# ESR Studies of Unstable Six-coordinated Cobalt(II) Complexes Produced by γ-Radiolysis of Glassy Solutions at 77 K

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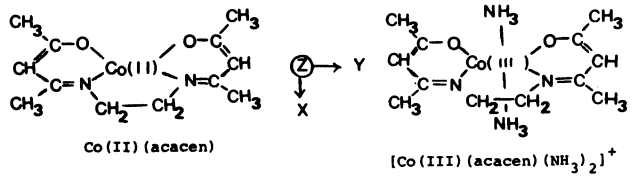
**Synopsis.** ESR spectra of γ-irradiated glassy solutions of cobalt(II) chelates of *N,N'*-bis(1-methyl-3-oxobutylidene)-ethylenediamine (acacen) having two $NH_3$ in the axial positions at 77 K show the formation of a metastable cobalt(II) complex in which two $NH_3$ are forced to be confined in the axial positions.

Fundamental researches on intra- and intermolecular electron transfer mechanisms of metal complexes are of great importance in relation to understanding of the redox reactions occurring in biological systems.[1-4] Numerous kinetics studies for the outer-sphere electron transfer between metal complexes have revealed that the complexes reorganize the ligand molecules with receiving or releasing electrons.[5-7]

Recently, unstable complexes having an anion in the axial position were reported to be formed by the radiation-chemical reduction of the metal complexes in rigid solutions at 77 K.[8-11] These complexes release the anions on warming the solution. In the present paper we wish to report the formation of an unstable six-coordinated complex, Co(II)(acacen)$(NH_3)_2$, having two neutral $NH_3$ molecules in the axial positions. The complex is considered to be an intermediate in the following reaction,

$$[Co(III)(acacen)(NH_3)_2]^+ + e^- \longrightarrow Co(II)(acacen) + 2NH_3, \quad (1)$$

where Co(II)(acacen) and Co(III)(acacen)$(NH_3)_2$ are represented, respectively, as




## Experimental

[Co(III)(acacen)$(NH_3)_2$]$^+$[$X^-$] (X=Cl and Br) was prepared according to the method reported by Costa *et al.*[12] Water was purified three times by distillation and ethylene glycol was used as supplied.

Radiolysis was performed with γ-rays from 1.2 kCi $^{60}Co$ source at 77 K at a dose rate of 57000 rad $min^{-1}$. ESR spectra were measured on a JEOL JES-FE-3AX X-band spectrometer.

## Results and Discussion

When a 1 : 1 mixture of ethylene glycol and water containing $10^{-3}$ M [Co(III)(acacen)$(NH_3)_2$]$^+$[$X^-$] was irradiated with γ-rays at room temperature, Co(II)-(acacen) was produced. As shown in reaction 1, this result indicates that [Co(III)(acacen)$(NH_3)_2$]$^+$ is reduced with electrons ejected from solvent molecules (S) upon γ-irradiation

$$S \longrightarrow S^{+\cdot} + e. \quad (2)$$

The use of a mixture of ethylene glycol and water in radiolysis has been applied to the selective formation of one-electron reduced species of solutes.[13]

The ESR spectrum *a* of Fig. 1 was observed for the γ-irradiated solution of [Co(III)(acacen)$(NH_3)_2$]$^+$[$Br^-$] at 77 K. Beside the intense signal from solvent radicals around 3250 gauss, four of the eight hyperfine lines due to the interaction of an unpaired electron and the cobalt nucleus ($I$=7/2) are clearly observed. The spectrum dramatically changed to *b* of Fig. 1 after warming the irradiated solution to room temperature and recooling it to 77 K. Since an authentic Co(II)-(acacen) solution shows an ESR signal identical with *b* of Fig. 1, it is evident that the reduced species giving the spectrum *a* of Fig. 1 produces Co(II)(acacen) at higher temperatures. The most probable structure of the species is Co(II)(acacen)$(NH_3)_2$ in which two $NH_3$ molecules are forced to be confined in the axial positions owing to the solvent rigidity at 77 K. The γ-radiolysis of a [Co(III)(acacen)$(NH_3)_2$]$^+$[$Cl^-$] solution gives the same ESR spectrum as *a* of Fig. 1. This result indicates that the anions, $Cl^-$ and $Br^-$, do not exert strong effect to the cobalt atom contrary to the case of constrained complexes.[8-10] Presumably, the anions are located far from the cobalt atom.

For preparing the solution of Co(II)(acacen)$(NH_3)_2$ using the reaction

$$Co(II)(acacen) + 2NH^3 \longrightarrow Co(II)(acacen)(NH_3)_2$$

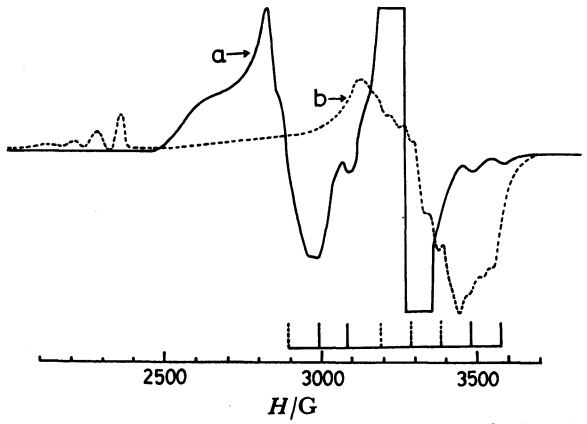



Fig. 1. ESR spectra of Co(II)(acacen) and Co(II)-(acacen)$(NH_3)_2$ in a 1 : 1 mixture of ethylene glycole and water at 77 K. a: ESR spectrum of Co(II)-(acacen)$(NH_3)_2$ obtained with γ-irradiating the solution of [Co(III)(acacen)$(NH_3)_2$]$^+$[$Br^-$] for 45 min at 77 K; b: ESR spectrum observed after warming the irradiated solution to room temperature and recooling it to 77 K.

Table 1. ESR parameters of Co(II)(acacen) and Co(II)(acacen)$(NH_3)_2$ in a 1 : 1 mixture of ethylene glycol and water at 77 K

| | $g_x$ [a] | $g_y$ [a] | $g_z$ | $A_x^{Co}$ [b] | $A_y^{Co}$ [b] | $A_z^{Co}$ [b] |
|---|---|---|---|---|---|---|
| Co(II)(acacen) | 3.157[c] | 1.930[c] | 2.006[c] | 110±5 | 36±2 | 36±2 |
| Co(II)(acacen)$(NH_3)_2$ | 2.3—2.5[d] | 2.3—2.5[d] | 2.023[c] | d) | d) | 90±4 |

a) x and y directions are arbitrary. b) Values are in units of $10^{-4}$ $cm^{-1}$. c) Experimental errors are 0.002. d) Values were not determined with precision because of poor resolution of the ESR spectrum.

Co(II)(acacen) was dissolved in ethanol saturated with $NH_3$ gass. However, the decomposition of Co(II)-(acacen) took place by dissolution and no formation of Co(II)(acacen)$(NH_3)_2$ was detected by ESR measurement. It is likely that the formation constant of Co(II)(acacen)$(NH_3)_2$ is very small.

In Table 1 are listed the ESR parameters of Co(II)-(acacen) and Co(II)(acacen)$(NH_3)_2$. The unpaired electron of Co(II)(acacen) has been established to be located in the $d_{z^2}$ orbital of the cobalt atom.[14-16] The **g** tensors are related to the excited state energies, $\Delta E(d_{yz} \rightarrow d_{z^2})$ and $\Delta E(d_{xz} \rightarrow d_{z^2})$, by equations[17]

$$g_x = 2.002 - 6k_x^2\lambda/\Delta E(d_{yz} \rightarrow d_{z^2}), \quad \text{(i)}$$

$$g_y = 2.002 - 6k_y^2\lambda/\Delta E(d_{xz} \rightarrow d_{z^2}), \quad \text{(ii)}$$

$$g_z = 2.002, \quad \text{(iii)}$$

where $\lambda$ is the spin-orbit coupling constant and $k_x$ and $k_y$, the orbital reduction parameters. The large in-plane $g$ anisotropy ($g_x \simeq 3$ and $g_y \simeq g_z \simeq 2$) of Co(II)(acacen) has been interpreted by assuming that the $d_{yz}$ lies closely below the $d_{z^2}$ and $d_{xz}$, far below.[14]

In contrast to Co(II)(acacen), the ESR spectrum of Co(II)(acacen)$(NH_3)_2$ indicates a nearly axial symmetry about the cobalt atom. The $d_{z^2}$ orbital probably interacts with the nonbonding orbitals of two $NH_3$ molecules in the axial positions. This interaction increases the $d_{z^2}$ orbital energy, resulting in a substantial decrease in the in-plane $g$ anisotropy as is predicted by equations i and ii. The reduction of out-of-plane puckering due to two $NH_3$ molecules would also has an effect on the decrease in the anisotropy as suggested in the case of Co(II)(acacen)(Py) (Py : pyridine).[14] Strict theories,[18,19] however, should be applied for complete understanding of the ESR spectrum of Co(II)(acacen)$(NH_3)_2$.

The present study shows that the unstable six-coordinated cobalt(II) complex produced after one-electron reduction undergoes reorganization and ejection of ligand molecules in the axial positions. This kind of unstable complexes should play an important role in the outer-sphere electron transfer of metal complexes as a reaction intermediate.

## References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