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ELECTROCHEMISTRY OF Cu(I) BIPYRIDYL COMPLEXES WITH ALKENE, ALKYNE, AND NITRILE LIGANDS. IMPLICATIONS FOR PLANT HORMONE ACTION OF ETHYLENE

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The redox behavior was evaluated for several (BIPY)Cu(I) complexes (BIPY = 2,2′-bipyridyl) with unsaturated ligands by means of cyclic voltammetry in CH_2Cl_2 at reduced temperatures (−78°, −23°, 0°C). The complexes studied are $[Cu(I)(BIPY)(C_2H_4)]PF_6$, $[Cu(I)(BIPY)(3\text{-hexyne})]PF_6$, $[Cu(I)(BIPY)(DEAD)]PF_6$, $\{[Cu(I)(BIPY)]_2DEAD\}[PF_6]_2$ (DEAD = diethyl acetylene dicarboxylate) and $[Cu(I)(BIPY)(CH_3CN)]PF_6$. The oxidations are quasi-reversible at −78°C for scan rates of 20 to 200 mV/sec. The reductions were irreversible on the CV time scale. Evidence is presented in support of a role for an electron transfer mechanism in the case of the plant hormone ethylene. Related literature data are also discussed.

KEY WORDS: Cu(I) unsaturated complexes, electrochemistry, electron transfer, ethylene plant hormone mechanism.

INTRODUCTION

There are a number of reported electrochemical studies on a variety of Cu(I) complexes that contain nitrogen and oxygen ligands.[1] We are interested in the redox properties of Cu(I) complexes with ethylene and alkyne ligands, since related Cu(I) complexes are believed to be involved in the hormonal action of ethylene and alkynes in plants.[2] However, we are not aware of any redox studies involving alkene or alkyne complexes of Cu(I).

Ethylene, a plant hormone, is intriguing because of its extreme simplicity. A large number of physiological responses are elicited, including abscission, fruit ripening, seed germination, extension growth, and root initiation.[3-6a] At the molecular level various effects have been noted involving enzymes, membranes, DNA synthesis, and protein synthesis.[3-6a] Although diverse hypotheses have been advanced, there is no general consensus regarding the mode of action of ethylene *in vivo*.[3,5,6c,7-12] Our approach is based on the proposal of Burg and Burg that binding entails a metal receptor.[10] This proposal has enjoyed continuing interest in subsequent years.[3,6b,7,9,13-15] An attractive receptor candidate would be copper[2,3,8,11,12,16-20] in the

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cuprous state, since Cu(I) is known to form fairly stable complexes with alkenes.[2,21] Evidence favors the bound ligand, rather than a metabolite, as the essential mediator.[9]

Our objective was to examine the electrochemical behavior (oxidation-reduction) of the Cu(I) complexes with unsaturated ligands: ethylene, 3-hexyne and diethyl acetylene dicarboxylate (DEAD). The bioactivity of these ligands would be expected to decrease in the order, ethylene > 3-hexyne > DEAD.[6b] For comparison, we also report data on $[Cu(I)(BIPY)(CH_3CN)PF_6$ and the unusual binuclear complex $\{Cu(I)(BIPY)]_2DEAD\}[PF_6]_2$. The data are compared with literature reports on related complexes. In addition, the electrochemical properties of the ethylene complex, which served as a model for the *in vivo* situation, are discussed in relation to the proposed mechanism of action for the ethylene plant hormone.

MATERIALS AND METHODS

The compounds studied here have been fully characterized and the synthetic procedures will be reported elsewhere.[22]

The cyclic voltametric measurements were performed with a PARC model 174A polarographic analyzer associated with a Houston instrument model 200 X-Y recorder. The operation of the instrument and the electrodes was checked against a ferrocene standard before each use. The scan rates range from 20 to 200 mV/sec. Solutions were purged of oxygen for 30 minutes with N_2 that was passed through an oxygen scrubbing column. The electrolytes used were tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium hexafluorophosphate (TBAH). The dichloromethane was freshly distilled from phosphorus pentoxide under N_2 and was passed through an alumina column (basic, activity I) to remove any acid or nucleophilic impurities present in the distillate.

A standard three electrode cell was used. The platinum flag working electrode had a surface area of $1.26\,cm^2$. The working electrode was cleaned in aqua regia before each use. The counter electrode was a platinum wire. The reference electrode was non-aqueous Ag/AgCl separated from the solution of the analyte by a salt bridge containing TBAH [Ag|AgCl, CH_2Cl_2, LiCl(sat), TBAP (0.1 M) || CH_2Cl_2, TBAH (0.1 M) || analyte (0.5 mM, TBAH (0.1 M)]. Solutions of the analyte were prepared by adding with a syringe a cooled solution of the electrolyte to the electrochemical cell which was loaded with a weighed sample of the analyte under a steady stream of N_2. The electrochemical cell was immersed in a dry ice-acetone (−78°C), dry ice-carbon tetrachloride (−23°C) or an ice bath (0°C). The temperature of the solution was monitored and verified with a calibrated thermocouple. The electrochemical apparatus was protected from light and was allowed to come to thermal equilibrium for 10 minutes before data were collected. Since the Cu(I) species are labile in solution at room temperature, ambient temperature measurements were found to be unsuitable for these complexes. Therefore, our electrochemical studies were carried out at low temperatures so that the complexes would not decompose and to permit the possibility of observing reversible radox processes on the CV time scale. We anticipated that the Cu(II) and Cu(0) products of the electrochemistry would be unstable.

The temperature dependence of the reference electrode potential is unknown. The $E^{0\prime}$ values are given *vs.* the Ag/AgCl reference, unless otherwise indicated. The following equations were used for the half-wave potentials, the difference in potentials, and the current function:

$$E^{0\prime} = (E_{pc} + E_{pa})/2, \qquad \Delta E_p = |E_{pc} - E_{pa}| \tag{1}$$

$$i_{pa}/i_{pc} = (i_{pa})_0/i_{pc} + 0.485(i_{sp})_0/i_{pc} + 0.086 \tag{2}$$

In Eq. (1), $E^{0\prime}$ is the formal equilibrium reduction potential; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively; ΔE_p is the difference between the cathodic and anodic peak potentials. In Eq. (2), i_{pa} and i_{pc} are the anodic and cathodic peak currents, respectively; $(i_{pa})_0$ is the uncorrected anodic peak current with respect to the zero current base line of the cyclic voltammogram and $(i_{sp})_0$ is the current observed at the switching potential, E_λ.

RESULTS AND DISCUSSION

Electrochemical Data

It was not possible to use standard electrochemical procedures, because of the instability of the substrates in solution at room temperature. Hence, experiments were carried out at low temperatures in a special apparatus.

Electrochemical results for the Cu(I) complexes are given in Table I. The oxidations exhibited varying degrees of quasi-reversibility at −78°C. They became less reversible at −23°C and exhibited irreversible waves at 0°C on the CV time scale in all cases. The Cu(II) species produced upon oxidation are apparently unstable. Reductions of the complexes exhibited irreversible waves at all scan rates including the shortest time scale of 200 mV/s. After scanning several times in the reductive direction, the surface of the working electrode is apparently poisoned with metallic Cu. Irreversibility is presumably due to precipitation of the Cu(0) species produced upon reduction.

TABLE I
Reduction and oxidation potentials of Cu(I) complexes[a]

Complex	Temp °C	$E^{0\prime}_{Cu}+1/+2$	i_{pc}/i_{pa}[a]	$E_{pCu}+1/0$
1. $[Cu(I)(BIPY)(C_2H_4)]PF_6$	−78	+0.80	0.94	−0.80
	−23	+0.76	0.73	−0.87
	0	+0.9[b]	–	–
2. $[Cu(I)(BIPY)(3\text{-hexyne})]PF_6$	−78	+0.65	0.75	−1.44
	−23	+0.63	0.59	−1.51
	0	+0.7[b]	–	–
3. $[Cu(I)(BIPY)(DEAD)PF_6$	−78	+0.46	0.90	−1.07
	−23	+0.43	0.82	−1.10
	0	+0.8[b]	–	–
4. $\{[Cu(I)(BIPY)]_2DEAD\}[PF_6]_2$	−78	+0.59	0.65	−1.14
	−23	+0.59	0.31	−1.12
	0	+0.6[b]	–	–
5. $[Cu(I)(BIPY)(CH_3CN)]PF_6$	−78	+0.77	0.61	−1.00
	−23	+0.78	0.48	−1.07
	0	+0.8[b]	–	–

[a] Values *versus* Ag/AgCl, 200 mV/s, Pt electrode, CH_2Cl_2, [substrate] = 0.5 mM. TBAH = 0.1 M.
[b] Approximate value.

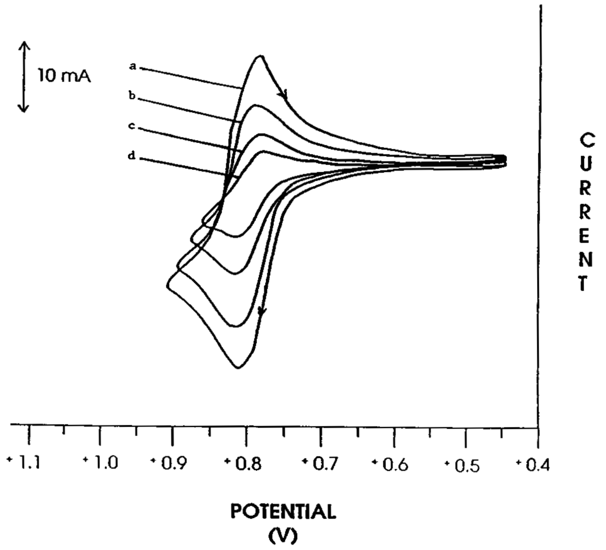

FIGURE 1 Electrooxidation of 0.5 mM [Cu(I)(BIPY)(C_2H_4)]PF_6 in CH_2Cl_2, Pt, *versus* Ag|AgCl, (a) 200, (b) 100, (c) 50, (d) 20 mV/s, 0.1 M TBAH, −78°C.

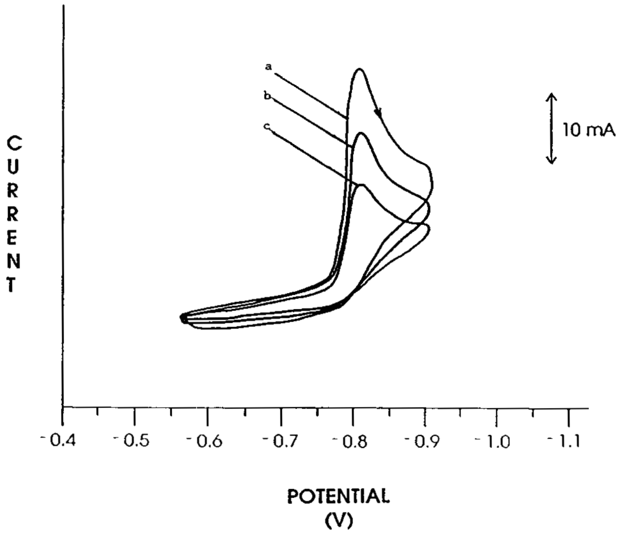

FIGURE 2 Electroreduction of 0.5 mM [Cu(I)(BIPY)(C_2H_4)]PF_6 in CH_2Cl_2, Pt, *versus* Ag|AlCl, (a) 200, (b) 100, (c) 50 mV/s, 0.1 M TBAH, −78°C.

[Cu(I)(BIPY)(C_2H_4)]PF_6: The complex oxidized at 0.8 V at −78°C with 94% reversibility (i_{pc}/i_{pa} × 100%) at 200 mV/s (Figure 1). The oxidation waves exhibited a ΔE_p value of 60 mV at scan rates of 200, 100 and 50 mV/s, thus indicating Nernstian behavior with $n = 1$. The complex reduces at −0.80 V (E_p), the most positive value obtained in the series of complexes examined (Figure 2).

[Cu(I)(BIPY)(3-hexyne)]PF_6: At $-78°$ this complex produced an oxidation wave at 0.65 V with an i_{pc}/i_{pa} value of 0.75. The reduction occurs at -1.44 V, the most negative value observed in the series.

[Cu(I)(BIPY)(DEAD)]PF_6: The complex containing the electron withdrawing DEAD ligand showed a quasireversible oxidation wave with 90% reversibility ($E^{0\prime} = 0.46$ V). The complex reduced more easily than in the 3-hexyne case with an E_p value of -1.07 V.

[Cu(I)$(BIPY)_2$DEAD]$[PF_6]_2$: This binuclear Cu(I) DEAD complex oxidized at a somewhat less positive potential than for the monomeric form ($E^{0\prime} = 0.59$ V). However, the oxidation is less reversible ($i_{pc}/i_{pa} = 0.65$) than for the monomer. The complex showed a reduction at an intermediate value ($E_p = -1.14$ V) between the electron rich alkyne complex 3 and the DEAD monomer.

[Cu(I)(BIPY)(CH_3CN)]PF_6: The Cu^+/Cu^{2+} couple exhibited a $E^{0\prime}$ value of 0.77 V for oxidation with 61% reversibility (200 mV/s, $-78°$). An irreversible peak was observed at -1.00 V upon reduction.

Others have studied the electrochemical behavior of the Cu^+/Cu^{2+} redox couple with various ligands[1] (*vs.* NHE). With pyridine, values of approximately $+0.2$ V were reported, in line with our data. However, the potentials vary appreciably with ligand concentration, over $+100$ mV for a change from 1 : 1 to 2 : 1 ligand to copper ratio in the case of benzimidazole.[1] The potential is also dependent on the nature of the ligand, e.g., for ethylenediamine, -0.38 V, and for benzimidazole, $+0.36$ V.[1] The potential of the Cu^+/Cu^{2+} couple is apparently dependent on solvent: in DMF, $+0.30$ V[23] and in acetone, $+0.75$ V.[1] The $E_{1/2}$ of the Cu^+/Cu^0 couple evidently depends strongly on the solvent employed in electrochemical measurements:[1] $+0.41$ V (methanol), -0.13 V (acetonitrile), and -0.43 V (pyridine). It is reported that good π acceptors complex Cu(I) preferentially and shift $E_{1/2}$ anodically, while good σ donors complex Cu(II) preferentially and $E_{1/2}$ is cathodically shifted.[24]

MECHANISM OF ETHYLENE HORMONAL ACTION IN PLANTS

Theoretically, ET processes involving Cu(I) · C_2H_4 could occur by either initial oxidation or reduction. Redox cycling would entail interconversion of Cu(I) and Cu(II) with a nearby donor serving to regenerate Cu(I). The hormonal response of the alkene might arise from a beneficial effect on oxidation potential or from a role as an ET bridge linking various cellular donors and acceptors. In relation to the reductive pathway, the energetics are attractive, since the potential (about -0.9 V, Table I) is near the range usually considered favorable for *in vivo* redox transformations.[25] Perhaps, the nature of the complex *in vivo* would permit Cu(0) to recycle, in contrast with the situation *in vitro*.

A number of other features are in keeping with a hormonal mechanism based on ET and electrical phenomena. Copper complexes, both in the endogenous[26] and exogenous (*vide infra*) categories, evidently participate in such processes. Since ET is known to occur over fairly long distances,[27] appreciable numbers of susceptible plant systems could be influenced resulting in the many and varied responses that are observed, as previously suggested by Burg *et al.* in their single mechanism proposal.[13] Furthermore, the response can be comparatively fast, with no lasting effect after ethylene is removed.[7] It is remarkable that a prior general electrochemical description of ethylene's behavior by Leshem is very much in accord with an ET approach.[4]

If ET events occur with ethylene, it is conceivable that other plant regulators act similarly, including the single mechanism approach.[3,13,28,29] Our application of the concept[29] to ethylene is treated in a forthcoming review by Sisler.[30] There is mounting evidence that metal complexes, particularly of Fe and Cu, function in part as ET agents in their roles as enzymes[26] and drugs.[23,31-37]

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