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Polarographic Studies on Bipyridine Complexes. IV. The Polarography of the Dicyanobis(2,2′-bipyridine)iron(II) Complex

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Synopsis. Each electron added to the oxidant in the first two reduction waves of a polarogram for dicyanobis(2,2′-bipyridine)iron(II) is concluded to occupy a π^*-orbital localized on a bipyridine molecule, on the basis of the number of the reversible waves and the half-wave potential shift caused by the methyl substitution of ligand bipyridines.

In Parts I—III of this series,[1–3] the molecular orbital occupied by the electron added or removed in the course of oxidation-reduction reactions of tris(bipyridine) complexes of transition metals was discussed on the basis of the polarographic half-wave potentials. In this paper, the same discussion will be extended to dicyanobis(2,2′-bipyridine)iron (II).

Experimental

4,4′-Dimethyl-2,2′-bipyridine (4-dmbipy) and 5,5′-dimethyl-2,2′-bipyridine (5-dmbipy) were prepared according to the method of Sasse and Whittle.[4] Dicyanobis(2,2′-bipyridine)iron(II) and its dimethyl derivatives were prepared by the method of Shilt.[5] *N*,*N*-Dimethylformamide (DMF) was used as a solvent. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP). The electrolysis cell[3] and the following experimental procedures have been described in previous papers: the preparation of TBAP and solutions,[6] the purification of DMF,[6] and the measurements of polarograms and cyclic voltammograms.[1] The measurements were carried out at room temperature. All the potentials were referred to a saturated calomel electrode (SCE).

Results and Discussion

Figure 1 shows a cathodic polarogram for $Fe(bipy)_2(CN)_2$ (bipy=2,2′-bipyridine). It exhibits three waves with half-wave potentials of −1.59, −1.90, and −2.6 V. The wave height at −2.6 V is higher than the others. The first two waves were concluded to be reversible one-electron wave on the basis of the cyclic voltammogram in Fig. 2, taken with an initial cathodic scan. They can be assigned to the following redox systems respectively: $Fe(bipy)_2(CN)_2/Fe(bipy)_2(CN)_2^-$ and $Fe(bipy)_2(CN)_2^-/Fe(bipy)_2(CN)_2^{2-}$.

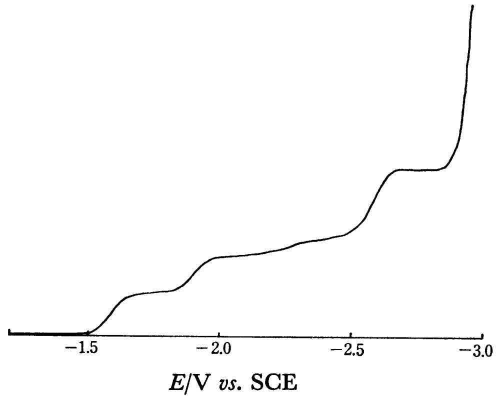

Fig. 1. Cathodic polarogram for 1 mM $Fe(bipy)_2(CN)_2$ in DMF containing 0.1 M TBAP.

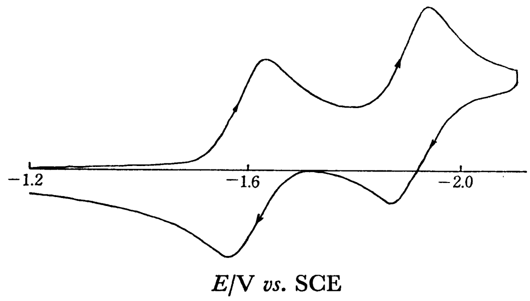

Fig. 2. Cyclic voltammogram with initial cathodic scan for 1 mM $Fe(bipy)_2(CN)_2$ in DMF containing 0.1 M TBAP. Scan rate: 0.1 V s^{-1}.

Table 1. The reversible half-wave potentials for $FeL_2(CN)_2$ (L=bipy, 4-dmbipy, 5-dmbipy), $E^{red}_{1/2,C}$, in DMF containing 0.1 M TBAP

Complex	$E^{red}_{1/2,C}$/V vs. SCE 1st wave	 2nd wave
$Fe(bipy)_2(CN)_2$	−1.59	−1.90
$Fe(4\text{-}dmbipy)_2(CN)_2$	−1.69	−1.98
$Fe(5\text{-}dmbipy)_2(CN)_2$	−1.73	−2.05

Similar polarograms and cyclic voltammograms were also obtained for the methyl-substituted complexes. The half-wave potentials of the redox systems, $FeL_2(CN)_2/FeL_2(CN)_2^-$ and $FeL_2(CN)_2^-/FeL_2(CN)_2^{2-}$ (L=bipy, 4-dmbipy, 5-dmbipy), became more negative in this order: bipy<4-dmbipy<5-dmbipy (Table 1). It should be noted that an empirical rule has been obtained concerning the order of the reversible half-wave potentials of tris(bipyridine) complexes of transition metals:[1] When an electron is added to a ligand π^*-orbital by the electrochemical reduction of a complex, the reduction half-wave potential, $E^{red}_{1/2,C}$, is shifted, on the methyl-substitution of ligand bipyridines, to a more negative potential in this order: bipy<4-dmbipy<5-dmbipy. The relation between the reduction half-wave potentials of free ligand molecules, $E^{red}_{1/2,L}$, and the $E^{red}_{1/2,C}$ for $FeL_2(CN)_2/FeL_2(CN)_2^-$ satisfies Eq. 3 in Part I,[1] as shown in Fig. 3. Consequently, it may be concluded that the electrons added to $FeL_2(CN)_2$ in the first two reduction steps occupy ligand π^*-orbitals.

It has been noted that there exsists a correlation be-

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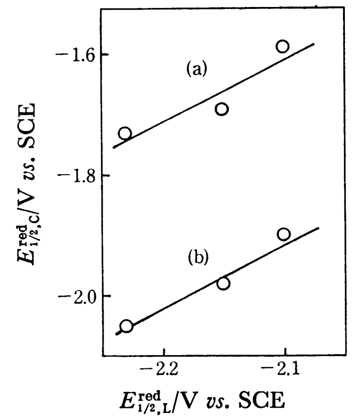

Fig. 3. Plot of half-wave potentials for (a) $FeL_2(CN)_2$/$FeL_2(CN)_2^-$ and (b) $FeL_2(CN)_2^-$/$FeL_2(CN)_2^{2-}$, $E^{\mathrm{red}}_{1/2,\mathrm{C}}$, *vs.* those for L/L⁻, $E^{\mathrm{red}}_{1/2,\mathrm{L}}$, in DMF containing 0.1 M TBAP. L=bipy, 4-dmbipy, 5-dmbipy. The $E^{\mathrm{red}}_{1/2,\mathrm{L}}$ data can be found in Ref. 1.

tween the number of reversible reduction waves of a complex and the number of its ligands of a π-character:[1,7] The polarogram of this kind of complex is characterized by nearly neighboring one-electron waves, the number of which is identical with that of the ligands. This correlation can be found in the polarograms for bis(2,2′,2″-terpyridine)iron(II),[1,8,9] tris(4,7-diphenyl-1, 10-phenanthroline)iron(II),[7,10] tris(2,2′-bipyridine)iron(II),[1,8,11] tris(2,2′-bipyridine)ruthenium(II),[1,9] and tris(2,2′-bipyridine)osmium(II).[1] It is evident that this rule holds also for Fe(bipy)$_2$(CN)$_2$. This fact suggests that the lowest π^*-orbitals are nearly doubly degenerate. Thus, in the two reversible reduction waves for Fe(bipy)$_2$(CN)$_2$, each added electron should occupy one of the nearly degenerate orbitals successively.

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