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An X-Ray Photoelectron Spectroscopic Study of Several Hydroxy Azo Metal Complexes

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The X-ray photoelectron spectra of the copper(II) and nickel(II) complexes of five *o*-hydroxy azo compounds were measured. The N(1s) electron spectra of the complexes of 1-phenylazo- and 1-(1-naphthylazo)-2-naphthols showed the presence of only one kind of nitrogen atom, suggesting an equalization in the electron densities on the two nitrogen atoms of an azo group. Such equalization was observed also in the complexes of 1-(8-quinolylazo)-2-naphthol. The N(1s) spectra of the complexes of 1-(2-pyridylazo)- and 1-(2-thiazolylazo)-2-naphthols, on the other hand, showed the presence of three kinds of nitrogen atoms, suggesting the non-equalization of the two nitrogen atoms of an azo group. These results were explained mainly on the basis of the mode of ligand coordination and the resonance structure of the sodium salt of the ligand. Furthermore, the relation between the structures of the complexes and the O(1s) chemical shifts was discussed.

o-Hydroxy azo dyes are very important in analytical chemistry, particularly in the spectrophotomeric and titrimetric determination of metal ions.[1] Furthermore, it is interesting to know whether the azo group is coordinated to the metal ion as a whole or through one of the component nitrogen atoms, since the N=N system is isoelectronic with the CH=CH group, which is capable of coordinating through the π-systems to transition metals, as in Zeise's salt.[2] Therefore, there have been several studies of the structures of their metal complexes by means of some physicochemical techniques.[3] It has been found by X-ray structural analysis that, in the complexes of *o*-hydroxy azo compounds with transition metal ions, one of the component nitrogen atoms of an azo group is coordinated to a metal ion.[3c–3g]

X-Ray photoelectron spectroscopy (XPS), which is sensitive to the charge distribution,[4] is suitable for the examination of the mode of ligand coordination in coordination compounds. The examination is based primarily upon the concept that the coordination of a ligand to a metal ion causes a decrease in the electron density on the coordination atom, giving rise to an increase in the core-electron binding energy of the atom. The XPS study of several hydroxy azo compounds has been reported.[5] The purpose of the present study is to examine the chemical structures of the copper(II) and nickel(II) complexes of several *o*-hydroxy azo compounds by means of XPS.

Experimental

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. Al $K\alpha$ (1486.6 eV) X-ray radiation was used as the excitation source. The samples were ground to a powder and dusted onto double-backed adhesive tape. The measurements were conducted at room temperature under a vacuum of about 10^{-7} Torr. The binding energy of the C(1 s) electron peak was used as the energy standard throughout the present work; it has been taken to be 285.0 eV. The reproducibilities of the values thus obtained were within ± 0.1 eV. No appreciable X-ray damage was observed throughout the experiments. All the compounds used and their binding energies measured are given in Table 1. 1-Phenylazo-, 1-(1-naphthylazo)-, 1-(2-pyridylazo)-, 1-(2-thiazolylazo)-, and 1-(8-quinolylazo)-2-naphthols (abbreviated as $\mathrm{L_AH}$, $\mathrm{L_BH}$, $\mathrm{L_CH}$, $\mathrm{L_DH}$, and $\mathrm{L_EH}$ respectively) were used as ligands. 1,1′-Azonaphthalene (abbreviated as L) was used as the reference compound. 1-(2-Thiazolylazo)-2-naphthol was obtained commercially and was used after recrystallization from an ethanol-water mixture. The sodium salt of 1-(2-pyridylazo)-2-naphthol (abbreviated as $\mathrm{L_CNa}$) was obtained by treating the naphthol with NaOH in a mixture of ethanol and water. This salt was fairly stable compared with the sodium salt of 1-phenylazo-2-naphthol (abbreviated as $\mathrm{L_ANa}$), which was subject to hydrolysis by water.[5] Attempts to prepare the sodium salts of $\mathrm{L_BH}$ and $\mathrm{L_EH}$ were unsuccessful. The other free azo compounds in Table 1 were obtained in the way indicated in the literature.[5] All the complexes were prepared based upon the literature.[3a] However, in the preparation of the complexes in a 1:1 ratio of an azo ligand to a metal ion, the chlorides were used instead of the acetates as metal salts. Furthermore, in the preparation of the complexes of $\mathrm{L_BH}$ and $\mathrm{L_EH}$, an *N*,*N*-dimethylformamide–ethanol mixture was used as the solvent because of the insuffcient solubility of $\mathrm{L_BH}$ and $\mathrm{L_EH}$ in ethanol only. When we attempted to prepare $\mathrm{Ni(L_C)Cl}$ and $\mathrm{Ni(L_D)Cl}$, these complexes were not obtained at all, but $\mathrm{Ni(L_C)_2}$ and $\mathrm{Ni(L_D)_2}$ were obtained. All the compounds used were dried in an air oven at 95 °C and were checked by elemental analysis.

Results

The N(1s) electron spectra of $\mathrm{L_AH}$, $\mathrm{L_CH}$, and their sodium salts are shown in Figs. 1 and 2. Eb in the figures indicates the binding energy. The peaks indicated by the broken lines in the spectra, as well as those in the other N(1s) spectra, were obtained by graphical resolution on the basis of the symmetrical peak with almost the same full-width at half-maximum height (FWHM) as that (1.6 eV) of L containing one type of nitrogen atom. The spectrum of $\mathrm{L_AH}$ as well as that of $\mathrm{L_BH}$ showed a single peak with an FWHM value of about 1.6 eV, while the spectrum of $\mathrm{L_ANa}$ showed two comparable peaks. The spectrum of $\mathrm{L_CH}$ as well as those of $\mathrm{L_DH}$ and $\mathrm{L_EH}$ showed two peaks with an intensity ratio of approximately 2:1, while the one of $\mathrm{L_CNa}$ showed peaks with a ratio of 1:2.

The N(1s) spectra of $\mathrm{Cu(L_A)_2}$, $\mathrm{Cu(L_C)_2}$, and $\mathrm{Cu(L_E)_2}$ are shown in Fig. 3. The spectrum of $\mathrm{Cu(L_A)_2}$, like those of $\mathrm{Ni(L_A)_2}$, $\mathrm{Cu(L_B)_2}$, and $\mathrm{Ni(L_B)_2}$, was almost the same as that of $\mathrm{L_AH}$ in shape. The spectrum of $\mathrm{Cu(L_C)_2}$, like those of $\mathrm{Ni(L_C)_2}$, $\mathrm{Cu(L_D)_2}$, $\mathrm{Ni(L_D)_2}$, $\mathrm{Cu(L_C)Cl}$, and $\mathrm{Cu(L_D)Cl}$, showed a broad

Table 1. Measured binding energies

Compound[a)]	Binding energy/eV			
	N(1s)	O(1s)	S(2p$_{3/2}$)	Metal(2p$_{3/2}$)
$Cu(L_A)_2$	400.1	531.5		934.5
$Ni(L_A)_2$	400.2	531.6		855.2
$Cu(L_B)_2$	400.1	531.6		934.6
$Ni(L_B)_2$	400.2	531.8		855.3
$Cu(L_C)_2$	400.6; 399.7; 399.0	531.0		934.2
$Ni(L_C)_2$	400.6; 399.7; 399.0	531.0		855.6
$Cu(L_D)_2$	400.6; 399.6; 398.9	531.1	164.8	934.3
$Ni(L_D)_2$	400.5; 399.6; 399.0	531.0	164.8	855.7
$Cu(L_E)_2$	400.0; 399.1	530.9		934.2
$Ni(L_E)_2$	400.0; 399.2	531.0		855.4
$Cu(L_C)Cl$	400.8; 399.8; 399.1	531.3		934.6
$Cu(L_D)Cl$	400.7; 399.8; 399.1	531.4	164.8	934.7
$Cu(L_E)Cl$	400.2; 399.4	531.5		934.4
$Ni(L_E)Cl$	400.1; 399.4	531.7		855.4
L_AH	400.5	533.1; 531.1		
L_BH	400.5	533.0; 531.0		
L_CH	400.5; 399.0	533.0; 530.9		
L_DH	400.5; 399.0	533.1; 531.1	164.8	
L_EH	400.3; 398.9	533.0; 530.8		
L_ANa	400.5; 399.0	531.0		
L_CNa	400.4; 399.1	530.9		
L	400.2			

a) L, L_AH, L_BH, L_CH, L_DH, and L_EH indicate 1, 1′-azonaphthalene, 1-phenylazo-, 1-(1-naphthylazo)-, 1-(2-pyridylazo)-, 1-(2-thiazolylazo)-, and 1-(8-quinolylazo)-2-naphthols respectively. L_ANa and L_CNa indicate the sodium salts of L_AH and L_CH.

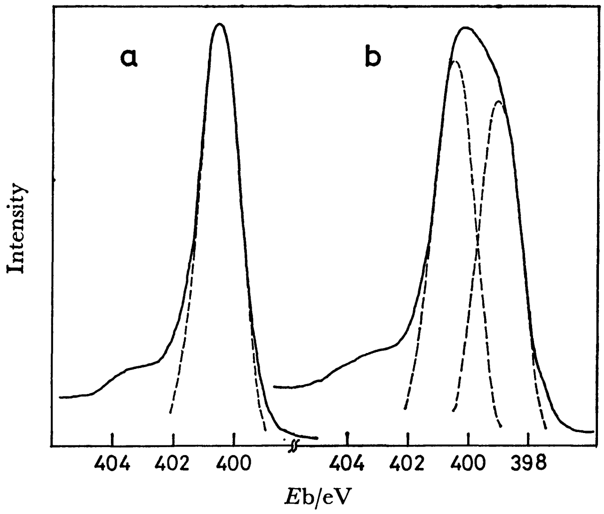


Fig. 1. N(1s) electron spectra of a: L_AH and b: L_ANa.

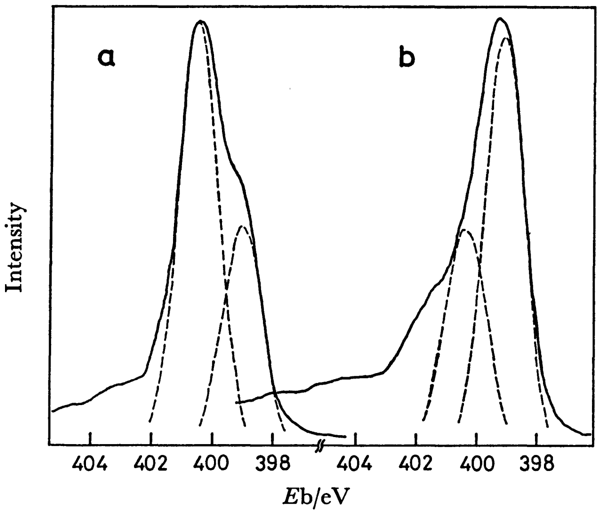


Fig. 2. N(1s) electron spectra of a: L_CH and b: L_CNa.

peak with an FWHM value of about 2.4 eV comprising three peaks with similar intensities. The spectrum of $Cu(L_E)_2$, like those of $Ni(L_E)_2$, $Cu(L_E)Cl$, and $Ni(L_E)Cl$, showed two peaks with an intensity ratio of approximately 2:1.

Satellite signals on the higher-energy side of the primary peak, as are seen in Figs. 1—3, were observed in the N(1s) spectra of all the compounds in Table 1.

The O(1s) spectra of L_AH and $Cu(L_A)_2$ are shown in Fig. 4. The spectrum of L_AH as well as those of L_BH, L_CH, L_DH, and L_EH showed two peaks with comparable intensities, while the spectrum of $Cu(L_A)_2$ as well as those of the other complexes showed one primary peak.

Discussion

All the N(1s) spectra of five free ligands indicated that the electron densities on the two nitrogen atoms of an azo group are almost the same. Here, the peak with the lower binding energy in Fig. 2a was easily

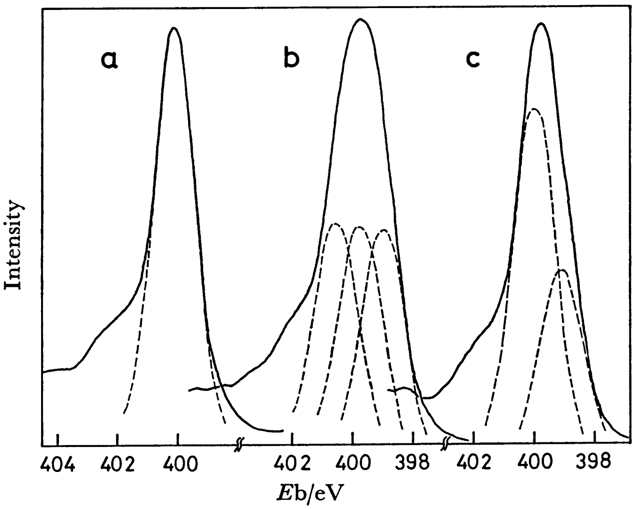


Fig. 3. N(1s) electron spectra of a: $Cu(L_A)_2$, b: $Cu(L_C)_2$, and c: $Cu(L_E)_2$.

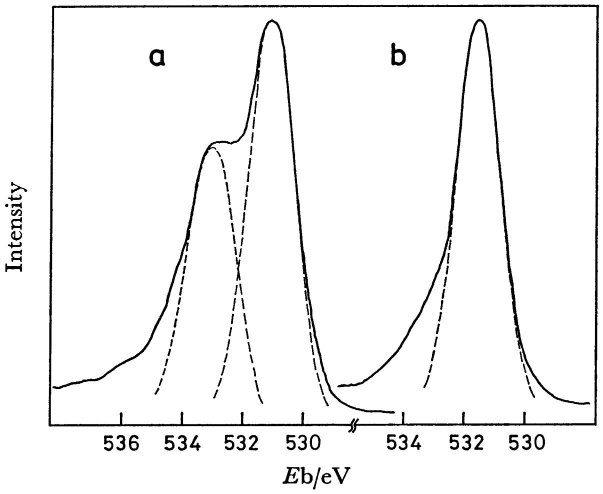
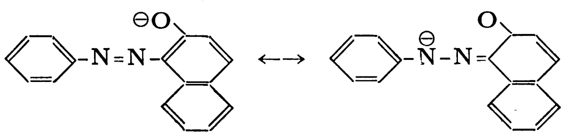


Fig. 4. O(1s) electron spectra of a: L_AH and b: $Cu(L_A)_2$.

assigned to the nitrogen atom of a hetero ring by comparing with Fig. 1a.

The presence of two kinds of peaks in Fig. 1b was due to the following resonance structures:[5]



This resonance suggests that the electron density on the nitrogen atom of an azo group farthest from a naphthalene ring is higher than that on the other nitrogen. Therefore, the peak with the lower binding energy in Fig. 1b can be assigned to the former nitrogen atom, and the other peak to the latter nitrogen.

The peak with the higher energy in Fig. 2b may be assigned to the nitrogen atom of an azo group nearest to a naphthalene ring, and the lower-energy peak, to the other nitrogen of the azo group in addition to the nitrogen of a pyridine ring, by considering the resonance structure of L_CNa to be similar to that of L_ANa. Such resonance structures as those in L_ANa may be expected also in the sodium salts of the other *o*-hydroxy azo compounds in this study.

The spectra of the complexes may be explained in the following way, based upon the structure of the sodium salt estimated above.

In the complexes of L_AH, the hydroxyl group and the nitrogen atom of an azo group farthest from a naphthalene ring are involved in chelate formation.[3c,3d] Therefore, such complex formation may be considered to act to equalize the electron densities on the two nitrogen atoms of an azo group due to the electron transfer from a coordinating atom to a metal ion.

The N(1s) binding energies of an azo group (400.1—400.2 eV) of the complexes of L_AH were slightly lower than the value (400.5 eV) of the nitrogen atom nearest to a naphthalene ring in L_ANa, which does not participate in bond formation. This may be due to the delocalization of π-electrons in the chelate ring suggested by the IR study of the metal complexes of 2-hydroxyazobenzene.[3a] Such delocalization may be supported also by the results of X-ray structural analysis that the N–N distances in $Cu(L_A)_2$ and $Ni(L_A)_2$ are 1.32 Å[3c] and 1.28 Å,[3d] while that of azobenzene is 1.23—1.24 Å.[6] That is, the distances for the complexes are slightly longer than that for azobenzene.

The mode of ligand coordination in the complexes of L_BH is considered to be almost the same as that in the complexes of L_AH, because the N(1s) spectra of the former complexes are very close to those of the latter.

In the complexes of L_CH and L_DH, each of the ligands acts as a terdentate ligand, the hydroxyl group, the nitrogen atom of an azo group nearest to a naphthalene ring, and the heterocyclic nitrogen atom, to give two five-membered chelate rings.[3e–3g] The nitrogen atom farthest from a naphthalene ring, which is expected to be rich in electron density, cannot be coordinated to a metal atom because of steric hindrance. This suggests that the electron densities on the two nitrogen atoms of an azo group cannot become equal on complex formation, unlike in the case of the complexes of L_AH and L_BH.

Therefore, it seems reasonable to assign the three peaks in the N(1s) spectra of the complexes of L_CH and L_DH to the nitrogen atom of an azo group nearest to a naphthalene ring, the nitrogen of a hetero ring, and the remaining nitrogen of the azo group, successively from the higher-energy side.

The N(1s) chemical shifts (0.6—0.8 eV) of the nitrogen atom of a hetero ring of the complexes of L_CH and L_DH, *i.e.* the difference between the N(1s) binding energies of the complex and the free ligand, were comparable with those (0.5—0.9 eV) of the copper and nickel complexes of 8-quinolinol and 2-pyridinecarboxylic acid.[7] This may support the above assignment of the three peaks in the N(1s) spectra. The N(1s) chemical shifts (<0.3 eV) of the nitrogen atom of an azo group which participates in bond formation were smaller than those of the nitrogen of a hetero ring. This seems to be associated with the coordination ability of the donor atoms.

In the complexes of L_EH, it is not known which nitrogen atom of an azo group is coordinated to a metal ion because of the absence of the data of the X-ray structural analysis. In this study, it may be easily expected from the following facts that the nitrogen atom farthest from a naphthalene ring participates in the bond formation, as in the complexes of L_AH and L_BH.

The spectra of the complexes of L_EH showed the presence of two kinds of nitrogen atoms in the proportion of 2:1, unlike the spectra of the complexes of L_CH and L_DH, which show three kinds of peaks. Furthermore, the binding energy (400.0—400.2 eV) of the peak with the larger intensity was very close to those (400.1—400.2 eV) of the nitrogen atoms of an azo group of the complexes of L_AH and L_BH. Therefore, it seems reasonable to assign the peak with the larger intensity to the two nitrogen atoms of an azo group, and the other peak, to that of a quinoline ring. Here, the equalization in the electron densities on the two nitrogen atoms of an azo group can be explained much as in the case of the complexes of L_AH and L_BH.

The N(1s) chemical shifts (0.2—0.5 eV) of a hetero ring in the complexes of L_EH were slightly smaller than those in the complexes of L_CH and L_DH. This may be due to the difference of the mode of the coordination of an azo group in the two groups of complexes.

In hydroxy azo compounds, two kinds of oxygen atoms, keto and enol forms, usually coexist as a result of tautomerism. The peak with the higher binding energy in the O(1s) spectra of L_AH, L_BH, L_CH, L_DH, and L_EH corresponds to the protonated oxygen atom, and the other to the deprotonated oxygen.[5)]

The O(1s) binding energies of $Cu(L_A)_2$, $Ni(L_A)_2$, $Cu(L_B)_2$, $Ni(L_B)_2$, $Cu(L_C)Cl$, $Cu(L_D)Cl$, $Cu(L_E)Cl$, and $Ni(L_E)Cl$, all of which are four coordinate species, were 0.3—0.9 eV higher than those of the deprotonated oxygen atom of the corresponding free ligands, while in the other complexes, which are all six-coordinate species, there were no appreciable chemical shifts of the O(1s) binding energies. Such a result suggests that the interaction between the metal and the oxygen atoms in the complexes of the former group is stronger than that of the latter group. This is consistent with the fact that the nickel–oxygen distance (1.85 Å)[3d)] in $Ni(L_A)_2$, one of the complexes of the former group, is slightly shorter than that (1.98 Å)[3f)] in $Ni(L_D)_2$, one of the complexes of the latter.

The differences of the metal($2p_{3/2}$) binding energies of the complexes were small throughout the present experiment; the values for all the copper complexes were 934.2—934.7 eV, and those for all the nickel complexes were 855.2—855.7 eV. Therefore, no notable information concerning the structures of the complexes could be obtained from the metal binding energies.

In the complexes of L_DH, the thiazole sulfer atom was not considered to participate in the chelate-ring formation, because there was no appreciable chemical shift in the S($2p_{3/2}$) binding energy. This agrees with the results of X-ray analysis.[3f,3g)]

The satellites at ≈4 eV on the higher-binding energy side of the primary peak in the N(1s) spectra in this study may be partly assigned to the shake-up satellite, which is mainly due to the co-excitations of valence electrons, n-π^*, π-π^*, on the ejection of the inner electrons, on the basis of the following facts. These satellites are observed in the spectra of both free ligands and their metal complexes. Such satellites have previously been observed in the N(1s) spectra only of compounds containing the unsaturated bonds with a hetero-atom.[8)] Furthermore, the electron spectra of the aromatic azo compounds generally show the absorption bands due to n-π^*, π-π^* transitions in a region of about $(17—40)\times10^3\ \mathrm{cm}^{-1}$, which approximately corresponds to 2—5 eV.[1a,9)]

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