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# The X-Ray Photoelectron Spectroscopy of *o*-Hydroxy Aromatic Azo Metal Complexes

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**Synopsis.** The photoelectron spectra of azo metal complexes were measured. There was no significant change in the profile or the binding energy of the N(1s) peak upon coordination. It was deduced that, in the bond between the azo-group and the metal, there is a contribution of a $\pi$-bonding.

*o*-Hydroxy aromatic azo compounds, which are bidentate complexing agents containing an azo-group and a hydroxy group *ortho* to the azo-group, are of considerable practical and theoretical interest because of their ability to form stable chelate complexes with some metal ions. There have been many studies of them by means of physico-chemical methods. Ueno[1] has reported an IR study of *o*-hydroxy azobenzene and its metal chelates, while Jarvis[2] and Alcock *et al.*[3] studied the structures of Cu(II)bis(1-phenylazo-2-naphthol) and Ni(II)bis(1-*m*-tolylazo-2-naphthol) by X-ray analysis.

In recent years a method of X-ray photoelectron spectroscopy (ESCA) has been developed; it is capable of yielding information pertinent to the study of chemical bonds in that the binding energy of an inner-shell electron is characteristic in both its elemental identity and the chemical environment of the atom. The differences in binding energies between coordinated and uncoordinated ligand atoms have been used to support arguments concerning $\pi$ back-bonding in some coordination compounds.[4] The purpose of this paper is to report the results of a study by this method of some *o*-hydroxy aromatic azo metal complexes.

The X-ray photoelectron spectra were measured on an AEI ES100 spectrometer under the control of a DS100/32 computer data-processing system. An AlK$\alpha$ (1486.6 eV) X-ray line was used as the excitation source. All the samples measured are given in Table 1. The 2-arylazophenol and 1-arylazo-2-naphthol derivatives were prepared by coupling diazotized amines with *p*-tolylphenol and $\beta$-naphthol respectively. Chelate compounds with a ligand-metal ratio of 2:1 were synthesized according to the procedures of Elkins and Hunter.[5] The samples were ground to powder, dusted onto a double-backed adhesive tape, and set inside the measuring chamber. The measurements were run at room temperature under a vacuum of about $10^{-6}$ Torr. A few volatile samples were introduced *via* a heatable reservoir shaft and condensed on a cooled copper holder.

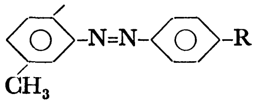
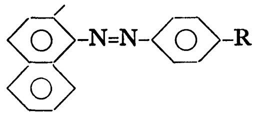
The binding energy of the C(1s) peak was used as the energy standard throughout the present experiments; it was taken to be 285.0 eV, the C(1s) binding energies for all the samples being assumed to be constant.

The N(1s) spectra of all the compounds were composed of single peaks with full-width half-heights of 1.6—1.8 eV in all the free azo compounds and Cu chelates, and 1.5—1.7 eV in all the Ni chelates. In view of these results, the difference between the charge densities on the two nitrogen atoms of an azo-group is considered to be so small that they can not be distinguished by ESCA in all these compounds.

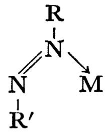
The measured values for the N(1s) binding energies are listed in Table 1. There were no remarkable changes in the N(1s) binding energy upon the coordination of all azo compounds to metals, although barely appreciable minus changes appear to be observed in 1-arylazo-2-naphthol derivatives. Therefore, it seems reasonable to assume that there is no significant change in the electron density around the azo-group on the complex formation.

There are chiefly two known modes of the formation of a bond between an azo-group and a metal atom. The one is Type (1), in which one lone-pair electron of a component nitrogen atom is coordinated to the

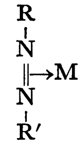
TABLE 1. N(1s) BINDING ENERGY VALUES

| Sample | R | B.E. of N(1s) (eV)[a] Free | B.E. of N(1s) (eV)[a] Cu-Chelate | B.E. of N(1s) (eV)[a] Ni-Chelate | $E$ (eV)[b] Cu-Chelate | $E$ (eV)[b] Ni-Chelate |
|---|---|---|---|---|---|---|
|  | $-OCH_3$ | 399.8 | 400.0 | — | +0.2 | — |
| | $-H$ | 400.0 | 400.1 | 400.2 | +0.1 | +0.2 |
| | $-NO_2$ | 400.2 | 400.1 | 400.2 | −0.1 | ±0.0 |
|  | $-OCH_3$ | 400.3 | 400.0 | 400.2 | −0.3 | −0.1 |
| | $-H$ | 400.6 | 400.1 | 400.3 | −0.5 | −0.3 |
| | $-NO_2$ | 400.5 | 400.0 | 400.2 | −0.5 | −0.3 |

a) Uncertainties are equal to ±0.1 eV. b) The differences between the N(1s) binding energies of the chelate and the free azo compounds.



type (1)



type (2)

metal, while the other is Type (2),[6] in which the whole of the N=N bond itself is coordinated to the metal, just as in metal-olefin complexes, in which the $\pi$-electrons of the carbon-carbon double bond are capable of coordination with a metal.

The results of the X-ray analysis[2,3] suggest that the bonds between the azo-group and the metals in the Cu and Ni chelates of 1-phenylazo-2-naphthol are of Type (1).

Aromatic compounds containing an N=N bond generally exhibit absorption bands at approximately 320—315 nm; these bands are attributed to the conjugation of the unsaturated nitrogen with the phenyl rings. Kleiman and Dubeck[7] have suggested that, on complex formation, the disappearance and the retaining of such absorption bands indicate that the nitrogen system in the complex is bonded to the metal as is shown in Type (2) and in Type (1) respectively.

The UV measurements in the above region for all the chelates listed in Table 1 indicate absorption peaks with almost the same intensities as those of free azo compounds.

Accordingly, it may be concluded that all the chelates used in this study belong to Type (1). In the case of Type (1), it appears that the charge densities on the nitrogen atoms of the azo-group are not equal. If this is really true, the ESCA spectrum of the N(1s) of the chelate should give a different profile from that of the free one, for instance, with two well-resolved peaks or a single broad peak. As has been stated previously, however, scarcely no such phenomena were observed in this study.

From these experimental facts, the data obtained in this experiment may be explained as follows.

In all the chelates in Table 1, there are two effects of opposing factors. One is the $\sigma$-bonding by the coordination of a lone-pair electron of a nitrogen atom to the bonding orbital of Cu or Ni; the other is the $\pi$-bonding by the coordination (back-donation) of the *d*-electrons of Cu or Ni to the vacant anti-bonding orbital of the azo-group. These effects result in a neat cancellation of the total electron drift and a small change in the total electron density in the neighborhood of the nitrogen atom. This is the explanation for the facts that the difference between the N(1s) binding energies of the free ligand and the chelate is too small in view of the stability of the chelates, and that the profile of the N(1s) of the chelate is almost the same as that of the free ligand.

Though the problem remains unsolved, it is noteworthy that the change in the N(1s) binding energies is very small throughout all the chelates.

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