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The Core-level Binding Energies and the Structures of Nickel Complexes

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Synopsis. The X-ray photoelectron spectra of thirty-two nickel complexes were measured in order to examine the relation between the structures and the core-level binding energies of the complexes. The differences between the energies of Ni(2p) and Ni(3p) electrons for the complexes with an octahedral structure were about 1 eV larger than for those with a square planar one.

There have been many reports on X-ray photoelectron spectroscopic studies of nickel compounds.[1] It has been established that paramagnetic complexes show intense shake-up satellites on the higher energy side of the primary peaks in the Ni(2p) electron region, but that diamagnetic ones do not. However, there have been few studies of the relationship between the binding energy and the stereochemistry.[1d] The purpose of this study is to examine the relation between the structure of nickel complex, square planar or octahedral, and the binding energies of its core-electrons.

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 powder and then dusted onto double-backed adhesive tape. The measurements were run 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 experiments; it was taken to be 285.0 eV. The reproducibilities of the values thus obtained were ± 0.1 eV. All the complexes used and their binding energies are given in Table 1. All the complexes were prepared based upon the literature.

The spectra in the Ni(2p)- and Ni(3p)-electron regions for the nickel complexes of 2-pyridinecarboxylic acid and dimethylglyoxime are shown in Fig. 1. E_b in the figure indicates the binding energy. The spectra of the 2-pyridinecarboxylic acid complex, like those of the complexes of Nos. 1—16 in Table 1, showed intense satellites on the higher energy side of each primary peak originating in the $2p_{1/2}$, $2p_{3/2}$, and 3p electrons, but the spectra of the dimetylglyoxime complex, like those of the complexes of Nos. 17—32, did not show such satellites. This suggests that the complexes of Nos. 1—16 are paramagnetic, while those of Nos. 17—32 are diamagnetic.

In general, the Ni(3p) spectrum does not show clear doublet peaks because of the small difference (about 2 eV)[2] between the binding energies of the Ni($3p_{1/2}$) and Ni($3p_{3/2}$) electrons. Therefore, the 3p binding energies in Table 1 correspond to the top of a main peak, as is shown in Fig. 1b.

On the basis of the results of X-ray structural analysis, IR, UV, and magnetic measurements, it has been proved that the structures of the complexes of Nos. 1,[3] 2,[4] 4,[5] 5,[5] 6,[5] 7,[6] 9,[7] 11,[8] 12,[8] 13,[8] 14,[9] 15,[8] and 16[10] are octahedral, while those of Nos. 18,[11] 23,[12] 24,[13] 25,[14] 26,[15] 27,[16] 29,[10] 30,[17] 31,[18] and 32[19] are square planar. The structure of the No. 3 complex may be considered to be octahedral in view of the structures of the corresponding copper and zinc complexes.[20] It seems reasonable to consider that the structures of the complexes of Nos. 8 and 10 are octahedral, because 1-(2-pyridylazo)- and 1-(8-quinolylazo)-naphthols as well as 1-(2-thiazolylazo)-2-naphthol are tridentate ligands. Furthermore, it seems that the structures of the complexes of Nos. 17, 19—21, and 28 are square planar in view of the structures of the complexes of Nos. 18 and 25—27. The structure of the No. 22 complex seems to be square planar. The square planar structure for the complexes of Nos. 17—32 are supported by the absence of intense satellites in their Ni(2p) and Ni(3p) electron spectra.

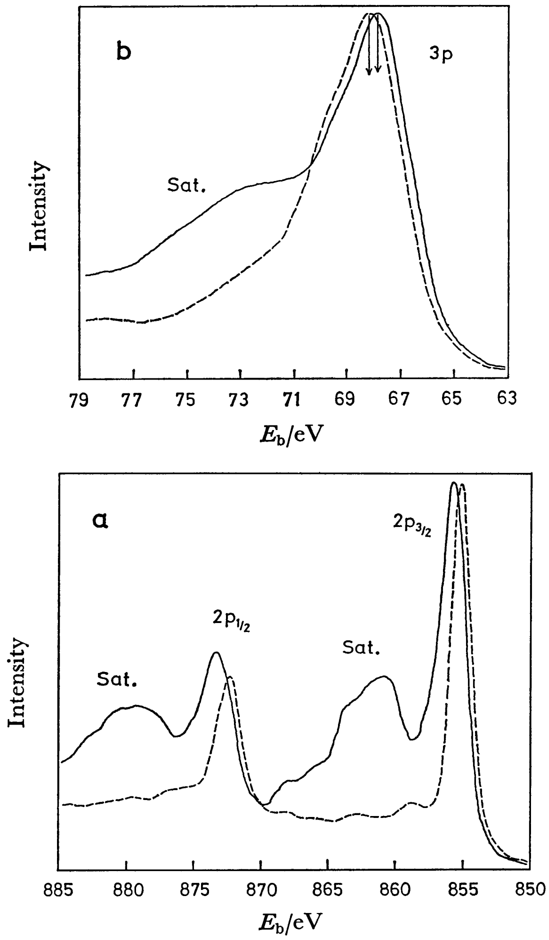

Fig. 1. XPS spectra of a: Ni(2p) and b: Ni(3p) electron regions. Solid line: *trans*-diaquabis(2-pyridinecarboxylato)Ni(II), broken line: bis(dimethylglyoximato)Ni(II).

It has been reported that, for the nickel complexes of NCS^- ligand, the Ni(2p) binding energies of octahedral compounds are a little higher than those of the square planar ones.[1d] Such a tendency was

Table 1. Measured binding energies

Sample No.	Ligand	Complex formula[a]	BE of Ni/eV			ΔE_1[c]	ΔE_2[c]
			$2p_{1/2}$	$2p_{3/2}$	3p[b]		
1	Ethylenediaminetetraacetic acid	A	872.7	855.1	67.2	805.5	787.9
2	Glycine	B	873.0	855.6	67.7	805.3	787.9
3	8-Quinolinol	B	873.6	856.0	68.0	805.6	788.0
4	2-Pyridinecarboxylic acid	B	873.4	855.7	67.9	805.5	787.8
5	3-Pyridinecarboxylic acid	C	873.7	856.1	68.3	805.4	787.8
6	4-Pyridinecarboxylic acid	C	873.9	856.2	68.4	805.5	787.8
7	2-Aminobenzoic acid	D	873.8	856.1	68.2	805.6	787.9
8	1-(2-Pyridylazo)-2-naphthol	D	873.1	855.6	67.9	805.2	787.7
9	1-(2-Thiazolylazo)-2-naphthol	D	873.3	855.7	68.0	805.3	787.7
10	1-(8-Quinolylazo)-2-naphthol	D	872.8	855.4	67.8	805.0	787.6
11	Ethylenediamine	E	872.4	855.0	67.2	805.2	787.8
12	Ethylenediamine	F	872.6	855.2	67.4	805.2	787.8
13	2,2′-Bipyridine	G	873.6	856.1	68.1	805.5	788.0
14	2,2′-Bipyridine	F	873.4	856.0	68.2	805.2	787.8
15	1,10-Phenanthroline	G	873.6	856.1	68.2	805.4	787.9
16	Biuret	F	874.3	856.9	68.9	805.4	788.0
17	2-(*p*-Nitrophenylazo)-4-methylphenol	D	872.6	855.5	68.6	804.0	786.9
18	1-Phenylazo-2-naphthol	D	872.7	855.5	68.6	804.1	786.9
19	1-(*p*-Methoxyphenylazo)-2-naphthol	D	872.6	855.4	68.5	804.1	786.9
20	1-(*p*-Nitrophenylazo)-2-naphthol	D	872.6	855.6	68.6	804.0	787.0
21	1-(1-Naphthylazo)-2-naphthol	D	872.5	855.3	68.4	804.1	786.9
22	1-(8-Quinolylazo)-2-naphthol	H	872.7	855.4	68.4	804.3	787.0
23	Salicylaldehyde oxime	D	873.4	856.1	69.0	804.4	787.1
24	Salicylideneamine	D	873.0	855.7	68.6	804.4	787.1
25	Dimethylglyoxime	D	872.3	855.1	68.2	804.1	786.9
26	2,3-Pentanedione dioxime	D	872.4	855.2	68.2	804.2	787.0
27	Benzil dioxime	D	872.9	855.9	68.8	804.1	787.1
28	1,2-Cyclohexanedione dioxime	D	872.7	855.5	68.4	804.3	787.1
29	Biuret	I	872.1	854.8	67.7	804.4	787.1
30	Rubeanic acid	J	871.8	854.5	67.4	804.4	787.1
31	2-Mercaptobenzothiazole	D	872.6	855.3	68.2	804.4	787.1
32	Diethyldithiocarbamic acid	D	871.6	854.3	67.4	804.2	786.9

a) A: $Ni(L\text{-}4H)Na_2 \cdot 2H_2O$, B: $Ni(L\text{-}H)_2 \cdot 2H_2O$, C: $Ni(L\text{-}H)_2 \cdot 4H_2O$, D: $Ni(L\text{-}H)_2$, E: $NiL_3Cl_2 \cdot 2H_2O$, F: NiL_2Cl_2, G: $NiL_3(ClO_4)_2$, H: $Ni(L\text{-}H)Cl$, I: $K_2Ni(L\text{-}2H)_2$, J: $Ni(L\text{-}2H)$. L, L-H, L-2H, and L-4H in the above formulas indicate a free ligand and mono-, di-, and tetra-deprotonated ligands respectively. b) The binding energy of a main peak. c) ΔE_1 and ΔE_2 indicate the binding energy differences, $2p_{1/2}-3p$ and $2p_{3/2}-3p$ respectively.

not observed in this study. This is probably due to the comparison among the complexes of a variety of ligands. Therefore, in this study the differences between the binding energies of core-electrons for each complex were compared in order to reduce the effect of the variety of ligand on the binding energies.

Two kinds of differences, $\Delta E_1 = Ni(2p_{1/2}) - Ni(3p)$ and $\Delta E_2 = Ni(2p_{3/2}) - Ni(3p)$, are given in Table 1. The ΔE_1 and ΔE_2 values for Nos. 1—16 were 805.0—805.6 eV and 787.6—788.0 eV respectively. Those for Nos. 17—32 were 804.0—804.4 eV and 786.9—787.1 eV respectively. That is, the ΔE_1 and ΔE_2 values for the complexes of the former group were about 1 eV larger than those of the latter. This indicates that the differences between the binding energies of core-electrons give valuable information on the stereo-structures of nickel complexes.

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