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Redox Characteristics of $[Co(N)_{6-x}(O)_x]$ Type Cobalt(III) Complexes (x = 0 and 2) in the Ground and the Excited States

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Introduction

It is anticipated from the electronic configuration of the central metal atom that cobalt(III) complexes may have reaction behavior and related properties in the excited state quite different from those in the ground state. However, there have been no studies on the properties in the excited state of the cobalt(III) complexes. The present article deals with the estimation of the redox potential and the stability constant of $[Co(N)_6{-_x}(O)_x]$ type cobalt(III) complexes in the $^1T_{1g}(O_h)$ excited state and in the $^1A_{1g}$-(O_h) ground state, and with efforts to find some correlation of these characteristics with geometrical structure.

Experimental

Cobalt(III) complexes were prepared and characterized according to the methods in the literature: $[Co(NH_3)_6]Cl_3$ [1], $[Co(en)_3]Cl_3\cdot 3H_2O$ [2], *mer*-$[Co(dien)_2]Cl_3$ and the mixture of *mer* and *fac* isomers [3], $[Co(bpy)_3]Cl_3\cdot 3H_2O$ [4], $[Co(phen)_3]Cl_3\cdot 7H_2O$ [5], *fac*-$[Co(amp)_3]Br_3$ [6], *fac*-$[Co(amq)_3]Br_3$ [6], *cis(N)*-$K[Co(ida)_2]\cdot 2.5H_2O$ [7], and $K[Co(edta)]\cdot 2H_2O$ [8], where en, dien, bpy, phen, amp, amq, ida, and edta denote ethylenediamine, diethylenetriamine, 2,2′-bipyridine, 1,10-phenanthroline, 2-(aminomethyl)pyridine, 8-aminoquinoline, iminodiacetate, and ethylenediamine-N,N,N′,N′-tetraacetate, respectively. Other chemicals used were of analytical or equivalent grade.

Electronic absorption spectra were recorded on the JASCO spectrophotometer, model UVIDEC-1. Cyclic voltammograms were recorded on the HOKUTO DENKO potentiogalvanostat, model HA-201, to which a linear potential scanner, model HB-103, was attached. A Pt wire or a hanging Hg drop microelectrode, a Pt wire counter electrode with sufficiently large surface area, and an Ag/AgCl reference electrode were used for the potentiostatic measurements in 1.0 mol dm^- aqueous sodium chloride solution at room temperature (25 ± 1 °C). The data were corrected to those obtained using the standard hydrogen electrode (SHE).

Results and Discussion

Cobalt(III) complexes of the $[Co(N)_{6-x}(O)_x]$ type in the $^1A_{1g}(O_h)$ state take one electron reduction to the corresponding cobalt(II) complexes in the $^4T_{1g}(O_h)$ state with a standard redox potential of $E^\circ_{III/II}$. These cobalt(III) complexes can be excited to the $^1T_{1g}(O_h)$ state with excitation energy of $\sigma_{III^*/III}$. Hence, a standard redox potential of the couple of the cobalt(III) complex in the $^1T_{1g}$-(O_h) state/the cobalt(II) complex in the $^4T_{1g}(O_h)$ state, $E^\circ_{III^*/II}$, can be correlated to $E^\circ_{III/II}$ and $\sigma_{III^*/III}$ by a thermodynamic cycle for their standard Gibbs free energy changes:

$$\Delta G^\circ_{III^*/II} = \Delta G^\circ_{III/II} - \Delta G^\circ_{III^*/III} \qquad (1)$$

$$E^\circ_{III^*/II} = E^\circ_{III/II} + (N_A hc/F)\sigma_{III^*/III} \qquad (2)$$

Here, $\Delta G^\circ_{III^*/II}$ and $\Delta G^\circ_{III/II}$ are the standard Gibbs free energy changes corresponding to $E^\circ_{III^*/II}$ and $E^\circ_{III/II}$, $\Delta G^\circ_{III^*/III}$ is the standard Gibbs free energy change caused by electronic transition from the $^1A_{1g}$-(O_h) to the $^1T_{1g}(O_h)$ state, N_A is the Avogadro number, and h, c, and F have general meanings.

$E^\circ_{III/II}$ was estimated by cyclic voltammetry, which gave well-defined voltammograms with nearly equal anodic and cathodic peak currents and the peak potential difference (ΔE_p) ranging from 69–71 mV ($[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$) for the reversible electrode process to 135–143 mV ($[Co(dien)_2]^{3+}$) for the quasireversible process. $\sigma_{III^*/III}$ was determined from the electronic absorption spectra.These data are summarized in Table I. Comparison of $E^\circ_{III^*/II}$ and $E^\circ_{III/II}$ indicates that the cobalt(III) complex in the $^1T_{1g}(O_h)$ state is an electron acceptor more powerful than that in the $^1A_{1g}(O_h)$ state. Furthermore, comparison of $E^\circ_{III^*/II}$ reveals that an increase in chelate rings and incorporation of aromatic structure in the chelate ring results in

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an enhancement of electron acceptor characteristics of the cobalt(III) complex.

Based on these redox characteristics, stability constants of the cobalt(III) complexes in the $^1A_{1g}(O_h)$ and $^1T_{1g}(O_h)$ states were calculated according to the following relations:

$$\log \beta_{III} = \log \beta_{II} + (F/2.303RT)(E^\circ_{III(aq)/II(aq)} - E^\circ_{III/II}) \quad (3)$$

$$\log \beta_{III*} = \log \beta_{III} - (N_Ahc/2.303RT)(\sigma_{III*/III} - \sigma_{III*(aq)/III(aq)}) \quad (4)$$

Here, β_{II} is the stability constant of the cobalt(II) complex in the $^4T_{1g}(O_h)$ state, β_{III} and β_{III*} are the stability constants of the cobalt(III) complex in the $^1A_{1g}(O_h)$ and the $^1T_{1g}(O_h)$ states, $E^\circ_{III(aq)/II(aq)}$ is the standard redox potential of the $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$ couple, $\sigma_{III*(aq)/III(aq)}$ is the transition energy of $[Co(H_2O)_6]^{3+}$ from the $^1A_{1g}(O_h)$ to the $^1T_{1g}(O_h)$ state, and R is the gas constant. The data of β_{II} were taken from the literature, as given in Table I. $E^\circ_{III(aq)/II(aq)}$ and $\sigma_{III*(aq)/III(aq)}$ were also taken from the literature, to be

$E^\circ_{III(aq)/II(aq)} = 1.83$ V (*vs.* SHE) [9]

$\sigma_{III*(aq)/III(aq)} = 16500\ cm^{-1}$ [10]

The estimated stability constants of the cobalt(III) complexes are given in Table I, together with some literature data. The estimated data of β_{III} for $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and $[Co(edta)]^-$ in the present work are in good agreement with those given in the literature.

Comparison of the stability constants gives the general trend $\beta_{III} > \beta_{III*} > \beta_{II}$ corresponding to electronic states for the central metal atom of $(t_{2g})^6$, $(t_{2g})^5(e_g)^1$, and $(t_{2g})^5(e_g)^2$ respectively. This trend agrees with the order of the crystal field stabilization energy [11]. Hence, it may be concluded from the stability constants and electronic structure that the cobalt(III) complexes in the excited state are less stable and more labile, *i.e.*, more reactive, than in the ground state.

Finally, it should be pointed out for $[Co(N)_6]$ type complexes that the incorporation of aromatic structure into the chelate ring reduces the stability of the cobalt(III) complex more in the $^1T_{1g}(O_h)$ state than in the $^1A_{1g}(O_h)$ state. This may be due to contribution of antibonding character between the metal d and ligand π orbitals to the coordinate bond in the excited state.

TABLE I. Redox Potential and Stability Constant of Cobalt(III) Complexes in the $^1A_{1g}(O_h)$ and $^1T_{1g}(O_h)$ States.

Complex	$E^\circ_{III/II}$ [a] V *vs.* SHE	ΔE_p [b] mV	$\sigma_{III*/III}$ $10^3\ cm^{-3}$	$E^\circ_{III*/III}$ [c] eV	$E^\circ_{III*/II}$ V *vs.* SHE	$\log \beta_{II}$ [d]	$\log \beta_{III}$ [e]	$\log \beta_{III*}$ [e]
$[Co(NH_3)_6]^{3+}$	0.108 [9]	–	21.01	2.605	2.713	4.39(0, 20 °C) [12]	33.5 34.36(1.0, 30 °C) [12]	24.0
$[Co(en)_3]^{3+}$	-0.205	89[f]	21.32	2.644	2.439	14.1(1.4, 25 °C) [12]	48.5 48.7(1.4, 30 °C) [12]	38.4
$[Co(dien)_2]^{3+}$	-0.214	143[g]	21.69	2.690	2.476	14.77 [12]	49.3	38.4
mer-$[Co(dien)_2]^{3+}$	-0.200	135[f]	21.60	2.678	2.478	–	–	–
fac-$[Co(amp)_3]^{3+}$	0.022	95[f]	21.65	2.684	2.706	–	–	–
fac-$[Co(amq)_3]^{3+}$	0.143	90[f]	21.74	2.695	2.838	–	–	–
$[Co(bpy)_3]^{3+}$	0.305	69[g]	22.22	2.755	3.060	16.18 [12]	42.0	30.0
$[Co(phen)_3]^{3+}$	0.368	71[g]	22sh	2.73	3.10	19.8(0.1, 25 °C) [12]	44.5	33.0
cis(N)-$[Co(ida)_2]^-$	0.36 [13]	100 [13][f]	17.78	2.205	2.57	22.23(0.1, 25 °C) [12]	37.1	34.4
$[Co(edta)]^-$	0.37 [14]	–	18.60	2.306	2.68	16.26(0.1, 25 °C) [12]	40.9 41.4(0.1, 25 °C) [12] 40.6(0.2, 25 °C) [14]	36.5

[a] 1.0 mol dm^{-3} aqueous NaCl, 25 °C. [b] Scan rate, 100 mV s^{-1}. [c] $E^\circ_{III*/III} \equiv (N_Ahc/F)\sigma_{III*/III}$. [d] Ionic strength of 1.0 mol dm^{-3} and 25 °C unless otherwise specified. [e] 1.0 mol dm^{-3}, 25 °C. Log β_{III} and log β_{III*} were calculated to the first decimal place by taking significant figures of $E^\circ_{III(aq)/II(aq)}$ and no correction for ionic strength differences for β_{II}, whose precise correction is impossible, into consideration. [f] Hg electrode. [g] Pt electrode. sh, shoulder.

References

1 J. Bjerrum and J. P. McReynolds, *Inorg. Synth.*, *2*, 216 (1946).
2 J. B. Work, *Inorg. Synth.*, *2*, 221 (1946).
3 Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, *45*, 179 (1972).
4 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).
5 P. Pfeiffer and B. Werdelmann, *Z. Anorg. Allgem. Chem.*, *263*, 31 (1950).
6 Y. Hiramatsu, K. Okamoto, H. Einaga and J. Hidaka, to be submitted.
7 J. Hidaka, Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, *35*, 567 (1962).
8 S. Kirschner, *Inorg. Synth.*, *5*, 186 (1957).
9 G. Milazzo and S. Caroli, ed., 'Tables of Standard Electrode Potentials', Wiley, New York, 1978, p. 337.
10 C. K. Jørgensen, *Adv. Chem. Phys.*, *5*, 94 (1963).
11 A. F. Williams, 'A Theoretical Approach to Inorganic Chemistry', Springer, Berlin, 1979, p. 269.
12 A. E. Martell and R. M. Smith ed., 'Critical Stability Constants', Plenum Press, New York, vol. 1 (1974), vol. 2 (1975) and vol. 4 (1976).
13 R. A. Rader and D. R. McMillin, *Inorg. Chem.*, *18*, 545 (1979).
14 N. Tanaka and H. Ogino, *Bull. Chem. Soc. Jpn.*, *38*, 1054 (1965).