Characterization and Spectral Properties of (7,8,16,17-Tetrahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecinato)cobalt(II)

KAZUNORI SAKATA* and MAMORU HASHIMOTO

Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804, Japan

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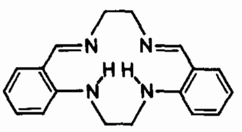
In connection with metal complexes of naturally occurring macrocycles, such as porphyrins and corrins, which play significant roles in biochemical metabolism, we have investigated metal complexes of synthetic macrocycles from the viewpoint of spectral properties [1]. The cobalt(II) complexes are of particular interest since we can often substitute these for hemoglobin and myoglobin complexes as oxygen carriers. Although the chemistry of dioxygen complexes of porphyrin and Schiff-base cobalt(II) complexes has been extensively studied [2], examples of cobalt dioxygen complexes of synthetic N_4-unsaturated macrocycles are rare. We reported the ESR spectrum of the cobalt dioxygen complex of a 16π-macrocyclic ligand, 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecine, in the presence of pyridine and O_2 at 77 K [1e].

In the present work, we employed the cobalt(II) complex (**1-Co**) of a N_4-macrocycle which changes a number of π-electrons placed in the interior molecular skeleton; a 12π-macrocyclic ligand, 7,8,15,16,17,18-hexahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecine (**1**). Green and Tasker reported only the synthesis of the cobalt(II) of **1** [3]. On account of the increasing interest in the chemistry of oxygen carriers in biological systems, we report here the characterization and the structural feature of the cobalt(II) complex of **1**, as examined by electronic, vibrational, ESCA and ESR spectroscopy. The characteristic behavior of the present 12π-macrocycle has been discussed in reference to the ligand property of the 16π-macrocycle.

Experimental

Spectral Measurements

A mass spectral measurement was carried out with a Shimadzu GCMS-9000 gas chromatograph–mass spectrometer at 70 eV. Electronic spectra covering the 12000–33000 cm^{-1} region were recorded on a Shimadzu UV-200S double beam spectrophotometer for *N,N*-dimethylformamide and pyridine solutions at room temperature. Infrared spectra in the range of 400–4000 cm^{-1} were measured with a JASCO IRA-2 grating spectrophotometer at room temperature, where a Nujol mull technique was adopted. ESCA spectroscopy was taken on a Du Pont 650B spectrometer using a Mg Kα irradiation unit. A signal due to Au 4f$_{5/2,7/2}$ was used for calibration. The ESR spectrum was performed on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The cobalt(II) complex was measured in *N,N*-dimethylformamide at 77 K, concentration being maintained at *ca.* 10^{-2} mol dm^{-3}. Manganese ion diffused into magnesium oxide was used to obtain the standard reference signals for all measurements.



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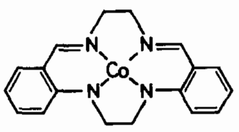

1 - Co

Preparation of Complexes

(7,8,16,17-Tetrahydrodibenzo[b,j][1,4,8,11]-tetraazacyclotetradecinato)cobalt(II) (1-Co)

The method of Green and Tasker [3] was modified for the preparation of this complex. 1,2-Ethanediamine (0.80 ml) dissolved in a mixed solvent composed of methanol (10 ml) and acetonitrile (10 ml) was added dropwise in 2 h to a mixture of cobalt(II) acetate tetrahydrate (0.80 g), 2,2′-(ethylenediimino)-dibenzaldehyde [4] (0.80 g), methanol (25 ml) and acetonitrile (25 ml) under reflux with stirring, while nitrogen was continuously bubbled through it. After the mixture was cooled down with ice-water, the precipitates were separated and washed three times with methanol (5 ml) and acetonitrile (5 ml) under a nitrogen atmosphere. The crystalline solid obtained was dried over phosphorus pentoxide *in vacuo* to give fine purple needles; yield 0.93 g (89%). *Anal.* Found: C, 61.67; H, 5.31; N, 16.07%; M^+, 349. Calc. for $C_{18}H_{18}N_4Co$: C, 61.89; H, 5.19; N, 16.04%; molecular weight 349.30.

Superoxo(7,8,16,17-tetrahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecinato)cobalt(II)

The color of (7,8,16,17-tetrahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**1-Co**) gradually turned dark purple on standing in the air at room temperature and the cobalt(III) complex was isolated. *Anal.* Found: C, 57.70; H, 5.12; N, 14.19%. Calc. for $C_{18}H_{18}N_4Co\cdot\frac{4}{5}O_2$: C, 57.66; H, 4.84; N, 14.94%.

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*Author to whom correspondence should be addressed.

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Results and Discussion

Electronic Spectra

The electronic absorption spectra covering the 15 000–33 000 cm^{-1} region are shown in Fig. 1 for (7,8,16,17-tetrahydrodibenzo[b,j] [1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**1-Co**). The absorption bands appearing in the energy range greater than 18 000 cm^{-1} are attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand as summarized in Table I. The reason for this conclusion is as hereunder. The molar extinction coefficients of the bands (10^3–10^4 mol^{-1} dm^3 cm^{-1}) are larger than those ordinarily assigned to $d \rightarrow d^*$ transitions [5]. A general spectral feature for **1-Co** in *N,N*-dimethylformamide is similar to those observed for the corresponding copper(II) and palladium(II) complexes [1a]. A low intensity band observed at 12 600 (ϵ 729) cm^{-1} is attributable to a ligand-field transition. This spectral behavior is consistent with a square-planar coordination. The electronic spectrum of **1-Co** did not undergo any significant change by changing the solvent from *N,N*-dimethylformamide to pyridine as shown in Fig. 1 and Table I. This fact shows that **1-Co** is no longer capable of binding an organic base at the axial site of the complex at room temperature. This spectral action differs from that observed for the cobalt(II) complex of the 16π-macrocycle already described by us [1d]. It may be pointed out that the difference in the extent of a π-conjugated system relates to the reactivity of an axial site in the cobalt(II) complex.

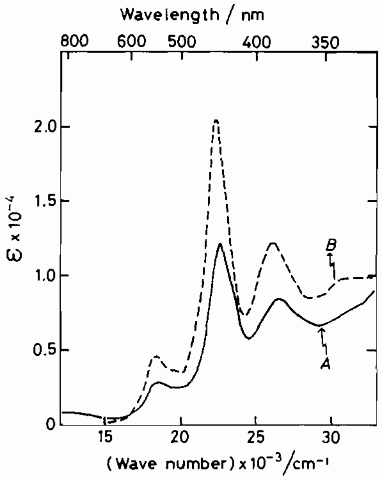

Fig. 1. Electronic absorption spectra for (7,8,16,17-tetrahydrodibenzo[b,j] [1,4,8,11]tetraazacyclotetradecinato)-cobalt(II) at room temperature: A, in *N,N*-dimethylformamide; B, in pyridine.

TABLE I. Characteristic Electronic Absorption Bands due to $\pi \rightarrow \pi^*$ and CT Transitions for (7,8,16,17-Tetrahydrodibenzo[b,j] [1,4,8,11] tetraazacyclotetradecinato)cobalt(II)[a]

Transition energy (cm^{-1}) (ϵ)	
N,N-Dimethylformamide	Pyridine
18600(2780)	18300(4640)
22600(12000)	22300(20400)
26500(8290)	26100(12200)

[a] The most intense band observed for metal-free ligand (**1**): 27800 cm^{-1} (ϵ 12700).

Vibrational Spectra

The characteristic IR bands are listed in Table II. A strong band due to the stretching mode of the C=N bond without metal coordination appears at 1623 cm^{-1}. The band is sensitive to metal coordination relative to other absorption peaks appearing in the 400–4000 cm^{-1} range and a spectral shift to lower frequency with respect to this band occurs upon formation of the cobalt(II) complex.

A strong band at 1063 cm^{-1} became observable for **1-Co** on standing in air. On the other hand, this strong band did not appear under a nitrogen atmosphere. We tentatively assign this band to an O–O stretching mode in a manner as observed for cobalt–dioxygen complexes [2f, h]. An O–O stretching frequency for the dioxygen complex of **1-Co** is similar to that obtained from $[Co(CN)_{10}(O_2)]^{-5}$ [2h]. Hence, this dioxygen complex is presumably a binuclear complex ($Co:O_2$ = 2:1) in a solid state.

Although allowed to stand for a long time in air, the 16π-macrocycle complex was not readily oxidized by atmospheric oxygen in a solid state owing to a π-conjugation effect more efficient than that for the macrocycle **1**.

ESCA Spectra

The present data are collected in Table III which contains the binding energies of carbon (C $1s_{1/2}$), nitrogen (N $1s_{1/2}$) and cobalt (Co $2p_{1/2}$, $2p_{3/2}$) together with those for 5,10,15,20-tetraphenylporphine, phthalocyanine and their cobalt(II) com-

TABLE II. Characteristic IR Absorption Bands for (7,8,16, 17-Tetrahydrodibenzo[b,j] [1,4,8,11]tetraazacyclotetradecinato)cobalt(II)[a]

Form	IR band (cm^{-1})	Assignment
Co–chelate	1515(m)	ν(C=C), (C=N) (macrocyclic skeletal)
	1599(s)	ν(C=N)
O_2–Co–chelate	1063(s)	ν(O–O)
	1528(w)	ν(C=C), (C=N) (macrocyclic skeletal)
	1601(s)	ν(C=N)

[a] Measured by a Nujol mull technique at room temperature. Relative intensities: s, strong; m, medium; w, weak.

TABLE III. Carbon 1s, Nitrogen 1s and Cobalt 2p Core-electron Binding Energies for Macrocycles and their Cobalt(II) Complexes[a]

Compound[b]	Binding energy (eV)				Reference
	C $1s_{1/2}$	N $1s_{1/2}$	Co $2p_{1/2}$	Co $2p_{3/2}$	
C atom	285				6
N atom		399			6
1	283.8	397.5			1a
1-Co	283.5	397.3	793.9	778.2	
H_2TPP	284.8	398.2, 400.2			7
CoTPP		397.2		778.8	8
H_2PC	284.8, 286.2	398.9, 400.4			7
CoPc		399.3			9

[a] Measured in the tablet state (5 mm diameter); for calibration, the signal of Au $4f_{5/2}$ and Au $4f_{7/2}$ was used. [b] **1**, 7,8,15,16,17,18-Hexahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecine; **1**-Co, (7,8,16,17-tetrahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecinato)cobalt(II); H_2TPP, 5,10,15,20-tetraphenylporphine; CoTPP, 5,10,15,20-tetraphenylporphinatocobalt(II); H_2PC, phthalocyanine; CoPC, phthalocyaninatocobalt(II).

plexes [7–9]. We find only one nitrogen 1s peak for **1** and **1-Co** as shown in Table III. This behavior suggests that the four nitrogen atoms of the macrocycle always become chemically identical and is different from that observed for the cobalt(II) complexes of the 16π-macrocycle, 5,10,15,20-tetraphenylporphine and phthalocyanine.

ESR Spectra

The ESR spectrum for (7,8,16,17-tetrahydrodibenzo[b,j][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II) (**1-Co**) in *N,N*-dimethylformamide containing pyridine and O_2 at 77 K is shown in Fig. 2. In this spectrum, a set of eight hyperfine lines on the parallel component of the g tensor ($g_\parallel$) was observed at low field. On the other hand, a set of hyperfine lines due to the perpendicular component of the g tensor ($g_\perp$) at high field was not plainly resolved. An analogous spectral feature has also been observed for the dioxygen complex of the 16π-macrocycle cobalt-(II), namely, (7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**2-Co**) [1e]. The present ESR spectral pattern is in agreement with the production of a monomeric dioxygen cobalt complex of a 1:1 molar ratio. The spin Hamiltonian parameters with those for a reference complex are compiled in Table IV. The superhyperfine lines based upon nitrogen donor atoms were not observed over the whole field region. The $g_\parallel$ value of the cobalt dioxygen complex is influenced by the character of the equatorial ligand. The isotropic hyperfine splitting constant ($\bar{A}^{Co}$) is immediately in proportion to

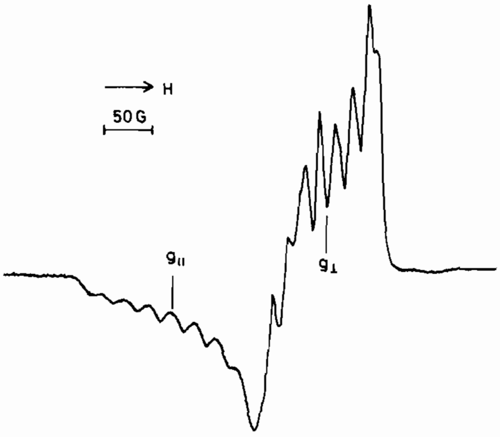

Fig. 2. ESR spectrum for (7,8,16,17-tetrahydrodibenzo[b,j]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(II) in *N,N*-dimethylformamide containing pyridine and O_2 at 77 K.

TABLE IV. Spin Hamiltonian Parameters for Macrocycle Cobalt(II) Complexes Containing Pyridine and O_2 at 77 K[a]

Complex[b]	$g_\parallel$	$g_\perp$	$A_\parallel^{Co} \times 10^4$ (cm^{-1})	$A_\perp^{Co} \times 10^4$ (cm^{-1})	$\bar{A}^{Co} \times 10^4$ [c] (cm^{-1})	Reference
1-Co	2.085	1.999	20.1	13.1	15.4	
2-Co	2.076	1.999	18.1	12.4	14.3	1e

[a] Maximum possible errors: g, ±0.005; $A_\parallel^{Co}$, $\pm 0.5 \times 10^{-4}$ cm^{-1}; $A_\perp^{Co}$, $\pm 0.5 \times 10^{-4}$ cm^{-1}. [b] See Table III for symboling the complex 1-Co; 2-Co, (7,16-diethyl-(*E*)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II). [c] Calculated from $\bar{A}^{Co} = 1/3(A_\parallel^{Co} + 2A_\perp^{Co})$.

the spin density on the cobalt nucleus. As for the equatorial ligand effect on $\bar{A}^{\mathrm{Co}}$, the dioxygen complex of **1-Co** affords a larger $\bar{A}^{\mathrm{Co}}$ value than that of **2-Co** with a pyridine base, as shown in Table IV. This indicates that the electron density on the cobalt nucleus is susceptible to change by varying the extent of π-conjugation in the equatorial ligand and is inclined to decrease as the π-conjugation is increased.

In conclusion, **1-Co** has no further ability for binding pyridine at the axial site of the complex at room temperature. Being permitted to stand in air, **1-Co** was readily oxidized by atmospheric oxygen in a solid state and is presumable a binuclear complex ($Co:O_2 = 2:1$) in a solid state. **1-Co** becomes the monomeric dioxygen complex of a 1:1 molar ratio in the presence of O_2 at 77 K. In the dioxygen complex, the electron density of the cobalt nucleus is subjected to change by varying the extent of π-conjugation in the equatorial ligand.

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