Electrolyte effects in electron transfer reactions of 1,8-bis(2-pyridyl)-3,6-dithiaoctane copper(II) with ferrocene in acetonitrile. Specific rate enhancement by tetrafluoroborate ion

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Abstract

The kinetics of electron transfer between 1,8-bis(2-pyridyl)-3,6-dithiaoctane copper(II), $Cu(pdto)^{2+}$, and ferrocene, $FeCp_2$, in acetonitrile have been studied by stopped-flow spectrophotometry, as a function of ferrocene concentration and the concentration of added electrolytes, $n\text{-}Bu_4NPF_6$, $n\text{-}Bu_4NBF_4$ and $NaCF_3CO_2$. The reactions exhibit different rate dependencies with the three salts. The second-order rate constant, $k_2=(2.1\pm0.2)\times10^4$ M^{-1} s^{-1}, measured in CH_3CN at 25 °C with excess ferrocene between 1.2×10^{-3} and 7.5×10^{-3} M is unaffected by $n\text{-}Bu_4NPF_6$ added up to 0.10 M. A lowered second-order rate constant, $k_2=(1.56\pm0.15)\times10^3$ M^{-1} s^{-1} is obtained with $[NaCF_3CO_2]$ between 0.01 and 0.10 M. Inner-sphere association of $CF_3CO_2^-$ with the Cu(II) center is proposed to explain the rate inhibition in trifluoroacetate solutions. Values of 15 and 0.25 M^{-1} s^{-1} have been estimated for the Cu(II)/Cu(I) self-exchange electron transfer rate constant in $n\text{-}Bu_4NPF_6$ and $NaCF_3CO_2$ media, using the Marcus cross relations. With added $n\text{-}Bu_4NBF_4$, the measured second order rate constant, k_2, increases with $[BF_4^-]$ reaching 1.75×10^5 M^{-1} s^{-1} at 0.050 M salt concentration. The rate data in BF_4^- solutions is fitted to a rate law involving ion-pair formation between BF_4^- and $Cu(pdto)^{2+}$, with the ion-paired species showing enhanced electron transfer reactivity. Spectral changes that accompany the addition of BF_4^- to $Cu(pdto)^{2+}$ solutions suggest that the association of BF_4^- facilitates electron transfer by modifying the energy of the electron acceptor orbital in the redox change.

Introduction

The use of copper complexes as models for Cu sites in blue copper proteins, particularly complexes having N and S donor ligands, has resulted in much recent attention being focused on the spectroscopic and redox properties of simple Cu complexes [1–5], and on the inner-sphere reorganization changes and solvent interactions [6–10] that are important in facilitating electron transfer by their Cu centers. Copper(II)/(I) self-exchange electron transfer rate constants have frequently been used to assess the extent to which the coordination site of the simple Cu model approaches the proteins proposed entatic state, and to explore the many factors contributing to the range of electron transfer rates exhibited by model copper complexes and blue copper protein molecules. Copper complexes that are subject to ligand constraints preventing coordination changes during the redox step and complexes that undergo major inner-sphere reorganizations during reaction, have both been targeted for study.

We have previously reported the electron transfer behavior of the complex $Cu(pdto)^{2+}$ (pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane) towards a variety of Ru(II) reductants in aqueous methanol [8], where loss of a coordinated water molecule is believed to make a major contribution to the structural barrier of the reaction. With the aim of exploring further the effect of reorganizational changes at the Cu center on the electron transfer rate, and particularly on electron exchange between oxidation states with substantially different coordination geometries, we have made a kinetic study of the reduction of $Cu(pdto)^{2+}$ by ferrocene in several donor solvents and ionic media. Loss of an inner-shell solvent molecule is expected to accompany the reduction of the five-coordinate $[Cu(pdto)(solvent)]^{2+}$ complex to the four-coordinate Cu(I) product during the reactions. With added electrolytes in low dielectric solvents however, additional inner-sphere coordination changes and outer-sphere ion-pairing interactions, involving anionic spe-

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cies from the medium, are possible for labile Cu(II) systems. We report here the result of both of these interactions on the electron transfer behavior of the Cu(pdto)$^{2+}$ complex. We describe a somewhat unusual case of rate enhancement through ion pairing.

Experimental

Materials

The ligand pdto and the complex [Cu(pdto)](ClO$_4$)$_2$ were prepared by the method of Goodwin and Lions [11]. The corresponding hexafluorophosphate, tetrafluoroborate and trifluoroacetate salts were similarly prepared using NH$_4$PF$_6$, NaBF$_4$ and NaCF$_3$CO$_3$, respectively as precipitants. Ferrocene (Sigma) was purified by sublimation at atmospheric pressure. The electrolyte tetra-n-butylammonium tetrafluoroborate was prepared from the bromide salt (Kodak) and NaBF$_4$ and was recrystallized three times from ethyl acetate/hexane [12]. Other tetra-n-butyl ammonium salts, n-Bu$_4$NPF$_6$ (Aldrich) and n-Bu$_4$NClO$_4$ (G.F. Smith), were recrystallized from ethanol/water and dried in vacuum. Acetonitrile (Aldrich 99+ spectroscopic grade) was dried over molecular sieves (3–4A) and distilled from P$_2$O$_5$ with only the middle fraction taken.

Kinetic measurements

Rate measurements were made with an Aminco stopped-flow spectrophotometer. Data were collected on a Nicolet 2090 digital oscilloscope and transferred to a microcomputer for data treatment and analysis using Nicolet transfer software. Reactions were carried out under pseudo first-order conditions with the reductant in at least ten-fold excess. First-order plots were linear to at least three half-lives. Three rate determinations were usually carried out for each filling of the stopped-flow syringes. Routine spectral measurements were made using a Hewlett-Packard 8452A diode-array spectrophotometer.

Electrochemical measurements

Determination of standard potentials for the Cu(pdto)$^{2+/+}$ and FeCp$_2$$^{0/+}$ couples in different solvents were obtained using a BAS CV-1B cyclic voltammetry unit. Potentials were measured at a glassy carbon electrode versus a saturated calomel reference electrode (SCE) using a platinum wire auxiliary electrode. Liquid junction potentials were not considered since only potential differences between Cu(pdto)$^{2+/+}$ and FeCp$_2$$^{+/0}$ couples were required. Standard potentials were determined from the mean of the anodic and cathodic peak potentials and are reported relative to the normal hydrogen electrode (NHE). The cyclic voltammograms observed for the Cu(pdto)$^{2+/+}$ couple using n-Bu$_4$NPF$_6$ and NaCF$_3$CO$_2$ as supporting electrolyte displayed quasi-reversible behavior with peak separations of 122 and 145 mV, respectively. With n-Bu$_4$NBF$_4$ as supporting electrolyte, a peak separation of 80 mV was obtained, indicative of a more reversible process.

Results and discussion

The Cu(pdto)$^{2+}$–FeCp$_2$ reaction was studied initially in acetonitrile as a function of ferrocene concentration and concentration of the added electrolytes NaCF$_3$CO$_2$, n-Bu$_4$NPF$_6$ and n-Bu$_4$NBF$_4$. Contrasting behavior was found in the three cases. A second-order rate constant $k_2 = (2.1 \pm 0.2) \times 10^4$ M^{-1} s^{-1}, was obtained with no added electrolyte and excess [FeCp$_2$] in the range 1.2×10^{-3} to 7.5×10^{-3} M. This value did not change significantly with n-Bu$_4$NPF$_6$ added up to 0.20 M. With NaCF$_3$CO$_2$ as electrolyte however, close to a ten-fold reduction in the second-order rate constant was noted at all salt concentrations employed between 5×10^{-3} and 0.10 M. With n-Bu$_4$NBF$_4$ present, the measured second-order rate constant increased with [BF$_4$$^-$] reaching a value of 1.75×10^5 M^{-1} s^{-1} at 0.050 M n-Bu$_4$NBF$_4$.

Representative rate data is shown in Table 1, and the electrolyte dependencies are illustrated in Fig. 1.

The complex [Cu(pdto)](ClO$_4$)$_2$ is near square pyramidal in the solid state. The two nitrogen and sulfur donor atoms of the bis(pyridyl)-dithiaether ligand provide essentially square planar coordination for the Cu(II) center, with the plane of the N and S donor atoms displaced 0.25 Å from the metal and with a perchlorate oxygen bound at the apex [13]. In aqueous solution, the coordinated perchlorate is expected to be replaced by a water molecule, and the relatively slow Cu(pdto)$^{2+/+}$ self-exchange electron transfer rate constants that have been determined in aqueous solution, have been attributed to the considerable reorganization energy involved for reduction of the five-coordinate Cu(II) center to the tetrahedral Cu(I) state [7, 8]. In weakly polar solvents such as acetonitrile, a tetragonal Cu(II) center with only weak axial association of solvent molecules is expected [4]. The ten-fold decrease in the measured rate constant when trifluoroacetate is added to acetonitrile solutions, however, suggests strong inner-sphere association of CF$_3$CO$_2$$^-$ with Cu(pdto)$^{2+}$ resulting in a coordination environment at the Cu(II) center more similar to that existing for Cu(pdto)$^{2+}$ in aqueous solution. The more extensive geometric change required on reduction is consistent with the lowered electron transfer rate found in trifluoroacetate solutions.

TABLE 1. Effect of added electrolytes on the second-order rate constant for $FeCp_2$–$Cu(pdto)^{2+}$ electron transfer in CH_3CN at 25.0 °C

Initial conc. × 10^4 (M)			$[NaCF_3CO_2]$ (M)	$10^{-3} \times k_2$ (M^{-1} s^{-1})
$[Cu(pdto)^{2+}]$	[pdto]	$[FeCp_2]$		
2.22	30.7	44.0	0	18.8
2.22	30.7	74.8	0	18.7
1.20	10.4	13.3	0.050	1.57
1.20	10.4	34.0	0.050	1.85
1.20	11.4	46.8	0.050	1.62
1.20	11.4	80.0	0.050	1.44
1.00	10.0	12.0	0.020	1.32
1.00	10.0	12.0	0.010	1.70
1.95	16.6	41.0	0.10	1.40
			$[n\text{-}Bu_4NBF_4]$ (M)	$10^{-4} \times k_2$ (M^{-1} s^{-1})
0.96	10.1	12.0	0	2.10
1.09	10.4	12.5	0.00212	2.50
1.16	10.9	11.6	0.0050	3.18
1.03	10.1	11.9	0.0100	4.66
1.13	10.9	23.2	0.0100	5.06
1.20	10.5	11.4	0.0201	7.29
0.97	10.6	11.5	0.0502	17.5
			$[n\text{-}Bu_4NPF_6]$ (M)	$10^{-4} \times k_2$ (M^{-1} s^{-1})
1.95	10.5	40.4	0	2.28
1.98	10.5	40.3	0.004	2.22
1.98	10.5	41.1	0.010	2.28
1.98	10.1	98.5	0.010	2.06
1.98	10.1	200.	0.010	1.74
2.10	10.5	40.4	0.020	2.40
1.95	10.5	39.9	0.050	2.18

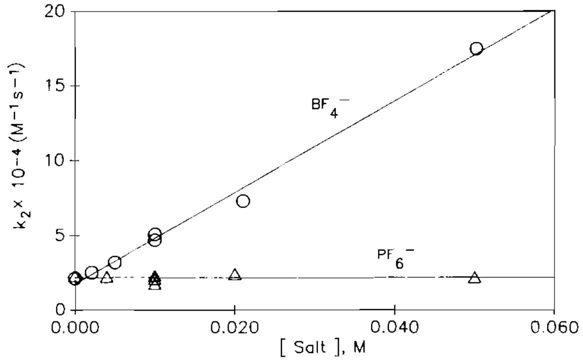

Fig. 1. Dependence of the second-order rate constant for the reduction of $Cu(pdto)^{2+}$ by $FeCp_2$ on the concentration of added tetra-n-butylammonium salts, $n\text{-}Bu_4NPF_6$ and $n\text{-}Bu_4NBF_4$.

Values determined for the $Cu(pdto)^{2+/+}$ redox potential in acetonitrile using 0.050 M solutions of $n\text{-}Bu_4NPF_6$, $n\text{-}Bu_4NBF_4$ and $NaCF_3CO_2$ as supporting electrolytes were 0.440, 0.444 and 0.415 V, respectively, versus SCE. Although association with the O-donor $CF_3CO_2^-$ ion appears to stabilize the Cu(II) state, the smaller driving force of the reaction with trifluoroacetate present does not by itself account for the rate advantage which PF_6^- shows over $CF_3CO_2^-$. Such an advantage exists even when the $Cu(pdto)^{2+}$–$FeCp_2$ electron transfer rate constants are corrected to zero driving force. Correspondingly, the $Cu(pdto)^{2+/+}$ self-exchange electron transfer rate constant, k_{22}, estimated with the Marcus cross relations $k_{12}=(k_{11}k_{22}K_{12}f)^{1/2}$, where $\ln f=\ln(K_{12})^2/4\ln(k_{11}k_{22}/Z^2)$, using $k_{11}FeCp_2/FeCp_2^+)=5.3\times10^6$ M^{-1} s^{-1} [14], and $Z=1\times10^{11}$, is found to be sixty-fold greater in CH_3CN alone ($k_{22}=15$ M^{-1} s^{-1}) than in 0.10 M $NaCF_3CO_2$ ($k_{22}=0.25$ M^{-1} s^{-1}). These values compare to a value of 0.63 M^{-1} s^{-1} obtained in aqueous methanol [8]. The lowered rate constant in trifluoroacetate media is consistent with a larger intrinsic reorganizational energy for reduction of five-coordinate $[Cu(pdto)(CF_3CO_2)]^+$ to four-coordinate $[Cu(pdto)]^+$.

In n-Bu_4NBF_4 solutions, the observed rate dependence on $[BF_4^-]$ is accounted for in terms of an equilibrium association between $Cu(pdto)^{2+}$ and BF_4^-, with both $Cu(pdto)^{2+}$ and ion-paired Cu(II) species being reactive towards ferrocene.

$$Cu(pdto)^{2+} + BF_4^- = [Cu(pdto):BF_4]^+ \qquad K_{IP1}$$

$$[Cu(pdto):BF_4]^+ + BF_4^- = [Cu(pdto):(BF_4)_2] \qquad K_{IP2}$$

$$Cu(pdto)^{2+} + FeCp_2 \xrightarrow{k_0} Cu(pdto)^+ + FeCp_2^+$$

$$[Cu(pdto):BF_4]^+ + FeCp_2 \xrightarrow{k_1} Cu(pdto)^+ + FeCp_2^+ + BF_4^-$$

$$[Cu(pdto):(BF_4)_2] + FeCp_2 \xrightarrow{k_3} Cu(pdto)^+ + FeCp_2^+ + 2BF_4^-$$

$$k_2 = \frac{(k_0 + k_1K_{IP1}[BF_4^-] + k_3K_{IP1}K_{IP2}[BF_4^-]^2)}{1 + K_{IP1}[BF_4^-] + K_{IP1}K_{IP2}[BF_4^-]^2} \qquad (1)$$

The observed k_2 dependence on $[BF_4^-]$, assuming an ion-pair association constant value of 10 M^{-1} for n-Bu_4NBF_4 in CH_3CN [15], yields best fit parameters, $k_0 = 2.1 \times 10^4$ M^{-1} s^{-1}, $k_1 = 1.1 \times 10^6$ M^{-1} s^{-1}, $k_3 = 2.6 \times 10^7$ M^{-1} s^{-1}, $K_{IP1} = 2$ M^{-1} and $K_{IP2} = 1$ M^{-1}. The values of K_{IP} are however expected to vary with the ionic strength according to the Fuoss equation

$$K_{IP} = \frac{4\pi N r^3}{3000} \exp[-w(r)/(k_b T)] \qquad (2)$$

$$w(r) = \frac{Z_1 Z_2 e^2}{D_s r(1 + Br\mu^{1/2})}$$

$$B = \left(\frac{8\pi N e^2}{1000 D_s k_b T}\right)^{1/2}$$

where D_s is the solvent dielectric constant (35.95 for CH_3CN), μ is the ionic strength, Z_1 and Z_2 are the charges on the ions and r is the distance between the center of the ions in the ion pair. The smallest K_{IP} values are obtained with $r = 9$ Å. Values in the range 12–32 M^{-1} are obtained for n-Bu_4NBF_4 between 0.0502 and 0.00212 M. An effective radius of 4.9 Å has been estimated for the structurally related complex, $Cu(bidhp)^{2+}$ [10], (bidhp = 1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane) and an ion size parameter of 3.5 Å has been determined for BF_4^- in acetonitrile [16]. A value of 6–7 Å has been estimated for the electron transfer distance during $Cu(bidhp)^{2+/+}$ self-exchange in DMSO. Although the aspherical nature and open structure of $Cu(pdto)^{2+}$ would allow apical association of BF_4^- at separations less than 9 Å, alternative values of r between 6 and 12 Å, do not vary K_{IP1} significantly, or give values closer to those obtained from the kinetic data. Agreement between values estimated for ion-pairing constants using the Fuoss equation and values determined experimentally is, in any event, often poor [17], particularly at the relatively high ionic strengths used in our study. When variable K_{IP} values, $K_{IP1} = 3.1$–1.3 M^{-1}, $K_{IP2} = 1.5$–1.2, are fitted to eqn. (1), to reflect the range of ionic strengths employed, modified rate parameters $k_0 = 2.1 \times 10^4$ M^{-1} s^{-1}, $k_1 = 7.6 \times 10^5$ M^{-1} s^{-1} and $k_3 = 6 \times 10^7$ M^{-1} s^{-1} are obtained. A plot of k_2 versus $[BF_4^-]$ is shown in Fig. 2, along with calculated values of k_2 at selected BF_4^- concentrations, using eqn. (1) and the above rate parameters and K_{IP} values.

The data at the lower salt concentrations, $[BF_4^-] = 2.12 \times 10^{-3}$ to 2.01×10^{-2} M, can be fitted equally well to a rate law excluding the k_3 term, to yield $k_1 = 5.1 \times 10^5$ M^{-1} s^{-1} and $K_{IP} = 5$ M^{-1}. An electron transfer rate constant, 1×10^4 M^{-1} s^{-1}, is estimated for self-exchange involving the $[Cu(pdto):BF_4]^+$ ion-pair.

The overall finding that the $[Cu(pdto):BF_4]^+$ ion-pair is more reactive towards ferrocene than $Cu(pdto)^{2+}$ itself, differs from most previously reported rate studies involving metal centers in non-aqueous solvents that have observed a lowering of electron transfer rate constants for ion-paired reactants formed on addition of electrolytes [9, 13, 15, 17, 18]. Reduced precursor complex stability or increased electron transfer distance have most frequently been invoked to explain such effects. Specific rate enhancement has been observed in the reduction

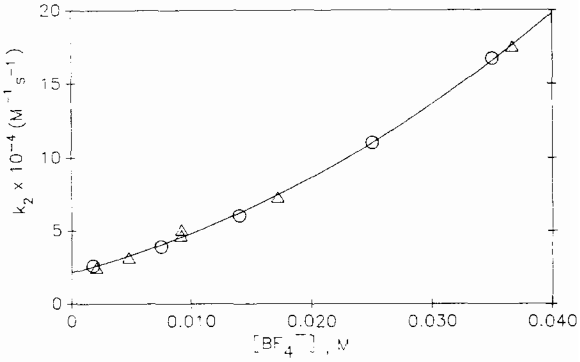

Fig. 2. Plot of second-order rate constant, k_2 vs. $[BF_4^-]$, for reaction of $Cu(pdto)^{2+}$ with $FeCp_2$. Comparison of observed (△) and calculated (○) values.

of neutral [Co(phen-SO$_3$)$_3$] by [Co(terp)$_2$]$^{2+}$ with added ClO$_4^-$ in ethylene glycol and attributed to ion pairing between ClO$_4^-$ and the Co(terp)$_2^{2+/+}$ couple [19].

Some insight into the effect of BF$_4^-$ in our study, and on the contrasting rate effects observed with BF$_4^-$ and PF$_6^-$, is afforded by the spectral changes that accompany the addition of BF$_4^-$ to Cu(pdto)$^{2+}$ solutions illustrated in Fig. 3. The spectrum of Cu(pdto)$^{2+}$, in common with other dithiaether copper(II) complexes, is characterized by a relatively intense d–d band ($\lambda = 594$ nm, $\epsilon = 820$), and a strong 'blue' band ($\lambda = 360$ nm, $\epsilon = 5.4 \times 10^3$) associated with a $S(\sigma) \rightarrow d_{x^2-y^2}$ LMCT transition, with the unusually large extinction coefficient of the d–d transition attributed to intensity borrowing from the blue band [2–4]. Since the LMCT transition absorbance at 360 is dependent on the degree of the 'in-plane' $S(\sigma) \rightarrow d_{x^2-y^2}$ overlap occurring with the two S atoms, it is expected to decrease with distortion from square planar and to be progressively weakened by apical association with the Cu(II) center. In our study, the association of both BF$_4^-$ and CF$_3$CO$_2^-$ with Cu(pdto)$^{2+}$, present at 2.0×10^{-4} M concentration, results in a shift in the energy of the 594 nm d–d band to longer wavelengths, reaching 720 nm at [BF$_4^-$] = 0.10 M and 680 nm at [CF$_3$CO$_2^-$] = 0.10 M. This is accompanied by a decrease in intensity of the 360 nm charge transfer band, though changes at 360 nm were much more marked with trifluoroacetate (85% reduction at 0.10 M CF$_3$CO$_2^-$) than with tetrafluoroborate (20% reduction at 0.20 M BF$_4^-$). Neither n-Bu$_4$NPF$_6$ nor n-Bu$_4$NClO$_4$ affect significantly the intensity of the 360 maximum or the energy of the d–d band, nor do they affect the rate of the FeCp$_2$–Cu(pdto)$^{2+}$ reaction in acetonitrile. The rate enhancement appears specific to BF$_4^-$. In the trifluoroacetate case, the red shifted d–d band, coupled with the lowered absorbance of the LMCT transition, are consistent with a five-coordinate square pyramidal structure, [Cu(pdto)CF$_3$CO$_2$]$^+$, being formed in trifluoroacetate solutions. Association of BF$_4^-$ with Cu(pdto)$^{2+}$ does not appear to significantly alter the ground state structural properties of the Cu(pdto)$^{2+}$ complex however, as evidenced by its much smaller influence on the intensity of the 'in-plane' 360 nm charge transfer transition. Rather, it appears to facilitate a more rapid electron transfer rate through lowering the energy of the $d_{x^2-y^2}$ orbital, the electron acceptor orbital in the reaction, without significant distortion of the planar environment at the Cu center. This behavior is also reflected in the more reversible cyclic voltammogram obtained for the Cu(pdto)$^{2+/+}$ redox couple in tetrafluoroborate solutions. Endicott *et al.* have demonstrated that weak ion-pair charge-transfer interactions between readily oxidizable anions and [Co(polypyridyl)$_3$]$^{3+}$ increase the electron transfer rate between [Co(PP)$_3$]$^{3+}$ and the Co(II) sepulchrate complex, Co(sep)$^{2+}$, by making the reaction more adiabatic [20]. A similar superexchange mechanism does not appear likely with BF$_4^-$, though its role does appear to be that of facilitating the electron transfer process by modifying the energy of the electron acceptor orbital in the redox change. An equilibrium inner-sphere association of BF$_4^-$ with Cu(pdto)$^{2+}$ could also account for the [BF$_4^-$] rate dependence, as well as the spectral changes observed for the 594 nm band. Although BF$_4^-$ is usually assumed to be a non-coordinating ligand, there are many examples in transition metal chemistry which involve the weak coordination of BF$_4^-$ to the metal [21–31]. These include several Cu(II) centers with both terminal and bridging BF$_4^-$ ions. Bis(2,5-dithiahexane)-Cu(II)bis(tetrafluoroborate) has two axial BF$_4^-$ fluorine atoms along with four in-plane thiaether sulfurs surrounding the tetragonal Cu(II) center in the crystal [23]. Bridging BF$_4^-$ groups are reported in polymeric [{Cu(μ-BF$_4$)(bpy)}$_n$](BF$_4$)$_n$ [22], and weakly associated BF$_4^-$ ions also bridge Cu(II) centers in both the difluorobridged Cu(II) dimer Cu$_2$F$_2$(mppzH)$_4$(BF$_4$)$_2$ (mppzH = 3-methyl-5-phenylpyrazole) [24] and Cu(ethylenediamine)$_2$(BF$_4$)$_2$ [25]. Although there is less evidence for BF$_4^-$ coordination in solution, a weak apically associated BF$_4^-$ ion in a square pyramidal [Cu(pdto)BF$_4$]$^+$ complex could also give rise to the shift in the energy of the 594 band to longer wavelengths which was observed. Such a large change for a d–d transition localized at the Cu(II) ion is perhaps more in line with what would be expected for an inner-sphere ligand association than for an outer-sphere ion-pairing interaction. For an intensity borrowing mechanism such as that proposed for Cu(pdto)$^{2+}$ however, increased

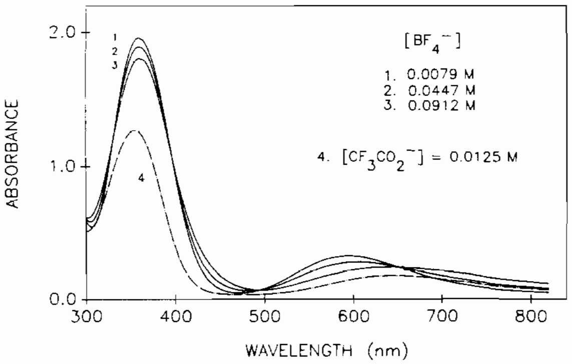

Fig. 3. Effect of added salts, n-Bu$_4$NBF$_4$ and NaCF$_3$CO$_2$, on the absorption spectrum of Cu(pdto)$^{2+}$ in acetonitrile. [Cu(pdto)$^{2+}$] = 4×10^{-4} M.

energy separation between the interacting transitions, the d–d band and the S(σ)–Cu(II) LMCT transition, is also expected to result from associations that reduce the intensity of the LMCT band [4]. Because of the significantly weaker solvation of copper(II) in low dielectric solvents, the difference between weak inner-sphere axial association and close contact ion-pair formation in acetonitrile is, in any event, likely to be small. Enhanced affinity of halide ions for Cu(II) centers has been demonstrated in acetonitrile ($K_f = 10^{9.7}$ for $Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ in CH_3CN and 1 in H_2O [32]). The slightly smaller size of BF_4^- as compared to PF_6^- appears the most likely reason for its stronger interaction with Cu(pdto)$^{2+}$. BF_4^- has been shown to exhibit a greater ion-pairing tendency towards Fe(phen)$_3^{3+}$ ($K_{IP} = 18$ M^{-1}) than PF_6^- ($K_{IP} = 1.4$ M^{-1}) in acetonitrile [33]. Amongst the examples of weak coordination by the anions BF_4^- and PF_6^- in the solid state, greater ligand binding strength has been generally demonstrated for BF_4^- than for PF_6^- [31]. A solid state structural determination of the hexafluorophosphate and tetrafluoroborate salts, [Cu(pdto)](PF$_6$)$_2$ and [Cu(pdto)](BF$_4$)$_2$ salts would be of interest.

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