm{L}_n \rightleftharpoons \mathrm{Cu^{II}(N_4)L}_n \quad n = 1, 2 \qquad (2a)$$

$$\mathrm{Cu^{I}(N_4)} + \mathrm{L} \rightleftharpoons \mathrm{Cu^{I}(N_4)L} \qquad (2b)$$

(L = monodentate ligand or solvent and charges are omitted for simplicity), interpretation of some of this data may require inclusion of terms for the solvent. Furthermore, virtually no information was available on zerovalent copper macrocycles at the time this project commenced. Recently Maroney et al.,[22] in a brief examination of the redox chemistry of copper complexes of iii, noted that two chemically reversible one-electron-reduction processes are observed in acetonitrile. In another study,[8] electrochemical reduction of iv in acetonitrile was said to give two reduction waves. However, the second reduction process with an $E_{1/2}$ value of −1.75 V vs. SCE was said to be irreversible and was not investigated further. In the case of v a second reduction step was shown to produce elemental copper.[23] Some examples of two-electron reduction of $\mathrm{Cu^{II}(N_4)}$ to the metal are also known.[23,24]

While chemical reduction of vi with metallic zinc in methanol[25] produces metallic copper in aprotic solvents, copper (I) complexes are produced in other solvents, indicating that formation of metallic copper is solvent-assisted disproportionation rather than direct reduction to the zerovalent complex and subsequent ligand loss.

In this work, consideration of known substituent effects, geometry requirements, charge effects, and solvent interactions in copper macrocyclic chemistry led to the belief that the virtually uncharacterized formally copper(0) macrocyclic complexes should be accessible. The literature data indicate that stability may be achieved if the following points are observed:

(i) The final formally copper(0) complex has a zero charge; i.e. the synthesized copper (II) species prior to reduction should have an overall charge of 2+.

(ii) The macrocyclic ligand should itself not be readily capable of undergoing reduction. An example would be a ligand containing conjugated α-diimine groups in a five-membered ring; furthermore, available data suggest that it may be advantageous if factors iii and iv are considered.

(iii) The fifth and possibly sixth coordination site should be blocked by a suitable ligand.

(iv) Reduction should be undertaken in a noncoordinating solvent.

A complex possibly meeting requirements i, ii, and iii may be derived from iii. In this present study, electrochemical and chemical redox studies are reported on the compound[(Cu(Me$_4$[14]1,4,8,11-tetraeneN$_4$)(*N*-MeIm)](PF$_6$)$_2$ in coordinating and noncoordinating solvents at platinum, gold, glassy-carbon, and mercury electrodes to determine whether formally copper(0) oxidation states are readily accessible and what factors are required to achieve this goal. This compound has been prepared independently by two research groups[21,22] and characterized by X-ray crystallography.[26] The abbreviation [Cu(N$_4$)MeIm]$^{2+}$ will be used for this compound where (N$_4$) = iii and MeIm = *N*-methylimidazole (vii). Finally, comparison with the redox chemistry of [Cu[14]aneN$_4$]$^{2+}$, (N$_4$) = viii, is included to complete a systematic investigation of factors leading to stabilization of formally low-oxidation-state copper macrocyclic complexes.

Experimental Section

Synthesis. [Cu(Me$_4$[14]1,4,8,11-tetraeneN$_4$)(*N*-MeIm)](PF$_6$)$_2$, [Cu(N$_4$)MeIm](PF$_6$)$_2$. [Cu(N$_4$)MeIm]$^{2+}$ was prepared and characterized by methods described by Khalifa[21] and Maroney et al.[22] The purity of the product was confirmed by elemental analysis.

[Cu([14]aneN$_4$)](ClO$_4$)$_2$. [Cu([14]aneN$_4$)](ClO$_4$)$_2$ was prepared by reaction of copper acetate and 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$ or cyclam) in methanol followed by addition of a 50:50 methanol–water mixture. The purity was confirmed by elemental analysis and comparison with the chemical, physical, and spectroscopic characteristics described for this complex in ref 23.

Hg(MeIm)$_6$(ClO$_4$)$_2$·2H$_2$O. Mercuric perchlorate trihydrate (0.453 g) was dissolved in acetone (20 mL) and the excess filtered off. This solution was added slowly, with stirring, to a solution of *N*-methylimidazole (0.5 g) in acetone (15 mL). The reaction mixture was stirred at ambient temperature for 30 min and then cooled to 0 °C. The white crystalline product was filtered and washed with methanol. The product was recrystallized three times from acetone and dried in vacuo. Anal. Calcd for $\mathrm{C_{24}H_{40}N_{12}Cl_2O_{10}Hg}$: C, 31.05; H, 3.9; N, 18.12. Found C, 30.93; H, 3.86; N, 18.25.

Other Compounds. Cobaltocene (ICN pharmaceuticals), *N*-methylimidazole (Aldrich Chemical Co.), and other compounds were used as supplied by the manufacturer.

Electrochemical Instrumentation and Techniques. Cyclic voltammetric experiments at platinum, gold, and glassy-carbon disk electrodes were undertaken with a Bioanalytical Systems CV 27 Voltammograph (West Lafayette, IN).

The reference electrode was Ag/AgCl (acetone, saturated LiCl), which was frequently calibrated by using the ferrocene, Fe(C$_5$H$_5$)$_2$, oxidation process

$$\mathrm{Fe(C_5H_5)_2} \rightleftharpoons [\mathrm{Fe(C_5H_5)_2}]^+ + e^- \qquad (3)$$

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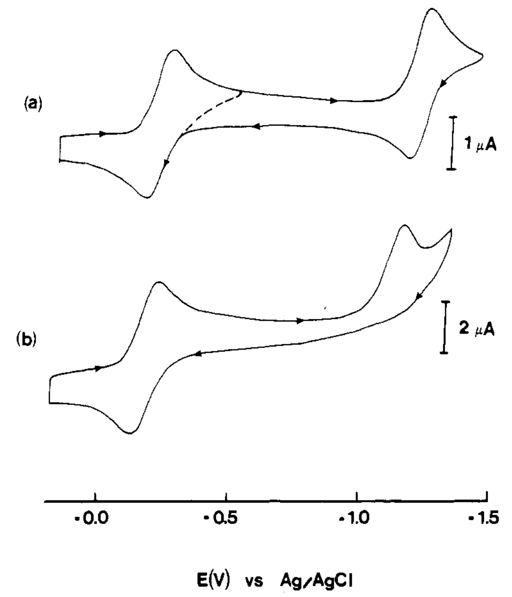

Figure 1. (a) Cyclic voltammogram at 20 °C for reduction of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetone (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 100 mV s^{-1}): (---) first reduction process; (—) both processes. (b) Cyclic voltammogram at 20 °C for reduction of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) in the presence of deliberately added water at a gold electrode (scan rate = 100 mV s^{-1}).

in the appropriate solvent. The auxiliary electrode was platinum wire.

Polarographic measurements using a dropping mercury electrode or voltammetric experiments with a hanging mercury drop electrode were undertaken with an EG & G PAR Model 174A polarographic analyzer (Princeton, NJ). The same reference and auxiliary electrodes were used as in cyclic voltammetry.

Controlled-potential electrolysis and coulometric experiments were undertaken with a PAR Model 173 potentiostat/galvanostat combined with a Model 179 digital coulometer. The working electrodes were either mercury pool or platinum-gauze basket electrodes, with a platinum-gauze auxiliary electrode separated from the test solution by a Vycor plug. The reference electrode was the same as for voltammetric and polarographic experiments. The course of electrolysis experiments was monitored voltammetrically or polarographically using the instrumentation described above.

The solvents used were dichloromethane, acetone, and acetonitrile, each containing 0.1 M Bu_4NClO_4 as the supporting electrolyte. Solvents, after purification by distillation, were dried and stored over 4A molecular sieves prior to use. The electrolyte was dried under vacuum at 60 °C for at least 12 h prior to use and stored in a drybox or vacuum desiccator. All solutions were degassed with argon for at least 15 min prior to recording electrochemical data. During the course of voltammetric experiments, an argon atmosphere was maintained above the solution. In controlled-potential electrolysis experiments, argon was bubbled continuously through the solution. Experiments undertaken in a drybox produced data essentially identical with that provided under argon in a conventional laboratory atmosphere.

Unless otherwise specified, data were obtained at 20 ± 0.5 °C. Solid electrodes were cleaned by polishing with alumina and applying a positive potential of +2 V vs. Ag/AgCl before recording voltammetric scans.

Results and Discussion

Figure 1a shows a cyclic voltammogram for reduction of $[Cu(N_4)MeIm]^{2+}$ in acetone (0.1 M Bu_4NClO_4) at a platinum electrode. At platinum, gold, mercury, or glassy-carbon electrodes, two well-defined chemically reversible reduction waves were observed in acetone or dichloromethane. These are referred to as processes 1 (less negative) and 2 (more negative) in the subsequent discussion. Data are summarized in Table I. Data for oxidation of 5×10^{-4} M ferrocene are also included, so that junction potential effects can be estimated and comparisions in different solvents made. The ratio of peak height for reduction and oxidation for both processes was unity for all scan rates (50–500 mV s^{-1}) and temperatures (20 to −70 °C) examined, and the separation in peak potential was close to the value expected for an electrochemically reversible one-electron process, as ascertained by comparison with data obtained for oxidation of ferrocene under the same conditions.

Table I. Cyclic Voltammetry for 5.0×10^{-4} M $[Cu(N_4)(MeIm)]^{2+}$ in Various Solvents (0.1 M Bu_4NClO_4) and Electrodes at a Scan Rate of 100 mV s^{-1} and at 20 °C[a]

	solvent																		
	dichloromethane							acetone							acetonitrile						
	process 1		process 2		process 3[b]		process 4[c]	process 1		process 2		process 3[b]		process 4[c]	process 1		process 2		process 3[b]		process 4[c]
electrode	$(E_{1/2}^{red})_1$, V	$(\Delta E_p)_1$, mV	$(E_{1/2}^{red})_2$, V	$(\Delta E_p)_2$, mV	$(E_{1/2}^{ox})_3$, V	$(\Delta E_p)_3$, mV	$(E_p^{ox})_4$, V	$(E_{1/2}^{red})_1$, V	$(\Delta E_p)_1$, mV	$(E_{1/2}^{red})_2$, V	$(\Delta E_p)_2$, mV	$(E_{1/2}^{ox})_3$, V	$(\Delta E_p)_3$, mV	$(E_p^{ox})_4$, V	$(E_{1/2}^{red})_1$, V	$(\Delta E_p)_1$, mV	$(E_{1/2}^{red})_2$, V	$(\Delta E_p)_2$, mV	$(E_{1/2}^{red})_3$, V	$(\Delta E_p)_3$, mV	$(E_p^{ox})_4$, V
platinum	−0.085	70	−1.160	70			1.820	−0.178	65	−1.173	65			1.505	−0.170	80	−1.145	70			1.702
gold	−0.080	80	−1.155	70			1.815	−0.175	70	−1.173	65			1.502	−0.168	65	−1.142	70			1.701
glassy carbon	−0.085	75	−1.155	80			1.803	−0.178	75	−1.175	70			1.504	−0.173	75	−1.148	75			1.703
mercury	−0.082	70	−1.159	70	0.580	65		−0.180	60	−1.180	65	0.430	65		−0.175	65	−1.152	70	0.485	70	

[a] Data for 5×10^{-4} M ferrocene at a platinum electrode: CH_2Cl_2, $E_{1/2} = 0.683$ V; CH_3COCH_3, $E_{1/2} = 0.618$ V; CH_3CN, $E_{1/2} = 0.578$ V. $E_{1/2}$ calculated as $(E_p^{red} + E_p^{ox})/2$. All potentials in V vs. Ag/AgCl. ΔE_p = peak-to-peak separation, mV. [b] Process 3 only observed at mercury electrodes. [c] Chemically irreversible.

Table II. Polarographic Data[a] for 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ at 20 °C

	dc polarography[b]						differential-pulse polarography[c]		
	redn process 1		redn process 2		oxidn process 3		redn process 1	redn process 2	oxidn process 3
solvent	$E_{1/2}$, V	$(E_{1/4} - E_{3/4})$, mV	$E_{1/2}$, V	$(E_{1/4} - E_{3/4})$, mV	$E_{1/4}$, V	$(E_{1/4} - E_{3/4})$, mV	E_p, V	E_p, V	E_p, V
CH_2Cl_2	−0.080	60	−1.160	55	0.570	−55	−0.075	−1.140	0.560
CH_3COCH_3	−0.180	60	−1.175	55	0.480	−55	−0.170	−1.160	0.470
CH_3CN	−0.170	60	−1.165	60	0.485	−60	−0.160	−1.150	0.465

[a] Data for 5.0×10^{-4} M ferrocene: CH_2Cl_2, $E_{1/2} = 0.685$; CH_3COCH_3, $E_{1/2} = 0.615$; CH_3CN, $E_{1/2} = 0.580$. All potentials in V vs. Ag/AgCl. [b] Drop time 0.5 s. [c] Drop time 0.5 s; amplitude ±50 mV.

Table III. Electrochemical Data for Reduction of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in the Presence of MeIm in Dichloromethane and at 20 °C

	dc polarography[a]						voltammetry[b]			
	process 1			process 2			process 1		process 2	
[MeIm], M	$(E_{1/2})_1$, V	i_d, μA	$(E_{1/4} - E_{3/4})$, mV	$(E_{1/2})_2$, V	i_d, μA	$(E_{1/4} - E_{3/4})$, mV	$(E_{1/1})_1$, V	$(\Delta E_p)_1$, mV	$(E_{1/2})_2$, V	$(\Delta E_p)_2$, mV
0	−0.083	1.52	63	−1.155	1.60	64	−0.080	70	−1.155	65
6.0×10^{-4}	−0.090	1.60	70	−1.152	1.65	60	−0.082	75	−1.151	70
2.4×10^{-3}	−0.117	1.45	60	−1.154	1.50	62	−0.110	75	−1.152	70
6.4×10^{-3}	−0.145	1.50	59	−1.152	1.55	58	−0.138	75	−1.153	70
5.0×10^{-2}	−0.200	1.50	60	−1.154	1.53	65	−0.188	70	−1.151	70
5.0×10^{-1}	−0.245	1.50	65	−1.155	1.52	60	−0.240	80	−1.150	70

[a] Drop time = 0.5 s^{-1} at a dropping mercury electrode. [b] Scan rate = 200 mV s^{-1} at a platinum electrode.

While acetone in principle may be a weakly coordinating solvent, CH_2Cl_2 should be noncoordinating and acetonitrile strongly coordinating. The absence of any major dependence of data for process 1 on electrode material and solvent after correction for the junction potential via ferrocene data suggests that neither specific electrode terms nor solvent terms are highly important in the thermodynamic sense. However, in the strongly coordinating acetonitrile solvent, cyclic voltammetric data are different with respect to the second reduction process. Figure 1b shows a cyclic voltammogram in acetonitrile in the presence of deliberately added water. Under these conditions, the second reduction process is chemically irreversible. Addition of similar concentrations of water does not produce the same change in data obtained in acetone or dichloromethane. In dried acetonitrile, a considerable, but not complete, degree of chemical reversibility is observed, unless scan rates of 200 mV s^{-1} or greater are used. Experiments to be described later suggest that the coordination of solvent and the presence of traces of water are both important factors in enhancing the rate of decomposition of the formally zerovalent complex. Data for a reversible oxidation process at mercury electrodes (process 3) and for an irreversible oxidation process (process 4), observed at very positive potentials at platinum, gold, and glassy-carbon electrodes, are also included in Table I and will be discussed later.

Polarographic studies in the three solvents also indicate the existence of two well-defined one-electron-reduction processes (Figure 2a). Polarographic data are summarized in Table II. After background correction, both reduction processes show the same limiting current per unit concentration. However, a one-electron-oxidation wave at mercury electrodes (process 3), not observed at platinum, gold, or glassy-carbon electrodes, is also present at about 0.5 V vs Ag/AgCl (Figure 2a). Cyclic voltammetry at the hanging mercury drop electrode (Figure 3a) confirms that all three processes are chemically reversible at mercury electrodes, and differential pulse polarograms for all three processes are consistent with reversible one-electron charge transfer (Figure 3b, Table II). In acetonitrile the second reduction step exhibits a small maximum, not present in acetone or dichloromethane. Small differences in data at mercury electrodes for process 2 in acetonitrile are characteristic of studies at all electrode surfaces.

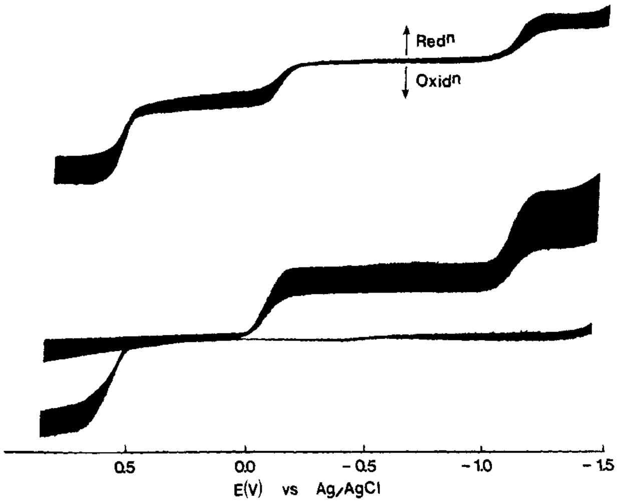

Figure 2. Lower curve: dc polarogram at 20 °C for reduction of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) (drop time = 0.5 s). Upper curve: dc polarogram after controlled-potential electrolysis of $[Cu(N_4)MeIm]_4^{2+}$ at −0.4 V vs. Ag/AgCl in acetone (0.1 M Bu_4NClO_4) at 20 °C (drop time = 0.5 s).

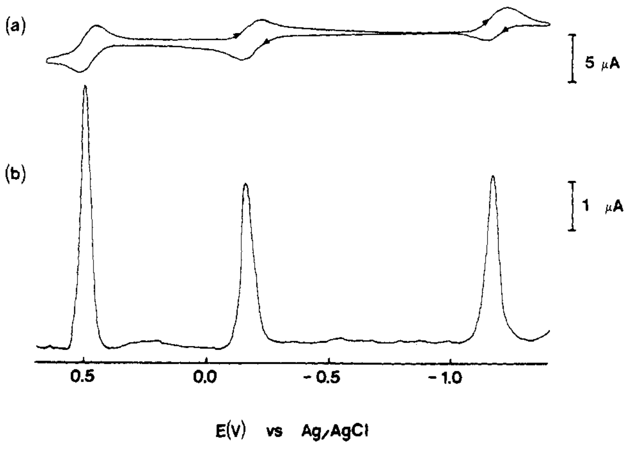

Figure 3. (a) Cyclic voltammogram at 20 °C for 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetone (0.1 M Bu_4NClO_4) at a hanging mercury drop electrode (scan rate = 200 mV s^{-1}). (b) Differential-pulse polarogram for 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetone (0.1 M Bu_4NClO_4) (drop time = 0.5 s; pulse amplitude = −50 mV).

At mercury electrodes the presence of process 3, which is absent at platinum, gold, or glassy-carbon electrodes, suggests that the formation of a mercury complex occurs at this electrode surface. Deliberate addition of MeIm to a solution containing 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in CH_2Cl_2(0.1 MBu_4NClO_4) has important influences on both polarographic and voltammetric data at all electrodes, and significantly aids mechanistic interpretation of processes 1–3. At the dropping mercury electrode, the dc limiting current of process 3 increases in height after addition of MeIm. For an equivalent concentration of both species, the limiting current doubles in height, whereas processes 1 and 2 are unaltered with respect to the limiting current. However, data in Table III demonstrate that $E_{1/2}$ for process 1 in dichloromethane is a function of MeIm concentration becoming more negative with increasing concentration. Similarly, $E_1/_2$ for process 1 at platinum electrodes shifts to more negative potential with increasing MeIm concentration (Table III). By contrast, process 2 is independent of MeIm concentration. The ratio of i_p^{red}/i_p^{ox} for both processes 1 and 2 remains unity at all concentrations of MeIm, indicating that chemical reversibility is maintained. A plot of $(E_{1/2})_1$ vs. the logarithm of the concentration of MeIm is a straight line of slope 57 ± 1 mV over the concentration range 5.0×10^{-3} to 1.0 M. The dependence of process 1 on the concentration of MeIm and the existence of process 3 at mercury electrodes imply that $[Cu(N_4)MeIm]^{2+}$ is an extremely labile complex and/or is almost completely dissociated to $[Cu(N_4)]^{2+}$ and MeIm in solution. The slope of 57 mV for the plot of $(E_{1/2})_1$ vs. the logarithm of the concentration of MeIm as well as the shift in $E_{1/2}$ to more negative potentials with increasing concentration of MeIm is explained by a decrease of one in the coordination number when a copper(II)

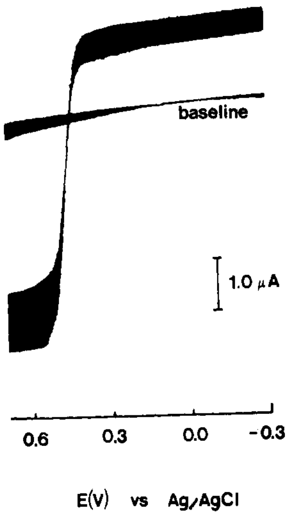

Figure 4. Dc polarogram at 20 °C for 5.0×10^{-4} M $Hg(MeIm)_6(ClO_4)_2 \cdot 2H_2O$ in acetone (0.1 M Bu_4NClO_4) (drop time = 0.5 s).

complex is reduced to copper(I) in the presence of a considerable excess of MeIm. The independence of process 2 on the concentration of MeIm suggests that no change in coordination number occurs[27] when further reduction to the formally copper(0) complex takes place.

Two possible explanations for data in the presence of excess MeIm may be proposed, as in eq 4 and 5.

$$[Cu(N_4)MeIm]^{2+} + MeIm \rightleftharpoons [Cu(N_4)(MeIm)_2]^{2+} \quad (4a)$$

$$[Cu(N_4)(MeIm)_2]^{2+} + e^- \rightleftharpoons [Cu(N_4)MeIm]^+ + MeIm \quad (4b)$$

$$[Cu(N_4)MeIm]^+ + e^- \rightleftharpoons [Cu(N_4)MeIm]^0 \quad (4c)$$

$$[Cu(N_4)MeIm]^{2+} \rightleftharpoons [Cu(N_4)]^{2+} + MeIm \quad (5a)$$

$$[Cu(N_4)MeIm]^{2+} + e^- \rightleftharpoons [Cu(N_4)]^+ + MeIm \quad (5b)$$

$$[Cu(N_4)]^+ + e^- \rightleftharpoons [Cu(N_4)]^0 \quad (5c)$$

$[Cu(N_4)]^{2+}$ and indeed $[Cu(N_4)]^+$ and $[Cu(N_4)]^0$ can of course be involved in an equilibrium reaction with the solvent or electrolyte as in eq 6.

$$\begin{gathered}[Cu(N_4)]^{2+} + S \rightleftharpoons [Cu(N_4)S]^{2+} \\ S = \text{weakly bound solvent or perchlorate}\end{gathered} \quad (6)$$

The presence of process 3 at mercury electrodes at the same position as the free ligand and the known chemistry of $[Cu(N_4)]^{2+}$ and related systems[9,22d,25] favor eq 5 as being the dominant pathway.

Addition of mercury(II) perchlorate to a solution of MeIm leads to reversible oxidation process 3 becoming a reversible one-electron-reduction step. In the presence of water, process 3 disappears and is replaced by a reduction step at a more negative potential. The new process presumably arises from formation and reduction of an hydroxy mercury complex. Process 3 is consistent with the mechanism

$$2MeIm + 2Hg \rightleftharpoons 2[HgMeIm]^+ + 2e^- \quad (7a)$$

$$2HgMeIm^+ \rightleftharpoons [Hg(MeIm)_2]^{2+} + Hg \quad (7b)$$

$$\text{overall:} \quad 2MeIm + Hg \rightleftharpoons [Hg(MeIm)_2]^{2+} + 2e^- \quad (7c)$$

Synthesis of $Hg(MeIm)_6(ClO_4)_2$ and addition to acetone produces a mixed oxidation–reduction response as shown in Figure 4. That is, equilibria of the kind

$$[Hg(MeIm)_6]^{2+} \rightleftharpoons [Hg(MeIm)_2]^{2+} + 4MeIm \quad (8)$$

are involved in solution. Addition of mercury(I) perchlorate to MeIm leads to formation of elemental mercury via disproportionation as required by eq 7b.

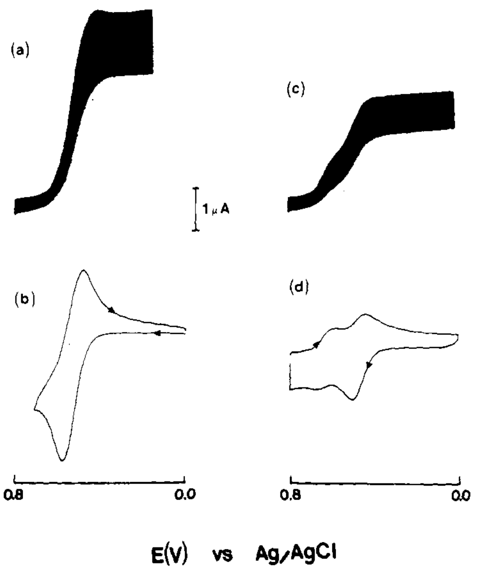

Figure 5. (a) Dc polarogram at 20 °C for reduction of 5.0×10^{-4} M $Cu(ClO_4)_2$ in acetone (0.1 M Bu_4ClO_4) (drop time = 0.5 s). (b) stripping voltammogram at 20 °C for oxidation of copper at a hanging mercury drop electrode (scan rate = 200 mV s^{-1}). (c) Dc polarogram at 20 °C for reduction of 5.0×10^{-4} M $Cu(ClO_4)_2$ in acetone (0.1 M Bu_4NClO_4) in the presence of water (drop time = 0.5 s). (d) Cyclic voltammogram at 20 °C for reduction of 5.0×10^{-4} M $Cu(ClO_4)_2$ in acetone (0.1 M Bu_4NClO_4) in the presence of water at a hanging mercury drop electrode (scan rate = 200 mV s^{-1}).

When $Hg(ClO_4)_2$ and $[Cu(N_4)MeIm]^{2+}$ are mixed in acetone, the color changes immediately from light blue to pink, which is the color[22c,28] of $[CuN_4S]^{2+}$. In this case S could be acetone, adventitious water, or perchlorate. Mercury(II) perchlorate is extremely hydroscopic, and complete elimination of water in this experiment is unlikely even if the solvent is sufficiently dry. Additionally, process 3 is converted from a one-electron-oxidation step to a reduction process. Controlled-potential electrolysis at a mercury pool electrode in acetone confirms that process 3 is a one-electron-oxidation step.

Thus process 3 is assigned to the reaction

$$2[Cu(N_4)MeIm]^{2+} \rightleftharpoons 2[Cu(N_4)]^{2+} + 2MeIm \quad (9a)$$

$$2MeIm + Hg \rightleftharpoons [Hg(MeIm)_2]^{2+} + 2e^- \quad (9b)$$

$$\text{overall:} \quad 2[Cu(N_4)MeIm]^{2+} + Hg \rightleftharpoons 2[Cu(N_4)]^{2+} + [Hg(MeIm)_2]^{2+} + 2e^- \quad (9c)$$

with the equilibrium position for the reaction

$$2[Cu(N_4)MeIm]^{2+} + Hg^{2+} \rightleftharpoons 2[Cu(N_4)]^{2+} + [Hg(MeIm)_2]^{2+} \quad (10)$$

lying to the right, and possible equilibria 5a and 6 are omitted for simplicity.

The most likely products of reduction, both in the presence and absence of excess MeIm, are hypothesized to be $[Cu(N_4)]^+$ and $[Cu(N_4)]^0$. In other studies on related complexes, elemental copper rather than solution-soluble complexes is frequently reported as a product (see introduction). It is therefore critical to demonstrate that low-valent copper complexes and not elemental copper are produced in the present case. A series of experiments has been undertaken to verify this suggestion.

Figure 5a shows a dc polarogram for reduction of anhydrous copper(II) perchlorate in acetone. Reduction of the solvated copper complex at a hanging mercury drop electrode leads to the formation of copper amalgam, which can be stripped at this

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Table IV. Stripping Data for Copper after Reduction of 5.0 × 10^{-4} M Copper(II) Perchlorate and $[Cu(N_4)MeIm]^{2+}$

$Cu(ClO_4)_2$ Data

solvent	dc polarography[a,b] ($E_{1/2}$, V)	cyclic voltammetry[b,c] at HMDE ($E_{1/2}$, V)	stripping at HMDE ($E_{1/2}$, V)	stripping at platinum electrode ($E_{1/2}$, V)
CH_3COCH_3	0.535	0.535	0.525	
CH_3CN	0.625	0.620	0.625	0.355

$[Cu(N_4)MeIm]^{2+}$ Stripping Data[d]

solvent	HMDE (20 °C)	platinum electrode (20 °C)	platinum electrode (−70 °C)
CH_3COCH_3	no	yes	no
CH_2Cl_2	no	yes	no
CH_3CN	yes	yes	

[a] For ferrocene values see footnote for Table II. [b] All potentials in V vs. Ag/AgCl. [c] For ferrocene values see footnote for Table I. [d] Potential held more negative than for process 2.

electrode (Figure 5b). In the presence of deliberately added water, two reversible one-electron steps rather than a reversible two-electron-reduction step are observed (Figure 5c,d). However, a stripping process due to formation of Cu(Hg) is still observed. Other studies on the reduction of copper(II) in nonaqueous solvents report one or two reduction steps.[29-31] The role of water in reduction of solvated metal ions appears to be crucial.[32] In the absence of deliberately added water the process is defined as

$$[CuS_x]^{2+} + Hg + 2e^- \rightleftharpoons Cu(Hg) + xS \qquad S = \text{acetone} \qquad (11)$$

Equivalent experiments in acetone for the complex $[Cu(N_4)MeIm]^{2+}$ show no evidence of formation of elemental copper as an amalgam (no stripping peak), irrespective of whether the potential is held more negative than either the first or second reduction processes. In these experiments, the hanging mercury drop electrode was transferred to an acetone (0.1 M Bu_4NClO_4) solution, containing no compound, followed by scanning to positive potential under conditions where a stripping peak is observed for equivalent experiments with $[CuS_x]^{2+}$. This confirms that the product at a mercury electrode is not elemental copper but rather solution-soluble monovalent and zerovalent complexes. In acetonitrile, at potentials more negative than process 2, when the hanging mercury drop electrode is used as described above, direct evidence for formation of copper amalgam can be found, indicating that at mercury electrodes in this solvent, the macrocyclic ligand and MeIm fall off after addition of the second electron and that the overall process for the second reduction step on long time scale experiments is given by eq 12.

$$[Cu(N_4)]^+ + e^- \rightarrow Cu(Hg) + (N_4) \qquad (12)$$

Figure 6 and data in Table IV demonstrate that a copper stripping peak is also observed in acetonitrile after reduction at potentials more negative than the second process at a platinum electrode in in situ experiments. In dichloromethane at 20 °C and at a platinum electrode, a stripping peak is also observed, which is enhanced by the presence of deliberately added water. Apparently, the platinum surface in the presence of trace amounts of water acts as a catalyst in the decomposition of the zerovalent complex to elemental copper. At −70 °C, no stripping peak is observed in dichloromethane or acetone, even when water is deliberately added.

Controlled-potential reductive electrolysis in acetone and dichloromethane at a potential of −0.4 V vs. Ag/AgCl with coulometric monitoring confirmed that the first reduction step is a one-electron process (n = 1.0 ± 0.1). Figure 2b shows a dc polarogram after controlled-potential electrolysis in acetone. $E_{1/2}$ values of all three processes are identical within experimental error before and after electrolysis. However, process 1 is now a reversible one-electron-oxidation process instead of a reduction process. Process 2 remains a reduction process, and process 3 is an oxidation process.

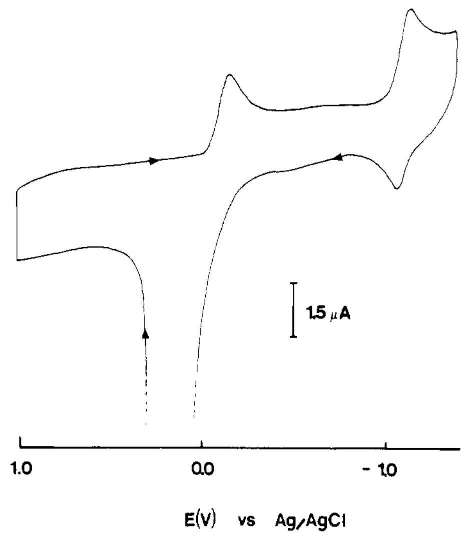

Figure 6. Stripping voltammogram after reduction of $[Cu(N_4)MeIm]^{2+}$ at 20 °C in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 200 mV s^{-1}; potential held at −1.4 V for 2 min).

Thus, as required by the proposed reaction scheme, the additional wave seen on mercury (but not on other electrodes) is still present after reductive electrolysis. That is, all three processes remain chemically reversible after the one-electron reduction. Cyclic voltammetric curves at platinum electrodes after electrolysis are identical with those before electrolysis except for the initial current sign of process 1.

During controlled potential reductive electrolysis in acetone or dichloromethane the solution changes color from very pale blue to an intense blue. Oxidation of this solution at +0.2 V vs. Ag/AgCl regenerates the starting material, confirming the chemical reversibility of the process.

In the presence of oxygen, the bright blue color of the reduced solution changes rapidly to yellow, and both reversible processes 1 and 2 disappear with process 3 (MeIm) remaining at mercury electrodes. That is, the reaction with oxygen does not regenerate the starting material $[Cu(N_4)MeIm]^{2+}$. The intense blue color is consistent with the formation of a four-coordinate copper(I) complex,[25] and the irreversible reaction with oxygen to produce uncharacterized yellow solutions has been observed previously with related reactions of copper(I) complexes.

A number of workers have reported the use of cobaltocene as a chemical reductant (see ref 33-35 for examples). The $E_{1/2}$ value in dichloromethane for the reversible one-electron-oxidation reaction

$$Co(C_5H_5)_2 \rightleftharpoons [Co(C_5H_5)_2]^+ + e^- \qquad (13)$$

is −0.57 V vs. Ag/AgCl. The potential is conveniently situated between processes 1 and 2. Figure 7 shows a titration of cobaltocene with $[Cu(N_4)MeIm]^{2+}$ in dichloromethane as monitored by dc polarography. The reaction

$$Co(C_5H_5)_2 + [Cu(N_4)MeIm]^{2+} \rightarrow [Co(C_5H_5)_2]^+ + [Cu(N_4)]^+ + MeIm \qquad (14)$$

is quantitative and selective.

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Table V. Cyclic Voltammetric Data for $[Cu[14]aneN_4]^{2+}$ at a Scan Rate of 100 mV s^{-1} and at 20 °C

		redn[a]		oxidn[a]		
solvent	electrode	$(E_p^{red})_1$, V	$(E_p^{red})_2$, V	$(E_p^{ox})_3$, V	$(E_p^{red})_3$, V	$(E_{1/2})_3$, V
CH_3CN	platinum	−0.90	−1.28	1.615	1.540	1.580
CH_3CN	gold	−0.90	−1.30	1.615	1.540	1.580
CH_3CN	glassy carbon	−0.78	−1.41	1.600	1.525	1.565
CH_2Cl_2	platinum	−0.72	*b*	*c*	*c*	*c*
CH_2Cl_2	gold	−0.72	*b*	*c*	*c*	*c*
CH_2Cl_2	glassy carbon	−0.76	−0.88	1.805	1.600	1.705
CH_3COCH_3	platinum	−0.96	−1.25	1.580	1.510	1.545
CH_3COCH_3	gold	−0.84	−1.15	1.575	1.500	1.540
CH_3COCH_3	glassy carbon	−0.79	−1.25	1.580	1.520	1.550

[a] For ferrocene values see footnote for Table I. All potentials in V vs. Ag/AgCl. [b] Unresolved irreversible two-electron-reduction processes. [c] Not observed prior to solvent limit.

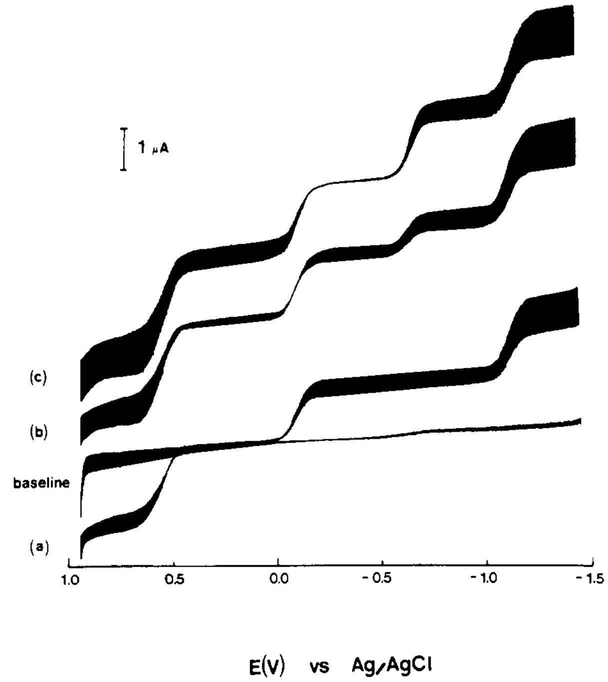

Figure 7. (a) Dc polarogram at 20 °C for reduction of 5.0 × 10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) (drop time = 0.5 s). (b) Dc polarogram at 20 °C for reduction of 5.0 × 10^{-4} M $[Cu(N_4MeIm]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) in the presence of 2.5 × 10^{-4} M cobaltocene (drop time = 0.5 s). (c) Dc polarogram at 20 °C for reduction of 5.0 × 10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in dichloromethane (0.1 M Bu_4NClO_4) in the presence of 5.0 × 10^{-4} M cobaltocene (drop time = 0.5 s).

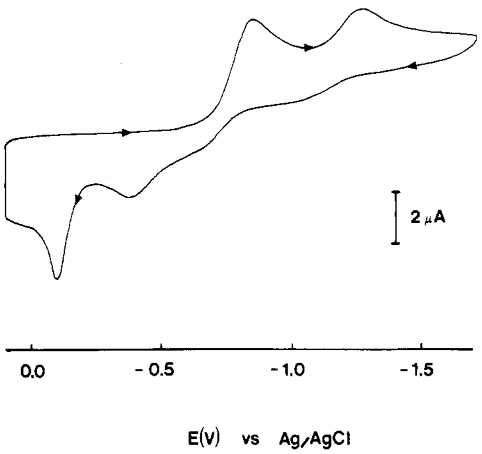

Figure 8. Cyclic voltammogram at 20 °C for reduction of 5.0 × 10^{-4} M $[Cu([14]aneN_4)]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 100 mV s^{-1}).

Controlled-potential electrolysis of $[Cu(N_4)MeIm]^{2+}$ at −1.3 V vs. Ag/AgCl in acetone at −70 °C generates a very air-sensitive formally copper(0) complex, via a two-electron reduction (n = 2.0 ± 0.1). A parallel experiment with initially generated $[Cu(N_4)]^+$ is a one-electron-reduction process. At 20 °C the platinum electrode is coated with metallic copper after controlled-potential electrolysis experiments, but this does not occur at −70 °C. The formally copper(0) complex rapidly turns yellow, presumably due to reaction with oxygen (as was the case with the copper(I) complex). Reaction with oxygen is faster than decomposition to elemental copper at low temperatures. The two-electron-reduced solution exhibits two reversible one-electron-oxidation waves at platinum, gold, or glassy-carbon electrodes, which have the same $E_{1/2}$ values as processes 1 and 2. The additional wave on mercury remains present after the two-electron reduction and decomposition. The formally copper(0) complex could only be detected electrochemically in small yields (10–20%) even under argon at −70 °C. At these temperatures, the activity of water in acetone may be reduced substantially. Acetone cannot be dried exhaustively since removal of water merely facilitates an aldol condensation that generates more water.[43,44] It is suggested that $[Cu(N_4)]^+$ is oxygen-sensitive but not water sensitive, whereas $[Cu(N_4)]^0$ is extremely sensitive to both on the synthetic time scale.

The above data are consistent with formation of a soluble four-coordinate copper(0) complex, $[Cu(N_4)]^0$ after a two-electron reduction of $[Cu(N_4)MeIm]^{2+}$. This complex is extremely air- and moisture-sensitive and prone to an enhanced rate of decomposition to elemental copper at platinum surfaces, particularly in the presence of traces of water. The presence of unsaturated macrocycles containing α-diimine have been reported to provide evidence for formation of formally low-oxidation-state complexes of nickel(0),[36] cobalt(0),[37,38] and iron(−1).[39,40] This ability to stabilize low oxidation states also appears to be true for copper. Of course, the formal description of $[Cu(N_4)]^0$ as a zerovalent copper species ignores the role of the macrocycle. The electron density may be delocalized onto the macrocyclic ligand in this complex.[22d] Unfortunately, the complex is too reactive to structurally characterize with facilities available in these laboratories.

Electrochemistry of $[Cu[14]aneN_4]^{2+}$ (viii). To further probe the factors providing substantial stabilization of the formally low-valent oxidation state $[Cu(N_4)]^0$ complex, the redox electrochemistry of the related species $[Cu[14]aneN_4]^{2+}$ (viii) is considered. The electrochemical reduction and oxidation of this complex has been reported in acetonitrile.[23c] Figure 8 and data in Table V summarize results that are now extended to other solvents. Two one-electron-reduction steps are observed in all solvents. However, in contrast to reduction of $[Cu(N_4)MeIm]^{2+}$,

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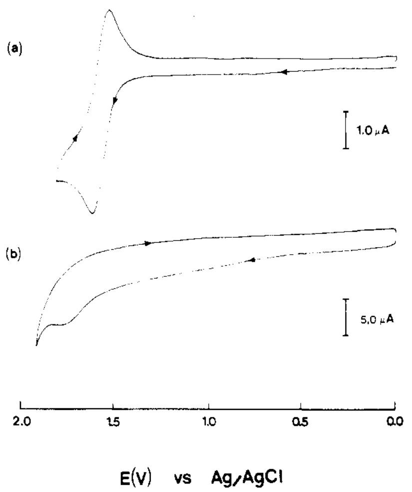

Figure 9. (a) Cyclic voltammogram at 20 °C for oxidation of 5.0×10^{-4} M $[Cu([14]aneN_4)]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 100 mV s^{-1}). (b) Cyclic voltammogram at 20 °C for oxidation of 5.0×10^{-4} M $[Cu(N_4)MeIm]^{2+}$ in acetonitrile (0.1 M Bu_4NClO_4) at a platinum electrode (scan rate = 200 mV s^{-1}).

both are chemically irreversible at all scan rates (20–500 mV s^{-1}) and temperatures (20 to −70 °C) examined. Furthermore, copper stripping peaks are observed even after the first reduction process in both coordinating and noncoordinating solvents. A chemically reversible one-electron oxidation is observed under voltammetric conditions in all solvents examined (Table V and Figure 9), confirming previous data in acetonitrile.[23a] Apparently, the macrocyclic ligand in $[Cu[14]aneN_4]^{2+}$ stabilizes higher oxidation states. $[Cu[14]aneN_4]^{3+}$ is unstable on longer time scale controlled-potential electrolysis experiments,[23a] giving rise to a multielectron oxidation process.[41] By contrast, $[Cu(N_4)MeIm]^{2+}$ is irreversibly oxidized even on the voltammetric time scale (20 °C, scan rate 500 mV s^{-1}, Table V, Figure 9). That is, factors that stabilize high-oxidation-state copper complexes seem to destabilize the lower oxidation states. Electrochemical oxidation[42] of the mercury(II) complex $[Hg[14]aneN_4](BF_4)_2$ at low temperature is consistent with the formation of a mercury(III) complex. Conversely, reduction of $[Hg[14]aneN_4]^{2+}$ produces elemental mercury without evidence for a zerovalent formally mercury(0) complex. A combination of an unsaturated macrocycle, the correct charge, and reduction in an inert solvent in the absence of moisture and oxygen are factors that appear to be required to stabilize formally zero oxidation state copper macrocyclic complexes. Data imply that it is not necessary to block the fifth or sixth coordination sites by a ligand such as MeIm. This role (if required) can be fulfilled by the solvent or anion of the electrolyte.

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Registry No. $[Cu(N_4)MeIm](PF_6)_2$, 84667-54-9; $[Hg(MeIm)_6](ClO_4)_2$, 106251-96-1; $Cu(ClO_4)_2$, 13770-18-8; $[Cu([14]aneN_4)](ClO_4)_2$, 71170-98-4; MeIm, 616-47-7; $Co(C_5H_5)_2$, 1277-43-6; $[Cu(N_4)]^0$, 106251-97-2; $[Cu(N_4)]^+$, 80502-51-8; Pt, 7440-06-4; Hg, 7439-97-6; Au, 7440-57-5; C, 7440-44-0; CH_2Cl_2, 75-09-2; CH_3COCH_3, 67-64-1; CH_3CN, 75-05-8.

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Contribution from the Department of Chemistry,
University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Two-Electron Reduction of (η^6-Naphthalene)tricarbonylchromium. Haptotropic Rearrangement to the (η^4-Naphthalene)tricarbonylchromium Dianion

Reuben D. Rieke,* William P. Henry, and Jon S. Arney

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The electrochemical and chemical reduction of (η^6-naphthalene)tricarbonylchromium is a two-electron ECE reduction. The chemical step is a haptotropic rearrangement, which leads ultimately to the (η^4-naphthalene)tricarbonylchromium dianion. The dianion displays some unusual ^{13}C NMR features that provide strong support for the proposed "slip-fold" mechanism. Reaction of the dianion with a proton source produces a (η^5-cyclohexadienyl)tricarbonylchromium anion species, which can be oxidized to the original naphthalene complex. Molecular orbital arguments support the "slip-fold" mechanism. Finally, complete electrochemical reductive properties of the naphthalene complex are presented.

Introduction

Considerable interest has been shown in recent years concerning the generation of anions of (arene)tricarbonylchromium complexes. Methods used include proton abstraction (eq 1),[1-15] nucleophilic addition (eq 2),[16-24] and direct electrochemical reduction (eq 3).[25-36]

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