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^{13}C and ^{14}N Nuclear Magnetic Resonance of $K_4[Re(CN)_7]\cdot 2H_2O$ and some Related Cyano Metal Complexes

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Quite a few cyano metal complexes have so far been prepared. The structures of these complexes have also been determined by X-ray analysis. As for the transition metal complexes, six coordination of the CN^- ligand is the most popular and four or two coordination exists for Ni^{2+}, Cu^{2+}, Ag^+, Au^+, etc. [1]. However, seven coordination of cyano metal complexes is only known for V, Re and Mo [2–4]. The structures are reported to be pentagonal-bipyramidal (D_{5h}) symmetry with a slight deformation for $K_4[V(CN)_7]\cdot 2H_2O$ [2], $K_4[Re(CN)_7]\cdot 2H_2O$ [3] and $Na_5[Mo(CN)_7]\cdot 10H_2O$ [4].

In the present work, the author investigated the structure of diamagnetic $K_4[Re(CN)_7]\cdot 2H_2O$ (Fig. 1) in solution and the properties of the coordinated cyano carbon and nitrogen by comparison with those of six coordinated cyano metal complexes, $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_3[Co(CN)_6]$. For this purpose, ^{13}C and ^{14}N NMR measurements were carried out. The chemical shifts of these spectra could help to clarify the electronic structure of the outer shell of the ligand atoms of transition metal complexes, which might reflect the electronic influence of metal ions and the structure of the complexes.

Experimental

Materials

$K_4[Re(CN)_7]\cdot 2H_2O$ was prepared according to the literature [5, 6]. $K_3[Co(CN)_6]$ was kindly provided by Dr K. Kashiwabara of Nagoya University. $K_4[Fe(CN)_6]\cdot 3H_2O$ was purchased from Wako Pure Chemical Industries, Japan and used without further purification.

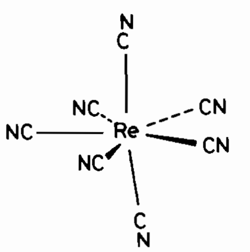

Fig. 1. Structure of $[Re(CN)_7]^{4-}$ in the solid state.

TABLE 1. ^{13}C and ^{14}N chemical shifts for $K_4[Re(CN)_7]\cdot 2H_2O$, $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_3[Co(CN)_6]$ in D_2O solution

Compound	δ (^{13}C) (ppm)[a]	δ (^{14}N) (ppm)[b]
$K_4[Re(CN)_7]\cdot 2H_2O$ (I)	140.3	−95 (850)[c]
$K_4[Fe(CN)_6]\cdot 3H_2O$ (II)	177.6	−94 (850)[c]
$K_3[Co(CN)_6]$ (III)	139.8	−94 (1450)[c]

[a] ± 0.1 ppm. [b] ± 1 ppm. [c] Linewidth in Hz, ±50 Hz.

All other chemicals used were of reagent grade.

Measurements

The ^{13}C and ^{14}N NMR spectra were recorded at ambient temperature (20–21 °C) on the D_2O solution of the complex anion (0.05–0.5 M). A Jeol JNM-GX400 NMR spectrometer was operated in the Fourier transform mode at 100.535 MHz for carbon-13 and at 28.884 MHz for nitrogen-14. For the ^{13}C NMR measurements, dioxane in D_2O, which was sealed in a 5 mm tube, was taken as an external reference (67.4 ppm from TMS), being kept inside the 10 mm sample tube during the accumulation. For ^{14}N NMR, $NaNO_3$ (0.0 ppm) in D_2O was used as a reference.

Results and Discussion

Table 1 shows the ^{13}C and ^{14}N chemical shifts of $K_4[Re(CN)_7]\cdot 2H_2O$ **(I)**, $K_4[Fe(CN)_6]\cdot 3H_2O$ **(II)** and $K_3[Co(CN)_6]$ **(III)**. The signals of all cyano carbons are observed quite sharply (though the signals of $[Co(CN)_6]^{3-}$ are octet as indicated in the literature [7]), but those of the cyano nitrogen are fairly broad ($\Delta\nu_{1/2}$ = 850–1450 Hz).

Figure 2 shows the ^{13}C NMR spectrum of $K_4[Re(CN)_7]\cdot 2H_2O$. The signal of this complex is a sharp singlet. The structure of this complex has a pentagonal-bipyramidal symmetry in the solid state, so that two different environments should exist (two axial CNs and five equatorial CNs), while $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_3[Co(CN)_6]$ have six equivalent CNs, which essentially show only one kind of sharp signal(s). The single peak of the coordinated CN carbon in $K_4[Re(CN)_7]\cdot 2H_2O$, clearly seen in Fig. 2, indicates that this pentagonal-bipyramidal (PB) complex is considered to be stereochemically nonrigid and flexible even though the PB structure could be maintained in solution [6, 8], and that the interchange rate of two non-equivalent sites (two axial

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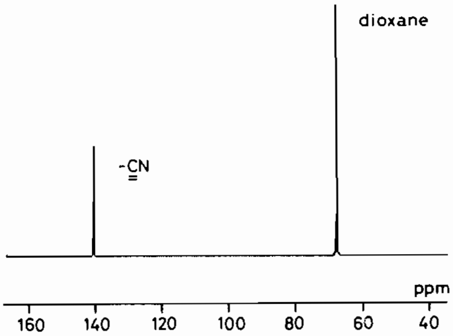

Fig. 2. ^{13}C NMR spectrum of $K_4[Re(CN)_7]\cdot 2H_2O$ in D_2O solution.

and five equatorial ligands) is faster than the time scale for ^{13}C NMR measurements at this temperature. Therefore, the chemical shift obtained for $K_4[Re(CN)_7]\cdot 2H_2O$ is an average of chemical shifts in different environments.

It is apparent in Table 1 that the ^{13}C chemical shift of **I** is similar to that of **III** but is quite different from **II**. According to the literature [7], the ^{13}C chemical shift of the cyano metal complexes varies depending on the central metal ion. This should be due to the influence of the metal ion on the charge distribution or the electronic structure of the coordinated cyano carbon. The results of Table 1 mean that the charge distribution (especially the charge in the p orbital of the outer shell) of the coordinated carbons is largely influenced by the central metal ion. The appearance of the signals of $[Re(CN)_7]^{4-}$ and $[Co(CN)_6]^{3-}$ in the upper field could be due to the heavier rhenium ion and the higher oxidation state, respectively; the former reason is confirmed by the similarity of the chemical shifts to $[W(CN)_8]^{4-}$ (146.9 ppm) and $[Os(CN)_6]^{4-}$ (142.8 ppm) [7]. In this work, the influence of the coordination number and the structure of the complex are not so pronounced in the ^{13}C chemical shift.

In contrast to the ^{13}C NMR chemical shift, the ^{14}N one is insensitive to the change of the central metal ion. A change in the concentration (0.05–0.5 M) does not give a different result. This suggests that the influence of the central metal ion on the electronic structure of the cyano nitrogen is not so distinctive. This means that the influence does not reach the nitrogen atom which is far from the metal ion. The linkage of C and N is not effective in the ^{14}N chemical shift.

The difference between seven and six coordination was not found in this work. However, it is clear that the ligand atoms are influenced drastically by coordination to the central metal ion on the ^{13}C NMR of coordinated carbons but not on the ^{14}N one.

Extensive studies are now in progress.

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