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# Preparation and Axial Ligation Behavior of Cyano(7,16-diethyl-(*E*)- or -(*Z*)-dipyrido[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(III)

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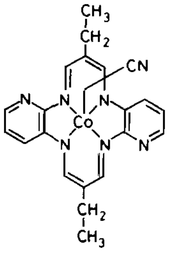
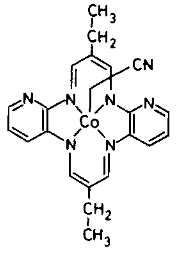
Although axial-ligation equilibria for porphyrin and corrinoid metal(II) complexes have been investigated extensively on account of their biochemical interest [1], little has been reported on the use of synthetic unsaturated $N_4$-macrocyclic cobalt(III) complexes.

The interaction of various organic bases with (dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II) has been studied [2]. The cobalt(II) complex was found to take up one amine base in its axial position, but was unable to form the corresponding hexa-coordinated complex in which both axial positions are occupied by amines.

In the present work, we prepared two cobalt(III) complexes of the unsaturated $N_4$-macrocycles: cyano(7,16-diethyl-(*E*)-dipyrido[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)cobalt(III) (Co(1-E)CN) and cyano(7,16-diethyl-(*Z*)-dipyrido[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)cobalt(III) (Co(1-Z)CN). Because of increasing interest in vitamin $B_{12}$ chemistry in biological systems, we report here the structural features of Co(1-E)CN and Co(1-Z)CN as examined by mass, electronic, vibrational and NMR spectroscopy. We also show that the penta-coordinated cyanocobalt(III) complexes Co(1-E)CN and Co(1-Z)CN form hexa-coordinated complexes with amine bases at their axial positions *trans* to the cyano group. The axial cyano ligand effect on the axial coordination behavior is effectively discussed by reference to those of the macrocyclic cobalt(II) complexes.



Co(1–E)CN



Co(1–Z)CN

## Experimental

### General Information

FD (field desorption) mass spectra were determined on a JEOL JMS-DX 300 gas chromatograph–mass spectrometer at 6 kV for the cathode and at 27 mA for the emitter. Infrared spectra in the range of 400–4000 $cm^{-1}$ were obtained on a Hitachi 260-10 spectrophotometer at room temperature, using a KBr disk method. Proton NMR measurements were recorded in the pulsed Fourier transform mode on a JEOL JNM-FX 60 spectrometer. The NMR spectra were run in dimethyl sulfoxide-$d_6$ ($D > 99.8\%$; Merck, Darmstadt) at 100 °C and in pyridine-$d_5$ ($D > 99.8\%$; Merck, Darmstadt) at room temperature; chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard. Electronic spectra covering the 15 000–35 000 $cm^{-1}$ range were carried out with a Shimadzu UV-200S double beam spectrophotometer at 25.0 ± 0.1 °C. 1,2-Dichloroethane as a solvent for spectroscopic measurements was prepared by the standard procedure [3]. Commercial liquid amines (pyridine, 2-methylpyridine, 4-methylpyridine and 2,6-dimethylpyridine) were refluxed with potassium hydroxide and then fractionally distilled. Commercially available solid amines (4-cyanopyridine and 4-aminopyridine) were recrystallized from aqueous ethanol and benzene, respectively. Melting points were observed on a Yamato hot-stage apparatus.

### Preparation of Macrocyclic Ligands

#### 5,14-Dihydro-7,16-diethyl-(E)-dipyrido[b,i]-[1,4,8,11]tetraazacyclotetradecine (1-E) and 5,14-dihydro-7,16-diethyl-(Z)-dipyrido[b,i]-[1,4,8,11]tetraazacyclotetradecine (1-Z)

Ligands of 1-E and 1-Z were synthesized as previously described [4].

### Preparation of Cobalt(II) and Cyanocobalt(III) Complexes

#### (7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]-tetraazacyclotetradecinato)cobalt(II) (Co(1-E)) and (7,16-diethyl-(Z)-dipyrido[b,i][1,4,8,11]-tetraazacyclotetradecinato)cobalt(II) (Co(1-Z))

Complexes of Co(1-E) and Co(1-Z) were prepared as previously reported [4].

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

Air was bubbled through a mixture of Co(1-E) (0.276 g), sodium cyanide (0.765 g) and acetone (150 ml) which was refluxed for 7 h. The reaction mixture was concentrated to *c.* 10 ml *in vacuo*. The concentrate was chromatographed on activated alumina column (200 mesh, Wako Pure Chemical Industries) and eluted with acetone. The second effluent was collected and evaporated to dryness under reduced pressure. The residue was recrystallized from benzene to give dark blue prisms; yield 0.035 g (12%), melting point >300 °C. The mass spectrum showed $M^+$ at *m/z* 429. IR (KBr disk): 2120 (C≡N str.), 1595 (C=N str. (conjugated ring)) and 1397 $cm^{-1}$ (macrocyclic skeletal str.). *Anal.* Found: C, 58.34; H, 4.50; N, 22.52. Calc. for $C_{21}H_{20}N_7Co$: C, 58.74; H, 4.70; N, 22.84%.

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

The reaction of Co(1-Z) (0.201 g) and sodium cyanide (0.488 g), following the above procedure, gave navy-blue prisms; yield 0.088 g (41%), melting point >300 °C. The mass spectrum showed $M^+$ at *m/z* 429. IR (KBr disk): 2120 (C≡N str.), 1596 (C=N str. (conjugated ring)) and 1390 $cm^{-1}$ (macrocyclic skeletal str.). *Anal.* Found: C, 58.49; H, 5.03; N, 22.56. Calc. for $C_{21}H_{20}N_7Co$: C, 58.74; H, 4.70; N, 22.84%.

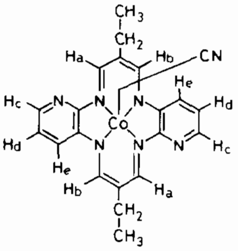
## Results and Discussion

### *Synthesis of Cyanocobalt(III) Complexes*

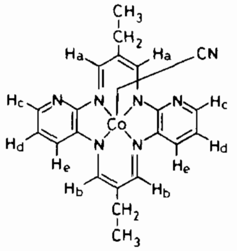
Elemental analyses of crystalline samples of Co(1-E)CN and Co(1-Z)CN were in fair agreement with compounds for the formula cyanocobalt(III) complexes, respectively. The two cyanocobalt(III) complexes showed mass spectra with the prominent parent peak at mass number 429, which was observed to have the same characteristic structure as that of $[Co(1\text{-}E)]^+$ or $[Co(1\text{-}Z)]^+$ shifted by 26 mass units to higher numbers. Consequently, this peak was assigned to $[Co(1\text{-}E)CN]^+$ or $[Co(1\text{-}Z)CN]^+$. The infrared spectrum of Co(1-E)CN and Co(1-Z)CN determined in a potassium bromide disk gave a strong band at 2120 $cm^{-1}$, which was attributed to the C≡N stretching mode [5].

### *NMR Behavior of Cyanocobalt(III) Complexes*

NMR data and their assignments for the cyanocobalt(III) complexes are summarized in Table 1. The shift positions of proton signals appearing in the 1.0–9.5 ppm range depend strongly on the solvent used for the NMR measurements. The proton signals for the methine $H_a$ and $H_b$ are shifted upfield by 0.87–1.21 ppm on transition from dimethyl sulfoxide-$d_6$ to pyridine-$d_5$. The proton signals of the aromatic $H_c$, $H_d$ and $H_e$ suffer an upfield shift of 0.71–0.90 ppm and the proton signals of the 7- and 16-ethyl groups suffer an upfield shift of 0.23–0.44 ppm in a similar manner as above. This unusual upfield shift suggests that in a solvent such as pyridine, the pyridine is coordinated to the cobalt atom at the axial site *trans* to the cyano group of the cyanocobalt(III) complex. Such coordination leads to predominantly upfield shifts, as observed, because of the shielding effect of the anisotropy of the magnetic susceptibility of pyridine.



Co(1–E)CN



Co(1–Z)CN

### *Interaction between Cyanocobalt(III) Complexes and Pyridine Bases*

The electronic spectra for the cyanocobalt(III) complexes were measured by changing the concentration of pyridine bases in a wide range (10–$10^4$-fold amounts relative to Co(1-E)CN or Co(1-Z)CN), while the concentration of Co(1-E)CN or Co(1-Z)CN was maintained constant ($\simeq 2 \times 10^{-5}$ mol $dm^{-3}$). The spectral changes of Co(1-E)CN upon addition of 4-methylpyridine are shown in Fig. 1 as an example, where isosbestic points are observed at 310, 455 and 590 nm. Since the spectral features are substantially identical to those of the pyridine adduct, it is assumed that Co(1-E)CN becomes hexa-coordinated by having a pyridine base in the axial position *trans* to the cyano group as the sixth ligand. The effect of pyridine concentration on the spectral change was in agreement with the following equilibrium

$$\mathrm{CoLCN} + \mathrm{B} \overset{K}{\rightleftharpoons} \mathrm{BCoLCN} \qquad (1)$$

where CoLCN and B stand for Co(1-E)CN or Co(1-Z)CN and a pyridine base, respectively. The unit slope for the plots of log([BCoLCN]/[CoLCN] versus log[B] is further evidence for the 1:1 complex formation for each of the pyridine ligands which were treated. The equilibrium constants (*K*) were obtained from the intensity change at 364 nm by using the Benesi–Hildebrand-type relation, as previously described [2]. Equilibrium constants for other pyridines and Co(1-Z)CN were obtained in a similar

TABLE 1. Proton NMR data for the cyanocobalt(III) complexes[a]

| Complex | Ethyl | | Aromatic | | | Methine | | Solvent |
|---|---|---|---|---|---|---|---|---|
| | $-CH_3$ | $-CH_2-$ | $-H_c$ | $-H_d$ | $-H_e$ | $-H_a$ | $-H_b$ | |
| Co(1-E)CN | 1.09(t)<br>($J$ = 7.3 Hz) | 2.26(q)<br>($J$ = 7.3 Hz) | 7.86(dd)<br>($J$ = 4.7 Hz)<br>($J$ = 1.4 Hz) | 6.62(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 4.7 Hz) | 7.69(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 1.4 Hz) | 8.48(s) | 7.68(s) | pyridine-$d_5$ |
| | 1.36(t)<br>($J$ = 7.3 Hz) | 2.70(q)<br>($J$ = 7.3 Hz) | 8.71(dd)<br>($J$ = 4.7 Hz)<br>($J$ = 1.4 Hz) | 7.36(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 4.7 Hz) | 8.45(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 1.4 Hz) | 9.35(s) | 8.89(s) | dimethyl sulfoxide-$d_6$ |
| Co(1-Z)CN | 1.14(t)<br>($J$ = 7.3 Hz)<br>1.05(t)<br>($J$ = 7.5 Hz) | 2.30(q)<br>($J$ = 7.3 Hz)<br>2.24(q)<br>($J$ = 7.5 Hz) | 7.84(dd)<br>($J$ = 4.7 Hz)<br>($J$ = 1.4 Hz) | 6.63(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 4.7 Hz) | 7.65(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 1.4 Hz) | 8.50(s) | 7.67(s) | pyridine-$d_5$ |
| | 1.37(t)<br>($J$ = 7.3 Hz) | 2.73(q)<br>($J$ = 7.3 Hz) | 8.74(dd)<br>($J$ = 4.7 Hz)<br>($J$ = 1.5 Hz) | 7.34(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 4.7 Hz) | 8.40(dd)<br>($J$ = 8.1 Hz)<br>($J$ = 1.5 Hz) | 9.40(s) | 8.82(s) | dimethyl sulfoxide-$d_6$ |

[a]Chemical shifts are given in ppm for TMS as an internal reference. The multiplicity of a proton signal is given in parentheses after the $\delta$ values: s = singlet; t = triplet; q = quartet; dd = doublet of doublets.

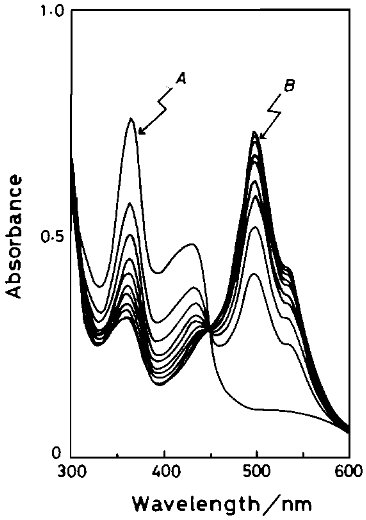


Fig. 1. Electronic spectra of Co(1-E)CN (2.43 × $10^{-3}$) in 1,2-dichloroethane at various concentrations of 4-methylpyridine: the absorption intensity in range A decreases as the 4-methylpyridine concentration increases from zero to higher, while that in range B increases as the 4-methylpyridine concentration is raised. 4-Methylpyridine concentrations: 6.03 × $10^{-3}$, 1.21 × $10^{-2}$, 1.81 × $10^{-2}$, 2.41 × $10^{-2}$, 3.01 × $10^{-2}$, 3.62 × $10^{-2}$, 4.22 × $10^{-2}$, 4.82 × $10^{-2}$, 5.42 × $10^{-2}$ and 6.03 × $10^{-2}$ mol dm$^{-3}$.

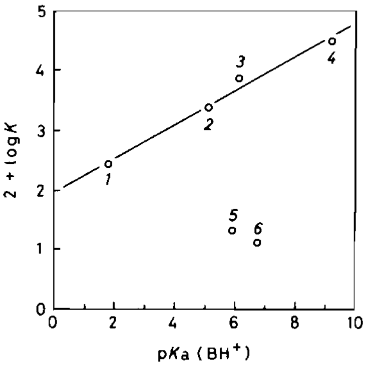


Fig. 2. Correlation between formation constant (log $K$) of Co(1-E)CN and pyridine basicity. Pyridines: (1) 4-CNPy; (2) Py; (3) 4-$CH_3$Py; (4) 4-$NH_2$Py; (5) 2-$CH_3$Py; (6) 2,6-$(CH_3)_2$Py (see Table 2 for abbreviations).

manner and are collected in Table 2. The equilibrium constants ($K$) for the formation of pyridine adducts of Co(1-E)CN and Co(1-Z)CN are somewhat larger in magnitude than those for a (dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co-B) [2]. This is due to a balance between the greater electrophilicity of nuclear cobalt in the trivalent state and the so-called *trans* effect by the cyano group, in a manner as observed for the axial ligation of pyridine to tetrakis(4-*N*-methylpyridyl)porphincobalt(III) [7]. The equilibrium constant can be correlated to the basicity of pyridine bases (p$K_a$) by eqn. (2) for the axial coordination of pyridine bases to Co(1-E)CN and Co(1-Z)CN, except for 2-methyl- and 2,6-dimethylpyridine, as shown in Fig. 2.

$$\log K = a\ \mathrm{p}K_a + b \qquad (2)$$

The $a$ and $b$ parameters thus evaluated are compiled in Table 3. The lower coordination ability of 2-methylpyridine and 2,6-dimethylpyridine with respect to the correlation line given by eqn. (2)

TABLE 2. Formation constants for the amine complexes of Co(1-E)CN and Co(1-Z)CN[a]

| Amine[b] | $pK_a(BH^+)$[c] | Co(1-E)CN | | Co(1-Z)CN | |
|---|---|---|---|---|---|
| | | $K$ (mol dm$^{-3}$) | log $K$ | $K$ (mol dm$^{-3}$) | log $K$ |
| 4-$NH_2$Py | 9.11 | $2.85 \times 10^2$ | 2.45 | $2.11 \times 10^2$ | 2.32 |
| 2,6-$(CH_3)_2$Py | 6.75 | $1.11 \times 10^{-1}$ | −0.95 | $1.88 \times 10^{-1}$ | −0.73 |
| 4-$CH_3$Py | 6.02 | $7.94 \times 10$ | 1.90 | $6.73 \times 10$ | 1.83 |
| 2-$CH_3$Py | 5.97 | $2.00 \times 10^{-1}$ | −0.70 | $2.62 \times 10^{-1}$ | −0.58 |
| Py | 5.19 | $2.69 \times 10$ | 1.43 | $2.60 \times 10$ | 1.41 |
| 4-CNPy | 1.90 | 2.79 | 0.45 | 2.66 | 0.42 |

[a]Measured in 1,2-dichloroethane at 25.0 ± 0.1 °C. [b]Abbreviations: 4-$NH_2$Py = 4-aminopyridine; 2,6-$(CH_3)_2$Py = 2,6-dimethylpyridine; 4-$CH_3$Py = 4-methylpyridine; 2-$CH_3$Py = 2-methylpyridine; Py = pyridine; 4-CNPy = 4-cyanopyridine. [c]Cited from ref. 6.

TABLE 3. Brønsted[a] and Hammett[b] parameters for the coordination of pyridine bases

| Coordination equilibrium | Cobalt complex system[c] | $a$ | $b$ | $-\rho$ | Reference |
|---|---|---|---|---|---|
| CoL + B $\rightleftharpoons$ BCoL | Co(II)-B | 0.32 | | 1.8 | 2 |
| CoLCN + B $\rightleftharpoons$ BCoLCN | Co(III) (1-E)CN | 0.28 | −0.01 | 1.54 | This work |
| | Co(III) (1-Z)CN | 0.27 | 0.02 | 1.47 | This work |

[a]Refer to eqn. (2). [b]Refer to eqn. (3). [c]Abbreviation: Co(II)-B = (dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II).

is attributable to the steric hindrance effect based on the interaction between the macrocyclic skeleton and the 2-methyl or 6-methyl group of the pyridine base. The free energy loss by the steric effect of the 2-methyl group was estimated to be *c.* 7.8 kJ mol$^{-1}$ (25 °C) for the penta-coordination step of Co-B [2], while *c.* 13 kJ mol$^{-1}$ (25 °C) was found for the hexa-coordination step of Co(1-E)CN and Co(1-Z)CN in the present work. The free energy loss for the latter is larger in magnitude than that for the former, so an extra steric effect would be expected for the latter. The free energy loss in the case of 2,6-dimethylpyridine was also estimated to be *c.* 15 kJ mol$^{-1}$.

The equilibrium data for the present set of pyridine bases can be referred to the Hammett equation for which the coordination equilibrium with pyridine ($K^0$) is taken as a reference.

$$\log K/K^0 = \rho\sigma \tag{3}$$

The evaluated $\rho$ values are compiled in Table 3 together with other reference data of relevant cobalt(II) complexes. It should be pointed out that the $a$ and $-\rho$ values for Co(1-E)CN and Co(1-Z)CN in the sixth coordination process are comparable to those for Co-B. This seems to indicate that the extent of $\sigma$- and $\pi$-bonding of the coordinate bond formed in the hexa-coordination step of Co(1-E)CN and Co(1-Z)CN is nearly the same as that in the penta-coordination step of Co-B, since the former complexes secure the *trans* effect of the coordinated cyano group.

## Conclusions

Penta-coordinated cyanocobalt(III) complexes exist as hexa-coordinated species in a solvent such as pyridine, as confirmed by NMR measurements. The coordination behavior of pyridine bases at the axial sites *trans* to the cyano group of cyanocobalt(III) complexes has been studied by measuring electronic spectra in 1,2-dichloroethane at 25.0 ± 0.1 °C. The formation constants were interpreted by the equations $\log K = a\,pK_a + b$ and $\log K/K^0 = \rho\sigma$ and by the so-called *trans* effect due to the cyano group.

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