XPS EVIDENCE FOR THE ORDER IN STABILITIES OF N,N,O-TERDENTATE COMPLEXES OF 2-(2-PYRIDYLAZO)PHENOLIC LIGAND WITH THE DIVALENT METALS

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The core electron binding energies of N(1s) and O(1s) in the eight complexes of an N,N,O-terdentate ligand, 5-dimethylamino-2-(2-pyridylazo)phenol, with divalent transition metals were measured by means of X-ray photoelectron spectroscopy (XPS). The results indicate that the thermodynamic stabilities of the N,N,O-terdentate chelates are controlled by the extent of the electron localization between the central metal and the donor nitrogen (azo and pyridyl) and oxygen (phenolate) atoms.

X-Ray photoelectron spectroscopy (XPS) is a powerful tool for the study of the coordination bonds of donor nitrogen and oxygen atoms with metal ions in various N,N- and/or N,O-bidentate complexes.[1,2] Since coordination with metal ions by sigma electron pair sharing of the donor atom in the ligand is expected to lead to a decrease in the electron density on the donor atom, the core electron binding energy (BE) of the donor atom should be increased upon formation of a coordination bond. It has been pointed out that the strength of the coordination bonds of the donor nitrogen atom with the metal ions determines the stabilities of the complexes of divalent metal ions with N,N- and N,O-bidentate ligands.[3,4]

In the present communication, we describe on the basis of XPS measurements the difference in the contribution of the M-N and the M-O bonds to the stabilities of the chelates of various divalent transition metals with an N,N,O-terdentate 2-(2-pyridylazo)phenolic ligand.

The complexes were prepared by mixing an ethanolic solution of the N,N,O-terdentate ligand, 5-dimethylamino-2-(2-pyridylazo)phenol (DAPAP), with an acidic solution of the divalent metal chloride. The compositions of the complexes were found to be $M(dapap)_nCl_{2-n}$ (n = 1 or 2). The visible absorption spectra in absolute ethanol of isolated complexes exhibited
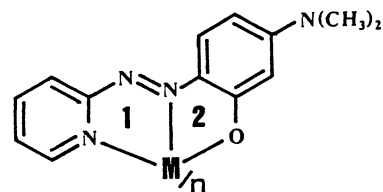

Fig. 1. The configuration of the 1 : n M(II)-DAPAP complexes. n = 1: M = Cu, Pd, and Cd; n = 2: M = Mn, Ni, Zn, and Cd. The N,N- and the N,O-chelate rings are respectively indicated by the numbers 1 and 2.
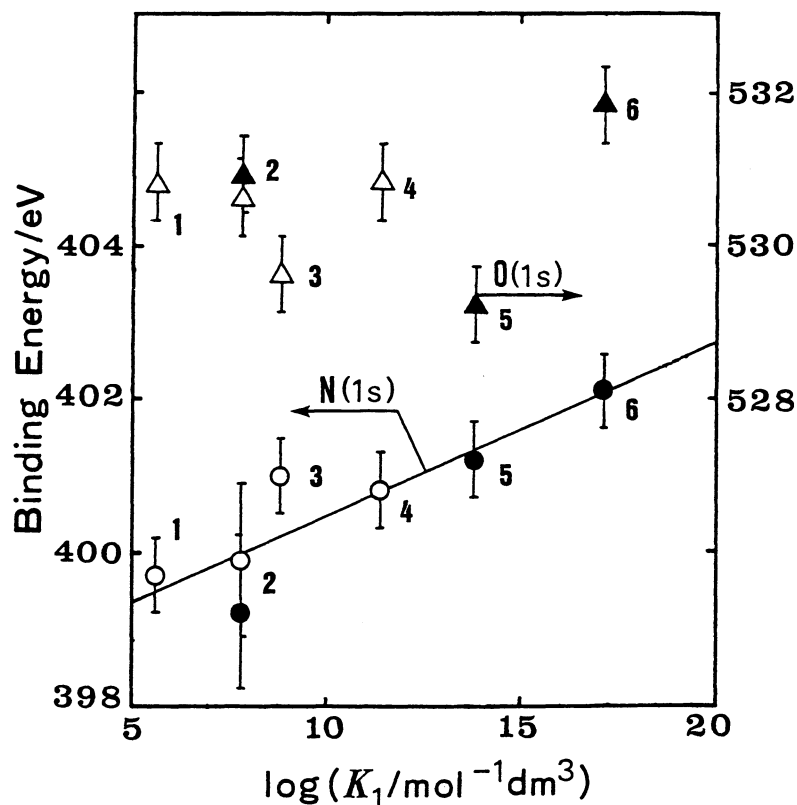
Fig. 2.   The plots of BE's of the donor atoms, the N(1s) (circle)
and the O(1s) (triangle), in the 1 : n M(II)-DAPAP complexes vs.
$\log(K_1/\text{mol}^{-1}\text{dm}^3)$ of the o-PAP complexes of the corresponding M(II)
atoms.   M = Mn(1), Cd(2), Zn(3), Ni(4), Cu(5), and Pd(6).   Full and
open circles or triangles denote the 1 : 1 and the 1 : 2 M(II)-
DAPAP complexes, respectively.

the double peak character in the range of 500 to 560 nm which is usually observed
for the N,N,O-terdentate complexes of DAPAP derivatives.[5]   The coordination mode
of DAPAP in the complexes is shown in Fig. 1.   The spectra of the core electron
BE's[6] of the N(1s) and the O(1s) were obtained with the powdered sample using a
VG ESCA 3 spectrometer employing MgKα radiation at room temperature under ca. 10^{-7}
Pa.

The observed N(1s) BE spectra in the complexes[7] were deconvoluted by Gaussian
curves into four peaks with a full widths at half-maximum, FWHM, 2.8 ± 0.2 eV.
Since the order of BE values of N(1s) in various chemical environments is reported
to be generally amino, pyridyl (uncoordinated) < azo (uncoordinated) < pyridyl
(coordinated) < azo (coordinated),[1,2,8] the highest N(1s) BE peak in the four
peaks was assigned to the peak of the coordinated azo nitrogen.   The O(1s) spectra
were deconvoluted into two major peaks (FWHM = 3.0 ± 0.3 eV[1]).   The O(1s) peak
with lower BE showing a considerable shift with the change of the central metal in
the complex was assigned to the peak of the coordinated phenolate oxygen.[9]

Figure 2 shows the plots of core electron BE values of the coordinated azo N-(1s) and the coordinated phenolate O(1s) in M(II)-DAPAP complexes against the logarithms of the stability constants of the 1 : 1 complexes of 2-(2-pyridylazo)phenol (o-PAP), $\log(K_1/mol^{-1}dm^3)$, of the corresponding metals in 50% aqueous methanol.[10,11] The term of $\log(K_1/mol^{-1}dm^3)$ could mainly reflect the enthalpy change for the complex formation of o-PAP with a metal ion because the entropy changes for the complex formations of the multidentate ligands such as ethylenediamine, 2,2',2"-triaminotriethylamine with divalent transition metal ions are generally almost constant.[12] The plot clearly indicates that the BE's of the coordinated azo N(1s) in the complexes of DAPAP increased with the increase in the stability, $\log(K_1/mol^{-1}dm^3)$, of the chelates.[13] The increase of the N(1s) BE's corresponded to that of the electronegativities of the central metal atoms except for the Cd(II) atom.[7] The higher values of the N(1s) BE's of the Zn(II), Cu(II), and Pd(II) complexes reveal that the extents of the electron donation of the pyridyl and the azo nitrogens to the central metal atoms are larger than those in the other metal complexes.[2] On the other hand, no linear relationship was obtained between the O(1s) BE and $\log(K_1/mol^{-1}dm^3)$ of o-PAP complexes. The higher BE values of the O(1s) in the Pd(II), Cd(II), and Mn(II) complexes suggest the larger electron donation of the phenolate oxygen of the ligand to the metal atoms. The higher O(1s) and N(1s) BE's of the N,N,O-terdentate complexes correspond to the fact that Mn(II) ion prefers the binding with oxygen atom and Ni(II), Cu(II), and Zn(II) ions prefer the binding with donor nitrogen; by replacing one donor nitrogen atom of an N,N-bidentate ligand in the complex with a donor oxygen atom, the stability of Mn(II) complex is enhanced, whereas the stabilities of Ni(II), Cu(II), and Zn(II) complexes are lowered.[3,4] From these facts, the higher O(1s) BE of the N,N,O-terdentate Mn(II) complex of DAPAP in Fig. 2 is ascribed to the larger contribution of the M-O(phenolate) bond to the stability in the Mn(II) complex compared with that in the Cu(II) and the Zn(II) complex.

The stabilization of the Mn(II) and the Cd(II) N,N,O-terdentate chelates is mainly caused by the increased strength of the M-O bond in the N,O-chelate moiety (Ring 2 in Fig. 1) (a). The stabilization of the N,N,O-terdentate chelates of the Cu(II) and the Zn(II) depends on the strength of the M-N bonds in the N,N-chelate moiety (Ring 1 in Fig. 1) (b) judging from the results of the higher N(1s) BE's. The Pd(II) complex is largely stabilized by the increased strength of both the M-N and the M-O bonds in the N,N- and the N,O-chelate moieties (c). The relative stability of the chelates investigated here was found to be in the order a < b < c. In conclusion, the thermodynamic stability of the chelates of the N,N,O-terdentate ligands is predominantly attributed to the increased strength of the covalent M-N bonds in the N,N-chelate ring; the strength of the M-N bonds is in turn controlled by the extent of the localization of electrons between the central metal atom and the donor oxygen atom in the N,O-chelate ring.

It is of interest that the above results could be applied to the determinations of stability constants of the complexes of low water solubilities. The undeconvoluted N(1s) and O(1s) BE peaks of Pt(II)-DAPAP complex, Pt(dapap)Cl, were observed at 401.4 and 534.9 eV, respectively. The Pt(II) complex can be classi-

fied to the group c and presumed to be very stable. This result is also in accordance with the fact that stabilities of Pt(II) complexes are generally much higher[14] than those of the corresponding complexes of the other metals discussed above.

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9) Since the higher O(1s) BE peaks at 533-534 eV were increased with the addition of water vapor at 77 K, the peaks were assigned to those of water of crystallization and/or adsorbed water molecules.

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11) It is reasonable to expect a linear relationship between the stability constants of the M(II) complexes of DAPAP and those of o-PAP, since DAPAP and o-PAP possess the same donor systems forming the same type of N,N,O-terdentate complexes with M(II) ions. Since only the value of $\log(K_1/\text{mol}^{-1}\text{dm}^3)$ for Ni(II)-o-PAP complex was not available, the value was roughly estimated to be one-half of $\log(\beta_2/\text{mol}^{-2}\text{dm}^6)$ (22.8). The estimation seems to be reasonable in the first approximation, since the value of $\log(K_1/\text{mol}^{-1}\text{dm}^3)$ thus estimated for the Ni(II) complex of o-PAP is consistent with the order of stability constants proposed by Irving and Williams,[3] Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II).

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