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An X-Ray Photoelectron Spectroscopic Study of Biuret Metal Complexes

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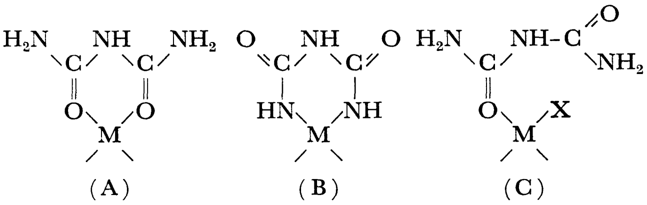
Synopsis. The mode of the co-ordination of biuret in biuret metal complexes has been examined by means of X-ray photoelectron spectroscopy. It has been found that the C(1s), O(1s), and N(1s) binding energies were clearly different among the bidentated, O-, and N-co-ordinated structures, and the monodentated O-co-ordinated one.

Biuret ($NH_2CONHCONH_2$) is known to form the following three types of complexes:



The structure (A) was found by the X-ray analysis for bis(biuret)copper(II) chloride[1] and bis(biuret)zinc(II) chloride.[2] The structure (B) was found for dipotassium bis(biureto)cuprate(II) tetrahydrate.[1] The structure (C) was found for bis(biuret)cadmium(II) chloride.[3] The structures of the other metal complexes have been studied in the solid state by various kinds of physicochemical techniques.[4]

The purpose of this study is to examine the mode of the co-ordination of biuret in the metal complexes by means of X-ray photoelectron spectroscopy(XPS).

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. AlK_α(1486.6 eV) X-ray radiation was used as the excitation source. The samples were ground to powder and then dusted onto double-backed adhesive tape. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. The binding energies were corrected by using the value of 285.0 eV for the C(1s) level resulting from the contaminated carbon. The reproducibilities of the values thus obtained were within ±0.1 eV. All the compounds used and their binding energies measured are given in Table 1. Biuret of an analytical grade was used after recrystallization from ethanol. All the complexes were prepared based upon the literature methods.[4c]

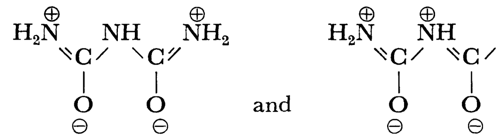
The C(1s), O(1s), and N(1s) electron spectra of biuret and all the biuret complexes except for $K_2[M(biureto)_2]$ (M : Cu, Ni) showed approximately symmetrical single peaks, whose full-widths at the half-maximum heights were 1.8—2.0 eV in the C(1s) and O(1s) spectra, and 2.1—2.2 eV in the N(1s). These results suggest the presence of only one kind of carbon, oxygen, and nitrogen atoms. The N(1s) spectrum of dipotassium bis(biureto)niccolate(II) showed an unsymmetrical peak, as is shown in Fig. 1. This suggests the presence of two kinds of nitrogen atoms as well as dipotassium bis(biureto)cuprate(II). The two peaks, a and b, shown by the broken lines in the figure were obtained by a graphical resolution.

TABLE 1. MEASURED BINDING ENERGIES

Compond	Binding energy (eV)				
	C(1s)	N(1s)	O(1s)	Cl($2p_{3/2}$)	Metal($2p_{3/2}$)
$Cu(LH_2)_2Cl_2$	290.1	400.6	533.0	198.5	936.0
$Ni(LH_2)_2Cl_2$	289.9	400.4	532.6	198.5	856.9
$Co(LH_2)_2Cl_2$	289.9	400.5	532.7	198.6	782.1
$Mn(LH_2)_2Cl_2$	289.9	400.4	532.6	198.5	642.3
$Cd(LH_2)_2Cl_2$	289.6	400.3	532.2	199.0	406.0[a]
$Hg(LH_2)_2Cl_2$	289.5	400.2	532.1	199.4	101.5[b]
K_2NiL_2	287.9	399.7; 398.2	530.8		855.0
$K_2CuL_2 \cdot 2H_2O$	288.1	399.7; 398.0	531.0		934.7
LH_2	289.5	400.2	532.2		
$NiCl_2$				199.4	856.9
$CuCl_2$				199.4	935.8
KCl				198.2	

LH_2 indicates $H_2NCONHCONH_2$. a) Cd($3d_{5/2}$). b) Hg($4f_{7/2}$).

Co-ordination through the two oxygen atoms of biuret can be expected to increase contributions from the structures of the following types:



This should result in an increase in the N(1s) binding energy of the complexes.

In fact, the N(1s) binding energies of $[M(biuret)_2]Cl_2$ (M: Cu, Ni, Co, Mn) were 0.2—0.4 eV higher than that of biuret. The presence of only one symmetrical peak in the N(1s) spectra suggests that the differences among the charges on the three nitrogen atoms in the molecule are not large enough to be detected by XPS. The increase in the C(1s) and O(1s) binding energies of the four complexes above, 0.2—0.4 and 0.4—0.6 eV respectively, compared with those of biuret may be explained by the displacement of

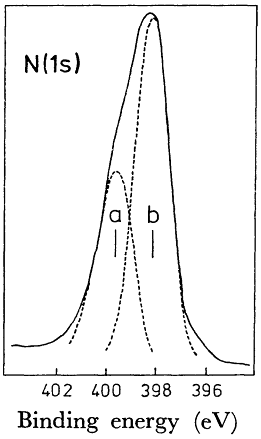


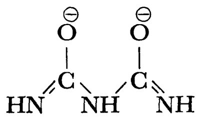
Fig. 1. N(1s) electron spectrum of dipotassium bis(biureto)niccolate(II).

the charge through the oxygen atom to the metal ion upon the complex formation. The Cl($2p_{3/2}$) binding energies of these complexes were 0.3—0.4 eV higher than that of KCl, and 0.8—0.9 eV lower than those of $NiCl_2$ and $CuCl_2$. This indicates that the bond character between the Cl^- ion and the metal ion in these complexes is more ionic than that in $NiCl_2$ and $CuCl_2$, but not so ionic as in KCl. This does not contradict the finding[1)] derived from the X-ray analysis for bis(biuret)copper(II) chloride.

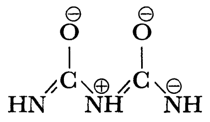
The XPS results presented above lead to the conclusion that the co-ordination modes of biuret are the same in the four metal complexes above.

The C(1s), O(1s), and N(1s) binding energies and the shape of each peak of M(biuret)$_2$Cl$_2$ (M: Cd, Hg) were almost the same as those of the biuret, and the Cl($2p_{3/2}$) binding energies were similar to those of $NiCl_2$ and $CuCl_2$. These suggest that, in the two complexes, the charge displacement on the complex formation occurs mainly between the metal and the Cl^- ions, and that the co-ordination mode in the Hg complex is the same as that[3)] in the Cd.

In the case of dipotassium bis(biureto)niccolate(II), it can be considered that two biuret molecules are co-ordinated to the metal atom, each through two nitrogen atoms of the amide groups, just as in the case of dipotassium bis(biureto)cuprate(II).[1)] This co-ordination mode can be expected to increase contributions from structures of the following types:



and



This should result in a decrease in the O(1s) binding energy of the complex and an appreciable separation of the N(1s) binding energies for the two kinds of nitrogen atoms, central and terminal.

In fact, the C(1s) and O(1s) binding energies of the complexes were 1.6 and 1.4 eV lower in the nickel complex, and 1.4 and 1.2 eV lower in the copper complex, than those of the biuret. Furthermore, the separation energies of the two kinds of peaks with the intensity ratio of about 1 : 2 observed in the N(1s) spectra of the nickel and the copper complexes were 1.5 and 1.7 eV respectively. The two peaks in both complexes could be assigned to the central and terminal nitrogen atoms respectively.

The difference (1.9 eV) between the Ni($2p_{3/2}$) binding energies of dipotassium bis(biureto)niccolate(II) and bis(biuret)nickel(II) chloride may be mainly due to the following differecnes in the bonding types. Firstly, the former complex contains biuret in an anionic species, while the latter contains biuret in a cationic species. That is, the possibility of increasing the electron density on the metal atom is larger in the former case than in the latter. Secondly, the coordination atoms in the two complexes are different, being nitrogen atoms and oxygen atoms respectively. That is, the covalent character of the coordination bond of dipotassium bis(biureto)niccolate(II) is larger than that in bis(biuret)nickel(II) chloride; the electron density on the metal atom is larger in the former complex than in the latter. The difference (1.3 eV) between the Cu($2p_{3/2}$) binding energies of the two analogous copper complexes may be explained in the same way.

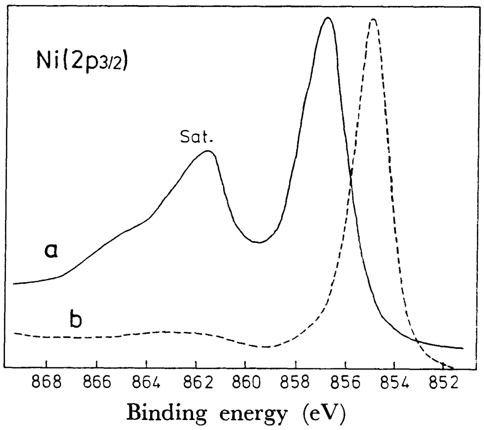


Fig. 2. Ni($2p_{3/2}$) electron region spectra.
a: Bis(biuret)nickel(II) chloride, b: dipotassium bis(biureto)niccolate(II)

XPS can differentiate specifically between the paramagnetic and diamagnetic characters of nickel(II) compounds.[5)] That is, the intense shake-up satellites due to the 3d→4s, 4p transition are found on the high-energy side of the primary peak in the former in the 2p electron region, but they are absent in the latter.

Figure 2 shows the spectra of bis(biuret)nickel(II) chloride and dipotassium bis(biureto)niccolate(II) in the $2p_{3/2}$ electron region. The former complex exhibited a strong satellite peak, but the latter did not. This satellite peak was similar to those of other paramagnetic nickel compounds[6)] in its intensity and its separation energy from the main peak. This suggests that the latter complex is of the low-spin type, and the former, the high-spin type. This agrees with the reported results[4c)] on their magnetic properties.

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