High-Resolution ^{13}C NMR Spectra of *trans*-[Co^{III}(2,3-Alkanedione dioximato)$_2$(pyridine)$_2$]I Complexes in the Solid State

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Synopsis. High-resolution ^{13}C NMR spectra of the title complexes showed two type signals based on the "packing effect" and the long-chain alkyl group of the dioximato ligand was found to be fixed near the axial pyridine ligand in the solid state.

To determine molecular structures in the solid state, X-ray crystal structure analyses are preferable. However, they are time consuming and are sometimes impossible because of the difficulty of making single crystals. Recently, high-resolution ^{13}C NMR techniques in the solid state (CP/MAS) have been developed, and attempts to apply these techniques are now being made.$^{1)}$ The CP/MAS measurement can readily give some information about the molecular conformations and the molecular packings even for such compounds in the solid state.

In the previous paper, we reported that the pyridine liberation-anation reaction of the series of *trans*-[Co(R,CH$_3$-dioxH)$_2$(py)$_2$]I (R,CH$_3$-dioxH$_2$: CH$_3$-C(=NOH)-C(=NOH)-R; R=CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$ and *n*-C$_4$H$_9$, py: pyridine) fitted well to the Taft's plot, indicating that the Co(III)-py bond is weakened not only by the electron-donating inductive effect of R but also by the steric effect of R.$^{2)}$ Therefore, the long-chain alkyl group, R, was expected to be fixed near the axial pyridine ligand in the solid state. On the other hand, ^{1}H and ^{13}C NMR Spectra and T$_1$ measurements of the complexes indicated that the R group was moving segmentally in dimethyl-d_6 sulfoxide (DMSO-d_6) solution.$^{3)}$

In this paper, CP/MAS is applied to these complexes and the molecular structure and the molecular packing of the complexes are estimated in the solid state.

Experimental

A JEOL NM-SH 200 spectrometer (50 MHz for ^{13}C) was used for the CP/MAS measurement. The complexes used were fine needle crystals obtained by slow evaporation of a saturated solution in methanol. The spectral assignments were made using Opella's method$^{4)}$ and in comparison with the spectra in DMSO-d_6 solution.$^{3)}$

Results and Discussion

As is shown in Fig. 1, the C^1 and C^2 resonances of the [Co(CH$_3$,CH$_3$-dioxH)$_2$(py)$_2$]I complex were separated into two peaks, respectively, though they appeared as a single peak in DMSO-d_6 solution. The [Co(C$_2$H$_5$,CH$_3$-dioxH)$_2$(py)$_2$]I complex showed a spectrum similar to that in DMSO-d_6 solution, but the [Co(*n*-C$_3$H$_7$,CH$_3$-dioxH)$_2$(py)$_2$]I showed a spectrum different from that in solution; the C^1 resonance was separated into two peaks, while the C^2 and C^3 resonances overlapped. The spectrum of [Co(*n*-C$_4$H$_9$, CH$_3$-dioxH)$_2$(py)$_2$]I complex was similar to that in solution. The numerical data for these spectra are summarized in Table 1.

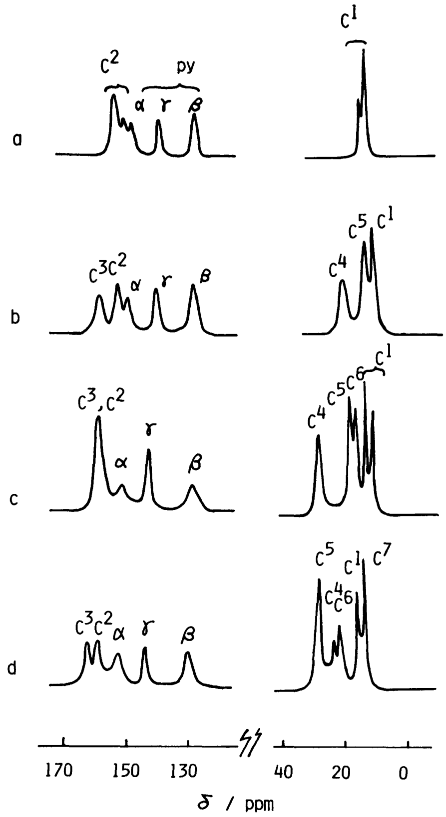

Fig. 1. High-resolution ^{13}C NMR spectra of [Co(R, CH$_3$-dioxH)$_2$(py)$_2$]I in the solid state.
a: R=CH$_3$, b: R=C$_2$H$_5$, c: R=*n*-C$_3$H$_7$, d: R=*n*-C$_4$H$_9$. Each carbon atom of the ligands is noted as a following example; C^{1}H$_3$-C^2(=NOH)-C^3(=NOH)-C^{4}H$_2$-C^{5}H$_2$-C^{6}H$_2$-C^{7}H$_3$.

The results obtained here are understandable if each carbon resonance of the complexes can show two type NMR signals, i.e., A type and B type, based on a "packing effect".$^{1)}$ The observed signals were assigned as follows: C^1, 14.9 ppm (A type), 17.1 ppm (B type); C^2, 155.2 ppm (A type), 158.5 ppm (B type); C^3, 161.6 ppm (A type), 162.5 ppm (B type). The C^4, C^5, C^6, C^7, resonances showed no observable splittings between A type and B type. The [Co(C$_2$H$_5$,CH$_3$-dioxH)$_2$ (py)$_2$] I and [Co(*n*-C$_4$H$_9$,CH$_3$-dioxH)$_2$(py)$_2$]I complexes showed only A type or B type signal, respectively. While, [Co(CH$_3$,CH$_3$-dioxH)$_2$(py)$_2$]I and [Co(*n*-C$_3$H$_7$,CH$_3$-dioxH)$_2$(py)$_2$]I complexes showed both A type and B type signals. As for the [Co(*n*-C$_3$H$_7$,CH$_3$-dioxH)$_2$-(py)$_2$]I complex, four signals, i.e., C^2(A), C^2(B), C^3(A),

Table 1. High-Resolution ^{13}C NMR Data of [Co(R,CH_3-dioxH)$_2$(py)$_2$]I Complexes in the Solid State

R	δ/ppm									
	C^1		C^2		C^3		C^4	C^5	C^6	C^7
CH_3	15.6	17.5	155.0	158.0	—	—	—	—	—	—
C_2H_5	14.9	—	155.3	—	161.6	—	21.4	12.9	—	—
n-C_3H_7	14.2	17.0	159.6				29.1	19.4	12.2	—
n-C_4H_9	—	16.9	—	159.0	—	162.5	25.1	28.9	23.2	14.6

Each carbon atom of the ligands is noted as a following example; C^1H_3-C^2(=NOH)-C^3(=NOH)-C^4H_2-C^5H_2-C^6H_2-C^7H_3.

C^3(B), were mixed up and appeared as a single peak at 159.6 ppm.

The splitting of an NMR signal based on a "packing effect" was also observed for [Co(CH_3,CH_3-dioxH)$_2$-(NH_3)$_2$] NO_3 complex: In D_2O solution, C^1 and C^2 appeared at 15.3 and 159.7 ppm, respectively, as a single peak, but, in the solid state, they appeared as a double peak, respectively. The X-ray structural analysis of the complex showed that two NH_3 ligands coordinate to Co(III) at trans positions and the space group is $P2_1/c$ with two molecules in the unit cell.[5] According to this X-ray structural analysis, there are two non-equivalent positions for the C^1 and C^2 carbons, respectively, which can cause the splitting of the NMR signals.

In DMSO solution, higher-field shifts were observed for both ^{1}H and ^{13}C resonances of the C^5, C^6, and C^7 groups on complex formation and the higher-field shifts of ^{13}C resonances were mainly attributable to the ring-current shielding of the axial pyridine ligand for these complexes.[3] In the solid state, the C^6 resonance of [Co(n-C_3H_7,CH_3-dioxH)$_2$(py)$_2$]I complex appears at 12.2 ppm, which is 4.0 ppm higher-field in comparison with that of free n-C_3H_7,CH_3-dioxH$_2$ ligand in the solid state. In DMSO solution, the corresponding peak shift was 1.3 ppm.[3] The amount of the shift caused by the above ring-current effect was the largest for C^6 carbon of [Co(n-C_3H_7,CH_3-dioxH)$_2$ (py)$_2$]I complex of all the carbons in the series of the complexes. Judging from these facts, the long-chain alkyl group in the equatorial plane may be assumed to be fixed near the axial pyridine ligand in the solid state. Such a location of the R group is susceptible to ring-current shielding of the pyridine ligand and the chain length is most advantageous for the complex including R=n-C_3H_7 to experience the largest shielding effect. This location is also in accord with the expectation, based on the kinetic study, that the R group is fixed so as to weaken the Co(III)-py bonding.[2] In solution, the long-chain alkyl group is moving freely and the effect of the ring-current shielding is smaller than that in the solid state.

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