

tion, it is supposed that the intensity and the pattern of CD spectra can be different in a certain absorption band region and hence no isodichroic point. Thus, for the chloride complex, it seems that the observed irregular CD changes at about 540 nm are attributed to coexistence of the dissociated and associated species.

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### Organocobalt(III) Complexes of the Tetraazamacrocyclic Ligand, $C_{32}H_{26}N_4^{2-}$ (I)

Young-ae Whang Park

Department of Chemistry, Sang Myung Women's University, Seoul 110. Received March 16, 1990

A major factor affecting Co-C bond stability in Organocobalt(III)  $B_{12}$  models as well as cobalamins appears to be the coordination number. Most of the low spin  $d^6$  cobalt(III) complexes are 6-coordinate with octahedral or pseudooctahedral structures, but 5-coordinate organocobalt(III) species have been suspected to exist either as reactive intermediates in ligand-exchange reaction or, less commonly, as relatively stable species.<sup>1-3</sup> However, the evidence for 5-coordinate cobalt (III) species is not clear. In connection with the research program toward the investigation of the effect of bases as the sixth ligands on the stability of Co-C bond in organocobalt(III) species, this paper reports on the chemistry of 5-coordinate organocobalt (III) complexes of completely conjugated dianionic macrocyclic ligand (L), 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinate.

As a starting material, Co(II)L was prepared by the addition of methanol solution of cobalt(II) acetate tetrahydrate to a solution of the ligand in DMF followed by 30 minutes reflux and obtained as a greenish brown crystal. The compound is air sensitive even in the solid state. The structure of Co(II)L determined by elemental analysis (Table 1), magnetic mo-

**Table 1.** Analytical Data for the Cobalt Complexes

Compound	Calcd, %			Found, %		
	C	H	N	C	H	N
Co(II)L·H <sub>2</sub> O	71.9	5.05	10.5	72.2	4.92	10.5
CH <sub>3</sub> Co(III)L	73.3	5.37	10.4	72.1	5.37	10.4
C <sub>6</sub> H <sub>5</sub> Co(III)L	75.7	5.15	9.30	74.9	5.10	9.34
C <sub>6</sub> F <sub>5</sub> Co(III)L	65.9	3.76	8.09	66.3	4.02	8.28

**Table 2.** Electronic Spectral Data for RCoL Complexes in the Range 16,000–30,000 cm<sup>-1</sup>

Compound	Solvent	Absorption in cm <sup>-1</sup> (ε)
CoL	CHCl <sub>3</sub>	27,800(47,400), 16,700(4,810)
CH <sub>3</sub> CoL	CHCl <sub>3</sub>	27,030(7,970), 23,810(3,910), 16,620(2,540)
C <sub>6</sub> H <sub>5</sub> CoL	CHCl <sub>3</sub>	27,970(9,440), 23,120(5,000), 15,870(930)
C <sub>6</sub> F <sub>5</sub> CoL	CHCl <sub>3</sub>	27,780(31,240), 22,990(6,650)

**Table 3.** Proton NMR Spectral Data for RCoL<sup>a</sup>

Compound	Co-CH <sub>3</sub>	Methyl 6.15-CH <sub>3</sub>	Methine -CH=	Aromatic
LH <sub>2</sub>		2.30 (s)	5.14 (s)	6.10–7.94(m)
CH <sub>3</sub> CoL	2.33(s)	2.53(s)	5.26(s)	5.76–7.16(m, benzenoid) 7.40(s, phenyl)
C <sub>6</sub> H <sub>5</sub> CoL		2.68(s)	4.89(s)	5.33–8.25(m)
C <sub>6</sub> F <sub>5</sub> CoL		2.45(s)	5.22(s)	6.17–8.30(m)

<sup>a</sup>Chemical shifts in ppm from internal TMS. Measured in CDCl<sub>3</sub>. s: singlet, m: multiplet.

ment (2.33 B.M.), IR spectrum and electronic spectrum is regarded as a 4-coordinate square planar complex which the macrocyclic ligand acts as a tetradentate chelating agent lying in the equatorial plane.

Five-coordinate organocobalt (III) complexes, RCo(III)L (where R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>F<sub>5</sub>), were prepared similarly to that described for the synthesis of (py)Co(III) (saloph)(R)<sup>1</sup>. These green organocobalt complexes are also gradually decomposed in the air. The infrared spectra of these complexes show the change in the C = N stretching mode of the ligand, which enables us to distinguish between the coordinated and the free ligand. The absorption band for C = N of the free ligand which appears at 1613 cm<sup>-1</sup> with very strong intensity is shifted to the lower frequency region with decreased intensity; 1571 cm<sup>-1</sup> for CH<sub>3</sub>CoL, 1570 cm<sup>-1</sup>, 1570 cm<sup>-1</sup> for C<sub>6</sub>H<sub>5</sub>CoL and 1575 cm<sup>-1</sup> for C<sub>6</sub>F<sub>5</sub>CoL. This result indicates that the ligand is coordinated through for nitrogen atoms to the metal. Visible and ultraviolet spectral data covering 16,000–40,000 cm<sup>-1</sup> range are shown in Table 2.

These absorption bands are assigned to  $\pi$ - $\pi^*$  transitions within the ligand molecule and charge transfer transitions from metal to ligand since they have larger extinction coefficients ( $10^2$ – $10^4$  mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>) than expected for ligand field transitions.<sup>4</sup> Five coordinate organocobalt (III) complexes are known to show a band at ~440 nm<sup>5</sup>. Indeed, the ~430 nm band has been observed in chloroform in all the complexes of this work. This particular band is attributed to the intramolecular CT transitions for which the Co-CH<sub>3</sub> bond is

concerned, since the position of the band is sensitive to the solvent nature.<sup>6</sup> This will be discussed in detail in the future. The complexes of this work are diamagnetic, indicating these are low-spin  $d^6$  complexes. The proton NMR spectral data are summarized in Table 3. The peak at 2.33 ppm is due to the resonance of the methyl group directly bonded to cobalt, which is in the range of the literature.<sup>7</sup> Thus, the peak at 2.53 ppm can be assigned to the methyl groups of the macrocyclic ligand. Furthermore, the ratio of the peak area of the former to the latter (1:2) confirms the above assignment. Upon formation of the cobalt complexes, methine and methyl peaks are shifted to downfield in general. This may be attributed to deshielding effect by positive charge of the cobalt on the macrocyclic ligand.<sup>8</sup>

In conclusion, Co(II)L is a low spin  $d^7$  complex with a 4-coordinate square planar structure and rare 5-coordinate RCo(III)L complexes have been synthesized and characterized to provide useful insight into the chemistry and biochemistry of cobalamins.

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