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## Unusual Charge Distributions in Some Bis(fulvalene)dimetal Complexes As Revealed by X-ray Photoelectron Spectroscopy

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A series of bis(fulvalene)dimetal species,  $[(C_{10}H_8)_2M_2]^{n+}$ , was studied by using X-ray photoelectron spectroscopy. Some of the complexes have metal binding energies which are lower than one would expect, assuming the ligands to be dianions. These data are rationalized by considering the metal atoms to be in reduced oxidation states and the fulvalene ligands to be partially oxidized. The metal 2p spectra of the mixed-valence compounds ( $n = 1$ ) of cobalt and nickel show line broadening indicative of two inequivalent core-ionized states. Most of the paramagnetic compounds show an increase in spin-orbit splitting and line broadening attributable to multiplet splitting. Satellite structure, arising from ligand-to-metal charge-transfer transitions, appears in the spectra of some of the paramagnetic compounds.

### Introduction

The electronic properties of the mixed-valence compound biferrrocene  $[Fe^{II}Fe^{III}]$  picrate and the doubly bridged bis(fulvalene)diiron complex have been studied by a wide variety of techniques,<sup>1-6</sup> including X-ray photoelectron spectroscopy (XPS). In this paper we present the results of an XPS study of several bis(fulvalene)dimetal complexes of cobalt and nickel and the corresponding dicyclopentadienylmetal complexes.

### Experimental Section

**XPS.** Spectra were obtained with three different spectrometers: the AEI Model E200, the DuPont Model 650, and the McPherson ESCA 36 electron spectrometer. The neutral complexes were run by subliming samples under vacuum onto a polished gold surface which, in the case of the dicyclopentadienylmetal complexes, was cooled to  $-50^\circ C$  to prevent evaporation during the irradiation process. The salts were run as powders brushed onto one side of double-stick Scotch tape. The contaminant C 1s line was used as a reference. This line was arbitrarily assigned a binding energy of 285.0 eV on the AEI spectrometer. Binding energies of compounds run on more than one spectrometer were compared with one another, and reference binding energies were chosen so that binding energies were consistent. On this basis, the contaminant C 1s line was assigned a binding energy of 285.6 eV for the DuPont and McPherson spectrometers.

In all cases, Mg  $K\alpha$  X-rays (1253.6 eV) were used. Binding energies were determined by fitting the data to Lorentzian curves with a least-squares computer program.<sup>7</sup> The uncertainties given in Table I are twice the standard deviations obtained by the fit.

**Syntheses.** Ferrocene,<sup>8</sup> cobaltocene,<sup>9</sup> cobaltocenium hexafluorophosphate,<sup>10</sup> nickelocene,<sup>11</sup> bis(fulvalene)diiron,<sup>12</sup> bis(fulvalene)dnicobalt and its salts,<sup>13</sup> and bis(fulvalene)dnicol and its salts<sup>14</sup> were prepared by previously described methods.

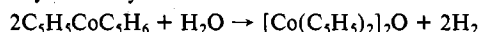
Ferrocenium hexafluorophosphate was made by dissolving 0.1 mol of ferrocene and 0.15 mol of ferric chloride hexahydrate in 100 mL of acetone and 300 mL of water. The solution was filtered and added to a concentrated aqueous solution of  $NH_4PF_6$ . The precipitate was recrystallized from acetone/ethanol, with some ferric chloride added to keep the product oxidized. Anal. Calcd: C, 36.29; H, 3.05. Found: C, 36.38; H, 3.12.

Under nitrogen, nickelocenium hexafluorophosphate was made by dissolving 3 mmol each of nickelocene and ferrocenium hexafluorophosphate in 40 mL of degassed acetone, filtering, and then adding the solution to 100 mL of hexane. The precipitate was recrystallized from acetone/hexane and washed with diethyl ether.

The complex  $(C_5H_5)_2Co(C_5H_6)$  was prepared by slowly adding, under nitrogen, 5.9 g of  $NaBH_4$  to a stirred mixture of 4.1 g of

$Co(C_5H_5)_2PF_6$  in 150 mL of tetrahydrofuran. The mixture was stirred and then filtered. Solvent was removed from the filtrate, and the resulting solid was sublimed at room temperature to a  $-78^\circ C$  cold finger. Red crystals were obtained, mp  $101-102^\circ C$  (lit.<sup>15</sup>  $98-99^\circ C$ ).

Decomposition of  $(C_5H_5)_2Co(C_5H_6)$  during its study in the spectrometer was indicated by the appearance of a peak at 781.7 eV which increased in relative intensity as scanning time increased. It is possible that the decomposition product is cobaltocenium ion, produced by an X-ray-induced reaction such as



### Results and Discussion

**Binding Energies.** The experimental binding energies are given in Table I. The relative binding energies of the iron compounds are in good agreement with the values reported by LeVanda et al.<sup>6</sup> In the case of the neutral and cationic dicyclopentadienyl complexes of the same metal, the metal  $2p_{3/2}$  binding energies follow the expected trend; i.e., the metal  $2p_{3/2}$  binding energies increase with increasing oxidation state. Close agreement is expected between the binding energies of the dicyclopentadienylmetal complexes and those of the corresponding fulvalene complexes, because the potential field at the metal atom is similar in the two types of compounds, with the metal atom sandwiched between two five-membered rings in each case. This agreement is observed within experimental error except for the neutral bis(fulvalene)dnicobalt complex and the dicationic bis(fulvalene)dnicol complex.

The fact that the bis(fulvalene)dnicol dication has a lower metal binding energy than the corresponding monocation was completely unexpected. This apparent anomaly can be explained by assuming that, in the dication, the nickel atoms are in the relatively stable  $2+$  oxidation state and that one pair of electrons has been removed from the two fulvalene dianions. The ligands are presumably equivalent, and the situation can be represented by the following resonance structures, in each of which one fulvalene dianion has been oxidized to a neutral fulvalene ligand.

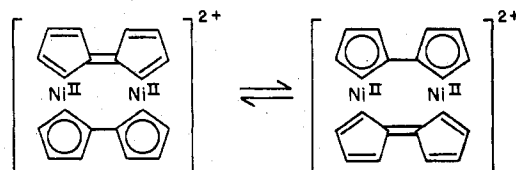


Table I. XPS Binding Energies and Line Widths<sup>a</sup>

	formal oxidn state of metal <sup>b</sup>	no. un- paired electrons	M 2p <sub>3/2</sub>	fwhm	Δ <sup>c</sup>	F 1s
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe	II	0	708.5 (1)	1.3 (2)	12.9 (1)	
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe]PF <sub>6</sub>	III	1	710.2 (2)	2.4 (4)	13.3 (1)	686.7 (1)
(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Fe <sub>2</sub>	II	0	708.5 (1)	1.1 (1)	12.8 (1)	
(C <sub>5</sub> H <sub>5</sub> )Co(C <sub>5</sub> H <sub>6</sub> )	I	0	779.7 (2)	1.3 (2)	14.8 (2)	
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co	II	1	780.2 (1)	1.4 (2)	15.1 (1)	
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co]PF <sub>6</sub>	III	0	781.7 (2)	1.9 (2)	15.1 (2)	686.6 (1)
(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Co <sub>2</sub>	II	0	779.5 (2)	1.2 (2)	14.9 (1)	
[(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Co <sub>2</sub> ]PF <sub>6</sub>	II, III	1	780.7 (2)	2.8 (4)	15.0 (2)	686.9 (1)
[(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Co <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	III	0	781.9 (1)	2.2 (2)	14.9 (2)	686.7 (1)
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ni	II	2	855.2 (1)	1.5 (2)	17.2 (1)	
[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ni]PF <sub>6</sub>	III	1	857.3 (2)	2.5 (3)	17.9 (2)	686.9 (2)
(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Ni <sub>2</sub>	II	0	854.9 (2)	1.3 (2)	17.2 (2)	
[(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Ni <sub>2</sub> ]PF <sub>6</sub>	II, III	1	856.7 (2)	3.3 (5)	17.7 (2)	686.9 (1)
[(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> Ni <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	III	0	856.2 (1)	2.1 (2)	17.3 (1)	686.8 (1)

<sup>a</sup> All values are given in electron volts (eV). Uncertainties in the last digit are given parenthetically. <sup>b</sup> Assuming C<sub>5</sub>H<sub>5</sub> ligands to be monoanions and C<sub>10</sub>H<sub>8</sub> ligands to be dianions. <sup>c</sup> Spin-orbit splitting; Δ = E<sub>B</sub>(2p<sub>1/2</sub>) - E<sub>B</sub>(2p<sub>3/2</sub>).

In view of this result, one might have expected that the bis(fulvalene) dinickel monocationic complex would also consist of two Ni<sup>2+</sup> ions and partially oxidized anionic ligands. However, the monocation appears to be a true Ni<sup>2+</sup>, Ni<sup>3+</sup> mixed-valence species; the nickel 2p<sub>3/2</sub> binding energy is approximately midway between the corresponding binding energies of nickelocene and the nickelocenium ion. Perhaps the data are best rationalized by assuming that the dication would exist as a Ni<sup>3+</sup>, Ni<sup>3+</sup> complex if it were not for the excessive electrostatic repulsion between the two highly positively charged metal ions. This strong repulsion is avoided by going to the Ni<sup>2+</sup>, Ni<sup>2+</sup> configuration. The nickel binding energy of the dication is lower than that of the monocation because of the lower average metal atom charge but higher than that of the neutral complex because of the less negative electrostatic potential of the oxidized fulvalene ligands.<sup>16</sup>

The cobalt binding energy of the neutral bis(fulvalene)-dicobalt is significantly lower than that of cobaltocene, suggesting an electronic structure with Co(I) atoms, exactly analogous to that of the isoelectronic nickel dication. Indeed, the binding energy of this complex is even slightly lower than that of the Co(I) complex, (C<sub>5</sub>H<sub>5</sub>)Co(C<sub>5</sub>H<sub>6</sub>). However, the binding energies of the mono- and dicationic bis(fulvalene)dicobalt complexes appear to be normal. The binding energy of the monocation lies between those of cobaltocene and the cobaltocenium ion, and that of the dication is slightly higher than that of the cobaltocenium ion.

**Line Shapes and Satellites.** The spectrum of the paramagnetic ferrocenium salt shows greater spin-orbit splitting than either ferrocene or bis(fulvalene)diiron. Such increased splitting is often found in the spectra of paramagnetic complexes.<sup>17</sup> The large line width of the ferrocenium salt is primarily due to the different method of sample mounting used. Samples mounted on Scotch tape give broader lines than sublimed samples because of greater sample charging. Relatively narrow lines were observed for all of the neutral complexes for this reason.

The spectra of the bis(fulvalene)dicobalt complexes are shown in Figure 1. The mixed-valence complex, [(C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Co<sub>2</sub>]PF<sub>6</sub>, has a significantly greater line width than the dicationic complex, probably because of unresolved peaks due to the presence of two oxidation states. Figure 1 shows the Co 2p<sub>3/2</sub> spectrum of [(C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Co<sub>2</sub>]PF<sub>6</sub> resolved into two lines, at binding energies 780.4 and 781.6 eV, which we attribute to transitions to different core-ionized excited states arising from the mixed valence. However, the data in Table I for this

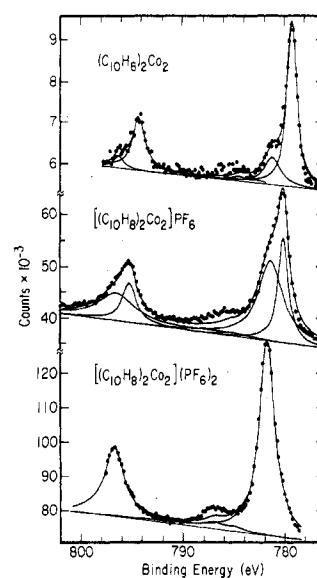
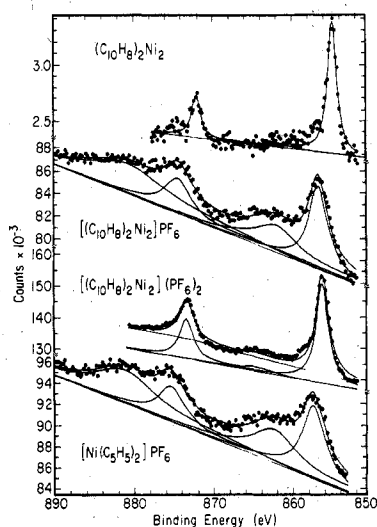


Figure 1. Co 2p spectra of the bis(fulvalene)dicobalt complexes. The spectrum of (C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Co<sub>2</sub> shows a small peak at higher binding energy due to an oxidation product. The spectrum of [(C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Co<sub>2</sub>]PF<sub>6</sub> is resolved into two lines arising from the mixed valency of this compound.

compound are obtained from fits of the experimental points to one peak.

Although nickelocene is paramagnetic, it does not show an increase in spin-orbit splitting. However, the nickelocenium salt and the monocationic bis(fulvalene)dinickel complex do show this increase, as well as an increase in line width, probably indicating the effects of multiplet splitting.<sup>17</sup> The latter complexes also are the only ones to show intense shake-up satellites. The separations of the satellites from the metal 2p<sub>3/2</sub> lines are the following: [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni]PF<sub>6</sub>, 4.9 eV; [(C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Ni<sub>2</sub>]PF<sub>6</sub>, 5.3 eV. The spectra of these compounds and the other bis(fulvalene)dinickel complexes are shown in Figure 2. The majority of evidence suggests that such satellite structure arises from ligand-to-metal charge-transfer transitions,<sup>18</sup> and we believe this to be the case for these complexes. The alternative, a metal 3d → 4s transition, is forbidden and would be expected to have a significantly higher energy than observed here.<sup>19</sup>

The line width of the mixed-valence nickel complex is much greater than that of the other nickel complexes; we believe this



**Figure 2.** Ni 2p spectra of the bis(fulvalene)nickel complexes and the nickelocenium salt, showing the unusual binding energy trend in the series. Intense shake-up satellites are seen in the paramagnetic complexes.

broadening is due to two unresolved lines arising from the mixed valence.

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Sciences, U.S. Department of Energy.

**Registry No.**  $(C_5H_5)_2Fe$ , 102-54-5;  $[(C_5H_5)_2Fe]PF_6$ , 11077-24-0;  $(C_{10}H_8)_2Fe_2$ , 11105-90-1;  $(C_5H_5)Co(C_5H_6)$ , 33032-03-0;  $(C_5H_5)_2Co$ , 1277-43-6;  $[(C_5H_5)_2Co]PF_6$ , 12427-42-8;  $(C_{10}H_8)_2Co_2$ , 69365-57-7;  $[(C_{10}H_8)_2Co_2]PF_6$ , 69365-59-9;  $[(C_{10}H_8)_2Co_2](PF_6)_2$ , 39333-80-7;  $(C_5H_5)_2Ni$ , 1271-28-9;  $[(C_5H_5)_2Ni]PF_6$ , 69365-60-2;  $(C_{10}H_8)_2Ni_2$ , 62518-80-3;  $[(C_{10}H_8)_2Ni_2]PF_6$ , 62873-73-8;  $[(C_{10}H_8)_2Ni_2](PF_6)_2$ , 62518-79-0.

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## Photoelectron Spectroscopic Study on Metalloctaethylporphyrins

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The UV photoelectron (PE) spectra of octaethylporphyrin ( $H_2OEP$ ) and its metallo derivatives containing a variety of divalent cations (Mg, Fe, Co, Ni, Cu, Zn, Pd) are presented. The spectral positions of the first two bands at 6–7 eV which correspond to an electron ejection from the porphyrin  $\pi$  system ( $A_{1u}$  and  $A_{2u}$  states) show a metal dependence. The first (and the second) ionization potential well correlates to the half-wave potential associated with the OEP ring oxidation obtained by cyclic voltametry. On the basis of this relationship, the ring oxidation potentials for the OEP derivatives with divalent Fe and Co atoms, which have still been beyond experimental observation, are estimated to be 0.4 V vs. SCE. The bands between 7 and 9 eV, which also exhibit a remarkable metal dependence, may be assigned to an electron ejection from the porphyrin  $\pi$  system.

### I. Introduction

Studies on the oxidation–reduction properties of metalloporphyrin complexes have long been a keen problem to the biochemist and chemist alike.<sup>2</sup> Prominent examples of such complexes are iron porphyrins serving as prosthetic groups in peroxidases, catalases, and cytochromes. The redox behavior of metalloporphyrins can be widely modified over a large potential range by changing the central metal ion, the coordinating ligands, and the porphyrin peripheral groups.

Many electrochemical studies have been performed with the aim of elucidating the relationship between the electronic structure and the redox properties of metalloporphyrins. Especially, in relation to the significance of an iron atom, the effect of the central metal ion on the ring redox characteristics has been vigorously studied by cyclic voltametry (CV)<sup>3,4</sup> in

nonaqueous solvents. The half-wave potentials of the porphyrin ring exhibit substantial variations with the central metal. On the contrary, in photoelectron spectroscopy (PES) which is relevant for obtaining ionization potentials (IP) directly, the IP values for *meso*-tetraphenylporphyrin (TPP)<sup>5</sup> and its metallo derivatives have been shown to be insensitive to the central metal ion.

In this paper we present some details of PE spectroscopic studies of octaethylporphyrin and its metallo derivatives (Figure 1) in the gas phase. OEP derivatives are more suitable than TPP for the investigation of the PE spectra of porphyrins for inquiry into the central metal dependence, since PE spectra of TPP derivatives show a complexity of bands above 7 eV resulting from the phenyl  $\pi$  electrons. We will also point out a relationship between ionization and redox potentials in