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A STUDY OF COBALT COMPLEXES BY X-RAY PHOTOELECTRON SPECTROSCOPY

Hiroki HARAGUCHI*, Kitao FUJIWARA, and Keiichiro FUWA
Department of Agricultural Chemistry, Faculty of Agriculture,
The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113
* Present Adress; Department of Chemistry and Physics, The National
Institute for Environment, Yatabe-machi, Tsukuba-gun, Ibaragi 300-21

Cobalt(II and III) complexes including Vitamin B_{12} have been investigated by X-ray photoelectron spectroscopy. Cobalt(II) and cobalt (III) complexes show the $2p_{1/2}$-$2p_{3/2}$ peak separation of 16.0 ± 0.3 eV and 15.1 ± 0.3 eV, respectively. The data of the binding energies for Co $2p_{1/2}$, Co $2p_{3/2}$, N 1s and S 2p in cobalt complexes are also presented.

X-ray photoelectron spectroscopy(XPS) or electron spectroscopy for chemical analysis(ESCA) has been extensively developed after the pioneering works of Siegbahn (1), and now applied to the various scientific fields. The application of XPS can be also found in the coordination chemistry. In this field, XPS is very useful for studying on the distributions of electrons in transition metal complexes. Cobalt complexes have been studied by several workers(2-8). Most of those studies, however, are preliminary, and have not yet given any systematic interpretation in a point of view from coordination chemistry. Hence, in this communication, we will report XPS study of cobalt(II and III) complexes, including Vitamin B_{12}(cyanocobalamin).

The complexes studied were prepared from the reagent grade chemicals according to the usual established methods. Their purities were examined by elemental analysis for ligands and EDTA titration and atomic absorption spectrometry for cobalt(9).

Measurements of XPS spectra were carried out using a McPherson ESCA 36 Spectrometer with Al Kα X-ray as the exciting radiation source. The samples were studied as fine powders thinly dusted on aluminium plate and/or scotch tape. The observed binding energies were calculated using Au $4f_{7/2}$ as the reference, the binding energy of which was taken as 84.0 eV.

The binding energies of the Co $2p_{1/2}$ and $2p_{3/2}$ lines obtained are listed in

Table 1, where the values of the $2p_{1/2}$-$2p_{3/2}$ peak separation are also given in the parentheses. The binding energies were reproducible to within ± 0.3 eV, and the separation within ± 0.2 eV for both cobalt(II) and cobalt(III) complexes. Several Co 2p photoelectron spectra of cobalt(II) and cobalt(III) complexes are shown in Figure 1. The spectrum of Co 2p in Vitamin B_{12} is also shown in Figure 2. As can be seen from Figure 1, cobalt(II) complexes show the significantly broad and intense Co $2p_{3/2}$ and $2p_{1/2}$ lines with some satellite lines. It has been interpreted that the shake-up processes involving the valence electrons occur on core ionization(10). The Co $2p_{1/2}$ and $2p_{3/2}$ lines of cobalt(III) complexes have the relatively narrow line widths compared to those of cobalt(II) ones, and their satellite lines are very weak or not observed. Cobalt complexes which show observable satellite peaks are signed by * or ** in Table 1. Cobalt(II) complexes investigated are paramagnetic and cobalt(III) ones diamagnetic. The appearance or no appearance of satellite

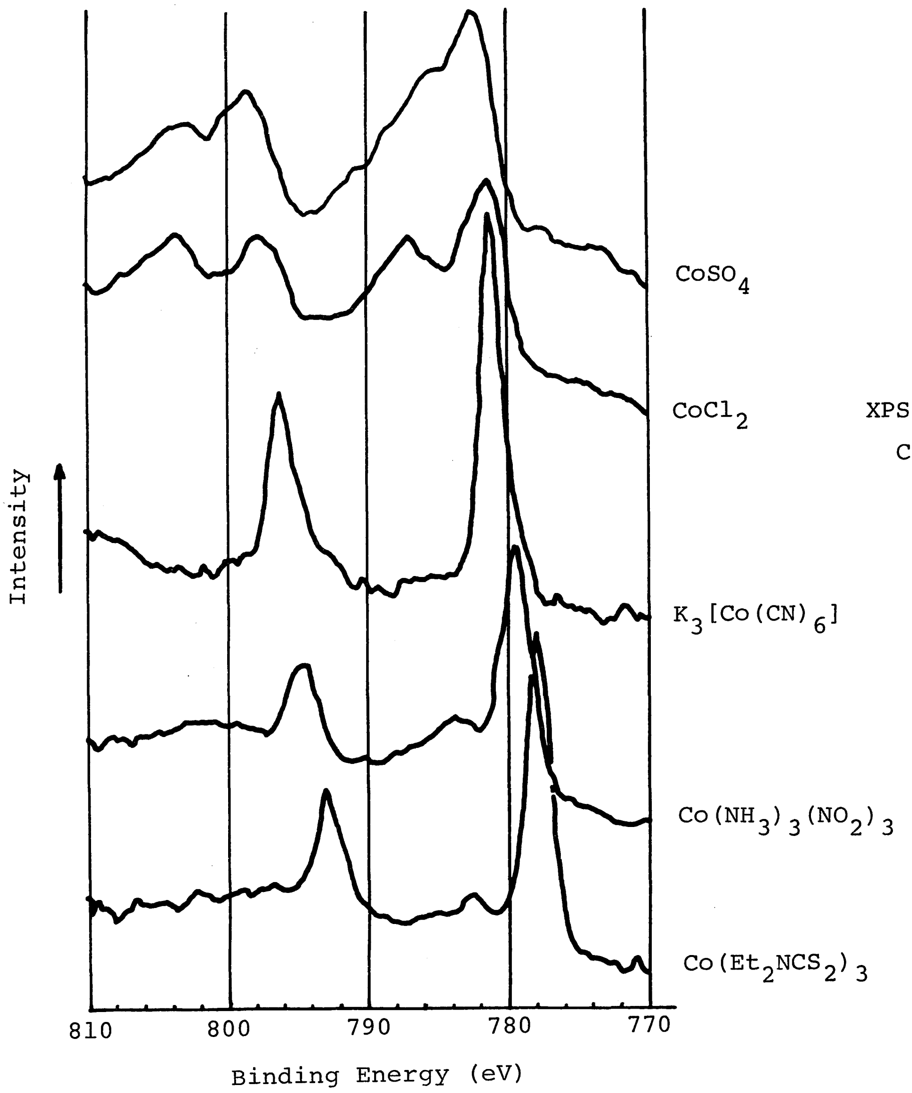

Figure 1

XPS Spectra of Co 2p for Cobalt Complexes.

peaks depending on the paramagnetic or diamagnetic compounds has been known with respect to copper(II) and nickel compounds(2,12).

The separations between Co $2p_{3/2}$ and $2p_{1/2}$ peaks are 16 ± 0.3 eV for cobalt(II) complexes and 15.1 ± 0.3 eV for cobalt(III) ones. That is to say, paramagnetic cobalt(II) complexes show the $2p_{3/2}$-$2p_{1/2}$ peak separation larger by about 1 eV than diamagnetic cobalt(III) complexes. A similar correlation has been known for nickel complexes, but not for copper compounds. Frost et al. attributed these change in the peak separations to the effect of multiplet splitting associated with the unpaired valence electrons in the case of the paramagnetic complexes(3). It should be noted here that the data for the Co $2p_{1/2}$-$2p_{3/2}$ peak separations give an important clue, along with the appearance of the satellite peaks, to distingish the oxidation state of cobalt in complexes.

In Table 1, the binding energies of Co $2p_{3/2}$ do not show any remarkable differences between cobalt(II) and cobalt(III) complexes, while those of Co $2p_{1/2}$ are somewhat larger in the former than in the latter. It is known that cobalt(II) complexes are in square-planar, and cobalt(III) ones in octahedral. The differences of metal oxidation states, stereochemical structures and magnetism might be expected to give the different binding energies of electrons in complexes. Indeed, the binding energies of Ni $2p_{3/2}$ in nickel complexes have been observed to differ according to the differences between them(12,13). In the case of cobalt complexes, it is difficult to know the oxidation states of cobalt only from the binding energies of Co 2p levels. Further investigation may be necessary in order to establish the correlation between the binding energies of Co 2p levels and and the electronic structures of cobalt(II) and cobalt(III) complexes, because the data for cobalt(II) complexes are few.

In Table 1, CoS_6-type complexes give the significantly small binding energies of Co 2p levels. Among other complexes, $NH_4[Co(en)(NH_3)_2(SO_3)_2]$ and $NH_4[Co(NH_3)_4(SO_3)_2]$, which are coordinated with sulfur atom, also give relatively smaller binding energies. According to the studies on cobalt(III) complexes by electronic spectra and cobalt-59 NMR(Nuclear Magnetic Resonance), it has been known that CoS_6-type complexes show the extraordinary behavior compared to other types of complexes(14-16). Fujiwara, Yajima and Yamasaki concluded from a theoretical treatment of cobalt-59 NMR chemical shifts using a molecular orbital theory that the radius of cobalt ion in CoS_6-type complexes is more expanded than those in CoC_6, CoN_6 and CoO_6-type complexes. It may, therefore, reduce the Coulomb potential even at the inner electron-

Table 1. Binding Energies of Photoelectrons in Cobalt Complexes.

	Binding Energy (eV)							
Complex a)	Co 2p		(ΔE) b)	N 1s				S 2p
	$2p_{1/2}$	$2p_{3/2}$		CN	NRR' d)	NO_2	NO_3	
$K_3[Co(CN)_6]$	797.1	782.2	(14.9)	398.6				
$K_3[Co(CN)_5(NO_2)]$	796.8	781.9	(15.1)	398.6		404.2		
$[Co(NH_3)_5(NO_2)]Cl_2$	796.8	781.9	(14.9)		400.3	404.3		
$[Co(dip)_3](ClO_4)_3$	796.8	781.7	(15.1)		400.0			
$[Co(NH_3)_6](NO_3)_3$	796.8	781.5	(15.3)		399.8		406.7	
$[Co(en)_3]Cl_3$	796.7	781.5	(15.2)		400.1			
$K[Co(edta)]$ *	796.5	781.2	(15.3)		400.3			
$[Co(NH_3)_5(CN)]Cl_2$ *	796.3	781.4	(14.9)	... c)	399.3			
$[Co(dien)(NO_2)_3]$ *	796.3	781.3	(15.0)		400.2	403.9		
$NH_4[Co(en)(NH_3)_2(SO_3)_2]$*	796.3	780.9	(15.4)		399.9			166.5
$[Co(acac)_3]$ *	796.2	781.2	(15.0)					
$Na_3[Co(NO_2)_6]$ *	796.2	781.1	(15.1)			404.2		
$NH_4[Co(NH_3)_4(SO_3)_2]$ *	796.1	781.4	(14.7)		400.5			166.2
$[Co(NH_3)_3(NO_2)_3]$ *	796.1	781.2	(14.9)		400.2	403.9		
$[Co(NH_3)_4(SO_3)(CN)]$ *	796.3	780.9	(15.4)	... c)	399.4			166.2
$[Co(EtOCS_2)_3]$ *	794.5	779.5	(15.0)					162.4
$[Co(PrOCS_2)_3]$ *	794.3	779.4	(14.9)					162.4
$[Co(Et_2NCS_2)_3]$ *	794.3	779.2	(15.1)		399.7			162.0
$[Co(Me_2NCS_2)_3]$ *	793.9	778.8	(15.1)		399.6			162.4
......								
$CoSO_4$ **	797.2	780.9	(16.3)					169.1
$CoCl_2$ **	797.4	781.2	(16.2)					
$Co(NO_3)_2$ **	796.8	780.9	(15.9)				406.4	
$[Co(acac)_2]$ **	797.5	781.3	(16.2)					

a) dip=bipyridine, en=ethylenediamine, edta=ethylenediaminetetraacetic acid, dien=diethylenetriamine, acac=acetylacetone, Me=methyl, Et=ethyl, Pr=propyl.

b) The peak separation between Co $2p_{1/2}$ and Co $2p_{3/2}$ in eV.

c) Clear signal could not be observed because of overlap with that of NH_3.

d) R and R' indicate H or alkyl group.

* Complexes which give the weak satellite lines.

** Complexes which give the strong satellite lines.

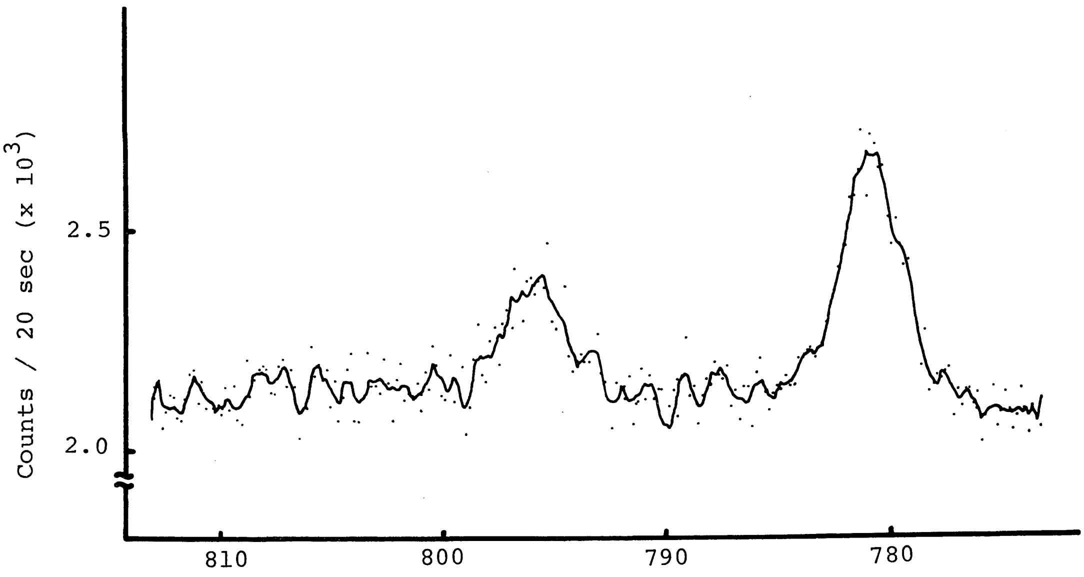

Figure 2 XPS Spectra of Co 2p for Vitamin B_{12}.

ic shell of cobalt, and reduce the binding energies of Co 2p electrons.

Siegbahn et al. reported the XPS spectrum of Co 2p in Vitamin B_{12}, but they did not mention the oxidation state of cobalt(1). In the spectrum shown in Figure 2, the binding energies of Co $2p_{1/2}$ and Co $2p_{3/2}$ are 795.8 eV and 780.9 eV, respectively. Therefore, the peak separation is 15.1 eV. Moreover, the satellite peaks can not be observed in the spectrum. According to the clue given before, these facts indicate that the oxidation state of cobalt in Vitamin B_{12} is $\underline{+3}$. This is consistent with the proposed oxidation state(17).

In addition, the binding energies of N 1s are different in order of $C\underline{N}$, $\underline{N}RR'$, $\underline{N}O_2$ and $\underline{N}O_3$. Those of S 2p are also varied with the kinds of species such as $\underline{S}O_4$, $\underline{S}O_3$ and $C\underline{S}_2$. Moreover, those results can be applied, along with their intensity data, to the state analysis in the various compounds. The data will be discussed elsewhere in near future.

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