Redox Chemistry of Cu(TIM) Complexes

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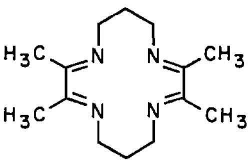
Our interest in the redox behavior of Cu complexes of the macrocyclic ligand TIM (*1*) was originally piqued by the known redox chemistry of methanol solutions of Fe(TIM)$^{2+}$, which is catalytic in the oxidation of methanol to formaldehyde [1]. In methanol $[Fe(TIM)(MeOH)_2]^{2+}$ is oxidized by molecular oxygen to $[Fe(TIM)OMe(MeOH)]^{2+}$ with the formation of water. The Fe(III) complex can be reduced in a photoassisted step to regenerate the Fe(II) complex and form a molecule of formaldehyde. This cycle may be repeated several times but eventually suffers from a competing process which leads to materials that are no longer active in the oxidation of methanol. Both of the Fe(TIM) complexes involved in the catalytic cycle feature low-spin iron centers [2]. It is therefore reasonable to assume that the observed chemistry is a reflection of a redox process centered in a π-symmetry orbital. It was hoped that by substituting Cu for the Fe center in the complexes, insight might be gained into the effects on the catalytic activity produced by altering the process to one involving an orbital of σ-symmetry. We wish to report the redox activity observed for Cu(TIM) complexes in methanol, and the results of cyclic voltammetry experiments conducted on several of the Cu complexes.



I, TIM

Experimental

The Cu(TIM)$^{2+}$ complexes were prepared as previously described [3]. Cyclic voltammetry at a platinum disk electrode employing a Pt wire auxiliary electrode was performed at ambient temperatures in acetonitrile solutions (deoxygenated by bubbling nitrogen through them) using a PAR-175 universal programmer and 174A polarographic analyzer. The supporting electrolyte used was 0.1 *M* tetrabutylammonium perchlorate. The reference electrode consisted of a silver wire immersed in a 0.1 *M* acetonitrile solution of $AgNO_3$. A salt bridge consisting of a 0.1 *M* acetonitrile solution of tetrabutylammonium perchlorate was employed between the reference electrode and the working compartment of the cell. The potentials measured *vs.* the Ag/Ag$^+$ reference were adjusted to the standard hydrogen electrode (SHE) via the conversion factor determined by Gagné and coworkers for this solvent system using the ferrocene Fe(II)/Fe(III) redox couple as an internal standard [5].

Results and Discussion

During the exploratory synthesis of Cu(TIM) complexes, it was observed that methanol solutions of $[Cu(TIM)1\text{-}MeIm](PF_6)_2$ changed color from pale pink to intense dark blue upon heating in the absence of air. These dark blue solutions were extremely air sensitive, losing the intense blue coloration instantly upon exposure to air. When other Cu(TIM) complexes, $Cu(TIM)(PF_6)_2 \cdot xH_2O$, $Cu(TIM)I_2$, $[Cu(TIM)py](PF_6)_2$, and $[Cu(TIM)Im](PF_6)_2$ were heated in methanol, only the Im adduct produced a dark blue solution. The colors of the other solutions were unchanged. This dependency on the axial ligand present was not anticipated since the spectra of methanol solutions of $[Cu(TIM)1\text{-}MeIm](PF_6)_2$ and $Cu(TIM)(PF_6)_2 \cdot xH_2O$ are identical and different from $Cu(TIM)(PF_6)_2 \cdot xH_2O$ in H_2O or acetone [3] indicating that the principal species present is a methanol complex, by analogy with the Fe(TIM) system. Since no formaldehyde could be detected in methanol solutions of $[Cu(TIM)1\text{-}MeIm](PF_6)_2$ after heating and exposure to air, the analogy with the Fe(TIM)–MeOH system does not extend to the redox chemistry of Cu(TIM). Further, no Cu(TIM)$^{2+}$ complex has ever been isolated from a completely reduced solution upon exposure to air, indicating that oxidation by O_2 is not reversible—an observation that is consistent with the irreversibility of the oxidation by O_2 of formally Cu(I) complexes of *2* [4, 5].

The intense blue color of methanol solutions of $[Cu(TIM)1\text{-}MeIm](PF_6)_2$ after heating is similar to that observed for reduction of $Cu(TIM)(BPh_4)_2$ [3], and is reported for the product of electrochemical reduction of Cu(II) complexes of *2* [4, 5]. The blue color of these compounds has been assigned to a

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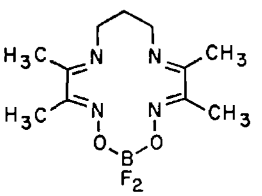

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MLCT transition of the formally Cu(I) complex [6]. This fact, coupled with the air sensitivity of the solutions, indicates that a formally Cu(I) species has been produced. The correlation between redox activity and the presence of 1-MeIm or Im implies that it is these molecules, not methanol, which are serving as reducing agents. If this were the case, no protons need be produced in the reaction, and the O_2^- or O_2^{2-} formed upon oxidation would not be scavenged. These powerful bases might then react with the 'acidic' protons of the TIM methyl groups [7] rendering the oxidation step irreversible.

A great deal of knowledge regarding the factors influencing the redox activity of Cu complexes has been obtained from the use of electrochemical techniques. The reduction potential of Cu(II) complexes has been found to be sensitive to a number of factors which may be classified as either structural or electronic effects. The geometry imposed by the ligands has a marked effect on the reduction potentials of Cu(II) complexes [8, 9]. Rigidly planar ligands have been shown to stabilize the Cu(II) oxidation state. Complexes with flexible ligands, which can adopt the planar geometry preferred by Cu(II) but distort in a tetrahedral direction to accommodate the preference for that geometry characteristic of Cu(I), are generally easier to reduce. Ligands which impose a tetrahedral geometry on Cu(II) centers have the least negative reduction potentials. Arguing on the basis of structural effects alone, the planar array of nitrogen atoms featured by TIM would be expected to stabilize the Cu(II) oxidation state and would be a rather poor environment for Cu(I). However, the nature of the donor atoms and ligand substituents also has an effect on the reduction potential of Cu(II) complexes [9]. Electron withdrawing substituents, such as $-CF_3$, would be expected to increase the effective charge at the metal and lead to more facile reduction of the metal center when the presence of these groups does not perturb the geometry of the complex significantly. The electronic effect of the donor atoms has been found to be in agreement with expectations based on Pearson's hard/soft and acid/base theory [10]. In general, 'hard' donor atoms stabilize Cu(II), while 'soft' donor atoms stabilize Cu(I). The reduction potentials of metal complexes of tetraazamacrocycles have been shown to be sensitive to the degree of unsaturation present in the ligand. Complexes of saturated tetraazamacrocycles are reduced at more negative potentials than those containing imines [11–14]. Further stabilization of the lower oxidation states of metals is achieved by macrocycles containing conjugated imines [15, 16], such as TIM and *2*.

The potentials ($E_{1/2}$) observed by cyclic voltammetry for the reduction processes of the $Cu(TIM)^{2+}$ complexes studied, are collected in Table I. In CH_3CN, $Cu(TIM)(PF_6)_2$ and $[Cu(TIM)1\text{-}MeIm](PF_6)_2$ feature reductions at –343mv and –488mv, respectively [17]. These values are comparable with values of –381mv and –486mv obtained for the analogous complexes of *2* under identical experimental conditions [4], and illustrate again the stabilization of the Cu(II) oxidation state that is achieved by adding a fifth σ-donor ligand [4, 5]. Both Cu(*2*) and $Cu(TIM)^{2+}$ display non-Nernstian behavior at the Pt electrode. The separation between the cathodic and anodic peak currents ($E_{pc} - E_{pa}$) for both compounds is significantly greater than the 58mv separation expected for a one electron reversible process. That these processes are reversible is supported by the values of I_{pa}/I_{pc}, which are near

TABLE I. Electrochemical Data[a].

Complex	$E_{1/2}$ (v)	$E_{pc} - E_{pa}$	Solvent
$Cu(TIM)(PF_6)_2\cdot xH_2O$	–0.343 –1.39	120 90	CH_3CN
$[Cu(TIM)1\text{-}MeIm](PF_6)_2$ + 19 equiv 1-MeIm	–0.488 –1.23	102 80	CH_3CN
$[Cu(2)]ClO_4\cdot\frac{1}{2}C_4H_8O_2$ [b]	–0.381	102	CH_3CN
$[Cu(2)]ClO_4\cdot\frac{1}{2}C_4H_8O_2$ [b] + 20 equiv 1-MeIm	–0.486	125	CH_3CN
$Cu(TIM)(ClO_4)_2$ [c]	–0.404	–	DMF

[a] All potentials are reported relative to the standard hydrogen electrode (SHE). [b] See ref. 5. [c] See ref. 17.

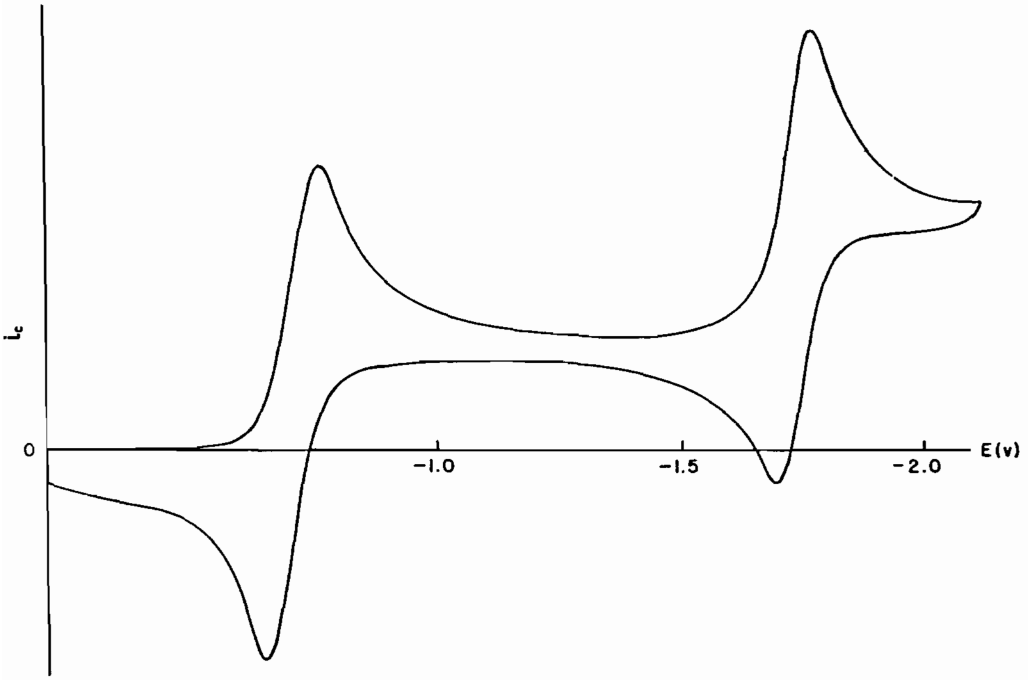

Fig. 1. Cyclic voltammagram of Cu(TIM)$(PF_6)_2 \cdot xH_2O$ in acetonitrile (potential in v *vs.* Ag/0.1 *M* Ag^+).

unity in each case. The reduction processes of Cu(*2*) complexes have been studied by constant potential electrolysis [4], and by voltammetry and polarography at mercury [5]. The results of these experiments are all consistent with a one electron process. By analogy, the reduction of $Cu(TIM)^{2+}$ complexes is assumed to be a one electron process.

In addition to the reduction process near –400mv, the TIM complexes also display another reversible reduction near –1.4v in CH_3CN solution (Fig. 1). Molecular orbital calculations reveal that the lowest unoccupied molecular orbital of the Cu(I) complexes is a π^* orbital that is largely ligand in character. The reduction process near –1.4v is assigned to reduction of the ligand on this basis. In contrast to TIM, the corresponding reduction of Cu(*2*) was reported to be irreversible [5].

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