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LOW-SPIN FIVE-COORDINATE Co(II) COMPLEXES OF A 14-MEMBERED MACROCYCLIC TETRAAMINE CONTAINING TWO DEPROTONATED AMIDES——A NEW REVERSIBLE OXYGEN CARRIER

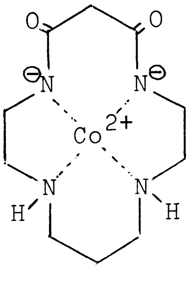
Kazuhiko ISHIZU, Junko HIRAI, Mutsuo KODAMA*, and Eiichi KIMURA**
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790
* Department of Chemistry, College of General Education, Hirosaki University, Hirosaki 036
** Institute of Pharmaceutical Sciences, School of Medicine, Hiroshima University, Kasumi, Hiroshima 734

A new 1:1 complex formed between Co(II) and doubly deprotonated 1,4,8,11-tetraazacyclotetradecane-5,7-dione exhibits an ESR spectrum typical of a low-spin square-planar Co(II) complex with the unpaired electron occupying d_{z^2} orbital. Addition of excess imidazole or pyridine yields five-coordinate square-pyramid complexes, which reversibly bind to O_2 at -70°C. The rigid planarity of the tetraamine macrocycle is compared with porphyrin chelates using ESR parameters.

Potential has been recognized of metal complexes of saturated macrocyclic tetraamines mimicking the biologically important porphyrin macrocycles.1) However, there exists an intrinsic difference in the ligand field strength between the two systems, as often reflected in distinctive electronic configuration of the metal ions. Thus, Co(II) is usually high-spin in the saturated macrocycles,2) while it is low-spin in porphyrin system.3)

In previous studies with Cu(II)4-6) we demonstrated that a modification of saturated macrocyclic tetraamines by incorporation of two carbonyl groups significantly restricts the original arbitrary coordination fashions to a stringent square-planar one comprising of two Cu-deprotonated amide nitrogen bonds (so the complexes formulated as $CuH_{-2}L^0$), thereby the tetraamines deviate to more like tripeptides or porphyrins. The study using an ESR technique is now extended to Co(II), which likewise forms a 1:1 $CoH_{-2}L^0$ complex with 1,4,8,11-tetraazacyclotetradecane-5,7-dione,4) in order to demonstrate a unique porphyrin-like ligand field by establishing i) low-spin Co(II) electronic state, ii) five-coordinate square-pyramidal geometry with an excess base, and iii) formation of a monomeric O_2 adduct in the presence of base.

The solution of a 1:1 Co(II) complex, $CoH_{-2}L^0$, was prepared as follows: The equimolar ethanol solutions of the ligand and $CoCl_2$ (2×10^{-2} M) were mixed at room temperature. The mixture was vigorously shaken with air. In 15 minutes, a clear green solution (probably of Co(III) complex) was formed. Upon reduction with $NaBH_4$, the solution turned to yellow to give a strong ESR absorption spectrum due to the Co(II) complex. Five-coordinate Co(II) complexes were prepared in situ in the presence



Co(II) complex of doubly deprotonated 1,4,8,11-tetraazacyclotetradecane-5,7-dione ($CoH_{-2}L^0$)

of excess amount of nitrogen bases at 77 K, which reversibly react with O_2 at dry-ice acetone temperature (-70°C). ESR spectra were obtained by a JEOL JES-ME-3X spectrometer (100 kHz magnetic field modulation). The magnetic field was calibrated by the splitting of Mn(II) in MgO ($\Delta H_{3-4} = 86.9 \times 10^{-4}$ T), and the g-values were standardized by using Li-TCNQ (g = 2.00252). The spectra were not computer-fitted, so the values of g and A are not known with great precision.

An ESR spectrum of the $CoH_{-2}L^0$ complex in the absence of base is shown in Fig. 1a. The observed hyperfine structures can be analyzed in terms of a near axial symmetry having the perpendicular branch ($g_\perp = 2.38$) and the parallel branch ($g_\parallel = 2.02$) split into eight lines due to hyperfine interaction with Co nucleus (I = 7/2).

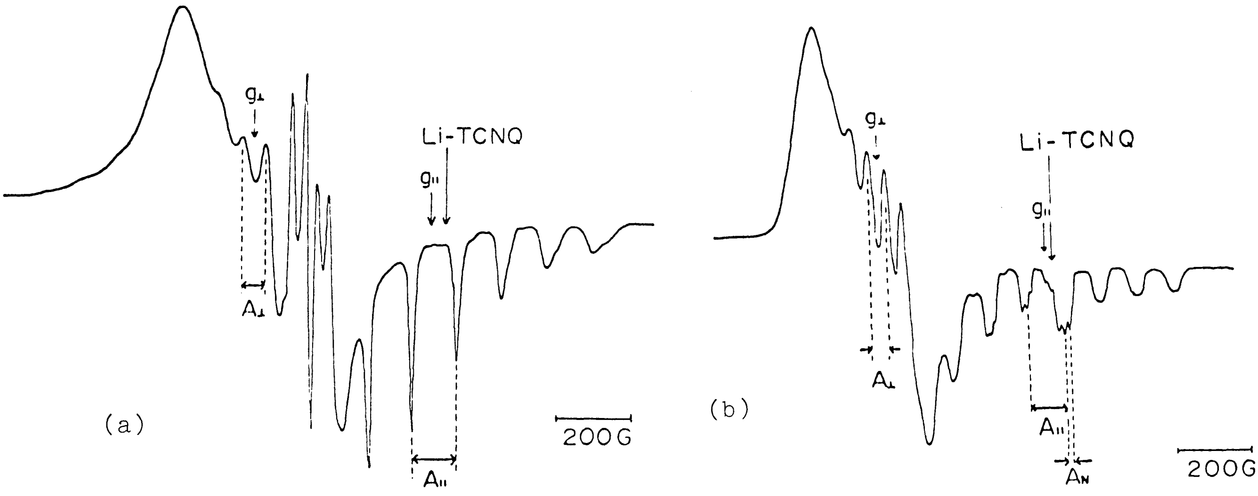


Fig. 1 ESR Spectra of $CoH_{-2}L^0$ complex in ethanol at 77 K (a) without imidazole and (b) with imidazole ($1G = 10^{-4}$ T)

The order of g-anisotropy, i.e., $g_\parallel < g_\perp$, indicates that the unpaired electron resides in a molecular orbital mostly made of d_{z^2} orbital of Co(II) in low-spin d^7 configuration. Theoretically,[7)] $g_\perp$ depends on the magnitude of energy separation between d_{z^2} (E_{a_1}) and d_{xz} or d_{yz} orbital (E_e), as expressed by Eq. 1

$$g_\parallel = g_e, \qquad g_\perp = 2 - 6\lambda/(E_{a_1} - E_e) \qquad (1)$$

where λ is the spin-orbit coupling constant of Co(II).

In the presence of excess nitrogen base such as pyridine or imidazole, a new superhyperfine splitting A_N (three lines in equal intensity), most likely due to the new axial nitrogen atom, appears at the $g_\parallel$ branch, which overlaps with $A_\parallel$ splitting of Co nucleus (see Fig. 1b for imidazole base). This is justifiably interpreted by the formation of five- rather than six-coordinate complexes. Perturbation of the ESR parameters (Table 1) is understood also by supposing an axial coordination. Reduction

Table 1. ESR parameters for five-coordinate Co(II) complexes

Ligand	N Base	$\lvert A_{\parallel}\rvert/10^{-4}cm^{-1}$	$\lvert A_{\perp}\rvert/10^{-4}cm^{-1}$	$g_{\parallel}$	$g_{\perp}$	$\lvert A_N\rvert/10^{-4}cm^{-1\Delta}$
L	none	114.6	70.6	2.02	2.38	——
L	pyridine	107.4	59.5	2.02	2.30	10.8
L	imidazole	95.2	50.6	2.02	2.34	11.9
[(p-OCH_3)TTP]	imidazole	76.4	12.0	2.030	2.307	16.2
[(p-OCH_3)TTP]	2,4-lutidine	89.4	42.6	2.019	2.363	12.7

[(p-OCH_3)TTP] = α,β,γ,δ-tetra-(p-methoxyphenyl)porphyrin[3a,b)]

in $|A_{\parallel}|$ and $|A_{\perp}|$ values is attributed to an enhanced delocalization of the unpaired electron to the axial nitrogen, which would result in a greater separation of E_{a_1} from E_e and hence the $g_{\perp}$ value is getting closer to 2.0 as derived from Eq. 1. Table 1 summarizes a similar square-pyramidal arrangement taken by the imidazole-capped $CoH_{-2}L^0$ and by the lutidine-capped porphyrin complex, although our tetraamine system has a weaker perturbation with the axial imidazole.

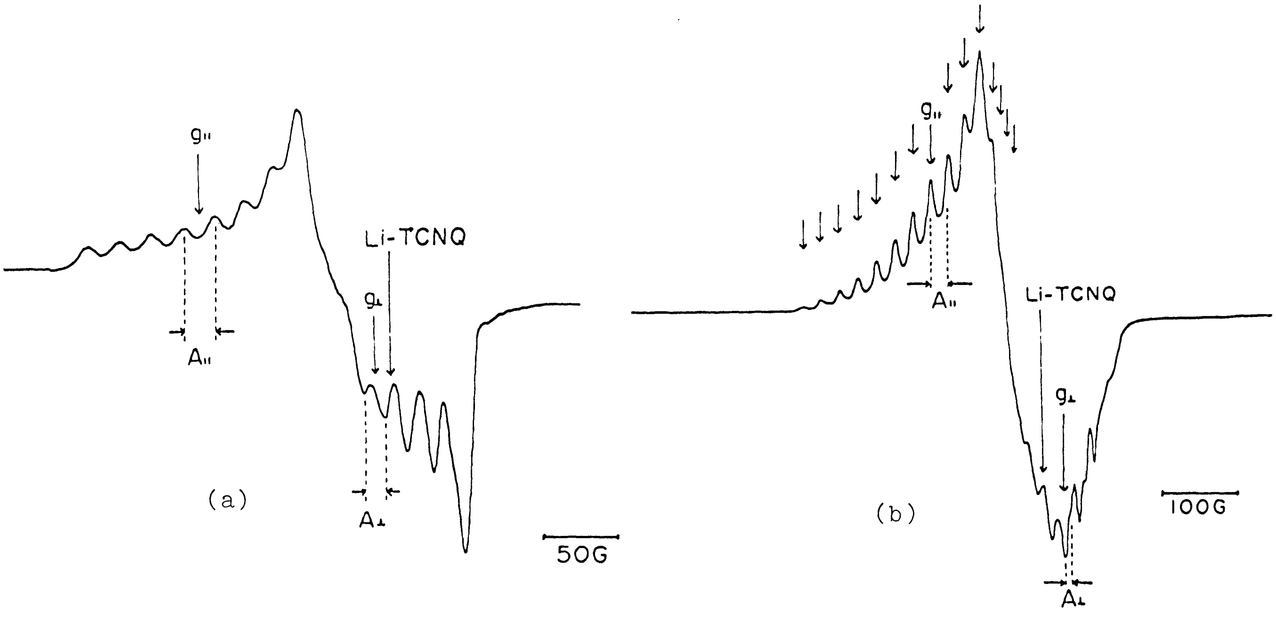


Fig. 2. ESR spectra of $CoH_{-2}L^0$ adducts in ethanol at 77 K (1G = 10^{-4} T)
(a) 1:1 complex (imidazole-capped)
(b) 1:2 complex (pyridine-capped)

When a frozen solution of the imidazole-capped complex is treated with O_2 at -70°C the ESR spectrum changes to the one assignable to a monomeric (1:1) O_2 adduct, see Fig. 2a (by pumping off O_2 the initial spectrum restores). The ESR parameters listed in Table 2 indicate a similar arrangement around Co for the present and porphyrin O_2 adducts. Formation of two different species of O_2 adducts was detected for pyridine-capped $CoH_{-2}L^0$ complex. At lower contents of pyridine (Co:pyridine = 1:50), equally spaced 15 hyperfine lines (attributed to the nuclear hyperfine interaction of two

Table 2. ESR parameters for O_2 adducts of Co(II) complexes

Ligand	Axial N base	$\lvert A_\parallel \rvert$ /10^{-4}cm^{-1}	$\lvert A_\perp \rvert$ /10^{-4}cm^{-1}	$^\Delta \lvert A_0 \rvert$ /10^{-4}cm^{-1}	$g_\parallel$	$g_\perp$
L	pyridine (1:1)	23.3	16.0	18.4	2.09	2.01
L	pyridine (2:1)	23.2	8.8	13.6	2.10	2.00
L	imidazole (1:1)	20.8	13.8	16.1	2.08	2.01
[(p-OCH_3)TTP]	imidazole (1:1)	17.7	10.6	13.0	2.077	2.003
[(p-OCH_3)TTP]	2,4-lutidine (1:1)	21.7	13.4	16.1	2.085	2.001

Δ : $A_0 = (A_\parallel + 2A_\perp)/3$

equivalent Co atoms) seen at the $g_\parallel$ branch identified a binuclear (2:1) Co-O_2 adduct (see Fig. 2b). With an increase in pyridine composition (Co:pyridine =1:100) the ESR spectrum altered to the one indicative of a (1:1) O_2 adduct. Their $\lvert A_\parallel \rvert$ and $\lvert A_\perp \rvert$ values were slightly larger than those for the imidazole O_2 complex. The imidazole-capped tetraamine system shows a weaker localization of the unpaired electron to O_2 than the imidazole-capped porphyrin. A detailed characterization of the O_2 adducts is in progress.

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