Contribution from the Department of Chemistry,
University of Maryland, College Park, Maryland 20742

X-Ray Photoelectron Spectroscopy of Some Nickel, Palladium, and Platinum Dithiene Complexes[1]

SAMUEL O. GRIM,* LUIS J. MATIENZO, and WILLIAM E. SWARTZ, Jr.

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Sulfur ($2p_{3/2,1/2}$), nickel ($2p_{3/2}$), palladium ($3d_{5/2}$), and platinum ($4f_{7/2}$) binding energies were measured by X-ray photoelectron spectroscopy for the compounds $[(C_2H_5)_4N][MS_4C_4(CN)_4]$, $[(C_2H_5)_4N]_2[MS_4C_4(CN)_4]$, $M[S_4C_4(C_6H_5)_4]$, $[(C_2H_5)_4N][MS_4C_4(C_6H_5)_4]$, and $(N_2H_5)_2[MS_4C_4(C_6H_5)_4]$, where M = Ni, Pd, and Pt. The results indicate that the charge on the particular metal remains essentially constant in the series of neutral, anionic, and dianionic complexes and that the additional electronic charge gained during the reduction sequence residues principally on the ligand and, in particular, on the sulfur atoms. Two compounds, $[(C_2H_5)_4N][PdS_4C_4(C_6H_5)_4]$ and $[(C_2H_5)_4N][PtS_4C_4(C_6H_5)_4]$, are reported for the first time. Both have the paramagnetism expected for one odd-electron species. Platinum ($4f_{7/2}$), nitrogen (1s), and chlorine ($2p_{1/2,3/2}$) binding energies are given for the series $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$, where n = 0–4.

Introduction

The synthesis and study of physical and chemical properties of metal dithiene compounds, $[M(S_2C_2R_2)_n]^z$, where M is a large variety of transition metals, n is generally 2 or 3, R is CF_3, CN, C_6H_5, H, CH_3, etc., and z is 0, 1−, or 2− (and sometimes 3− when n is 3), have been actively investigated because of the remarkable oxidation–reduction behavior of these compounds and the theoretically challenging bonding system.[2-9] Formally, the ligand can be pictured as a neutral 1,2-dithio ketone, as a monoanionic species, or as a dianionic 1,2-dithiolate, and the metal could have a variety of possible oxidation states which would appropriately satisfy the stoichiometry and charge of the complex. The theories of bonding in these complexes have been reported extensively, including molecular orbital calculations.[7-9]

X-Ray photoelectron spectroscopy seemed to be an appropriate method to gain new physical data of substantial significance for understanding the bonding in these compounds since the binding energies measured by XPS can be related to the charges on the atoms.[10,11] We report here the results of studies for some nickel, palladium, and platinum compounds $[M(S_2C_2R_2)_2]^z$ where R is CN (z = 1−, 2−) and C_6H_5 (z = 0, 1−, 2−).

Experimental Section

The compounds used in this investigation were prepared, purified, and characterized according to published methods (*cf.* references given in Tables I and II). Those compounds for which no preparative method is given were reagent grade chemicals used without further purification.

Preparation of Tetraethylammonium Bis(*cis*-1,2-diphenyl-1,2-ethylenedithiolato)platinate, $[(C_2H_5)_4N]\{Pt[S_2C_2(C_6H_5)_2]_2\}$. This compound was prepared by a method similar to that of the nickel analog.[12] $Pt[S_2C_2(C_6H_5)_2]_2$ (1.62 g, 2.38 mmol) and *p*-phenylenediamine (0.735 g, 6.80 mmol) were dissolved under N_2 in *ca.* 8 ml of freshly distilled oxygen-free dimethyl sulfoxide. An intense reddish brown color developed immediately. This solution was poured into a solution of 1.20 g of tetraethylammonium bromide in 30 ml of absolute ethanol. From the resulting green solution, brown crystals with metallic luster began to form. The crystals were filtered, washed with ethanol, and dried *in vacuo* for several hours. This product was recrystallized from hot acetonitrile to give crystals (1.64 g, 2.02 mmol, 85% yield) which melted at 306° with decomposition. *Anal.* Calcd for $[(C_2H_5)_4\{Pt[S_2C_2(C_6H_5)_2]_2\}$, $C_{36}H_{40}NS_4Pt$: C, 53.30; H, 4.98; N, 1.73. Found: C, 53.05; H, 4.89; N, 1.86.

Preparation of Tetraethylammonium Bis(*cis*-1,2-diphenyl-1,2-ethylenedithiolato)palladate, $[(C_2H_5)_4N]\{Pd[S_2C_2(C_6H_5)_2]_2\}$. $Pd[S_2C_2(C_6H_5)_2]_2$ (1.00 g, 1.86 mmol) and pure *p*-phenylenediamine (0.593 g) were dissolved under nitrogen in *ca.* 5 ml of freshly distilled oxygen-free dimethyl sulfoxide. This solution was poured into a solution of tetraethylammonium bromide (0.535 g, 4.95 mmol) in 40 ml of absolute ethanol. Shiny purple platelets which formed were kept at 0° for about 24 hr. This product was filtered and rinsed with a mixture of ethanol–diethyl ether, dried *in vacuo*, and handled under nitrogen. The crystals (1.19 g, 1.64 mmol, 88% yield) melted at 292–293°. *Anal.* Calcd for $[(C_2H_5)_4N]\{Pd[S_2C_2(C_6H_5)_2]_2\}$, $C_{36}H_{40}NS_4Pd$: C, 59.94; H, 5.59; N, 1.94. Found: C, 60.58; H, 5.74; N, 2.03.

Physical Measurements. Solid-state magnetic susceptibilities were measured at 297°K with a Faraday balance by Dr. George Candela, National Bureau of Standards, Gaithersburg, Md. The platinum compound, $[Et_4N][PtS_4C_4Ph_4]$, has an uncorrected magnetic susceptibility $\chi^M = 764.9 \times 10^{-6}$ cgsu. Diamagnetic corrections[13] (each ligand, -127.2×10^{-6} cgsu; $[Et_4N]^+$, -112.2×10^{-6} cgsu; Pt^{2+}, -40×10^{-6} cgsu) applied according to the Pascal equation give a corrected molar susceptibility, $\chi^M{}_{cor}$, of 1172 cgsu. The magnetic moment, $\mu_{eff} = 2.84(\chi^M{}_{cor}T)^{1/2}$, is 1.68 BM. Corresponding values for the palladium compound, $[Et_4N][PdS_4C_4Ph_4]$, are $\chi^M{}_{uncor} = 887.4 \times 10^{-6}$ cgsu, $\chi^M{}_{cor} = 1279 \times 10^{-6}$ cgsu, and $\mu_{eff} = 1.75$ BM. These values can be compared with the values previously obtained[12] for the corresponding nickel compound, $[Et_4N][NiS_4C_4Ph_4]$: $\chi^M{}_{cor} = 1397$ cgsu; $\mu_{eff} = 1.82$ BM.

Photoelectron spectra were taken with a Varian IEE-15 electron spectrometer. The samples were run as fine powders dusted onto double-sided tape. Air-sensitive samples were loaded in a glove bag under nitrogen. Since the available metallic samples were superficially oxidized as detected from their photoelectron spectra, it was necessary to sputter clean the powder with Ar^+ to remove the surface oxides. The reported binding energies were recorded in triplicate and, in most cases, are accurate to ±0.1 eV. The binding energies

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Table I. Metal and Sulfur Binding Energies (eV) in Metal Dithiolate Complexes[a]

	M = Ni		M = Pd		M = Pt	
Compd	Ni($2p_{3/2}$)	S($2p_{1/2,3/2}$)	Pd($3d_{5/2}$)	S($2p_{1/2,3/2}$)	Pt($4f_{7/2}$)	S($2p_{1/2,3/2}$)
[$MS_4C_4Ph_4$][b]	852.9 (1)	161.1 (1)	336.4 (1)	161.9 (1)	71.5 (1)	161.8 (2)
[Et_4N][$MS_4C_4Ph_4$][c]	852.5 (1)	160.8 (1)	335.9 (1)	161.2 (1)	71.2 (1)	161.1 (2)
[N_2H_5]$_2$[$MS_4C_4Ph_4$][b]	852.8 (1)	160.5 (1)	335.8 (1)	161.3 (1)	71.1 (1)	161.3 (2)
[Et_4N][$MS_4C_4(CN)_4$][c]	853.1 (1)	161.3 (2)	335.3 (1)	161.1 (1)	71.2 (1)	161.8 (2)
[Et_4N]$_2$[$MS_4C_4(CN)_4$][d]	853.1 (1)	161.4 (1)	335.8 (1)	161.2 (1)	71.5 (1)	161.8 (1)

[a] Relative to 83.0 eV for Au($4f_{7/2}$). [b] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 87, 1483 (1965). [c] Reference 12. [d] J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 86, 4339 (1964).

reported here correspond to the Ni($2p_{3/2}$), Pd($3d_{5/2}$), Pt($4f_{7/2}$), and S($2p_{1/2,3/2}$) levels. The carbon (1s) binding energies were not determined because of the variety of carbons in the compounds, as well as possible extraneous carbon impurities, which would make assignment of the chelate ring carbon energies very difficult. To compensate for sample charging, the spectra were referenced to the Au($4f_{7/2}$) electrons (E_b = 83.0 eV) as previously described.[14]

Results and Discussion

The nickel ($2p_{3/2}$) binding energies in the series [Ni($S_4C_4Ph_4$)]^0, [Ni($S_4C_4Ph_4$)]$^-$, and [Ni($S_4C_4Ph_4$)]$^{2-}$ are 852.9 (1), 852.5 (1), and 852.8 (1) eV, respectively. These values are remarkably constant and rather low energy for nickel compounds and fall generally in the range of energies associated with nickel(0) compounds[15,16] (*e.g.*, for Ni(s), 852.8 eV; for Ni($Ph_2PCH_2CH_2PPhEt$)$(CO)_2$, 852.9 eV). Since a fair correlation between binding energy and oxidation state is expected, it was earlier suggested[17] that all of these nickel dithiolate species contained nickel(0) with the electrons added on reduction residing mainly on the ligands. However, additional studies with nickel[16] and other elements[11,18,19] have indicated that a more reasonable correlation exists between the binding energy and charge on the metal, which, in turn, depends not only on formal oxidation state (which is often arbitrary) but on the electronegativity of the ligands, polarizability, covalency, and possibly other factors, such as stereochemistry.[20] Indeed, studies of over 100 nickel compounds show that the range of Ni($2p_{3/2}$) binding energies in nickel(II) compounds overlaps with the range in Ni(0) compounds,[15,16] with sulfur and arsenic ligands especially leading to lower metal binding energies than expected for a particular oxidation state. Further, a good correlation between the nickel binding energies and the electronegativities of the ligands has been found.[16] A similar correlation has been established for copper compounds.[11]

By applying the equation relating nickel binding energy ($BE = BE_{NiF_2} - 5.22 + 4.57q$)[16] to the charge, q, on nickel in the case of Ni[$S_4C_4(CN)_4$]$^{1-,2-}$ complexes, which both have binding energies of 853.1 eV, a charge of 0.25+ is obtained for nickel. It is interesting to note the remarkable agreement (which is probably mainly fortuitous) with Gray's[6] calculations from MO theory, which give a charge of 0.26+ in Ni[$S_4C_4(CN)_4$]$^-$ and 0.27+ in Ni[$S_4C_4(CN)_4$]$^{2-}$. The assignment of [$S_4C_4(CN)_4$] < Br < Cl in the spectrochemical series from uv and visible spectroscopy[6] is also in agreement with the XPS results.[16]

The palladium ($3d_{5/2}$) binding energies are fairly constant (*viz.*, 336.4, 335.9, and 335.8 eV) in the series [$MS_4C_4Ph_4$]$^{0,1-,2-}$, as are the platinum ($4f_{7/2}$) energies of 71.5, 71.2, and 71.1 eV. However, unlike the nickel results, these energies are significantly higher than those of representative Pd(0) compounds (*e.g.*, Pd(s), 334.5 eV; $(Ph_3P)_4Pd$,[21] 334.3 eV) and Pt(0) compounds (*e.g.*, Pt(s), 70.1 eV; $(Ph_3P)_4Pt$,[22] 70.1 eV) but slightly less than those of some representative Pd(II) compounds (*e.g.*, *trans*-$(Bu_3P)_2PdCl_2$, 336.9 eV; K_2PdCl_4, 337.3 eV) and Pt(II) compounds (*e.g.*, *cis*-$(Bu_3P)_2PtCl_2$, 72.4 eV; K_2PtCl_4, 72.2 eV).

The Madelung energy effect of an ionic lattice on the binding energy of photoelectrons has been discussed,[10] but calculations to compensate for such effects require the knowledge of extensive structural parameters. *A priori*, one would expect that an ionic lattice would slow down photoelectrons more than a neutral molecular lattice resulting in a lower measured kinetic energy for the electron and consequently an artificially high binding energy. Thus, the metal binding energy in [M($S_4C_4Ph_4$)]$^{2-}$ might be larger than otherwise anticipated (from the oxidation state, for example) due to the 2− charge on the ions and the two compensating monovalent cations. This effect might fortuitously offset the lower energy expected for the lower oxidation state in going from the monoanion to the dianion. In an attempt to ascertain the possible lattice effect on the platinum binding energy, we have measured the XPS of the following series: $K_2[PtCl_4]$, $K[Pt(NH_3)Cl_3]$, *trans*-$Pt(NH_3)_2Cl_2$, $[Pt(NH_3)_3Cl]Cl$, $[Pt(NH_3)_4]Cl_2$. The results are given in Table II. It is seen that the four ionic species have only slightly higher Pt($4f_{7/2}$) binding energies (about 0.5 eV) than the neutral compound. There is no significant difference between the monovalent and divalent cations and anions. The nitrogen (1s) binding energies in the same series of compounds reveal no discernible difference. The chlorine ($2p_{1/2,3/2}$) binding energy is lower in the compounds containing the ionic chlorides, *i.e.*, $[Pt(NH_3)_3Cl]Cl$ and $[Pt(NH_3)_4]Cl_2$, as expected, although different peaks for the two different chlorines in $[Pt(NH_3)_3Cl]Cl$ are not detectable. Again the covalently bound chlorine atoms in $[PtCl_4]^{2-}$ and in $[Pt(NH_3)Cl_3]^-$ have higher binding energies by about 0.7 eV than in neutral *trans*-$Pt(NH_3)_2Cl_2$. These results indicate that the ionic lattice effect may contribute a variation of about 0.5 eV in certain cases.

The sulfur ($2p_{1/2,3/2}$) binding energies decrease in the series [Ni($S_4C_4Ph_4$)]$^{0,1-,2-}$ as follows: 161.1 (1), 160.8 (1), 160.5 (1) eV. This indicates that the charge on reduction in the series is delocalized on the ligands and resides in large part on the sulfur (equally distributed over the four equivalent sulfur atoms). The trend in the palladium and platinum

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Table II. Platinum, Nitrogen, and Chlorine Binding Energies in $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$

Compd	$Pt(4f_{7/2})^a$	$N(1s)^a$	$Cl(2p_{1/2,3/2})^a$
K_2PtCl_4	72.2 (1)		197.9 (1)
$K[Pt(NH_3)Cl_3]^b$	72.0 (1)	398.8 (1)	197.9 (1)
trans-$Pt(NH_3)_2Cl_2{}^c$	71.6 (1)	398.6 (1)	197.2 (1)
$[Pt(NH_3)_3Cl]Cl^d$	72.3 (1)	399.0 (2)	196.9 (1)
$[Pt(NH_3)_4]Cl_2{}^c$	72.2 (1)	398.9 (1)	196.8 (1)

[a] Relative to 83.0 eV for $Au(4f_{7/2})$. [b] T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, **80**, 536 (1958). [c] R. N. Keller, *Inorg. Syn.*, **2**, 250 (1946). [d] K. I. Gildengershel, *Zh. Prikl. Khim.* (*Leningrad*), 39, 223 (1966).

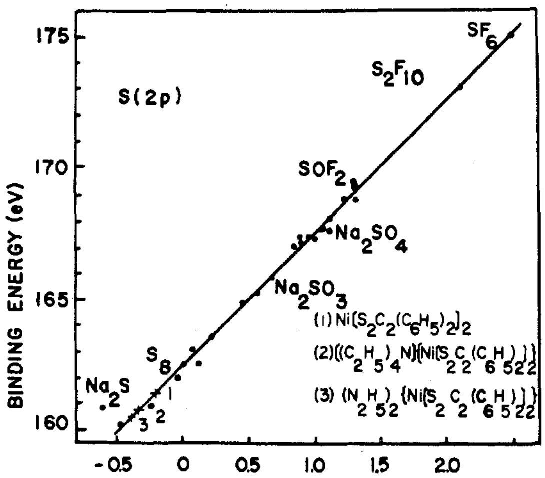

Figure 1. Sulfur $(2p_{3/2,1/2})$ binding energies *vs.* calculated charge on sulfur.

series begins the same way; *i.e.*, from the neutral to monoanionic complex the sulfur binding energy decreases by about 0.7 eV and then remains essentially constant in going to the dianionic species.

The sulfur binding energies are very low reflecting a high electron density on sulfur. Figure 1 according to Siegbahn[10] shows the binding energies of sulfur in a wide variety of sulfur compounds plotted against the calculated charge on sulfur. The stepwise decrease in energy in the series $[Ni(S_4C_4Ph_4)]^{0,1-,2-}$ is reflected in the increasing negative charge on sulfur. Points 1, 2, and 3 were placed on the line in Figure 1 according to their binding energies.

The metal binding energies in the series $[MS_4C_4(CN)_4]^{1-,2-}$ are essentially constant for each metal in agreement with the phenyl compounds. However, the sulfur binding energy is also constant in each metal series, perhaps indicating that the electron gained on reduction mainly residues in the electronegative cyano group of the ligand rather than largely on the sulfur as in the phenyl case.

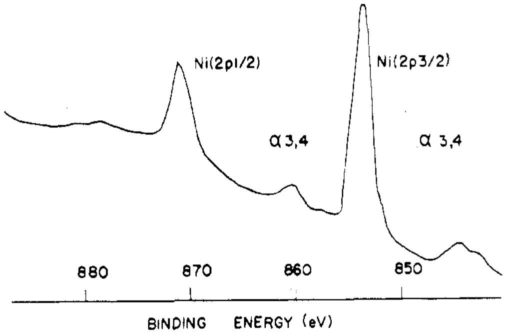

Figure 2. XPS of $[Et_4N][NiS_4C_4Ph_4]$.

An independent and convincing observation that the odd electron in the paramagnetic monoanionic nickel compounds, $[NiS_4C_4Ph_4]^-$ and $[NiS_4C_4(CN)_4]^-$, resides on the ligand rather than on nickel is confirmed by the shape and fine structure of the photoelectron spectra of these compounds (see Figure 2). In all the cases of paramagnetic nickel compounds observed by XPS previously,[16,23] it was found that lines are broadened and shake-up satellites occur, whereas narrow lines and no shake-up satellites occur for diamagnetic nickel compounds. These two paramagnetic dithiene compounds behave like diamagnetic square-planar nickel(II) compounds. Specifically, the lines are narrow and there are no shake-up satellites observable. Hence the odd electron could only be associated with the nickel atom to a very minor extent.

In conclusion, XPS results for metal dithiene compounds of nickel, palladium, and platinum of the type $[MS_4C_4R_4]^{0,1-,2-}$ indicate that the charge on the metal remains essentially constant in the reduction with the added electronic charge residing mainly on the ligands.

Registry No. $[NiS_4C_4Ph_4]$, 28984-20-5; $[PdS_4C_4Ph_4]$, 21954-15-4; $[PtS_4C_4Ph_4]$, 15607-55-3; $[Et_4N][NiS_4C_4Ph_4]$, 42847-28-9; $[Et_4N][PdS_4C_4Ph_4]$, 42846-96-8; $[Et_4N][PtS_4C_4Ph_4]$, 42846-97-9; $[N_2H_5]_2[NiS_4C_4Ph_4]$, 42847-29-0; $[N_2H_5]_2[PdS_4C_4Ph_4]$, 42847-30-3; $[N_2H_5]_2[PtS_4C_4Ph_4]$, 42847-31-4; $[Et_4N][NiS_4C_4(CN)_4]$, 15077-50-6; $[Et_4N][PdS_4C_4(CN)_4]$, 21328-88-1; $[Et_4N][PtS_4C_4(CN)_4]$, 15711-74-7; $[Et_4N]_2[NiS_4C_4(CN)_4]$, 15665-90-4; $[Et_4N]_2[PdS_4C_4(CN)_4]$, 15665-98-2; $[Et_4N]_2[PtS_4C_4(CN)_4]$, 15711-73-6; K_2PtCl_4, 10025-99-7; $K[Pt(NH_3)Cl_3]$, 13820-91-2; *trans*-$Pt(NH_3)_2Cl_2$, 14913-33-8; $[Pt(NH_3)_3Cl]Cl$, 13815-16-2; $[Pt(NH_3)_4]Cl_2$, 13933-32-9.

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