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CARBON-13 NUCLEAR MAGNETIC RESONANCE OF METAL COMPLEXES. I.

Michio HIROTA, Yasuo KOIKE*, Hidehiro ISHIZUKA, Akira YAMASAKI, and Shizuo FUJIWARA
Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Tokyo, 113

Carbon-13 chemical shifts were measured for 15 cyanometallate complexes in aqueous solution with Fourier-Transform NMR spectroscopy. The chemical shift values are distributed between -50.3_3 ppm (from external benzene standard) for $Fe(CN)_6^{4-}$ and $+2.6_6$ ppm for $Pt(CN)_4^{2-}$. The coupling constant $^1J_{C-Co}$ was found to be 126 ± 4 Hz for $Co(CN)_6^{3-}$.

In this note, we report a carbon-13 nuclear magnetic resonance study of cyanometallate complexes in aqueous solution. A brief discussion will be made in terms of these results on the chemical bonding of these complexes.

Carbon-13 Fourier-Transform nuclear magnetic resonance spectra were obtained at 25°C with a JEOLCO PS-100 NMR spectrometer operating at 25.15 MHz equipped with a JEC-6 spectrum computer. All diamagnetic cyanometallate complexes were prepared by the standard method. In most cases, saturated solutions were used for the measurement. A small amount of heavy water (D_2O) was added to the samples as the source of a lock signal.

Chemical shifts obtained are shown in Table I, where benzene is used as the external standard. Carbon-13 chemical shifts of the free cyanide ion and coordinated cyanide are lower than those of organic nitriles. The chemical shifts for the cyanometallate complexes range from -50.3_3 ppm for $Fe(CN)_6^{4-}$ to $+2.6_6$ ppm for $Pt(CN)_4^{2-}$. It should be noted that the chemical shift of $Fe(CN)_6^{4-}$ is much lower than that of the free cyanide ion. This result suggests that a simple explanation of the observed chemical shifts in terms of the ionic character of the metal-ligand bond is not adequate; if we assume that organic nitriles and the free cyanide ion give the chemical shifts representing the purely covalent and purely ionic state, respectively.

The complexes having central ions with the same electron configuration which lie along the vertical direction in the periodic table show two types of the change of chemical shift. In VIA and VIII groups, the heavier the central ion, the more positive the chemical shift, i.e., Mo(IV) $<$ W(IV), Fe(II) $<$ Ru(II) $<$ Os(II), and Ni(II) $<$ Pd(II) $<$ Pt(II). In VIII group, the difference between the first and second transition metal complexes was smaller than that of the second and third transition metal complexes. In central ions with d^{10} configuration, the heavier central ion corresponds to the more negative chemical shift, i.e., Ag(I) $>$ Au(I), Zn(II) $>$ Cd(II)

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*) Present address: Central Research Institute, Mitsubishi Chemical Industry, Mizonokuchi, Takatsu-ku, Kawasaki.

> Hg(II), the the range of chemical shifts is small. Along the horizontal direction in the periodic table, the larger oxidation number of the central ion gives the more positive chemical shift, i.e., Fe(II) < Co(III), and Cu(I) < Zn(II).

Since the d^{10} cyanometallate complexes are labile in aqueous solution, the excess of potassium cyanide was added in the case of zinc and cadmium complexes. In these cases, the signal of free cyanide ion was not observed. This is probably due to the rapid exchange between coordinated and free cyanide ions. When the fraction of free cyanide ion and coordinated cyanide to zinc(II) ion is equal, the life time of CN in $Zn(CN)_4^{2-}$ is about 0.9 x 10^{-4} sec from the half width of the signal. Using -37.5_6 ppm for free cyanide ion, the chemical shifts of coordinated cyanide to zinc and cadmium ions can be estimated at -18.0 and 20.6 ppm, respectively.

Multiplet spectra due to central ions with non-zero spin was not observed except for the hexacyanocobaltate(III). For metals with a high abundance of non-zero spin isotopes, this is probably due to the rapid ligand exchange and/or the rapid quadrupolar relaxation of the central ions.

Table I

Carbon-13 chemical shifts of cyanometallate complexes in aqueous solution.
(external benzene = 0)

Complex	Chemical Shift ppm	Complex	Chemical Shift ppm	Complex	Chemical Shift ppm
		$Mo(CN)_8^{4-}$	-24.6_3	$W(CN)_8^{4-}$	-18.4_4
$Fe(CN)_6^{4-}$	-50.3_3	$Ru(CN)_6^{4-}$	-34.5_8	$Os(CN)_6^{4-}$	-14.3_1
$Co(CN)_6^{3-}$ a)	-11.6_9				
$Ni(CN)_4^{2-}$	-8.0_0	$Pd(CN)_4^{2-}$	-3.5_1	$Pt(CN)_4^{2-}$	$+2.6_6$
$Cu(CN)_4^{3-}$ b)	-33.7_5	$Ag(CN)_2^{-}$	-21.9_6	$Au(CN)_2^{-}$	-25.9_6
$Zn(CN)_4^{2-}$	-18.0 c)	$Cd(CN)_4^{2-}$	-20.6 c)	$Hg(CN)_4^{2-}$	-24.6_0
NaCN (satd.)	-38.4_6	CH_3CN	+10.8 1)		
KCN (1 M)	-37.5_6	C_6H_5CN	+8.0 2)		

a) octet, $^1J_{C-Co}$ = 126 ± 4 Hz.

b) Cu(I) = 0.5 M, total CN = 3.0 M, The signal of coexisting free cyanide is also observed.

c) estimated value.

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1) G. E. Maciel and D. A. Beatty, J. Phys. Chem., 69, 3920 (1965).

2) G. L. Lebel, J. E. Laposa, B. G. Sayer and R. A. Bell, Anal. Chem., 43, 1500 (1971).

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