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Preparation and Characterization of a Cyanocobalt(III) Complex with Tetraaza[14]annulene

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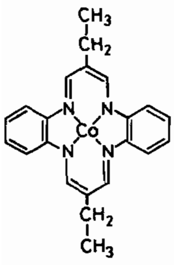
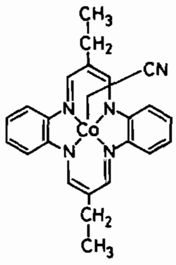
Though the chemistry of cobalt(III)–porphyrin and cobalt(III)–corrin complexes has been extensively investigated up to the present time owing to their biochemical interest [1], instances of synthetic macrocyclic ligand complexes to cobalt(III) are rare. Deger *et al.* simply presented the synthesis and X-ray diffraction study for cyano(dibenzo[b,i][1,4,8,11]-tetraazacyclotetradecinato)cobalt(III) without the research of spectral properties [2]. We have also studied oxovanadium(IV), isothiocyanatomanganese(III) and chloroiron(III) complexes of unsaturated N_4-macrocycles which are pentacoordinated by having ligands in the axial position [3–5].

In the present work, we prepared two cobalt complexes of the unsaturated N_4-macrocyclic tetraaza[14]annulene ligand; (7,16-diethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**Co(1)**) and cyano(7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecinato)cobalt(III) (**Co(1-CN)**). We characterized the spectral properties for the cobalt(II) and the cyanocobalt(III) complexes of the present macrocycle by the use of vibrational, electronic and NMR spectroscopy.



Co(1)



Co(1-CN)

Kosower reported that the *Z* value was established as an empirical measure of solvent polarity based on the transition energy for the charge transfer (CT) band of the 1-ethyl-4-methoxycarbonylpyridinium iodide complex in a variety of solvents [6]. Murakami *et al.* also studied the solvent effect for the CT transition of the dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III) [1a]. Since there is no systematic research of the solvent effect for the CT transition of cobalt(III)–tetraaza[14]annulene complexes, we report the solvent effect of the CT transition for the cyanocobalt(III) complex in the 530–560 nm range, too.

Experimental

Physical Measurements

EI mass spectrum (at 70 eV) of the cobalt(II) complex and FD mass spectrum (at 6 kV for cathode and at 33 mA for emitter) of the cyanocobalt(III) complex were obtained on a Jeol JMS-DX 300 gas chromatograph–mass spectrometer. Infrared spectra in the 400–4000 cm^{-1} range were carried out with a Hitachi 260-10 spectrophotometer at room temperature by a KBr disk method. Proton NMR measurements were taken on a Jeol JNM-FX 60 spectrometer operating in the Fourier transfer mode. The NMR spectra were measured in pyridine-d_5 and chemical shifts are given in ppm from tetramethylsilane as an internal reference standard. Ultraviolet and visible spectra covering the 12 500–35 000 cm^{-1} region were performed on a Shimadzu UV 200S double beam spectrophotometer at room temperature.

Preparation of the Macrocycle

5,14-Dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine (1)

The synthetic procedure for **1** has been reported previously [5].

Preparation of the Cobalt Complex

(7,16-Diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co(1))

After a 0.87 g sample of cobalt(II) acetate tetrahydrate dissolved in *N,N*-dimethylformamide (15 ml) was added dropwise with stirring for 1 h at 110 °C into a mixture of **1** (1.00 g) and *N,N*-dimethylformamide (8 ml), the reaction mixture was heated under reflux for 4 h with stirring. Upon cooling the mixture with ice-water, the crystalline solid was recovered by filtration, washed twice with methanol (10 ml) and recrystallized from *N,N*-dimethylformamide to give navy blue needles; yield 0.89 g (76%), melting point > 300 °C. The mass spectrum showed M^+ at m/z 401 and peaks for $[M-CH_3]^+$ and $[M-2CH_3]^+$ at m/z 386 and 371, respectively. IR (KBr disk): 1641 (C=C str.), 1597 (C=C str. (conjugated ring)) and 1466 cm^{-1} (macrocyclic

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skeletal str.). *Anal.* Found: C, 65.48; H, 5.61; N, 13.96. Calc. for $C_{22}H_{22}N_4Co$: C, 65.83; H, 5.52; N, 13.96%.

Cyano(7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(III) (Co(1-CN))

A mixture of **Co(1)** (0.20 g), sodium cyanide (0.55 g) and acetone (150 ml) was heated under reflux for 7 h while air was continuously bubbled through it and then concentrated to one tenth of the volume. The concentrate was applied to the top of a chromatographic column of activated alumina (Wako Pure Chemical Industries, Ltd.) and eluted with acetone. The second effluent was evaporated to dryness *in vacuo* to obtain navy blue needles; yield 0.09 g (48%), melting point > 300 °C. The mass spectrum showed M^+ at m/z 427 and the peak for $[M - Co - CN + 2H]^+$ at m/z 344. IR (KBr disk): 2112 (C≡N str.), 1590 (C=N str. (conjugated ring)) and 1429 cm^{-1} (macrocyclic skeletal str.). *Anal.* Found: C, 64.69; H, 5.32; N, 16.27. Calc. for $C_{23}H_{22}N_5Co$: C, 64.62; H, 5.20; N, 16.39%.

Results and Discussion

Mass Spectra

Mass spectra data for the cobalt(II) and the cyanocobalt(III) complexes are given in 'Experimental'. The EI mass spectrum for the cobalt(II) complex indicates the existence of a molecular ion M^+ at m/z 401 which becomes the base peak in the mass spectrum. The masses for the major fragment at m/z 386 and 371 correspond to $[M - CH_3]^+$ and $[M - 2CH_3]^+$, respectively. When the cyanocobalt(III) complex was analyzed using the EI mass spectrum, the complex did not exhibit a molecular ion but a cluster of ions corresponding to $[M - CN]^+$. On the other hand, the FD mass spectrum for the cyanocobalt(III) complex shows the presence of a molecular ion M^+ at m/z 427 that is the base peak. The mass of the fragment ion at m/z 344 is equivalent to $[M - Co - CN + 2H]^+$.

Vibrational Spectra

The cyanocobalt(III) complex shows a strong absorption band at 2112 cm^{-1} which is attributed to the C≡N stretching mode of the coordinated CN group. The C≡N stretching band for this complex is given in Table I together with the comparable data for CN^-(free), $K_3[Co(CN)_6]$, $Co(TDHC)(CN)_2$ and Co(DBTA)(CN) [1a, 2, 7, 8]. The C≡N stretching frequency of free CN^- anion is 2080 cm^{-1} [7]. Upon coordination to the cobalt(III), the C≡N stretching band shifts to higher frequency, as shown in Table I. The CN^- ion functions as a σ-donor by donating electrons to the metal and also as a π-acceptor by accepting electrons from the metal. σ-Donation is inclined to increase the C≡N stretching frequency because electrons are removed from the 5σ orbital, which is weakly antibonding, while π-back-bonding is inclined to decrease the C≡N stretching frequency since the electrons enter into the antibonding 2pπ* orbital. Hence the CN^- ion is a better σ-donor and a poorer π-acceptor than CO. The CN^- group of the cyanocobalt(III) complex acts as a σ-donor, because the C≡N stretching frequency of this complex is higher than the value for free CN^-.

TABLE I. Vibrational Frequencies of Cyanocobalt(III) Complexes (cm^{-1})

Complex[a]	ν(C≡N)	Reference
CN^-(free)	2080[b]	7
Co(1-CN)	2112	this work
$K_3[Co(CN)_6]$	2129	8
$Co(TDHC)(CN)_2$	2128	1a
Co(DBTA)(CN)	2116	2

[a] **Co(1-CN)**, cyano(7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(III); $Co(TDHC)(CN)_2$, dicyano-(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III); Co(DBTA)(CN), cyano(dibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(III). [b] Aqueous solution.

NMR Spectra

Proton NMR data and their assignments for the macrocycle and the cyanocobalt(III) complex are collected in Table II. Upon cobalt(III) coordination the signal for the amine proton was found to fade away and the methine proton signal obtained in the lowest field for the macrocycle turned out to be a singlet from a doublet on account of the absence of coupling with an amine proton. Moreover, the methine proton peak is shifted upfield by 0.31 ppm on complex formation. The abnormal upfield shift may result from the shielding effect caused by the magnetic anisotropy of the coordinated pyridine ring in a solvent of pyridine.

Electronic Spectra

The visible and ultraviolet spectra covering the 12 500–35 000 cm^{-1} region are shown in Fig. 1 for the cobalt(II) and the cyanocobalt(III) complexes of 5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine. The absorption bands observed above 15 000 cm^{-1} range are reasonably attributed to π → π* transitions within a ligand molecule and CT transitions from metal to ligand and not to d → d* transitions in the cobalt complexes since the molar extinction coefficients of these bands ($10^3 \sim 10^4$ mol^{-1} dm^3 cm^{-1}) are larger than those normally assigned to d → d* transitions [9].

Compared with the cobalt(II) complex, the cyanocobalt(III) complex was observed to indicate a strong

TABLE II. Proton NMR Data for the Macrocycle and the Cyanocobalt(III) Complex[a]

Compound	Ethyl		Aromatic	Methine $-CH=N-(=CH-NH-)$	Amine $-N-H$
	CH_3-CH_2-	CH_3-CH_2-			
1	1.09(t, J = 7.6 Hz)	2.22(q, J = 7.6 Hz)	6.8–7.4(m)	7.85(d, J = 5.9 Hz)	14.04(t, J = 5.9 Hz)
Co(1-CN)	1.11(t, J = 7.3 Hz)	2.24(q, J = 7.3 Hz)	6.6–7.5(m)	7.54(s)	

[a]Chemical shifts are given in ppm for TMS as an internal reference. Multiplicity of a proton signal is given in parentheses after the δ value; s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Measured in pyridine-d_5.

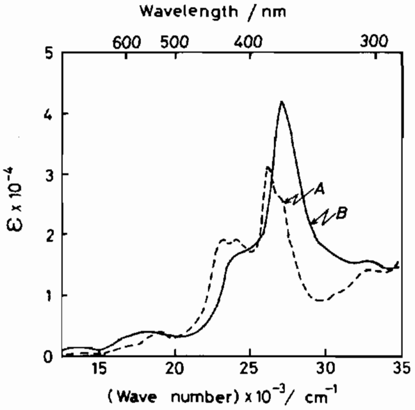

Fig. 1. Electronic spectra for 5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine cobalt complexes in chloroform at room temperature: A, cobalt(II) complex; B, cyanocobalt(III) complex.

absorption band in a longer wavelength range such as λ_{max} 549 nm with $\epsilon = 4.03 \times 10^3$ mol^{-1} dm^3 cm^{-1} in chloroform. This band is attributable to the intramolecular CT transition with which the Co–CN bond is associated, because the transition energy is moderately sensitive to the solvent nature as given in Table III. In addition, the behavior of the present cyanocobalt(III) complex is similar to that observed for isothiocyanatomanganase(III) and chloroiron(III) complexes of tetraaza[14]annulenes [4, 5]. The transition energy (E_T, kcal mol^{-1}) is thoroughly concerned with a solvent polarity parameter (Z value), as shown in Fig. 2, though finding no linear relationship with the solvent dielectric constant (D value). The Z value was confirmed as an experimental measure of solvent polarity based on the CT band of the 1-ethyl-4-methoxycarbonylpyridinium iodide complex in a variety of solvents, by Kosower [6]. The transition energy for the CT band of the pyridinium iodide complex measures the extent of its interaction with a cybotactic range of a solvent. Accordingly, the present absorption band is assigned to the intramolecular CT transition and the present finding is very useful for examining the character of a coordinate bond.

In conclusion, the cyanocobalt(III) complex has the pentacoordination structure in the trivalent state of the nuclear cobalt and maintains a low-spin d^6 ($S = 0$) state as judged by NMR data. In the infrared spectrum, the prominent absorption peak which has been observed at 2112 cm^{-1} is associated with the C≡N stretching mode and the CN group coordinates the cobalt through the carbon judging from the C≡N stretching frequency. A strong absorption band in the 530–560 nm region is assigned to the intramolecular CT transition correlated to the Co–CN bond.

TABLE III. Solvent Effects on CT Bands for the Cyanocobalt(III) Complex (Co(1-CN))

Solvent	Z value[a]	E_T [b] (kcal mol^{-1})
1,2-$Cl_2C_6H_4$	60.0	51.8
$CHCl_3$	63.2	52.2
$ClCH_2CH_2Cl$	63.9	52.2
CH_2Cl_2	64.2	52.4
$(CH_3)_2CO$	65.7	52.4
$(CH_3)_2NCHO$	68.5	52.5
CH_3CN	71.3	52.8
C_2H_5OH	79.6	53.4

[a]Cited from ref. 6a. [b]Calculated from E_T (kcal mol^{-1}) = $2.859 \times 10^5/\lambda_{max}$ (in Å).

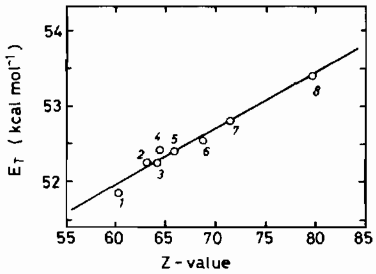

Fig. 2. Correlation between CT transition energy of cyanocobalt(III) complex and solvent polarity parameter (Z value): 1, 1,2-dichlorobenzene; 2, chloroform; 3, 1,2-dichloroethane; 4, dichloromethane; 5, acetone; 6, N,N-dimethylformamide; 7, acetonitrile; 8, ethanol.

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