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Mixed Valence Spectrum and Cyclic Voltammetry of Binuclear Iron Cyano Complexes

Sir:

The vast majority of mixed valence compounds is represented by polynuclear crystalline compounds.[1] Complexes with only two metallic centers exhibiting intervalence electron transfer spectra have been recently studied by Taube and by Cowan.[2] In our search for simple systems showing intervalence electronic transitions, we investigated the reaction of $Fe^{III}(CN)_5NH_3{}^{2-}$ with $Fe^{II}(CN)_6{}^{4-}$. Job's method[3] has been applied to solutions containing the two mononuclear complexes showing that a binuclear species is formed. Since the hexacyano complex of low-spin iron(II) is extremely unlikely to undergo ligand substitution, it is assumed that the ammonia molecule of the prusside species is replaced by one nitrogen end of the hexacyanoferrate(II). Thus the binuclear ion $[(CN)_5Fe^{III}NC)Fe^{II}(CN)_5]^{6-}$ is formed, abbreviated as [III-II]. For preparative purposes equivalent solutions of the two mononuclear constituents (1 mmol) were passed over an ion-exchange column (Dowex 50) in the acid form. The resulting solution was titrated with an appropriate base to pH 7 and evaporated to dryness under reduced pressure. *Anal.* Calcd for $Na_6[Fe_2(CN)_{11}]\cdot 2H_2O$: Fe, 19.5; C, 23.1; H, 0.7; N, 27. Found: Fe, 19.4; C, 23.1; H, 1.4; N, 29.1. Identical results were obtained by the combination of $Fe^{II}(CN)_5NH_3{}^{3-}$ and $Fe^{III}(CN)_6{}^{3-}$.

Aqueous solutions of [III-II] show a moderately intense (log $\epsilon \approx 3$) band at 1300 nm (7.7 kK). This band obeys Beer's law at concentrations higher than 10^{-2} *M*. Small deviations at lower concentrations are attributed to partial dissociation of the [III-II] dimer. We assign this low energy band to an intervalence charge transfer [III-II] → [II-III]*. This band is observed at the same wavelength in solution as well as in KBr pellets of the solid binuclear compound. The assignment as charge transfer band is supported by the fact that there is no loss of intensity observed upon cooling a KBr pellet of [III-II] to liquid nitrogen temperature. Evidence for a bridge assisted charge-transfer mechanism is furnished by comparing the spectrum of [III-II] with the one of a solution containing a 1:1 mixture of $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$. The extension of earlier work[4] into the near-infrared part of the spectrum did not reveal any band in the 700–1500 nm range.

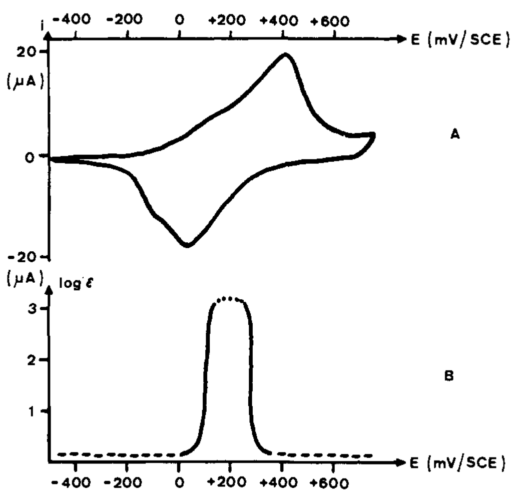

Figure 1. (A) Cyclic voltammogram of 4.5×10^{-4} *M* $Na_6[Fe_2(CN)_{11}]$ in 1 *M* $NaClO_4$, scan rate 0.1 V/min. (B) Extinction coefficient of the 1300-nm intervalence band of $Na_6[Fe_2(CN)_{11}]$ (4.5×10^{-4} *M* in 1 *M* $NaClO_4$) as function of the minigrid potential.

When the asymmetry of the bridging cyanide is neglected the results derived by Hush[5] for symmetrical binuclear mixed valence complexes can be applied. The parameters of the intervalence band (ν, 7.7 kK; ϵ, 3180 M^{-1} cm^{-1}, half-width, 5.1 kK) lead to a delocalization of the optical electron of only about 3%. In fair agreement with the observed value the calculated half-width of the band is 4.2 kK. The small degree of delocalization shows class II behavior[1] of [III-II]. Evidence for trapped valences is also furnished by the infrared spectrum. Two distinct frequencies are observed for the CN stretching vibration at 2060 and 2130 cm^{-1} (KBr pellet of $Na_6Fe_2(CN)_{11}$). These values are to be considered as characteristic for cyano complexes of a two- and three-valent metal.[6]

The electronic spectrum of [III-II] is very similar to that reported for the oxidized form of the dimer of $Fe(CN)_5H_2O^{3-}$.[7] The resulting binuclear species, however, was formulated with two bridging cyanide ligands.

In order to elucidate the optical and electrochemical properties of [III-II], a controlled potential experiment was performed by means of a transparent thin-layer cell.[8] A 0.2-mm flow cell was equipped with a gold minigrid[9] having an optical transparency of 60% (500 lines per in.). The minigrid operates as the working electrode in a potentiostatic circuit used for cyclic voltammetry within the sample compartment (thermostated to 25 ± 0.1°) of a Cary 17 spectrophotometer.

Repeated potential cycling from −400 to +700 mV (*vs.* sce) showed the binuclear species to be readily oxidized and reduced. The overall charge stoichiometry corresponds to

$$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$$

the complex [III-II] being formed as an intermediate at potentials near +200 mV/sce (Figure 1). This re-

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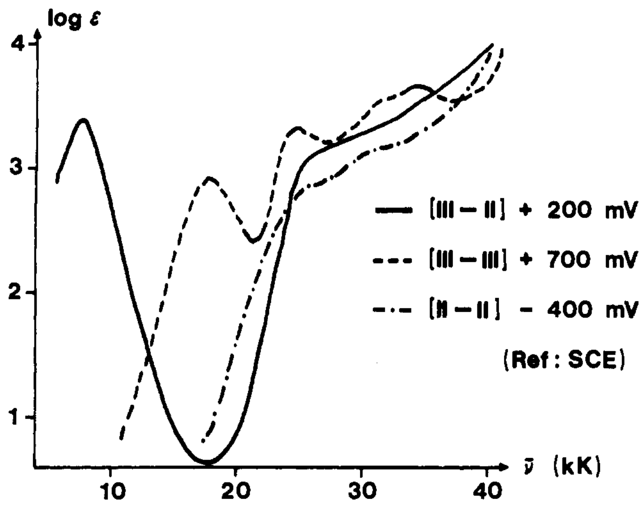

Figure 2. Absorption spectra of $Fe_2(CN)_{11}^{x-}$ at different, constant minigrid potentials.

peatedly and reversibly scanned reaction can be conveniently followed by recording the intensity of the 1300-nm band as a function of time, *i.e.*, the minigrid potential. The optical density at this wavelength is zero at −400 mV/sce, reaches a maximum around +200 mV/sce, and vanishes again at higher potentials (Figure 1). This redox behavior is interpreted in terms of a two-step mechanism involving the binuclear species [II-II], [III-III], and [III-II] as an electrochemical intermediate according to

$$[\text{III-III}] \overset{+e}{\rightleftarrows} [\text{III-II}] \overset{+e}{\rightleftarrows} [\text{II-II}]$$

$$Fe_2(CN)_{11}^{5-} \overset{+e}{\rightleftarrows} Fe_2(CN)_{11}^{6-} \overset{+e}{\rightleftarrows} Fe_2(CN)_{11}^{7-}$$

The spectra recorded at the different potentials are accordingly assigned to these three binuclear complexes (Figure 2). Defined oxidation states of this binuclear iron cyano complex can thus be produced which otherwise are difficult to obtain.[10] Similar complexes having pyrazine as bridging ligand are presently investigated in our laboratory. In the case of $[(CN)_5Fe^{III}pyrFe^{II}(CN)_5]^{5-}$ (pyr is pyrazine) an intervalence band is observed at 1180 nm.[11]

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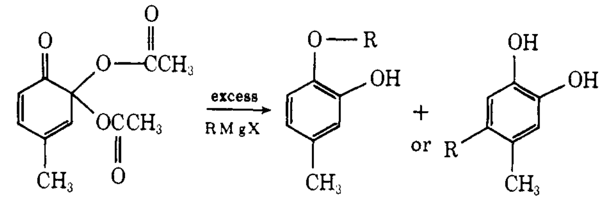
Attack of Carbanionoid Reagents at the Oxygen Atoms of Carbonyl Groups in *o*-Quinol Acetates[1]

Sir:

It is commonly observed that Grignard and lithium reagents add to the carbonyl carbons of ketones or to the β carbons of α,β-unsaturated ketones. In contrast, attack by these reagents at the oxygen atoms of carbonyl groups is almost unknown. One striking exception is the report by Wessely and Kotlan that ethylmagnesium bromide reacts with the quinol diacetate **1** to give principally the corresponding ethyl ether **2**. In contrast, methyl- and phenylmagnesium bromides reacted with **1** to give good yields of **3**, resulting from the expected conjugate addition to the unsaturated ketone.[2] Quinol monoacetates, such as **4**, were reported to react with lithium and Grignard reagents (including ethylmagnesium bromide) to give the normal conjugate addition. No formation of ethers was observed in these reactions.[3]



1 2 3

In this communication it is reported that ether formation in the reaction of carbanionoid reagents with *o*-quinol monoacetates is a general phenomenon. Remarkably, as the reagent employed changes from primary to secondary, and then to tertiary or benzylic Grignard or lithium reagents, ether formation changes from a very minor process to the major process, and frequently is the only observable addition reaction.

The products obtained from reaction of quinol acetates with carbanionoid reagents are listed in Table I. The final column in the table lists the ratio of attack at the carbonyl oxygen to conjugate addition. Since the presence of isomeric reaction products interfered with attempts to estimate the maximum possible yield of **6** from reaction with **4c**, the column is blank in those cases.

Wessely and Kotlan[2] originally suggested that **2** was formed by initial 1,2 addition of ethylmagnesium bromide to the carbonyl group of **1**, followed by rearrangement of the ethyl group from carbon to oxygen. An attempt to explain the data in Table I by a similar "reverse Wittig rearrangement" mechanism would require the assumption that the ratio of 1,2 to 1,4 addition to unsaturated ketones should increase sharply as the degree of substitution at the carbanionoid center of the organometallic reagent increases. Little support for such a proposition is available. Indeed, appreciable evidence suggests that the opposite is true.[4] Furthermore, it seems improbable that the *tert*-butyl Grignard reagent would add to the carbonyl of **4b** in preference to the much less hindered β carbon of the double bond. Finally, the observation that the reaction of the *sec*-butyl Grignard with **4c** is complete within a few seconds seems inconsistent with a mechanism for ether formation requiring attack at the highly crowded carbonyl carbon.

The data in Table I suggest that the ratio of formation of ethers to meta-substituted phenols from aliphatic

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