

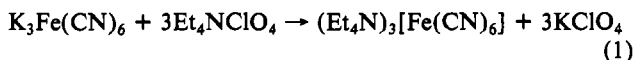
Communications

Convenient Synthesis of Tris(tetraethylammonium) Hexacyanoferrate(III) and Its Use as an Oxidant with Tunable Redox Potential

Sir:

Though the redox behavior of the hexacyanoferrate(III)-hexacyanoferrate(II) system has been studied in great detail,¹ the solubility characteristics of the common potassium or sodium salt restrict the use of $\text{Fe}(\text{CN})_6^{3-}$ as an oxidant in organic solvents like acetonitrile, DMF, benzene, and chloroform. The syntheses of tetraalkylammonium salts of hexacyanoferrate(III)² allowed the use of this oxidant in organic solvents. The reported procedure, however, requires the formation of the free acid $\text{H}_3\text{Fe}(\text{CN})_6$ in a cation-exchange-resin column and neutralization of the acid with the corresponding tetraalkylammonium hydroxide. The free acid decomposes fairly rapidly in aqueous solution even in the absence of light. Such decomposition can be prevented by saturating the aqueous solution with hydrogen cyanide gas, which is highly toxic. In this communication, the improved and convenient synthesis of tris(tetraethylammonium) hexacyanoferrate(III), $(\text{Et}_4\text{N})_3[\text{Fe}(\text{CN})_6]$ (**1**), is reported.³

The present synthesis makes use of two commercially available ingredients, namely, tetraethylammonium perchlorate, TEAP (Kodak Chemical), and $\text{K}_3\text{Fe}(\text{CN})_6$ (Mallinckrodt). When a mixture of TEAP (6.9 g, 30 mmol) and $\text{K}_3\text{Fe}(\text{CN})_6$ (3.3 g, 10 mmol) was stirred in methanol (200 mL), the latter slowly dissolved since the resulting potassium perchlorate is more insoluble in methanol as compared to $\text{K}_3\text{Fe}(\text{CN})_6$ (eq 1).



After 24 h of stirring under nitrogen, the mixture was filtered through a pad of Celite and the clear yellow filtrate was concentrated to ca. 10 mL under reduced pressure (rotary evaporator, 40 °C). The resulting orange oil was shaken with 100 mL of diethyl ether when **1** separated out as a yellow powder, which was filtered and dried under vacuum (yield 90%). Recrystallization from acetonitrile afforded large yellow blocks that lost crystallinity when dried under vacuum at room temperature.⁴ The infrared spectrum of **1** exhibited one sharp $\text{C}\equiv\text{N}$ stretching frequency at 2112 (s) cm^{-1} . The electronic spectrum in acetonitrile consisted of bands λ_{max} (ϵ) at 418 (950), 400 sh (850), 320 (1100), 303 (1500), 285 sh (1150), and 260 (1300) nm.⁵

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- (2) Jaselskis, B.; Diehl, H. *J. Am. Chem. Soc.* **1958**, *80*, 4197.
- (3) The procedure described here has also been followed to synthesize other $(\text{R}_4\text{N})_3[\text{Fe}(\text{CN})_6]$ salts.
- (4) Anal (sample dried under vacuum). Calcd for $\text{FeC}_{30}\text{H}_{60}\text{N}_6$: C, 59.78; H, 10.03; N, 20.92; Fe, 9.27. Found: C, 59.61; H, 10.11; N, 21.02; Fe, 9.19.
- (5) In water, the bands appear at 420 (1000), 400 sh (850), 320 sh (1150), 303 (1600), 285 sh (1200), and 260 (1180) nm.

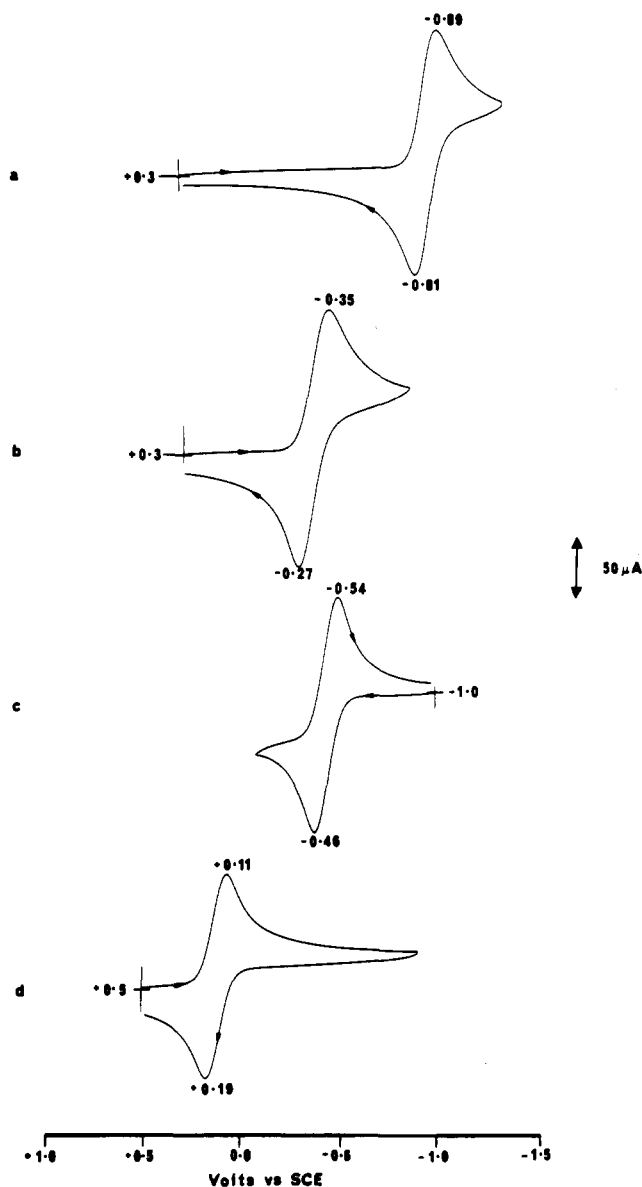


Figure 1. Cyclic voltammograms in 0.1 M TBAP/acetonitrile + $x\%$ (v/v) water at 50 mV/s with a glassy-carbon electrode: (a) **1** in acetonitrile ($x = 0$); (b) **1** in acetonitrile + 6% (v/v) water; (c) **2** in acetonitrile + 6% (v/v) water; (d) **1** in water (0.1 M TEAP, $x = 100$).

The $E_{1/2}$ values of **1** in different solvents have been reported to reflect the electron-accepting property of the solvent:⁶

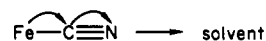


Table I. Half-Wave Potential for the Reduction of **1** in Solvent A Containing *x*% (v/v) Solvent B and 0.1 M Tetraalkylammonium Perchlorate^a

<i>x</i>	$E_{1/2}^a$		
	A = acetonitrile, B = water (TBAP)	A = acetonitrile, B = methanol (TBAP)	A = DMF, B = methanol (TEAP)
0	-0.85	-0.85	-0.90
1.5	-0.55	-0.71	-0.84
3	-0.43	-0.66	-0.78
6	-0.31	-0.61	-0.71
9	-0.23	-0.57	-0.67
12	-0.18	-0.53	-0.63
25	-0.08	-0.46	-0.53
100	+0.15 (TEAP)	-0.30	-0.30

^a Conditions: V vs. SCE; 25 °C; glassy-carbon electrode; scan rate 50 mV/s; concentration of **1** 1 mM.

The N atoms in $[\text{Fe}(\text{CN})_6]^{4-}$ are stronger donors as compared to those in $[\text{Fe}(\text{CN})_6]^{3-}$,⁷ and outer-sphere complex formation with the solvent molecules stabilizes the reduced form. The reduction potential of **1** is thus more positive in water or methanol than that in acetonitrile or DMF. In the present study, the variation of reduction potential of **1** in several mixed-solvent media has been studied by cyclic voltammetry, CV⁸ (Table I, Figure 1). The redox system exhibited nearly reversible behavior⁹ in all cases. The $E_{1/2}$ values in Table I are quoted vs. SCE and are not corrected for liquid-junction potential. However, these values can be readily compared with the $E_{1/2}$ values reported for various metallochromophores and their synthetic analogues.¹⁰

Table I exhibits a regular shift of half-wave potentials to more positive values due to addition of the protic partner to the solvent mixtures. Changes in dielectric constant of the mixed-solvent media are not adequate to account for such shift. For example, addition of methanol to acetonitrile brings about very small change in dielectric constant (from 36.01 to 32.63 for 0–100 wt % of methanol)¹¹ whereas such addition shifts the $E_{1/2}$ value for **1** from -0.85 to -0.30 V vs. SCE.¹² Gutmann et al.⁶ had shown that the $E_{1/2}$ values for **1** in different single-solvent media follow trends in *Z* values of Kosower¹³ and E_T values of Dimroth and Reichardt,¹⁴ both of which are empirical measures of the "polarity" of solvents based on charge-transfer energy of certain organic molecules dissolved in those solvents. Such numbers for mixed solvents are not available. However, if any linear relationship exists for these measures of "polarity" of solvents, $E_{1/2}$ values for **1** in Table I qualitatively follow the acceptor properties of the mixed-solvent media.¹⁵

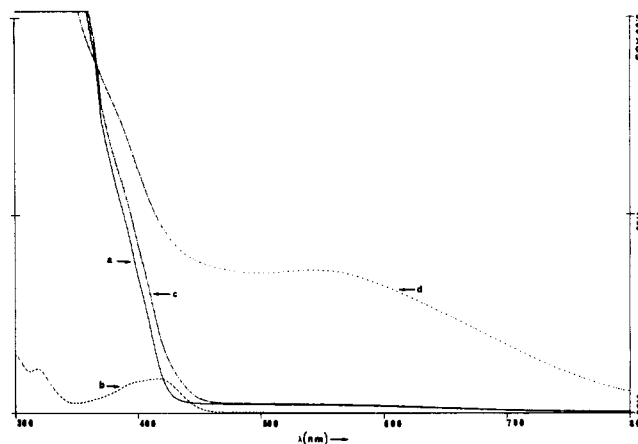


Figure 2. Electronic absorption spectra: (a) **2** in acetonitrile; (b) **1** in acetonitrile; (c) 1 equiv of **1** + 1 equiv of **2** in acetonitrile; (d) 1 equiv of **1** + 1 equiv of **2** in acetonitrile containing 6% (v/v) water. The spectra were recorded ca. 5 min after the solutions were prepared. Concentrations of **2** and **1** were 3 mM in (a) and (b) respectively. In the case of (c) and (d), concentrations were adjusted (for volume corrections) such that the final concentrations of **2** and **1** were again 3 mM. This choice of 3 mM was just to record an appreciable change in absorbance around 550 nm.

A close look at Table I reveals that **1** is not a strong oxidant in organic solvents like acetonitrile or DMF. However, the potential can be "tuned" to more positive value by introduction of water or methanol.

That such a system can indeed be used as a "tunable oxidant" has been successfully demonstrated in the present study. The cyclic voltammogram of the reduced rubredoxin analogue $(\text{Et}_4\text{N})_2[\text{Fe}(\text{SPh})_4]$ (**2**)¹⁶ in acetonitrile containing 6% (v/v) water is shown in Figure 1 (in MeCN, $E_{1/2} = -0.51$ V vs. SCE¹⁶). The CV experiments indicated that addition of water to a solution of **1** in acetonitrile could lower its $E_{1/2}$ value such that **2** could be oxidized smoothly in a predominantly organic solvent. This expected oxidation of **2** was followed spectrophotometrically. Under strictly oxygen-free conditions, addition of 1 equiv of **1** to a solution of **2** in pure acetonitrile caused a very small increase in absorption around 500 nm in the electronic spectrum (Figure 2). When the same addition was performed in acetonitrile containing 6% (v/v) water, the initial pale yellow color changed dramatically to deep red brown and the strong absorption band centered at 550 nm due to $[\text{Fe}(\text{SPh})_4]^{-17}$ was recorded (Figure 2). **2** alone, in the same acetonitrile/water mixture, had no absorption in this region. The oxidation of **2** was more than 80% complete within 15 min. Very similar behavior has been observed in DMF/methanol mixtures.

Clean oxidation in organic solvents often offers problems related to choice of suitable oxidant. **1** can be used over a wide range of redox potential depending on the solvent composition. The various combinations of a protic and an aprotic solvent, as exemplified by Table I, make such oxidation possible in a variety of solvent mixtures.

In conclusion, a straightforward, inexpensive, high-yield route to $(\text{Et}_4\text{N})_3[\text{Fe}(\text{CN})_6]$ has been discovered. The variable redox potential of this oxidant in mixed solvents has been successfully used to oxidize $(\text{Et}_4\text{N})_2[\text{Fe}(\text{SPh})_4]$. Efforts to use this oxidant with "tunable" potential to oxidize metal-containing active sites in the hydrophobic regions of folded and partially unfolded proteins in mixed-solvent media are in progress.

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- CV experiments were performed on a PAR Model 174A instrument connected to a Houston Instruments X-Y recorder. All the solvents were purified and thoroughly degassed. CV characteristics were practically identical on both glassy-carbon and platinum electrodes (freshly cleaned). The solutions were prepared fresh and used within 15 min. $[\text{Fe}(\text{CN})_6]^{4-}$ is reported to be unstable in acetonitrile.⁶ In the case of mixed-solvent systems, both the electrochemical cell and the bridging tube contained the same ratio of the two solvents.
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Acknowledgment. Financial support by Faculty Research Funds granted by the University of California, Santa Cruz, CA, is gratefully acknowledged.

Registry No. 1, 14837-73-1; 2, 77403-03-3; $K_3Fe(CN)_6$, 13746-66-2.

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Received May 28, 1985

Delayed Fluorescence and Triplet-Triplet Annihilation in a Diphosphate(II) Pyrophosphite Complex

Sir:

The luminescence from salts of the tetrakis(μ -pyrophosphito)diphosphate(II) ion is of current interest.¹⁻⁸ In addition to the known fluorescence and the phosphorescence, we have observed, for the first time, anti-Stokes delayed fluorescence for crystals of the potassium salt, $K_4[Pt_2(P_2O_5H_2)_4]$, at 4.2 K. When the crystalline complex, prepared as described previously,⁶ is excited by 450-nm dye laser light in its triplet state at 4.2 K, delayed fluorescence shown in Figure 1 is observed around 395 nm. The spectrum consists of a progression of the 120-cm^{-1} Pt-Pt stretching vibration, and the whole spectral distribution is exactly identical with the normal fluorescence observed at 4.2 K. Thus it is clear that the first singlet excited state (S_1) is somehow created from the first triplet excited state (T_1). At such a low temperature (4.2 K) thermal excitation from T_1 to S_1 is impossible. The most reasonable interpretation, therefore, appears to be that S_1 is created by the annihilation of two T_1 's. Taking this viewpoint, we will see if the intensity and decay behaviors of the phosphorescence and the delayed fluorescence are satisfactorily interpreted in terms of this mechanism.

The kinetic equations for the populations of T_1 and S_1 are

$$dn_T/dt = -k_P n_T - k_{TT} n_T^2 \quad (1)$$

$$dn_S/dt = -k_F n_S + f k_{TT} n_T^2 \quad (2)$$

where k_P and k_F are respectively the first-order decay rate constants for T_1 and S_1 and k_{TT} is the rate constant for the triplet-triplet annihilation. Further, f stands for the fraction of the annihilation rate constant yielding S_1 among the total annihilation rate constant. From these rate equations we have the following expressions for n_T and n_S :

$$\frac{1}{n_T(t)} = \left(\frac{1}{n_T(0)} + \frac{k_{TT}}{k_P} \right) \exp(k_P t) - \frac{k_{TT}}{k_P} \quad (3)$$

$$\left(\frac{1}{n_S(t)} \right)^{1/2} = \left[\left(\frac{1}{n_S(0)} \right)^{1/2} + \left(\frac{k_F k_{TT}}{f k_P^2} \right)^{1/2} \right] \exp(k_P t) - \left(\frac{k_F k_{TT}}{f k_P^2} \right)^{1/2} \quad (4)$$

We first focus attention on the phosphorescence decay. If we plot the reciprocal of the phosphorescence intensity with respect to $\exp(k_P t)$, we would expect a straight line with a negative in-

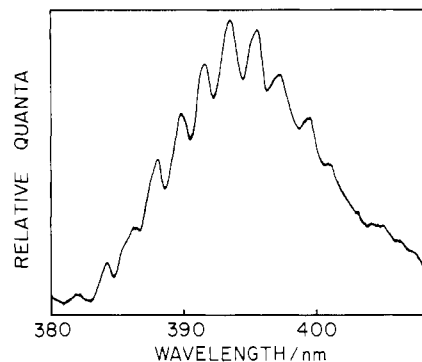


Figure 1. Delayed fluorescence spectrum of crystalline $K_4[Pt_2(P_2O_5H_2)_4]$ at 4.2 K. Excitation was by a nitrogen pumped dye laser (Moletron UV24 and DL14P) at 450 nm. The output from a Hamamatsu R928 photomultiplier tube was recorded with a PAR 162 boxcar integrator with 2-ms delay from the excitation and 200- μ s window. The spectral distribution is exactly identical with the normal fluorescence, which is known to decay with a lifetime of less than 1 ns.

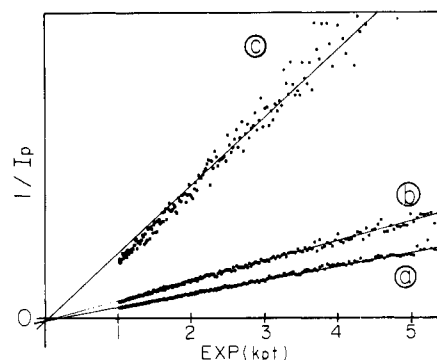


Figure 2. Plots of the reciprocal of the phosphorescence intensity with respect to $\exp(k_P t)$, where k_P is the first-order phosphorescence decay rate constant. The decay was obtained with an Iwatsu DM901 digital memory. The three plots labeled as a, b, and c correspond to three decays obtained with different exciting light intensities with a ratio of 1:0.48:0.12. In accord with eq 3, all the three plots are linear with the same negative intercept.

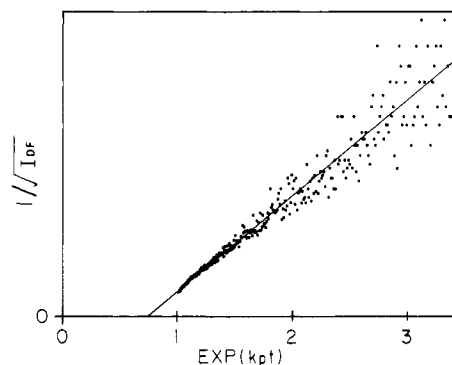


Figure 3. Plot of the reciprocal of the square root of the delayed fluorescence intensity with respect to $\exp(k_P t)$. The decay was obtained by a photon-counting system composed of a Hamamatsu C767 photon counter, C716 preamplifier, R649 photomultiplier tube, and an Ortec 6240B multichannel analyzer. In accord with eq 4, the plot is linear with a negative intercept.

tercept. Such plots are attempted in Figure 2, where $1/k_P = 6.5$ ms determined from the decay obtained in a weak exciting light limit is used. The three plots correspond to three decays obtained with different exciting light intensity. All the three plots are linear and extrapolate to the same intercept. Further, the initial triplet populations obtained from the slopes and the intercept of the experimental plots are roughly in the ratio of the exciting light intensity.

We next examine the decay of the delayed fluorescence. The reciprocal of the square root of the delayed fluorescence intensity

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