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Investigation on Low-spin Cobalt(II) Complexes. X. [1] An ESR Study on Six-coordinate Complexes

YUZO NISHIDA, KAZUHIKO IDA and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan

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ESR spectral measurements were carried out for several low-spin six-coordinate cobalt(II) complexes. Tetragonally compressed octahedral structures were assumed for some bis(terdentate) and tris*(bidentate) type complexes studied here.*

Introduction

Octahedral complexes of copper(II) ($3d^9$) and low-spin cobalt(II) ($3d^7$) are generally distorted from regular octahedron due to the Jahn–Teller effect. In almost all cases, copper(II) complexes assume tetragonally elongated octahedron with a small orthorhombic component superimposed [2, 3]. In some cases, however, tetragonally compressed copper(II) complexes exist. For example, copper(II) ion has such an environment when it is doped in a host lattice composed of complex ions with a compressed octahedral geometry [4, 5] such as $[CuCl_4(NH_3)_2]^{2-}$ [6]. Recently, ESR and crystal structural analysis of $[Cu(terp)]X_2$ and $[Co(terp)_2]X_2$ (terp = terpyridine, X = halide ions such as Cl^-, and Br^-, etc.) has shown that the rigid structure of the terdentate terpyridine induces a tetragonal compression of the MN_6 polyhedron [7–9].

For low-spin cobalt(II) complexes, however, only few ESR studies have been published concerning the distortion of octahedral coordination [10, 11]. In this study, in order to see the coordination geometry we have measured the ESR and electronic spectra of three different types of six-coordinated low-spin cobalt(II) complexes, such as (A): $[Co(dmg)_2B_2]$ (Hdmg = dimethylglyoxime, B = pyridine or imidazole), (B): $[Co(terdentate\ ligand)_2]I_2$, and (C): $[Co(bidentate)_3](PF_6)_2$. Of these complexes, it was found that B and C types are of compressed octahedral coordination.

Experimental

The six-coordinated cobalt(II) complexes used in this paper are classified into three types, (A), (B) and (C) (*cf.* Fig. 1).

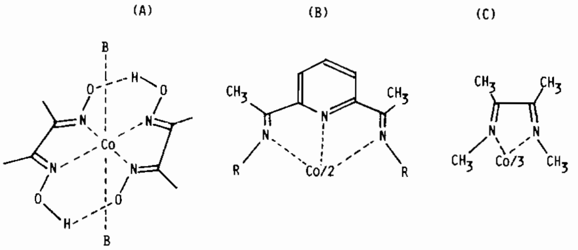

Fig. 1. The cobalt(II) complexes used in this study. (A): $[Co(dmg)_2B_2]$; (B): $[Co(dhap)_2]^{2+}$ (R = NH_2) and $[Co(dbap)_2]^{2+}$ (R = CH_2-C_6H_4); (C): $[Co(bmi)_3]^{2+}$.

TABLE I. Abbreviations of the Ligands Cited in This Paper.

Abbreviation	
py	pyridine
Hdmg	dimethylglyoxime
im	imidazole
dhap	2,6-diacetylpyridinebishydrazone
dbap	2,6-diacetylpyridinebisbenzylimine
bmi	diacetylbismethylimine
terp	terpyridine

(A): $[Co(dmg)_2B_2]$; Hdmg = dimethylglyoxime, B = pyridine and imidazole

The structures of these complexes are shown in Fig. 1. For the ESR measurements, these cobalt(II) complexes were diluted in the corresponding diamagnetic iron(II) complexes [12].

(B): Bis(terdentate) Type Complexes, $[Co(dhap)_2]I_2$ and $[Co(dbap)_2]I_2$ (cf. Fig. 1 and Table I)

These ligands, dhap and dbap, are illustrated in Fig. 1 and were obtained from the reaction mixture of 2,6-diacetylpyridine and hydrazine or benzylamine, according to Curry *et al.* [13]. We could not dilute these cobalt(II) complexes into the analogous iron(II) complexes. Therefore, ESR measurements of these complexes were carried out for DMF frozen solutions.

(C): Tris(bidentate) Type Complex, $[Co(bmi)_3](PF_6)_2$

The ligand, bmi, represents Schiff base derived from diacetyl and methylamine [14]. ESR measurement was performed for the diluted sample in the corresponding iron(II) complex.

ESR spectra of these complexes were measured with a JEOL ESR apparatus model MEX-3X at liquid nitrogen temperature. Electronic reflectance spectra were obtained with a Shimadzu multipurpose model MPS-5000 at room temperature.

Results and Discussion

From the studies of magnetic properties it was shown that $[Co(dhap)_2]I_2$, $[Co(dbap)_2]I_2$ and $[Co(bmi)_3]I_2$ are in spin-equilibrium of high-spin and low-spin at room temperature and are almost of low-spin type at the liquid nitrogen temperature [14–16].

In distorted octahedral low-spin cobalt(II) complexes, it is apparent that an unpaired electron resides in d_{z^2} or $d_{x^2-y^2}$ orbital. For these cases Maki *et al.* have given the following equations, taking spin–orbit coupling into consideration [17]:

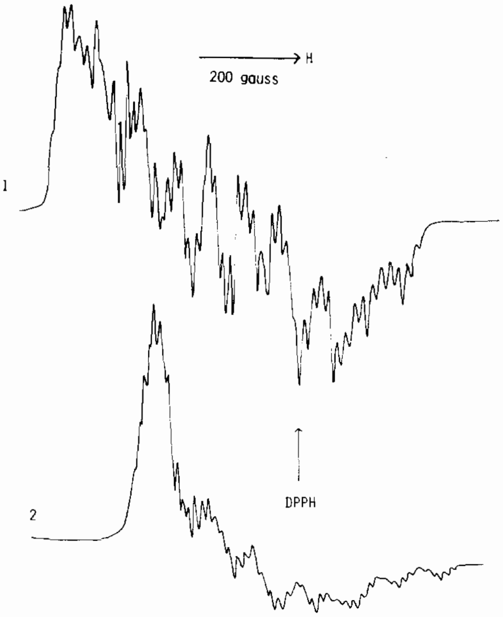

Fig. 2. ESR spectra of (A) type complexes (77 K). 1: $[Co(dmg)_2(im)_2]$; 2: $[Co(dmg)_2(py)_2]$.

For $(d_{x^2-y^2})^2(d_{z^2})^1$ configuration

$$g_\parallel = 2.0 \qquad a_1 = \frac{\zeta}{\Delta(z^2 - xz, yz)} \tag{1}$$

$$g_\perp = 2 - 6a_1 \tag{2}$$

For $(d_{z^2})^2(d_{x^2-y^2})^1$ configuration

$$g_\parallel = 2 - 8b_1 \qquad b_1 = \frac{\zeta}{\Delta(\{x^2 - y^2\} - xy)} \tag{3}$$

$$g_\perp = 2 - 2b_2 \qquad b_2 = \frac{\zeta}{\Delta(\{x^2 - y^2\} - xz)} \tag{4}$$

where ζ is the one-electron spin–orbit coupling constant of cobalt atom, and $\Delta(z^2 - xz)$, *etc.* represent the energy separation between $(d_{x^2-y^2})^2(d_{z^2})^1$ and $(d_{x^2-y^2})^2(d_{xz})^1$, *etc.*

In Fig. 2, the ESR spectra of (A) type complexes diluted in homologous iron(II) complexes are shown. These spectra are much more resolved compared with those in a frozen solution previously reported [18]. The spectrum of $[Co(dmg)_2(py)_2]$ is of a typical axial symmetry, and similar to spectra of cobalt(II) complexes whose ground state electronic configuration was established to be $(d_{x^2-y^2})^2(d_{z^2})^1$ [19–21]. The superhyperfine structure is observed in the $g_\parallel$ region. Five superhyperfine components for each ^{59}Co hyperfine component clearly indicate the axial coordination of pyridine molecules. The g values ($g_\parallel = 2.02$, $< g_\perp \sim 2.2$) well conform to equations (1) and (2), but not to equations (3) and (4) which predict $g_\parallel > g_\perp > 2.0$. Although $\Delta(z^2 - xz)$ is not estimated experimentally, the value $\Delta(z^2 - xz) = 16000\ cm^{-1}$ calculated from $g_\perp = 2.2$ and $\zeta = -510\ cm^{-1}$ according to (2) appears to be reasonable.

As seen in Fig. 2, $[Co(dmg)_2(im)_2]$ shows a little more complicated spectrum. This may be due to the fact that imidazole is stronger ligand than pyridine, so that the ligand field around cobalt atom is more isotropic for $[Co(dmg)_2(im)_2]$ than for $[Co(dmg)_2(py)_2]$. However, the ground state configuration of this complex should also be $(d_{x^2-y^2})^2(d_{z^2})^1$, because the general spectral pattern resembles that of $[Co(dmg)_2(py)_2]$, whereas it is entirely different from those of (B) and (C) type complexes whose ground state configuration was assigned to the $(d_{z^2})^2(d_{x^2-y^2})^1$ ground state (*vide infra*).

As obviously seen in Fig. 3, the ESR spectra of (B) type complexes are quite different from those of (A) type complexes. The relation $g_\parallel > g_\perp > 2.0$ is obviously seen for these spectra ($g_\parallel = 2.35$, and $g_\perp =$

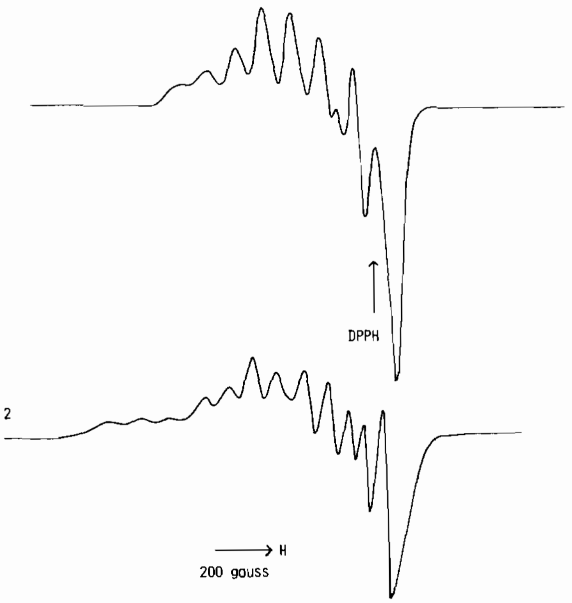

Fig. 3. ESR spectra of (B) type complexes (77 K). 1: [Co-(dhap)$_2$]I$_2$; 2: [Co(dbap)$_2$]I$_2$.

2.12 in the case of [Co(dbap)$_2$]I$_2$). This is compatible with the theoretical prediction (equations (3) and (4)) based on the $(d_{z^2})^2(d_{x^2-y^2})^1$ electronic configuration. Therefore, these complexes are of compressed octahedral coordination. It is to be noted that this is the first example of such symmetry for low-spin cobalt(II) complexes determined by use of ESR spectra. In order to examine the above conclusion, we have measured the ESR spectrum of [Cu-(dhap)$_2$]Cl$_2$ in a DMF frozen solution (*cf.* Fig. 4). The spectrum obtained is similar to that of [Cu-(terp)$_2$](NO$_3$)$_2$ [7], showing one g-component at $g \sim 2.0$ ($g_3 = 2.02$) which is indicative of $(d_{z^2})^1$ ground state [4, 6, 22]. This shows that the coordi-

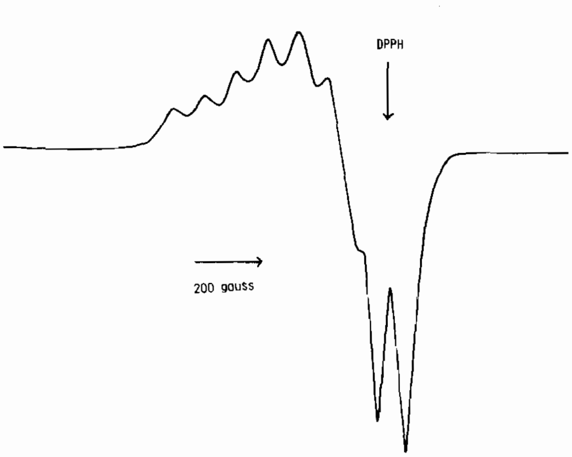

Fig. 5. ESR spectrum of [Co(bmi)$_3$](PF$_6$)$_2$ (77 K).

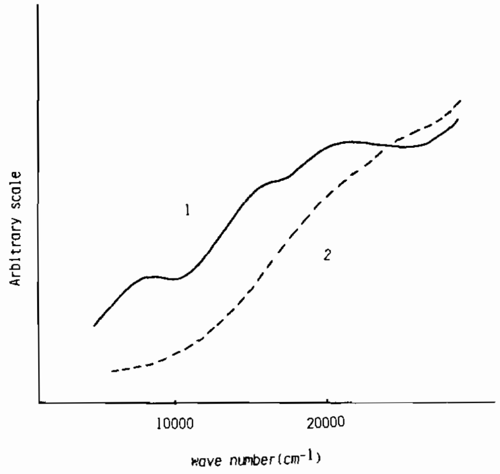

Fig. 6. Reflectance spectra of the cobalt(II) complexes 1: [Co(dhap)$_2$]I$_2$; 2: [Co(bmi)$_3$](PF$_6$)$_2$.

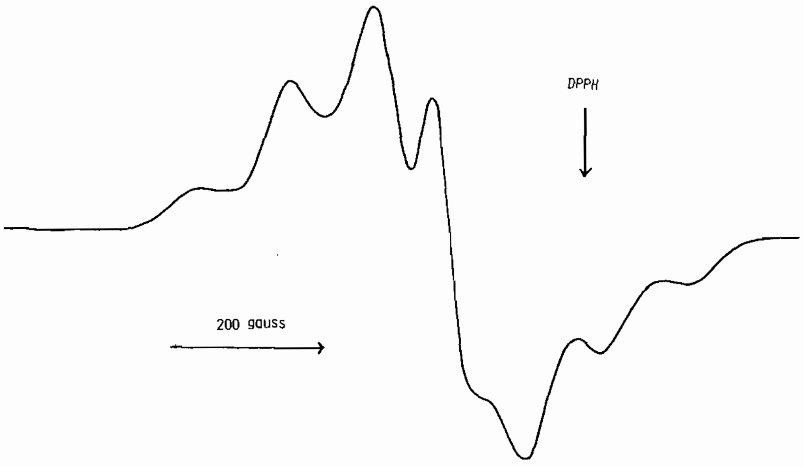

Fig. 4. ESR spectrum of [Cu(dhap)$_2$]Cl$_2$ (77 K).

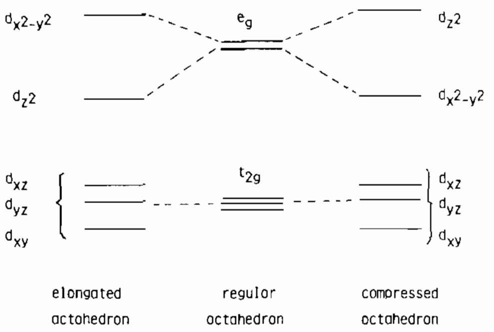

Fig. 7. Splitting scheme of d-orbitals in the distorted octahedron. 1: tetragonally compressed distortion. 2: tetragonally elongated distortion.

nation geometry of $[Co(dhap)_2]^{2+}$ and $[Cu(dhap)_2]^{2+}$ complexes are both compressed octahedron.

In Fig. 5, the ESR spectrum of $[Co(bmi)_3](PF_6)_2$ is shown. This is entirely different from those of (A) type complexes, but resembles those of (B) type complexes, and hence $(d_{z^2})^2(d_{x^2-y^2})^1$ configuration is expected for this complex. In Fig. 6, the electronic reflectance spectra of $[Co(dhap)_2]I_2$ and $[Co(bmi)_3](PF_6)_2$ are shown. Three absorption bands are observed for $[Co(dhap)_2]I_2$. These bands are assigned tentatively to the electronic transitions, $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{xz}, d_{yz}, d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz}, d_{xy} \rightarrow d_{z^2}$ for the bands at 8000, 16000 and 21000 cm^{-1}, respectively. Above assignments may be supported by the spectral study on $[Cu(terp)_2](NO_3)_2$ complex. For the latter complexes, two bands at 6550 and 14500 cm^{-1} were assigned to the $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{xz}, d_{yz}, d_{xy} \rightarrow d_{z^2}$, respectively [7] (*cf.* Fig. 7).

The spectrum of $[Co(bmi)_3](PF_6)_2$ shows no band in the near-infrared region ($5 \sim 10 \times 10^3$ cm^{-1}), and the band in the visible region is higher in energy than that of $[Co(dhap)_2]I_2$. This can be interpreted in terms of the smaller energy separation between d_{z^2} and $d_{x^2-y^2}$ orbital in $[Co(bmi)_3](PF_6)_2$ than that in $[Co(dhap)_2]I_2$.

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