November, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 3257—3260 (1978) 3257

An X-Ray Photoelectron Spectroscopic Study of Dioxime Metal Complexes

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(Received June 13, 1978)

The O(1s) and N(1s) electron-binding energies were measured for the dioxime complexes of several transition metals by means of the X-ray photoelectron spectroscopic method. On the basis of their chemical shifts, the strength of the intramolecular hydrogen bonds and the charge distribution around the nitrogen atoms in the complexes are discussed. Two kinds of oxygen atoms were observed for all the complexes, and their binding energy differences were in the range of 1.3—1.9 eV. This difference was found to decrease with the increase in the strength of the hydrogen bonds. However, only one kind of nitrogen atom was observed for all the compounds except one. The N(1s) chemical shifts were in the range of 0.2—0.8 eV, and were found to increase slightly in the order of $\mathrm{Cu^{II}} < \mathrm{Ni^{II}} < \mathrm{Pd^{II}} < \mathrm{Pt^{II}}$.

It is well known that dimethylglyoxime is the first selective organic reagent[1)] applied in the analyses of metals. In order to establish the structure of dimethylglyoxime complexes of transition metals, several complexes have been investigated by X-ray diffraction,[2-7)] infra-red spectrophotometry,[8-14)] magnetic[15-17)] and stability[18,19)] measurements. These investigations confirmed the square planar structure of the dimethylglyoxime complexes with a metal-ligand ratio of 1:2 of nickel, palladium, platinum, and copper. Furthermore, these investigations proved more important factors stabilizing the dioxime complexes to be the intramolecular hydrogen bonds in the planar configuration and the metal→ligand donor-acceptor π bonds in the chelate rings.

There have been two different opinions regarding the intramolecular hydrogen bonds in the Ni complex of dimethylglyoxime; one is that they are symmetric,[2,8,14,20)] and the other that they are unsymmetric.[11)] These conflicting results are due to the complexity of assigning the band of a hydroxyl group in IR. The former opinion is based only on the apparent centrosymmetric structure of the complex, the short O–O distance, and the low OH stretching frequency. No direct location of the protons has been carried out.

It has been known that X-ray photoelectron spectroscopy (XPS) is suitable for the detection of a protonated atom.[21)] The purpose of the present study is to examine the hydrogen bonds and the π bonds in several dioxime complexes of transition metals 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. Samples were ground to a powder and then dusted onto a double-backed adhesive tape. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. Dimethylglyoxime, benzil dioxime, 1,2-cyclohexanedione dioxime (abbreviated as LH, L′H, and L″H) were used as ligands, and nickel(II), palladium(II), platinum(II), copper(II), and cobalt(III), as metal ions. All the free ligands were commercially available and of an analytical grade, and were used without further purification. All the complexes were prepared by the literature methods, and were checked by elemental analysis.

All the C(1s) electron spectra showed nearly symmetrical single peaks with the full-width at a half-maximum height (FWHM) of 1.8—2.0 eV for benzil dioxime and 1,2-cyclohexanedione dioxime and their metal complexes, and of 2.0—2.2 eV for dimethylglyoxime and its metal complexes. It is reasonable to assume that the C(1s) binding energy is nearly constant within the complexes with the same ligand. Furthermore, as only the relative binding energies were considered in the present study, the binding energy of the C(1s) peak was used as the energy standard throughout the experiments; it was taken to be 285.0 eV. The reproducibilities of the values thus obtained were within ±0.1 eV.

Results

The O(1s) and N(1s) electron-binding energies measured are given in Table 1.

The O(1s) Spectra. The O(1s) electron spectra of the dimethylglyoxime complexes are shown in Figs.

TABLE 1. MEASURED BINDING ENERGIES

Compound[a)]	Binding energy (eV)			N(1s) chemical shift (eV)[c)]
	N(1s)	O(1s)	ΔE[b)]	
$\mathrm{PtL_2}$	400.8	532.8; 531.0	1.8	0.8
$\mathrm{PdL_2}$	400.7	532.8; 531.0	1.8	0.7
$\mathrm{NiL_2}$	400.5	532.5; 531.2	1.3	0·5
$\mathrm{CuL_2}$	400.3	532.8; 531.1	1.7	0.3
$\mathrm{Co^{III}L_3}$	400.3	532.9; 531.0	1.9	0.3
$\mathrm{[Co^{III}(NH_3)_2L_2]Cl}$	400.7; 399.4	532.6; 531.2	1.4	0.7
$\mathrm{HCo^{III}L_2Cl_2}$	400.7	532.8; 531.2	1.6	0.7
$\mathrm{PtL'_2}$	401.4	533.4; 531.7	1.7	0.6
$\mathrm{PdL'_2}$	401.2	533.4; 531.7	1.7	0.4
$\mathrm{NiL'_2}$	401.1	533.0; 531.7	1.3	0.3
$\mathrm{CuL'_2}$	401.0	533.4; 531.7	1.7	0.2
$\mathrm{PtL''_2}$	400.9	533.1; 531.2	1.9	0.7
$\mathrm{PdL''_2}$	400.8	533.1; 531.2	1.9	0.6
$\mathrm{NiL''_2}$	400.6	532.6; 531.2	1.4	0.4
$\mathrm{CuL''_2}$	400.4	533.0; 531.1	1.9	0.2
LH	400.0	532.8		
L′H	400.8	533.5		
L″H	400.2	533.0		

a) LH, L′H, and L″H indicate dimethylglyoxime, benzil dioxime, and 1,2-cyclohexanedione dioxime respectively. b) The binding-energy difference of the two O(1s) peaks. c) The N(1s) binding-energy difference of a complex and a free ligand.

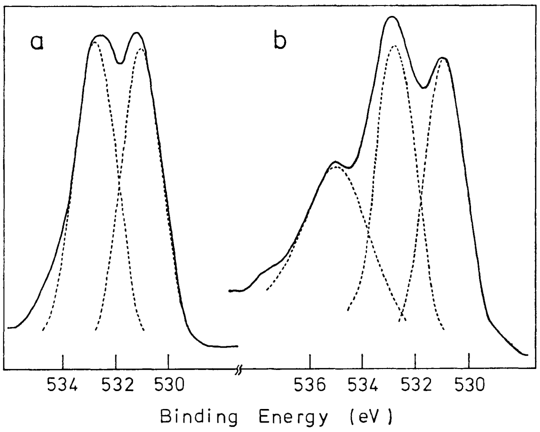

Fig. 1. O(1s) electron spectra.
a: PtL_2, b: PdL_2.

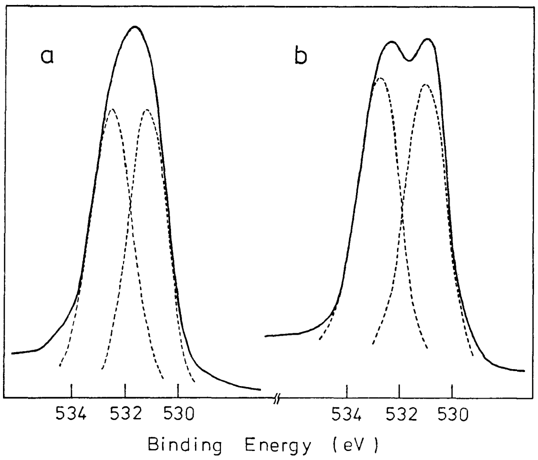

Fig. 2. O(1s) electron spectra.
a: NiL_2, b: CuL_2.

1—3. All the spectra showed multiple peaks, or one broad peak with the FWHM of 2.7—2.9 eV. The peaks with the FWHM of about 1.8 eV, indicated by the broken lines in the figures, were obtained by a graphical resolution. The peak with the highest binding energy of the three peaks in Fig. 1b can be assigned to the Pd($3p_{3/2}$) electron. As is seen in Figs. 1—3, at least two kinds of oxygen atoms were observed for all the complexes. The intensity ratio of the two kinds of oxygens was nearly 1:1 for all the complexes except for $HCoL_2Cl_2$, for which the ratio was about 3:1.

The O(1s) spectra of the benzyl dioxime and 1,2-cyclohexane-dione dioxime complexes of each metal ion were very similar in appearance to that of the corresponding dimethylglyoxime complex. The O(1s) spectra of all the free ligands showed nearly symmetrical single peaks with an FWHM of 2.0—2.1 eV.

The N(1s) Spectra. Figure 4 shows the N(1s) spectra of NiL_2 and $[Co(NH_3)_2L_2]Cl$. The peaks indicated by the broken lines were obtained as in the case of the O(1s) spectra.

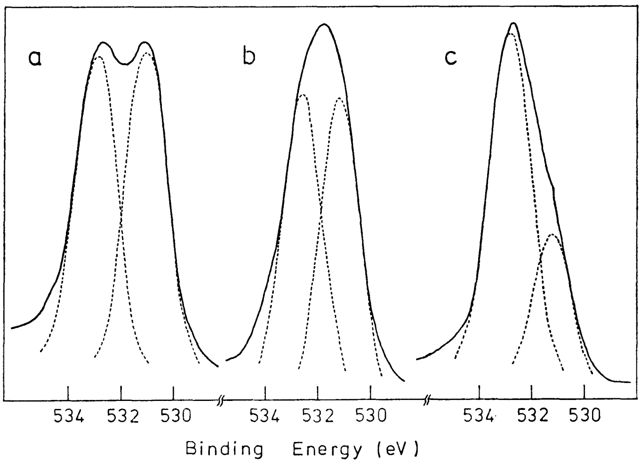

Fig. 3. O(1s) electron spectra.
a: CoL_3, b: $[Co(NH_3)_2L_2]Cl$, c: $HCoL_2Cl_2$.

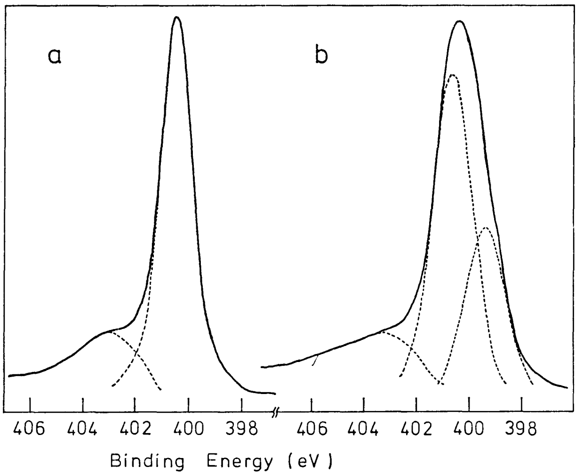

Fig. 4. N(1s) electron spectra.
a: NiL_2, b: $[Co(NH_3)_2L_2]Cl$.

The N(1s) spectrum of NiL_2 showed a single main peak with an FWHM of 1.6 eV and a broad satellite with a low intensity in the region of higher energies than the main peak. The N(1s) spectra of all the other compounds were similar in appearance to that of NiL_2 except for the $[Co(NH_3)_2L_2]Cl$ shown in Fig. 4b. This indicates the presence of only one kind of nitrogen atom in all the compounds studied here except for $[Co(NH_3)_2L_2]Cl$.

The N(1s) spectrum of $[Co(NH_3)_2L_2]Cl$ showed an unsymmetrical broad peak with an FWHM of 2.3 eV (Fig. 4b). This suggests the presence of two kinds of nitrogen atoms. The intensity ratio of about 2:1 of the two peaks clearly indicates that the peak with the higher binding energy is due to the nitrogen atom of dimethylglyoxime, and the other, to the nitrogen of ammonia.

Discussion

The O(1s) Spectra. For all the metal complexes of the three ligands, the peaks with high and low binding energies may be assigned to the protonated and deprotonated oxygen atoms, –OH and $-O^-$ respectively, because the binding energy of the former was close to that of the free ligand.

The magnitude of the O(1s) binding-energy differences between the above two peaks may be correlated with the difference in the electronic charge between the two oxygen atoms. That is, the binding energy difference becomes large as the charge difference becomes large.

An increase in the strength of an OH···O hydrogen bond results in decreases in the O–O distance and the charge difference between the two oxygen atoms, giving rise to a small binding-energy difference between the two O(1s) peaks. Therefore, it may be considered that the hydrogen bond in the Ni complex, which has the smallest binding-energy difference, is stronger than those of the Pt and Pd complexes. This coincides with the results previously obtained by X-ray analysis[2–4] and IR studies.[8,20]

The O–O distances of the Pt, Pd, and Ni complexes of dimethylglyoxime, as determined by the X-ray analyses, were 3.03, 2.59, and 2.44 Å respectively.[2–4]

It is striking that the binding-energy differences of the two peaks for both the Pt and Pd complexes of dimethylglyoxime are the same, while there is an appreciable difference in the O–O distance between the two complexes.

The binding-energy difference between the two peaks for $[Co(NH_3)_2L_2]^+$, in which the O–O distance is 2.65 Å,[6] is 1.4 eV. The binding-energy differences between the two peaks in the O(1s) spectra for *o*- and *p*-aminobenzoic acids,[22] in which the O–O distances of the intermolecular hydrogen bonds are 2.54[23] and 2.61—2.64 Å,[24] were 1.4 and 1.5 eV respectively. Therefore, it seems that the binding-energy difference for PdL_2 was fairly large compared with those for the compounds stated above with O–O distances similar to that of PdL_2. Though the reason for this cannot be explained clearly as yet, it is possibly due to the difference in the bonding type of the hydrogen bond, such as a bent or straight hydrogen bond. That is, the former type may be supposed for the Pd complexes, and the latter type, for the complexes quoted above as comparison and the Pt complexes.

It seems reasonable that the binding-energy differences observed in the complexes in Table 1 which have the intramolecular hydrogen bonds are equal to or smaller than that for CoL_3, in which the presence of a hydrogen bond analogous to those in the above complexes cannot be expected.[10a,10c]

It is very interesting that the present experiment for the three Ni complexes showed the presence of two kinds of oxygen atoms. In a symmetrical O···H···O hydrogen bond, the equivalence of the two oxygen atoms may be expected, because the proton occupies a central position between the two oxygen atoms. Therefore, it seems that the hydrogen bonds in the three Ni complexes are unsymmetrical.

The crystal-structure analysis[5] of CuL_2 showed that this complex exists as a dimer bridged by two oxygen atoms, and that it involves two kinds of intramolecular hydrogen bonds: weak and strong ones. Therefore, four kinds of oxygen atoms should be present in the complex. However, the O(1s) spectrum for CuL_2 could roughly be divided into only two peaks, like the other two Cu complexes.

It is clear from the dominant presence of the protonated oxygen atom over the deprotonated one, as may be seen in Fig. 3c, that, in the $HCoL_2Cl_2$ complex, an additional proton exists near an oxygen atom. This agrees with the results obtained by IR studies[10c,12] of the complex.

In the intramolecular hydrogen bonds studied here, the protons may be considered to be rapidly changing in their position from near one oxygen atom to near the other. In general, the lifetime of proton tautomers is much longer than the time (10^{-16}—10^{-18} s) needed in an ionization process in XPS.[25] Therefore, it was considered that the two kinds of oxygen atoms, the individual tautomers could easily be detected in this experiment.

The N(1s) Spectra. The N(1s) spectra of all the complexes were expected to show two well-resolved peaks or a single broad peak, because the complexes contain two kinds of nitrogen atoms bonded with different groups, –OH and $-O^-$. However, only a single peak with almost the same FWHM as the free ligand was observed in the N(1s) spectrum for all the complexes. This is probably due to the cyclic delocalization[13,18,19,26] based upon the metal→ligand donor-acceptor π bond in the five-membered rings. Such delocalization is considered to equalize the charges on the four nitrogen atoms.

The positive N(1s) chemical shift, which is the difference between the N(1s) binding energies of the complex and the free ligand, is, in all the complexes, considered to be due to the change in the electron density on the nitrogen atom caused by the coordination of lone-pair electrons of the nitrogen atom to the metal and the above-stated cyclic delocalization of electrons.

The magnitudes of the N(1s) chemical shifts were found to increase gradually in the order of Cu<Ni<Pd<Pt complexes. This indicates that, of the four complexes, the electron density around the nitrogen atom is the smallest in the Pt complex and the largest in the Cu complex. This order corresponds well to the decreasing order of the C=N frequencies of these complexes, where fewer frequencies indicate more conjugation in a chelate ring.[13]

The weak peak observed about 2.5 eV on the higher-energy side of the main peak, as is seen in Fig. 4, may be partly assigned to the shake-up satellite peak, which is mainly due to the co-excitations of valence electrons (L-L transition) on the ejection of the innner electrons, on the basis of the following facts. Such a weak peak was also observed in the N(1s) spectrum of each free ligand in the present study. In our laboratory, such peaks have previously been observed in the N(1s) spectra only of compounds containing unsaturated nitrogen groups in addition to the compounds listed in Table 1.[27] Furthermore, the electron spectra of the compounds containing the unsaturated bonds with a hetero-atom in the molecule generally show the absorption bands due to n-π^*, π-π^* transitions in a region of about $(10—50)\times10^3$ cm^{-1}.[28] In the case of NiL_2, such bands are observed in the vicinity of 20×10^3 and 40×10^3 cm^{-1},[29,30] which approximately correspond to 2.5 and 5.0 eV respectively.

The Estimation of the Charge Difference. In the point charge model,[31] a core-binding energy can be expressed by

$$Eb = kq_i + V_i + l + E_r, \qquad (1)$$

where Eb is the binding energy for a particular core level in a given atom (the "ionized" atom), q_i is the charge of the ionized atom, $V_i(=\sum_{i \neq j} q_j/R_{ij})$ is the Coulomb potential energy at the site of the ionized atom due to the other charged atoms of the molecule, k and l are empirical constants for the studied atom, and E_r is the relaxation energy associated with the shift of electrons toward the core hole.

The O(1s) binding energies of two oxygen atoms in the nickel dimethylglyoxime complex can be given by

$$\mathrm{B.E.}(\mathrm{O_1}) = k_\mathrm{O} q_{\mathrm{O_1}} + V_{\mathrm{O_1}} + l_\mathrm{O} + E_r, \qquad (2)$$

$$\mathrm{B.E.}(\mathrm{O_2}) = k_\mathrm{O} q_{\mathrm{O_2}} + V_{\mathrm{O_2}} + l_\mathrm{O} + E_r. \qquad (3)$$

The following equation can be obtained by using the interatomic distances previously reported[2] and by considering the D_{2h} symmetry of the complex:

$$\Delta q = \frac{1}{k_\mathrm{O} - 0.42}\{\Delta E - q_\mathrm{H}(1/R_{\mathrm{O_1H}} - 1/R_{\mathrm{O_2H}})\}, \qquad (4)$$

where $\Delta q = q_{\mathrm{O_1}} - q_{\mathrm{O_2}}$ and where $\Delta E = \mathrm{B.E.}(\mathrm{O_1}) - \mathrm{B.E.}(\mathrm{O_2}) = 1.3$ eV. By substituting $R_{\mathrm{O_1H}} = 1.15$ Å and $R_{\mathrm{O_2H}} = 1.29$ Å, obtained by the application of Lippincott's model equation,[32] and $k_\mathrm{O} = 25.8$ eV/(unit charge), determined empirically by Siegbahn *et al.*,[33] into Eq. 4, Δq was estimated as follows:

$$\Delta q = \frac{1}{25.4}(1.3 - 0.003 q_\mathrm{H}) \approx \frac{1}{25.4} \times 1.3 \risingdotseq 0.051.$$

Therefore, it seemed that the intramolecular hydrogen bond of the nickel dimethylglyoxime complex was slightly unsymmetrical, with a charge difference of about 0.05 unit charge.

The author wishes to thank Drs. Kiyoshi Yamasaki and Shigemasa Sawada for their many helpful discussions and suggestions during this work, and Mr. Taichiro Hirohara for the elemental analysis of all the samples.

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