Synthesis of a Novel π-Conjugated Cyclic Trinuclear Complex of Cobalt(III) and Intramolecular Electronic Interactions in Its Reduced Forms

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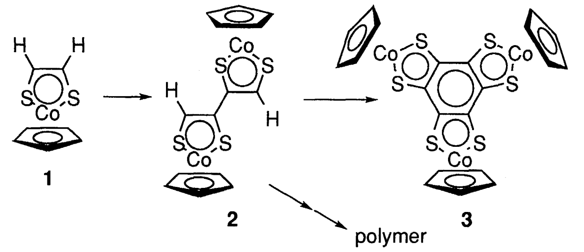
An oligomerization reaction of an ethylene-1,2-dithiolato-cobalt complex, [$CoCp(S_2C_2H_2)$] (Cp = η^5-cyclopentadienyl)) (**1**) in HBr-MeCN-H_2O in air affords a conjugated trinuclear complex, [$Co_3Cp_3(S_6C_6)$] (**3**), that undergoes reversible three-step $1e^-$ reductions in aprotic solvents. Electrochemical, optical and magnetic properties of **3** and its reduced forms are reported.

Intramolecular electronic interaction in transition metal multi-nuclear complexes are of recent growing interest with respect to discovery and development of new molecular mateials for electronics.[2] We present here a preparation of a novel cobalt(III) trinuclear complex with four fused rings, **3**, by oxidative condensation of **1**,[3,4] and its unique electrochemical, optical and magnetic properties.

A typical procedure of the oligomerization of **1** is as follows. Stirring a solution of **1** (268 mg, 1.25 mmol) in a mixture of 48% HBr aq. (49 cm^3) and MeCN (145 cm^3) at room temperature for 18 h in the presence of air afforded a dark purple solution. After the reaction was quenched by neutralization with Na_2CO_3, CH_2Cl_2 was added to the solution and the components soluble in the organic layer were extracted. There remained 21.6 mg of insoluble black polymeric material. Silica gel column chromatography of the soluble part in CH_2Cl_2 followed by recrystallization gave a greenish blue dinuclear comlex, [$CpCo(S_2C_2H)]_2$ (**2**) and a blue cyclic trinuclear complex, [$CpCo(S_2C_2)]_3$ (**3**) in the yield of 8.2 mg (3.1%) and 8.7 mg (3.3%), respectively, besides 46.7 mg (17.4%) of **1** recovered. IR, ^1H-NMR and FD-mass spectra and elemental analysis data were consistent with the structures of **2** and **3** as given in Scheme 1.[5] The oligomerization of **1** proceeded faster in MeCN than in THF or CH_2Cl_2-EtOH (1:3). HBr and HCl provided **2** and **3** but H_2SO_4, HNO_3, HI and CH_3COOH were ineffective for the oligomerization.



Scheme 1. The oligomerization process of **1**.

A cyclic voltammogram of **3** in Bu_4NClO_4-THF at a glassy carbon disk (5-mm o.d.) is shown in Figure 1. Reversible three-step reduction takes place at $E^{0'}$ = -1.06, -1.30 and -1.74 V *vs.* $E^{0'}$(Fc^+/Fc, Fc = ferrocene), suggesting formation of two mixed-valent states, Co(III)Co(III)Co(II) and Co(III)Co(II)Co(II), before all Co sites converting to the divalent state. Coulometry of **3** in this electrolyte at -1.23, -1.56 and -2.03 V gave 1.1, 1.9 and 3.4 as the number of electrons per molecule passed in reduction, confirming the three-step one-electron process as noted above. Comproportionation constants, K_{c1} for Eq. 1 and K_{c2} for Eq. 2, estimated from the $E^{0'}$ values are $10^{4.1}$ and $10^{7.4}$, respectively.

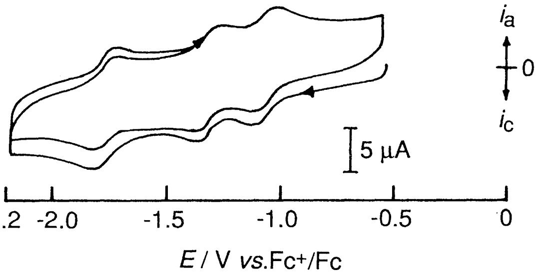


Figure 1. A cyclic voltammogram of **3** (6.9×10^{-5} mol dm^{-3}) at glassy carbon in 0.1 mol dm^{-3} Bu_4NClO_4-THF at a scan rate of 0.1 V s^{-1}.

Table 1. Redox Properties of **3**

Electrolyte solution[a]	$E^{0'}$ / V *vs.* Fc^+/Fc 1st	2nd	3rd	log K_{c1}	log K_{c2}
Bu_4NClO_4-THF	-1.06	-1.30	-1.74	4.1	7.4
$NaBPh_4$-THF	-1.11	-1.25	-1.36	2.4	1.9
$NaBPh_4$-THF[b]	-1.11	-1.43	-1.80	5.4	6.3
Bu_4NClO_4-MeCN	-0.96	-1.22	-1.61	4.4	6.6
Et_4NClO_4-MeCN	-1.01	-1.21	-1.54	3.4	5.6
Me_4NClO_4[c]-MeCN	-1.00	-1.21	-1.50	3.5	4.9
$NaBPh_4$-MeCN	-0.96	-1.19	-1.33	3.9	3.4
Bu_4NClO_4-DMF	-0.99	-1.27	-1.68	4.7	6.9
$NaBPh_4$-DMF	-1.00	-1.29	-1.63	4.9	5.7
Bu_4NClO_4-DMSO	-0.95	-1.22	-1.60	4.6	6.4
$NaBPh_4$-DMSO	-0.95	-1.22	-1.60	4.6	6.4

[a] Electrolyte concentration was 0.1 mol dm^{-3} unless otherwise stated. [b] Containing 18-crown-6 (0.14 mol dm^{-3}). [c] Saturated (< 0.1 mol dm^{-3}).

$$2 \times 3^- = 3 + 3^{2-} \qquad (1)$$

$$2 \times 3^{2-} = 3^- + 3^{3-} \qquad (2)$$

Similar three-step $1e^-$ reductions of **3** occur in other electrolytes but K_c valules depend markedly on electrolyte cations and solvents as shown in Table 1. In this table, K_{c2} is larger than K_{c1} except in $NaBPh_4$-THF and in $NaBPh_4$-MeCN. Addition of 18-crown-6 to $NaBPh_4$-THF increases both K_c values, indicating a crucial effect of the cation size on K_c's.

Electronic absorption spectra of 3^- and 3^{2-} electrochemically formed in Bu_4NClO_4-THF show an intervalence transfer (IT) band at λ_{max} = 1280 nm ($\varepsilon = 7.2 \times 10^2$ mol^{-1}dm^{-3}cm^{-1}, bandwidth $\Delta\nu_{1/2} = 6.0 \times 10^2$ cm^{-1}) and 1445 nm ($\varepsilon = 3.0 \times 10^3$ mol^{-1}dm^{3}cm^{-1}, $\Delta\nu_{1/2} = 1.5 \times 10^3$ cm^{-1}), respectively. The higher λ_{max}, ε and $\Delta\nu_{1/2}$ values of the latter than those of the former indicate that the donor-acceptor interaction is stronger in the Co(III)Co(II)Co(II) state than in the Co(III)Co(III)Co(II) state.[6] On the contrary, in $NaBPh_4$-THF, $\mathbf{3}^{2-}$ does not exhibit any distinct peaks assignable to the IT band while $\mathbf{3}^-$ does a similar IT band as noted above. These results and the electrochemical data in Table 1 indicate that the electrochemical stability given by K_c is roughly corresponding to the magnitude of donor-acceptor interaction estimated from IT bands.

Preliminaly ESR results for the reduced forms of **3** are as follows. Chemical reduction of **3** with sodium mirror in THF shows three-step changes in electronic spectra same to those for electroreduced forms in $NaBPh_4$-THF. ESR spectra of the chemically reduced forms were measured at 77 K with monitoring the electronic spectrum. The monoanion, $\mathbf{3}^-$, shows an $S = 1/2$ signal with a hyperfine structure due to $S = 7/2$ of Co at $g_{//} = 2.225$ and $g_\perp$ = ca. 2.00 (Figure 2*(a)*). The dianion, $\mathbf{3}^{2-}$, is ESR silent, and the trianion, $\mathbf{3}^{3-}$, affords a spectrum characteristic of not $S = 1/2$ but $S = 3/2$ in the nearly axial field with $g = 2.057$ and $D = 0.102$ cm^{-1} (Figure 2*(b)*)[7] implying an intramolecular ferromagnetic spin-spin interaction. A further investigation on magnetic properties of reduced forms of **3** are currently in progress.

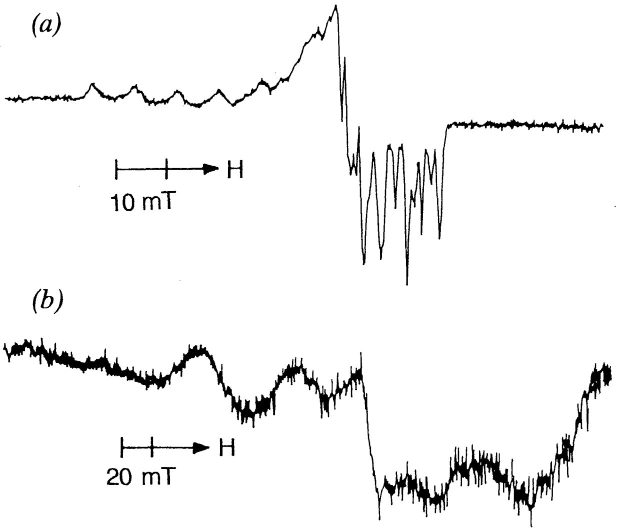


Figure 2. ESR spectra of $\mathbf{3}^-$and $\mathbf{3}^{3-}$(2×10^{-5} mol dm^{-3}) in THF at 77 K.

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References and Notes

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5 Satisfactory elemental analysis were obtained for compounds, **2** and **3**. **2**: MS(FD) m/z 426 (M^+); ^{1}H NMR (in $CDCl_3$): δ 9.28 (s, 2H), 5.34 (s, 10H); IR δ(C-H, out of plane) 776, 762 cm^{-1}; λ_{max} (ε) (in CH_2Cl_2) 236 (2.4×10^4), 300 (4.5×10^4), 354 (sh, 1.1×10^4), 640 (1.9×10^4), 780 (sh, 4.9×10^3). **3**: MS(FD) m/z 636 (M^+); ^{1}H NMR (in $CDCl_3$): δ 5.45 (s, 15H); λ_{max} (ε) (in CH_2Cl_2) 234 (3.0×10^4), 308 (9.8×10^4), 360 (sh, 7.2×10^3), 688 (2.9×10^4).
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