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Redox Potentials of Cobalt(III) Mixed-Ligand Complexes with Sulfur, Phosphorus, and Nitrogen Donor Atoms and a Correlation with Their Electronic Spectra

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Reduction($E_{1/2}$(red)) and oxidation($E_{1/2}$(ox)) potentials of 32 cobalt(III) mixed-ligand complexes with sulfur, phosphorus, and nitrogen donor atoms were obtained. A good linear relationship was found between the potential difference, ΔE(redox) $\equiv e[E_{1/2}(\mathrm{ox}) - E_{1/2}(\mathrm{red})]$, and the first d-d transition energy.

Few papers have been published on relationship between redox potentials and ligand field energies of metal complexes.[1)] To investigate such relationship, the data on both reduction and oxidation potentials will be necessary.[2)] In this letter, we have measured oxidation potentials as well as reduction ones of a large number of $[\mathrm{Co^{III}(S)_x(N)_y(P)_z}]$($x+y+z=6$)-type complexes, and examined relationship between the data and the ligand field transition energies. Although oxidation potentials of cobalt(III) complexes often exceed the voltage limit of a measurement system, those of the present dithiocarbamato complexes are in the measurable range, since dithiocarbamato ligands stabilize the high oxidation state of metals.[3)]

Electrochemical measurements were carried out by cyclic voltammetry (CV), rotating disk electrode voltammetry (RDE), and conventional DC polarography. Experimental details are given in the footnote of Table 1.

Table 1 lists the reduction $E_{1/2}$(red) ($\mathrm{Co^{3+} + e \rightarrow Co^{2+}}$) and the oxidation $E_{1/2}$(ox) ($\mathrm{Co^{3+} \rightarrow Co^{4+} + e}$) half-wave potentials of the complexes measured here. Reversible or quasi-reversible one-electron reduction waves were observed for most of the complexes, and values $(E_{pc} + E_{pa})/2$ by CV and $E_{1/2}$ by RDE were the same within the experimental error. On the other hand, oxidations of the complexes were irreversible in CV and no cathodic peak currents were observed. However, quasi-reversible waves with a small $(E_{1/4} - E_{3/4})$ value were obtained by RDE.

In Fig. 1 are plotted the $E_{1/2}$(ox) and $E_{1/2}$(red) values vs. the charge of the complexes. Both $E_{1/2}$(ox) and $E_{1/2}$(red) values are shifted to the positive side as the positive charge of the complexes increases. For the present octahedral Co(III) complexes, the HOMO and LUMO which correspond, respectively to redox potentials for the oxidation and reduction can be assigned to the $d\pi(d^6)$ and $d\sigma^*(d^0)$ orbitals of Co(III), respectively. Thus the charge-dependence of redox potentials indicates that the Co-3d orbital energies ($d\pi$ and $d\sigma^*$) are largely affected by the electrostatic potential due to the negative charge of ligands; the energies are lowered by replacing a negatively charged ligand with a neutral one and the lowering of d orbital energies causes the positive shift for either potential. The variation of potentials with the kind of ligand is small for the $E_{1/2}$(ox) values,

Table 1. Electrochemical$^{a)}$ and Absorption Spectral$^{b)}$ Data of the Co(III) Complexes $^{c,d)}$

Complexes	$E_{1/2}$(red) / V	$E_{1/2}$(ox) / V	ΔE(redox) / eV	ν_{d-d} / eV
[Co(dtc)$_3$]	-1.35$^{e)}$	0.56	1.91	1.91
[Co(pyrdtc)$_3$]	-1.28$^{e)}$	0.53	1.81	1.90
[Co(iPrdtc)$_3$]	-1.56$^{e)}$	0.45	2.01	1.97
mer-[Co(pyt)$_3$]	-0.93	0.68	1.61	1.85
[Co(dtc)$_2$(dmpm)]$^+$	-1.26	0.84	2.10	2.43
[Co(dtc)$_2$(dmpe)]$^+$	-1.38	0.97	2.35	2.57
[Co(dtc)$_2$(dmpp)]$^+$	-1.35	1.01	2.36	2.39
[Co(dtc)$_2$(dppm)]$^+$	-1.12	1.02	2.14	2.26
[Co(dtc)$_2$(dppe)]$^+$	-1.26	1.11	2.37	2.33
[Co(dtc)$_2$(dppp)]$^+$	-1.14	1.14	2.28	2.29
[Co(dtc)$_2$(dppb)]$^+$	-0.93	1.12	2.05	2.17
[Co(dtc)$_2$(dmope)]$^+$	-1.24	1.09	2.33	2.69
[Co(dtc)$_2$(en)]$^+$	-1.11	1.04	2.15	2.13
[Co(dtc)$_2$(bpy)]$^+$	-0.96	1.22	2.18	2.16
[Co(pyrdtc)$_2$(bpy)]$^+$	-0.92	1.19	2.11	2.13
[Co(iprdtc)$_2$(bpy)]$^+$	-1.12	1.18	2.30	2.11
trans-[Co(pyt)$_2$(en)]$^+$	-0.86	1.13	1.99	2.02
trans-[Co(pyt)$_2$(bpy)]$^+$	-0.69	1.19	1.88	2.03
[Co(dtc)(dmpm)$_2$]$^{2+}$	-1.11	1.41	2.52	2.70
[Co(dtc)(dmpe)$_2$]$^{2+}$	-1.10	1.54	2.64	2.81
[Co(dtc)(dmpp)$_2$]$^{2+}$	-0.95	f)		2.67
[Co(dtc)(dmope)$_2$]$^{2+}$	-1.11	1.62	2.73	3.04
[Co(dtc)(en)$_2$]$^{2+}$	-0.86	1.61	2.47	2.41
[Co(dtc)(bpy)$_2$]$^{2+}$	-0.55	f)		2.21
[Co(pyrdtc)(bpy)$_2$]$^{2+}$	-0.53	f)		2.23
[Co(iprdtc)(bpy)$_2$]$^{2+}$	-0.63	f)		2.26
[Co(pyt)(dmpe)$_2$]$^{2+}$	-0.84	1.38	2.22	2.42
[Co(pyt)(en)$_2$]$^{2+}$	-0.70	1.32	2.02	2.11
[Co(pyt)(bpy)$_2$]$^{2+}$	-0.37	1.58	1.95	2.03
[Co(dmope)$_3$]$^{3+}$	-1.26	g)		4.03
[Co(en)$_3$]$^{3+}$	-0.61	g)		2.64
[Co(bpy)$_3$]$^{3+}$	+0.01	g)		2.74

a) RDE measurements were carried out on CH_3CN solutions([Co]: 1.0×10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} Bu_4NBF_4) at 25 ± 1 °C by using a FUSO HECS 321B potential sweep unit and a FUSO HECS 317B potentiostat. A grassy-carbon rotating-disk(1500 rev min^{-1}) attached to a Yanako P10-RE Mark II head, a platinum-wire, and a Ag/Ag^+ electrode(Ag/0.01 mol dm^{-3} $AgNO_3$) were used as the working, auxiliary, and reference electrodes, respectively. The oxidation wave of ferrocene was observed at +0.08 V vs. Ag/Ag^+. CV measurements were performed at a scan rate, 200 mV s^{-1} with a grassy-carbon working electrode. Other experimental conditions were the same as those for RDE measurements. b) In the case where the first d-d band ($^1T_{1g} \leftarrow {}^1A_{1g}(O_h)$) is split, the lowest energy component was taken. c) Most of the complexes are new, and the preparative methods will be reported in a subsequent paper. d) Abbreviations in the Table are dmpm: $(CH_3)_2PCH_2P(CH_3)_2$; dmpe: $(CH_3)_2P(CH_2)_2P(CH_3)_2$; dmpp: $(CH_3)_2P(CH_2)_3P(CH_3)_2$; dppm: $(C_6H_5)_2PCH_2(C_6H_5)_2$; dppe: $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$; dppp: $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$; dppb: $(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2$; dmope: $(CH_3O)_2P(CH_2)_2P(OCH_3)_2$; dtc: $(CH_3)_2NC(S)S^-$; pyrdtc: $\overline{CH_2CH_2CH_2CH_2N}C(S)S^-$; iprdtc: $(CH_3)_2CHNC(S)S^-$; pyt: 2-pyridinethiolate; en: $NH_2CH_2CH_2NH_2$; bpy: 2,2'-bipyridine. e) $(E_{pc}+E_{pa})/2$ value on CV. f) The value was not determined because of a complex voltammogram. g) The value is more positive than the voltage limit of CH_3CN(ca. +1.8 V vs. Ag/Ag^+).

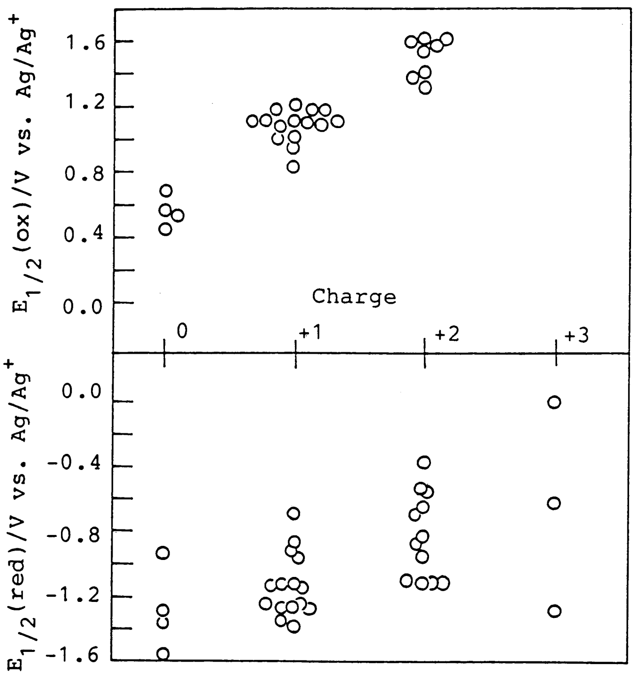

Fig. 1. Plots of $E_{1/2}(ox)$ and $E_{1/2}(red)$ values vs. the charge of the Co(III) complexes.

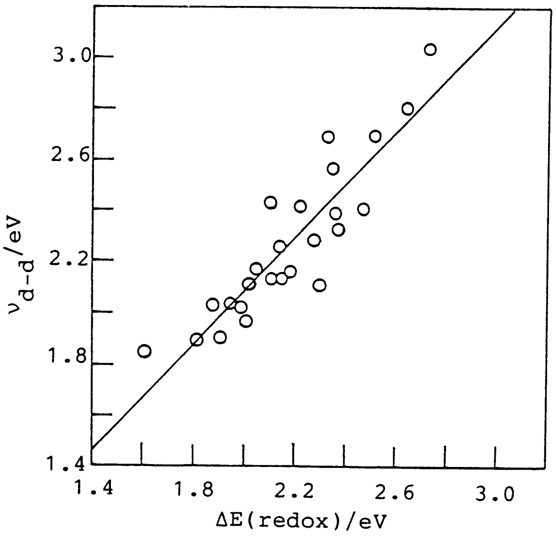

Fig. 2. Plot of ν_{d-d} vs. ΔE(redox).

while fairly large for the $E_{1/2}$(red) values. The small variation of $E_{1/2}$(ox) with ligands indicates that the dπ orbitals have no strong π-interaction with ligands in the complexes studied here. On the other hand, the $E_{1/2}$(red) values should depend on the kind of ligand, since the energy of anti-bonding $d\sigma^*$ orbitals varies with the ligand field strength; the higher the energy of $d\sigma^*$ orbital, the more negative the $E_{1/2}$(red) value. As seen in the spectral data of Table 1, diphosphines give stronger ligand fields than those given by ethylenediamine(en) and 2,2'-bipyridine(bpy), and the $E_{1/2}$(red) values of diphosphine complexes become more negative than those of en and bpy complexes with the same charge. Figure 1 represents features of the HOMO(non-bonding dπ) and LUMO(anti-bonding $d\sigma^*$) in the cobalt(III) complexes studied here.

Since the energy difference between the HOMO and LUMO can be estimated from the first d-d transition energy of the complex(ν_{d-d}), the ν_{d-d} value is expected to have a correlation with the potential difference between the $E_{1/2}$(ox) and $E_{1/2}$(red), $\Delta E(\text{redox}) \equiv e[E_{1/2}(\text{ox})-E_{1/2}(\text{red})]$. As shown in Fig. 2, a good linear relationship between them is obtained for the 25 $[\mathrm{Co(S)_x(N)_y(P)_z}]$-type complexes measured here. The least-squares line is

$$\nu_{d-d} = 1.05\,\Delta E(\text{redox}) - 0.003\ [\text{eV}],\ \text{correlation coefficient: } 0.90.$$

The redox potential E(red or ox) corresponds to the free energy difference between the reactant and the reduced or oxidized product, while the ν_{d-d} gives an approximate energy difference between the HOMO(dπ) and LUMO($d\sigma^*$) of the Co(III) complex. However, the fact that the good linear relationship exists between the ΔE(redox) and ν_{d-d} values indicates that energy changes resulting from physicochemical changes such as spin-pairing, solvation or coordination environment attended by redox reactions are small or nearly constant for the present complexes. Similar linear relationships have been reported between the charge-transfer energies and the ΔE(redox) of Ru(II)$^{4)}$- and Mo(0)$^{5)}$-diimine complexes.

Thus the good correlation between the ΔE(redox) and ν_{d-d} will provide useful information on not only the absolute HOMO and LUMO energies, but also magnitude of the σ or π interaction between the Co-d and ligand donor orbitals in these complexes.

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