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Quinone Imine Complexes with Pentacyanoferrate(II)

F. FELIX and A. LUDI*

Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland

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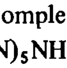
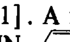
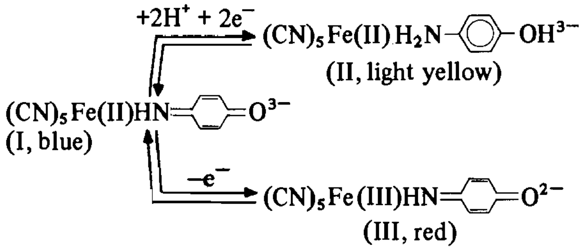
It has been shown that *p*-phenylenediamine and related aromatic amines react with ruthenium ammine complexes to form stable quinone-diimine compounds showing strong absorption bands in the visible [1]. A similar intensely colored species has been isolated when *p*-phenylenediamine reacts with amminepentacyanoferrate. The resulting compound has been described as a binuclear complex without specifying, however, the electronic structure of the ligand [2]. Considering the many analogies between the Ru(II)$(NH_3)_5$ and Fe(II)$(CN)_5$ moieties [3] it seems likely that the ligand in the iron complex is also represented by *p*-benzoquinonediimine.

The aromatic diamines *p*-phenylenediamine, *p*-aminophenol, 1,8-diaminenaphthalene, and N,N-dimethyl*para*phenylenediamine react very rapidly with $Fe(CN)_5NH_3^{3-}$ in aqueous solution. The visible spectrum of the resulting complexes is dominated by a strong (ϵ approximately 10^4) absorption band at about 14,000 cm^{-1} which is assigned to a $t_{2g} \rightarrow \pi^*$ charge transfer in analogy to pentacyanoiron complexes with heterocyclic nitrogen donors [4]. Job plots of the system $Fe(CN)_5L$ demonstrate the formation of mononuclear complexes $Fe(CN)_5L^{2-}$ (L = aminophenol, 1,8-diaminonaphthalene, and N,N-dimethyl*para*phenylenediamine) in solution and of the binuclear complex when L is *p*-phenylenediamine. In the case of N,N-dimethyl*para*phenylenediamine a mononuclear complex could be isolated as the zinc salt Zn[$Fe(CN)_5NH$==$N(CH_3)_2$]·$2H_2O$. *Anal.* Calculated Fe: 13.3, C: 36.0, N: 23.5, H: 3.2; found Fe: 13.1, C: 36.0, N: 23.2, H: 3.3.

In analogy to the corresponding ruthenium compounds the iron complexes described above are considered to be the quinone imine complexes of pentacyanoferrate(II). This conclusion has been verified by a spectroelectrochemical study using a thin-layer optical cell equipped with a transparent working electrode [1]. A freshly prepared solution of $Na_3[(CN)_5$-Fe(II)HN==O] (10^{-3} *M* in 1 *M* $NaClO_4$, pH adjusted to 9.7 with NaOH) was studied in the potential range –1.0 to 0.8 V *versus* SCE. The coulometric evaluation of the cyclic voltammograms agrees with the following redox reactions



The species occurring in these redox equilibria are identified by their absorption spectra [1, 4] (*cf.* Table I and Fig. 1). By monitoring the intensity of the 14.4 kK band of I it was shown that species I

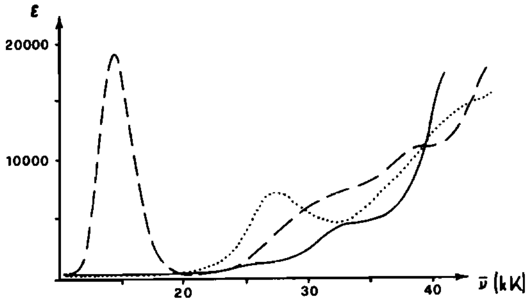
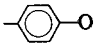
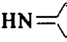
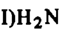
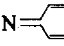


Figure 1. Absorption spectra of the $Fe(CN)_5$–H_2N––OH system at various potentials.

(----- $(CN)_5$Fe(II)HN==O^{3-},

—— $(CN)_5$Fe(II)H_2N––OH^{3-},

..... $(CN)_5$Fe(III)HN==O^{2-}).

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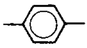
*To whom correspondence should be addressed.

TABLE I. Spectroelectrochemical Data of the $Fe(CN)_5$–H_2N––OH System.

Potential (V, *versus* SCE)	Species	ν_{max} (ϵ_{max}) (kK)
0	I	14.4 (19,000), 33.3 (6,000), 40.0 sh (9,500), 45.5 (17,000)
–1.0	II	24.4 (500), 33.9 sh (3,500), 45.4 (20,000)
+0.76	III	25.6 (6,500), 37.0 (16,000), 39.2 sh (16,000), 45.4 sh (12,000)

is regenerated to about 85% after a complete oxidation–reduction cycle.

Acknowledgment

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