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XPS Study of Bis(1,2-diaryl-1,2-ethylenedithiolato)nickels

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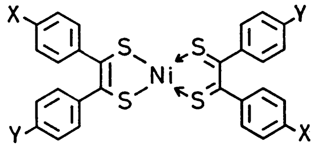
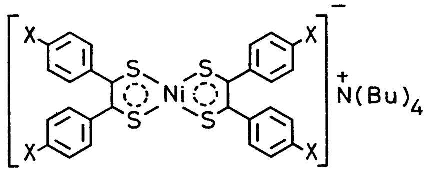
Synopsis. The binding energies of S 2p and Ni 2p of the bis(1,2-diaryl-1,2-ethylenedithiolato)nickels were measured by means of X-ray photoelectron spectroscopy using a silicone oil as a reference. The results indicated that a reasonable correlation exists between Hammett substituent constants σ_p on phenyl group in the nickel complexes and the binding energy and between charge of complexes and the binding energy.

Bis(1,2-diaryl-1,2-ethylenedithiolato)nickels **1** are useful as organic functional dyes for optical data storages, due to their characteristics of near infrared absorption and abilities of singlet oxygen quenching.[1,2] We have reported the substituent effects on both the absorption maxima and the reduction potential of these complexes, and suggested that the phenyl rings in the complex **1** are conjugated with the chelate rings.[1] The substituent effects on the nickel-sulfur stretching frequencies in **1** were also examined by means of the resonance Raman technique.[3]

X-Ray photoelectron spectroscopy, XPS, is a powerfull method for the study of the bonding energy in these complexes. In the present study, we have applied the XPS to the ethylenedithiolato nickel complexes **1** and **2**, in order to evaluate the detailed electronic state of sulfur atoms in **1** and **2**, and the substituent effects on the binding energies of S 2p and Ni 2p.



1a: X=Y=H
1b: X=Y=Me
1c: X=Y=Cl
1d: X=Y=OMe
1e: X=Y=CF$_3$
1f: X=H, Y=N(Me)$_2$



2a: X=H
2b: X=OMe
2c: X=CF$_3$

Experimental

The XPS spectra were taken on a Shimadzu ESCA 850 spectrometer. Mg $K\alpha$ radiation was used as the excitation source. The measurements were conducted at room temperature under a vacuum of about 10^{-5} Pa. The nickel complex dissolved in benzene was put on silicon single crystal plate. After drying, thickness of a sample layer was about 100 μm. About 3×10^{-3} cm^3 of silicone oil (Shin-etsu Kagaku Corp. KF851) solution in benzene (1 wt%) was added to the sample layer using a capillary. The binding energies of the complexes were calibrated by assigning 102.2 eV to the Si 2p peak of silicone oil. First, the binding energy of Ni 2p and S 2p of the complex was determined by using the energy reference of the Si 2p peak. Second, the binding energy of C 1s of the complex without silicone oil was calibrated by using the energy reference of Ni 2p, determined above, because the C 1s peak of the complex with silicone oil was broadened by the shoulder peak assigned to the C 1s of silicone oil.

The reproducibility of the binding energies thus obtained was within±0.1 eV. Appreciable X-ray damage was not observed throughout the experiments. Ethylenedithiolato nickel complexes were previously prepared.[1,4]

Results and Discussion

The C 1s level or Au 4f$_{7/2}$ level is generally used as the reference energy in XPS spectra, however, there are some disadvantages. The binding energy of C 1s of substituted benzene derivatives are shifted by the substituent group.[5] For the nonconducting materials, the gold depositions tend to result in islands which are uneven in size and have uneven chargings. This unevenness causes an uncertain evaluation of binding energy due to the broadening of the Au 4f peak or the apparent shifts of the binding energies of the samples.[6,7] On the other hand, homogeneous dispersion of silicone oil into the sample layer is very easy, and its concentration in sample layer can be controlled with the dilution. Silicone oil seems, therefore, to be a suitable energy reference for nonconducting materials. We have attempted the application of Si 2p level of silicone oil to an energy reference in XPS spectra.

The binding energies measured by this method are given in Table 1. The S 2p electron spectrum of **1a** clearly showed two peaks, as shown in Fig. 1. The S 2p peak of **1a** can be graphically separated into two peaks having an intensity ratio of 10:7 with full-width of 1.0 eV at half-height, as indicated by the broken lines in Fig. 1. The interval between the two peaks was 1.2 eV. The two peaks were assigned to S 2p$_{1/2}$ and S 2p$_{3/2}$ electrons, respectively, from comparison of those of known sulfur compounds.[8] This indicates that four sulfur atoms in **1a** are equivalent in

Table 1. Binding Energies for Ethylenedithiolate Nickel Complexes

Compd.	Binding energy$^{a)}$/eV		
	C 1s	S $2p_{3/2}$	Ni $2p_{3/2}$
1a	284.6(1.3)	162.6(1.0)	855.4(1.4)
1b	285.0(1.5)	162.3(1.1)	855.2(1.4)
1c	285.1(1.5)	162.8(1.2)	855.7(1.5)
1d	284.7(2.5)$^{b)}$	162.2(1.1)	855.1(1.5)
1e	285.5(1.5)	163.1(1.2)	855.9(1.4)
1f	284.2(2.4)$^{b)}$	162.0(1.3) 163.1(1.3)	854.8(1.9)
2a	284.3(2.1)$^{b)}$	161.7(1.5)	854.5(1.9)
2b	284.3(2.2)$^{b)}$	161.6(1.3)	854.4(1.7)
2c	285.0(1.9)$^{b)}$	162.2(1.8)	854.9(2.1)

a) Full width at half-height (eV) are given for each element in parenthese. b) Broadening is due to shoulder peak assigned to methyl or butyl groups.

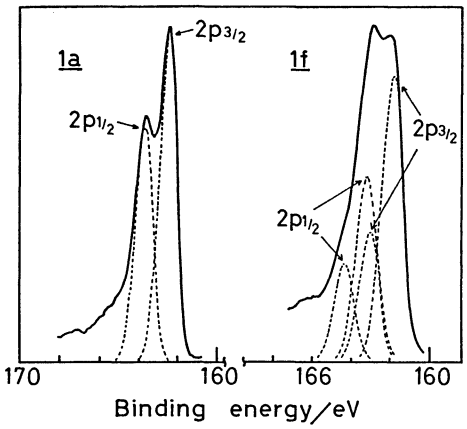
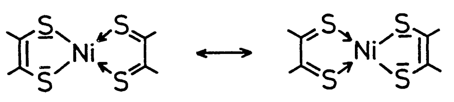


Fig. 1. The XPS spectra of S 2p for **1a** and **1f**.



Scheme 1.

solid state. Two peaks on the spectra were similarly observed for the other ethylenedithiolato nickel complexes **1b**—**1e** and **2a**—**2c**. Thus, the structure of **1** is represented by using Kekulé-type structures which are assumed to be delocalized aromatic 10-π electron system with neutral planar structure, as shown in Scheme 1. On the other hand, in the S 2p spectrum of **1f** having unsymmetrical ligands two kinds of sulfur atoms are found by similar wave analysis (Fig. 1). The two S $2p_{3/2}$ peaks, which have the intensity ratio of 3:1, were observed at 162.0 and 163.1 eV. The higher binding energy in **1f** suggests that one sulfur atom is cationic, as the S 2p peak of cationic sulfur atom in aromatic sulfur compounds is higher by ca. 1.0 eV than that of neutral sulfur atom.$^{9)}$ Therefore, it is concluded that four sulfur atoms in **1f** are not equivalent in solid state.

As shown in Fig. 2, good linear relationships exist between the binding energy of the Ni $2p_{3/2}$ or S $2p_{3/2}$ of **1** and Hammett substituent constants σ_p (correlation coefficient: 0.96—0.98). The slope of these linear substituent effects is similar to that of binding energy of C 1s in substituted benzene derivatives to σ.$^{5)}$ A reasonable correlation exists also between the binding energy of C 1s of **1** and Hammett substituent constants σ_p. This result indicates that the phenyl groups of complex **1** are conjugated with both the chelate ring and nickel, and is consistent both with the PPP-MO calculation and with the experimental results from absorption and Raman spectra, as reported previously.$^{1,3,10)}$

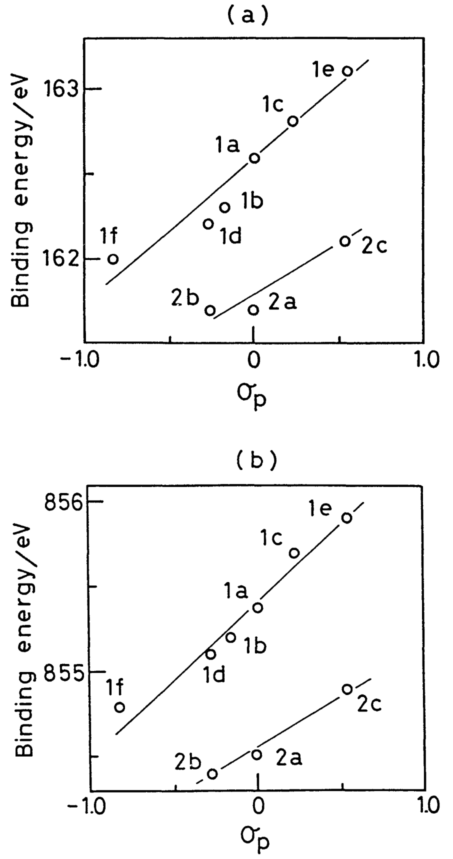


Fig. 2. Correlation between Hammett Substituent constants σ_p and the binding energy of (a): S $2p_{3/2}$ and (b): Ni $2p_{3/2}$.

The reduced species **2a**—**2c** have clearly lower binding energy of S $2p_{3/2}$ and Ni $2p_{3/2}$ than the corresponding neutral species. This shift was about 0.8 eV. The slope of the binding energy of S $2p_{3/2}$ to σ was same to that the Ni $2p_{3/2}$. These results are consistent with the conclusion from the hyperfine splitting in the ESR spectrum of **2a**,$^{4)}$ that is, the charge in **2** is delocalized over both nickel and the ligands.

Grim et al. reported that the binding energies of Ni $2p_{3/2}$ and S 2p of **1a** are 852.9 and 161.1 eV, respectively, and that those of $[Et_4N][NiS_4C_4Ph_4]$ are 852.5 and 160.8 eV, respectively.$^{11)}$ These values were determined by the gold-deposited method, and the energy difference in Ni 2p or S 2p between **1a** and $[Et_4N][NiS_4C_4Ph_4]$ are slightly different from the data in Table 1. We also measured the binding energies of Ni 2p and S 2p for the complexes **1a**—**1f** by the gold-deposited method, however, no significant substituent effect on XPS spectra was observed. These disagreements between the gold-deposited method and the silicone oil dispersed method may be due to the disadvantage of gold-deposited method, described above.

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