

Intramolecular Interactions between Two Non-conjugated Metal Complex Moieties in Alkylene-bridged Ferrocene and (η -Cyclopentadienyl)-(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III)

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Bimetallic complexes, A-CH₂-B(1) and A-(CH₂)₂-B(2), were synthesized in which (η -cyclopentadienyl)(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III)(A) and ferrocene(B) moieties are bound at the cyclopentadienyl(cp) rings by -CH₂-. Their cyclic voltammograms show the presence of the intramolecular interaction between the two metal complex moieties, A and B. Moiety B (oxidized form) promotes decomposition of the oxidized form of A. The MS fragment patterns of 1 and 2 suggest the presence of a species in which two sulfur atoms of the dithiolene ligand bridge the two metal atoms.

The organometallic complexes containing two transition metal atoms have recently been intensively studied,¹⁻³⁾ since the systems which contain two different transition metal atoms are expected to exhibit unique physical and chemical properties which cannot be observed in monometallic analogs because these properties derive from the cooperative metal-metal interactions. However, all of these reports were limited only to metal carbonyl complexes, or to the complexes having conjugated ligands; no report has appeared on the bimetallic non-conjugated system with a dithiolato ligand which might interact with more than one metal atoms. Hence, in order to obtain the evidence for the intramolecular metal-metal interaction and intramolecular ligand migration in non-conjugated, and sterically unfixed -CH₂- bridged bimetallic dithiolato complexes, A-CH₂-B(1) and A-CH₂-CH₂-B(2), were prepared.⁴⁾ Their electrochemical⁵⁾ and mass spectral data⁷⁾ were examined in view of the effect of bridge length on the intramolecular interactions.

We report here some results which support the presence of the proximity effects of the two metal complex moieties: (1) the comparisons of the

cyclic voltammograms (CV) of the complexes, 1 and 2, and monometallic complexes, $[\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)]$ (3) and ferrocene (4), suggest that the interaction between the two metal complex moieties, A and B, is "through space" fashion when A and B are bound by $-\text{CH}_2-$, and (2) the characteristic fragmentation peak, ($\text{M}^+ - \text{C}_5\text{H}_5$), implies the presence of the species in which two sulfur atoms bridge the cobalt and iron atoms.

A remarkable phenomenon for showing the proximity effects is the acceleration of the oxidative decomposition of the dithiolato metal moiety (A) by the ferrocene moiety (B) (in oxidized form). The complexes 1 and 2 show one reduction and two oxidation waves in CV (Fig. 1⁵). The values of the reversible half-wave potentials of 1, 2, 3, and 4 are listed in Table 1. In the case of 1, the processes corresponding to A/A^- and B/B^+ are reversible, while the A/A^+ process is irreversible. Therefore, the presence of ferrocenium nearby situated causes the decomposition of the dithiolato moiety in the oxidized state. This effect is also observed for 2, but the rate of decomposition of $[\text{2}]^{2+}$ is slower than in the case of $[\text{1}]^{2+}$. The reversible half-wave potentials in Table 1 show that the $E^{\text{r}}_{1/2}(\text{A}/\text{A}^-)$ of 1 and 2 are shifted to more negative values than that of monometallic complex, 3, since the $-(\text{CH}_2)_n-\text{B}$ moiety is electron-donating to the A moiety in 1 and 2. The magnitude of the negative shift of the potential, $\Delta E^{\text{r}}_{1/2}$ (red) { = $E^{\text{r}}_{1/2}(\text{A}/\text{A}^-)$ (1 or 2) - $E^{\text{r}}_{1/2}(\text{A}/\text{A}^-)$ (3) } should be balanced by the magnitude of the positive shift of the potential, $\Delta E^{\text{r}}_{1/2}$ (ox) { = $E^{\text{r}}_{1/2}(\text{B}/\text{B}^+)$ (1 or 2) - $E^{\text{r}}_{1/2}(\text{B}/\text{B}^+)$ (R-B)⁶ (R = $-\text{C}_2\text{H}_5$, or $-\text{CH}_3$) }, if the charge is transferred through the C-C bond of the bridge. The values of $\Delta E^{\text{r}}_{1/2}$ (red) and $\Delta E^{\text{r}}_{1/2}$ (ox) of 1 and 2 are shown in Fig. 2. In the case of 2, the $\Delta E^{\text{r}}_{1/2}$ (red) (80 mV) and the $\Delta E^{\text{r}}_{1/2}$ (ox) (66 mV) roughly compensate each other, whereas in the case of 1, the $\Delta E^{\text{r}}_{1/2}$ (ox) value (101 mV) is about twice as large as that of $\Delta E^{\text{r}}_{1/2}$ (red) (52 mV). This extra large positive shift of $E^{\text{r}}_{1/2}(\text{B}/\text{B}^+)$

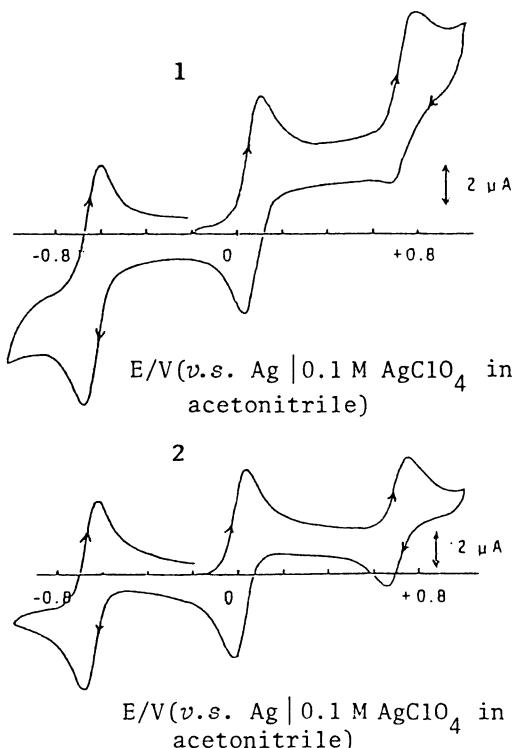
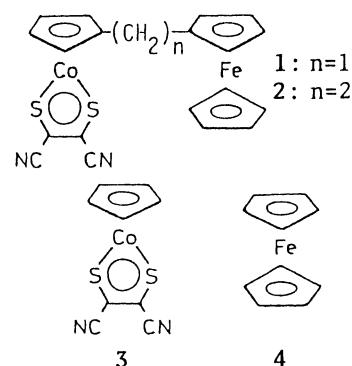


Fig. 1. Cyclic voltammograms of 1 (above) and 2 (below) in acetonitrile solutions. Scan rate = 0.1 V s^{-1} .

can be explained by the "through space" interaction between the iron atom in B moiety and the sulfur atom in A moiety. Therefore, the unbalanced potential shift of B moiety in 1 can be considered as the result of the proximity effect of the two metal complex moieties, A and B. The fact that both of the second oxidation potentials, $E_{1/2}^r(A/A^+)$, of A moiety in 1 and 2 show the same value as that of the monometallic complex, 3, indicates that at this potential the iron atom of B moiety is already oxidized and that the B moiety is no longer an electron-donating group.

A related phenomenon showing this proximity effect was observed in the fragmentation patterns of the complexes in MS.⁷⁾ The following characteristic bond cleavages were observed: (1) the cleavage of the bonds between unsubstituted ($\eta\text{-C}_5\text{H}_5$) and Fe (Scheme 1,(a)) occurs in preference to that of the bonds between substituted ($\eta\text{-C}_5\text{H}_4^-$) and Fe, while the latter occurs preferentially in monosubstituted ferrocene with an electron attracting group,⁸⁾ (2) the cleavage of the S-C bonds (Scheme 1,(b)) occurs only after the cleavage of the bonds between ($\eta\text{-C}_5\text{H}_5$) and Fe occurs (the former is the most favorable cleavage in 3), and (3) the cleavages of the two Co-S bonds occur stepwise (Scheme 1,(c)), while they occur simultaneously in 3.

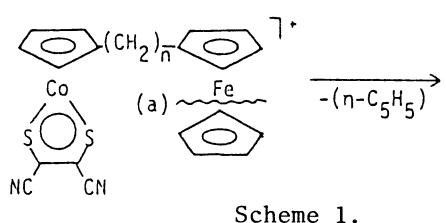


Table 1. Reversible Half-Wave Potentials of the Complexes^{a)}

Complex	$E_{1/2}^r(\text{B/B}^+)/\text{V}^b)$	$E_{1/2}^r(\text{A/A}^+)/\text{V}^b)$	$E_{1/2}^r(\text{A/A}^-)/\text{V}^b)$
1	0.066	(0.74) ^{c)}	-0.642
2	0.030	(0.74) ^{c)}	-0.670
3	-	-	-0.590 ^{d)}
4	0.025	-	-

a) Conditions are given in Ref.5. b) Volt *v.s.* $\text{Ag}|\text{0.1 mol dm}^{-3}\text{ AgClO}_4$ in acetonitrile.

c) $(E_p^a + E_p^c)/2$. d) M.Kajitani et al., *J.Electroanal. Chem.*, 251, 421 (1988).

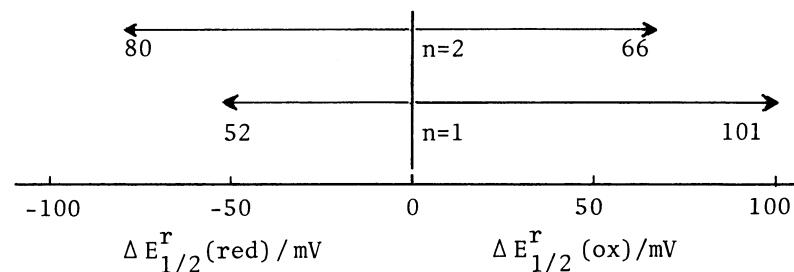


Fig.2. The magnitude of the shift of reduction and oxidation potentials of the complexes 1 and 2. Definitions of $\Delta E_{1/2}^r(\text{red})$ and $\Delta E_{1/2}^r(\text{ox})$ are given in the text.

These characteristic cleavages (1)-(3) suggest the formation of the

species(I). In the case of 2, the fragment patterns are similar to those of 1, except for the presence of fragments which originated from the cleavage of C-C bond of the bridge and the fragments which correspond to the loss of metal- $S_2C_2(CN)_2$ unit from I {I-Co $S_2C_2(CN)_2$ (m/z, 212) and I-Fe $S_2C_2(CN)_2$ (m/z, 215)}. These results suggest that the interaction between the two metal complex moieties, A and B, exists even in the non-conjugated alkylene-bridged bimetallic system, such as 1 and 2, when an electron is removed from the system.

References

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- 4) The complexes, 1 and 2, were prepared according to the literature method (organic ligands: A.Cassens, P.Eilbracht, A.Nazzal, W.Prössdorf, and U.T. Mueller-Westerhoff, *J.Am.Chem.Soc.*, **103**, 6367 (1981); dithiolato ligand: H.Bönnemann et al., "Transition-Metal-Catalyzed Synthesis of Heterocyclic Compounds," in "Catalysis of Organic Reactions," 1st Ed, ed by J.R.Kosak, Marcel Dekker, Inc., New York, Basel (1984), pp.60-61.).
- 5) All the cyclic voltammograms of the complexes were obtained in the acetonitrile(AN) - 0.1 mol dm⁻³ (C₂H₅)₄NClO₄ solutions at 25 °C. A platinum disk of 2.0 mm diameter embedded in glass was used as a test electrode. A spiral platinum wire was used as an auxiliary electrode.
- 6) Calculated based on the reported E_{T/4} values of methyl- and ethyl-ferrocene which are 60 and 61 mV more negative than that of ferrocene. W.F.Little, C.N.Reilley, J.D.Johnson, K.N.Lynn, and A.P.Sanders, *J.Am.Chem.Soc.*, **86**, 1382 (1964).
- 7) The relationships between daughter ions and their precursor ions were established by MS-MS spectral data. MS-MS Spectra of 1 were recorded on a Finnigan MAT TSQ-70 spectrometer, and those of 2 were recorded on a JEOL JMS-SX102 using the linked scan method.
- 8) D.W.Slocum and C.R.Ernst, "Electronic Effects in Metallocenes and Related Systems," in "Advances in Organometallic Chemistry," Academic Press, Inc., New York, N.Y.(1972), Vol.10, pp.95-97.

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