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X-Ray Photoelectron Spectroscopy of 1,10-Phenanthroline Metal Chelates

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Synopsis. Photoelectron spectra of several phenanthroline metal chelates were measured and the shifts of the N(1s) binding energy were plotted against the electronegativities of the metals. The plotted points appeared to fall into two groups, one for transition-metal chelates and the other for the other metal chelates.

The use of X-ray photoelectron spectrometry (XPS) to determine the effect of co-ordination on the electron density of a ligand is based on the fact that changes in the electron density about an atom are reflected in changes of the binding energies of the core electrons. The authors have previously reported results on the XPS of several metal chelate compounds.[1—3] It is well known that 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), both having electron-donating and accepting capabilities, form very stable complexes with various cations, especially the Fe(II) ion.[4]

In this note, the results for several phen and bipy metal chelates using an XPS method will be presented.

Binding energies were measured employing an AEI ES200 photoelectron spectrometer under the control of a DS100/32 computer data-processing system using AlK$_\alpha$ radiation (E=1486.6 eV) as the photon source. All the metal complexes given in Table 1 were prepared according to the procedures of Schilt and Taylor.[5] The samples were ground to powder, dusted onto double-backed adhesive tape, and set inside the measuring chamber. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. However, a freezing technique was used for a few volatile samples.

The binding energy of the O(1s) peak was used as the energy standard throughout the present experiments; it was taken to be 532.0 eV, the O(1s) binding energies for all the samples being assumed to be constant. The C(1s) peak was, however, used for compounds having no perchlorate group as a constituent.

TABLE 1. N(1s) ELECTRON BINDING ENERGY VALUES

Samples	B.E. of N(1s)[a] (eV)	ΔE[b] (eV)	χ[c]	r[d] (Å)	pK[e]
phen	398.9				
phen(H_2O)	398.9				
phen($HClO_4$)	401.2; 398.9				
Mn(II)(phen)$_3$(ClO_4)$_2$	399.6	0.7	1.5	0.80	10.1
Fe(II)(phen)$_3$(ClO_4)$_2$	399.9	1.0	1.8	0.74	21.3
Co(II)(phen)$_3$(ClO_4)$_2$	399.7	0.8	1.8	0.72	19.9
Ni(II)(phen)$_3$(ClO_4)$_2$	399.7	0.8	1.8	0.69	24.8
Cu(II)(phen)$_2$(ClO_4)$_2$	399.9	1.0	1.9	0.72	11.0
Zn(II)(phen)$_3$(ClO_4)$_2$	399.7	0.8	1.6	0.71	17.5
Cd(II)(phen)$_3$(ClO_4)$_2$	399.5	0.6	1.7	0.97	14.3
Hg(II)(phen)$_3$(ClO_4)$_2$	399.0	0.1	1.9	1.10	23.3
Cu(I)(phen)$_2$(ClO_4)	399.4	0.5	1.7[f]	0.96	—
Ag(I)(phen)$_2$(ClO_4)	399.1	0.2	1.8[f]	1.31	12.0
bipy($HClO_4$)	401.2; 398.9				
Fe(II)(bipy)$_3$(ClO_4)$_2$	399.9	1.0			
Ni(II)(bipy)$_3$(ClO_4)$_2$	399.6	0.7			

a) Uncertainties are less than or equal to ±0.2 eV. b) Chemical shift of the N(1s) electron binding energy. c) Pauling electronegativity of the metal. d) Ionic radius of the metal. e) The logarithms of the overall stability constants of the chelates.[10] f) The value corrected according to Pauling.[12]

The measured values for the N(1s) electron binding energies are listed in Table 1 with other constants reported in the literature. Figure 1 shows the N(1s) electron spectra of phen($HClO_4$) and Fe(II)(phen)$_3$(ClO_4)$_2$. As can be seen from the figure, there are two kinds of nitrogen atoms in phen($HClO_4$), in addition to those observed in bipy($HClO_4$). The N(1s) spectrum of phen is a single peak with a full width at half height (FWHH) of 1.4 eV, and its binding energy value, 398.9 eV, agrees well with that of the peak with the lower binding energy of the two in phen($HClO_4$). Therefore, it can be concluded that the higher binding energy peak of the two in phen($HClO_4$) can be assigned to the protonated nitrogen atom and the lower to the unprotonated nitrogen atom.

The N(1s) binding energy value of phen(H_2O) is the same as that of phen, so the effect of the presence of a hydrogen bond in the molecule cannot be detected by XPS. The N(1s) spectrum of Fe(II)(phen)$_3$(ClO_4)$_2$ is a single peak with a FWHH of 1.4—1.5 eV, as are those of all other metal chelates. It can be concluded that all nitrogen atoms in the chelate molecule have equivalent charge densities.

The O(1s) electron spectra of all the compounds containing a perchlorate group are single peaks with a FWHH of 1.7—1.9 eV.

The chemical shifts ΔE are the differences between the N(1s) electron binding energies for the free phen and that for the chelates. Figures 2 and 3 show the chemical shifts which are plotted against the Pauling electronegativity of the metal and the ionic radius, respectively. In Fig. 2, the points appear to fall into two groups. The points for the transition-metal chelates (d^5, d^6, d^7, d^8, and d^9 complexes) Mn(II), Fe(II), Co(II), Ni(II), and Cu (II) fall near one straight line. On the other hand, the points for the Zn(II), Cd(II), Cu(I), Hg(II), and Ag(I) chelates (d^{10} complexes) fall near another straight line having a negative slope, the chemical shift in this case decreasing with increasing electronegativity of the metal. In Fig. 3, the points for all the chelates fall near one straight line, the chemical shift decreasing with increasing ionic radius.

In the charge-potential model,[6] the chemical shift can be expressed in terms of the charge on the atom and the Coulomb potential energy of an electron due to the other atoms in the molecule. In general, the neglect of the Coulomb potential energy may cause serious errors for ionic compounds, but for the covalent compounds as studied here, the chemical shift should be dominated by the charge on the atom concerned.

The difference just noted in Fig. 2 suggests that a fundamental difference of some sort may exist between the structures of the two groups of chelates. The most obvious difference between the transition-metal cations

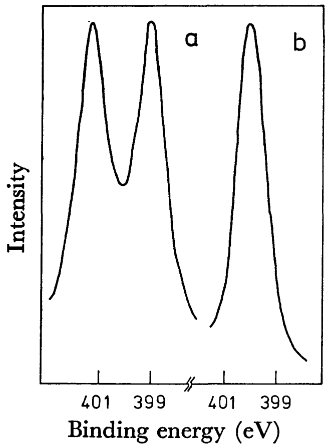

Fig. 1. N(1s) electron spectra of (a) phen($HClO_4$), and (b) Fe(II)$(phen)_3(ClO_4)_2$.

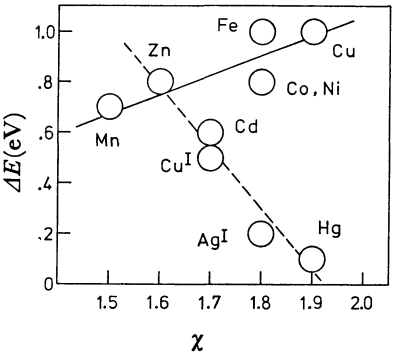

Fig. 2. Relation between electronegativity and chemical shift.

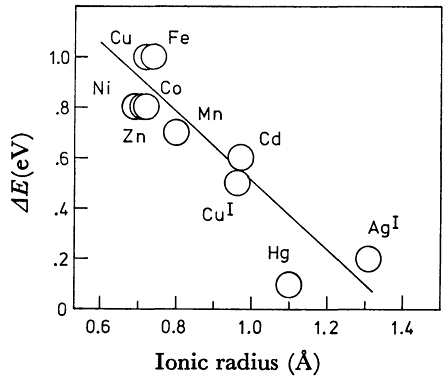

Fig. 3. Relation between ionic radius and chemical shift.

and the other metal cations mentioned is the presence of available 3d orbitals in the former. A possible explanation, then, for the difference noted is the participation of 3d orbitals in the metal–ligand bonding. However, Craig *et al.*[7] have reported on the basis of magnetic susceptibility measurements of $Ni(bipy)_3^{2+}$ that 3d-orbitals may not be involved in metal–ligand bonding for this chelate, and even if involved, not to the extent of forming a $3d^24s4p^3$ hybridized bond.

In general, the bond between a ligand and a metal for coordinate compounds is explained by a σ-bonding (the coordination of a lone pair electrons of a ligand to a metal) and a π-bonding (back-domation from filled metal ion orbitals to empty ligand orbitals) in many cases. These two effects work in opposite directions as for the electron density on the donor atom of the ligand.

If the σ-bonding is more important in the complex formation than the π-bonding, it can be said that the covalent character of the bonds between the metal ions and the ligand increases with the metal ion electronegativity, and that the degree of complex stability is affected by this character.[8] Furthermore, more covalent coordinate bonding is considered to decrease the electron density on the donor atoms, which appears in the increase of the electron binding energies.

When the π-bonding is important, there is no longer correlation between the metal ion electronegativity and the electron density of the donor atoms, as was stated above.

For EDTA, anthranilic acid and oxine chelates in which the double bond with the metal atom is not present or is weak, the plots of the N(1s) chemical shift as a function of the electronegativity of the metal actually showed that all the points for the transition and the other metal chelates appeared to fall near one straight line.[1,2,9]

It has been reported by Busch *et al.*[10] that the chemical behavior and properties of phen and bipy complexes are best described in terms of σ-bonds formed between the metal and the methine nitrogens, and of π-bonds resulting from interaction of the unhybridized d-electron pairs of the metal atom with the π-system of the ligand.

In this study, the fact that the N(1s) chemical shifts of the Hg(II) and the Ag(I) chelates are small compared to those of the Ni(II) and the Cu(II) chelates, as is seen in Fig. 2, which have stabilities similar to the former two chelates (the logarithms of the stability constants of the Hg(II) and the Ag(I) chelates are 23.3 and 12.0, respectively, while those of the Ni(II) and the Cu(II) chelates are 24.8 and 11.0, respectively)[11] may be attributed in part to the greater contribution of the dative π-bond in the metal-ligand bond of the Hg(II) and the Ag(I) chelates.

In the phen metal chelates, the ionic radii of metal ions may be one of the important factors that affect the electron density of the donor atom in view of the relation in Fig. 3. This may be correlated with the geometrical structure characteristic of the phen molecule that the distance between the two donor nitrogen atoms is invariable.

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