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X-Ray Photoelectron Spectra of Inorganic Molecules. 18.¹ Observations on Sulfur 2p Binding Energies in Transition Metal Complexes of Sulfur-Containing Ligands

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The S 2p binding energies of a series of nickel(II), palladium(II), and platinum(II) complexes of 1,2-ethanedithiol and benzenedithiol occur between 163.5 and 161.5 eV. A comparison between data for the square-planar sulfur-bridged polymers $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{S})]_n$ and $[\text{M}(\text{SPh})_2]_m$, where M = Ni, Pd, or Pt, and square-planar monomers of the type $\text{Ni}(\text{SCH}_2\text{CH}_2\text{S})\text{L}_2$ and $\text{M}(\text{SPh})_2\text{L}_2$, where L = $\text{C}_6\text{H}_{11}\text{NC}$, PMe_2Ph , or $1/2$ dppe, shows that the bridging sulfur atoms usually have S 2p binding energies which are higher than those of sulfur atoms in terminal thiol ligands (i.e., $\text{R}-\text{S}_b^- \approx \text{R}-\text{S}_t^-$). For the ligand methionine, which contains a thioether moiety, coordination of the sulfur atom to platinum(II) causes a S 2p chemical shift of +1.2 eV. However, in methionine complexes of cobalt(II), nickel(II), copper(II), and zinc(II), in which the sulfur atoms are not complexed, the S 2p binding energies (S $2p_{3/2}$ = 163.0 eV) are unchanged from that of the free ligand. Related data for molecules such as $[\text{Fe}(\text{SCH}_3)(\text{CO})_3]_2$, $[\text{Fe}(\text{SC}_2\text{H}_5)(\text{NO})_2]_2$ and a variety of dithiocarbamate- and dithiene-metal complexes have also been obtained. These results are discussed in the light of some recent XPS results for several sulfur-containing metalloproteins.

Introduction

As a result of our recent work on the x-ray photoelectron spectra of a wide variety of transition metal chlorides and bromides,^{1,3,4} we have been able to demonstrate the feasibility of using this technique to differentiate halogen environments in bridging M-X bonds from those in terminal M-X bonds and halide ion X^- . In view of the isoelectronic nature of Cl^- and S^{2-} , we became interested in the possibility that thiol groups ($\text{R}-\text{S}^-$) which are bound to a metal center could be differentiated from the related unbound groups. This possibility is of considerable significance in the identification of metal binding sites in metalloproteins, as recent results of the XPS of cobalt and copper plastocyanins⁵ and cytochrome *c*⁶ have attested. In these two latter studies it was concluded that binding of sulfur (from cysteine or methionine residues) to the

metal shifts the S 2p binding energy peaks by ~ 5 eV to higher energy. The magnitude of this shift is unexpectedly large in view of our previous findings concerning the Cl 2p binding energies of metal chlorides.⁷ Although extensive investigations of the S 2p binding energies of organosulfur compounds have been published,⁸ no systematic studies have been reported on the S 2p binding energies of stable metal complexes of thiol ligands. It seemed to us that such investigations were essential if conclusions concerning the 5-eV S 2p chemical shifts in plastocyanins and cytochrome *c* were to be substantiated. In the present paper we describe the results of our studies on the XPS of a wide variety of metal complexes of sulfur-containing ligands.

Experimental Section

Metal Complexes. Samples of the nickel(II), palladium(II), and

Table I. Metal and Sulfur Core Electron Binding Energies of Metal Complexes of Thiol Ligands^a

No.	Compd	Energy, eV			No.	Compd	Energy, eV		
		S 2p _{3/2}	Metal ^b	Source ^c			S 2p _{3/2}	Metal ^b	Source ^c
I	[Ni(SCH ₂ CH ₂ S)] _n	162.6	854.5 (1.3)	A	XII	Pt(SPh) ₂ (dppe)	161.9	72.9 (1.4)	A
II	Ni(SCH ₂ CH ₂ S)(dppe)	162.0	854.8 (1.8)	A	XIII	Pt(SPh) ₂ (CyNC) ₂	162.2	73.4 (1.2)	A
III	Ni(SCH ₂ CH ₂ S)(PMe ₂ Ph) ₂	162.6	854.5 (1.3)	A	XIV	[Fe(SCH ₃)(CO) ₃] ₂ ^d	163.5 ^e	708.8 (1.8)	B
IV	[Ni(SPh) ₂] _n	162.9	854.8 (1.1)	A	XV	[Fe(SC ₂ H ₅)(NO) ₂] ₂ ^d	163.5	709.2 (1.9)	B
V	Ni(SPh) ₂ (dppe)	161.5	854.7 (1.6)	A	XVI	Methionine	163.0 ^f		A
VI	Ni(SPh) ₂ (PMe ₂ Ph) ₂	162.9	854.7 (1.6)	A	XVII	Co(Met) ₂	163.0	780.3 (~2.0)	A
VII	Ni(SPh) ₂ (CyNC) ₂	162.8	854.6 (1.9)	A	XVIII	Ni(Met) ₂	163.0	855.4 (1.9)	A
VIII	[Pd(SPh) ₂] _n	163.4	337.9 (1.4)	A	XIX	Cu(Met) ₂	163.0	934.8 (1.7)	A
IX	Pd(SPh) ₂ (dppe)	161.8	338.0 (1.3)	A	XX	Zn(Met) ₂	163.0 ^f	1021.7 (0.9)	A
X	Pd(SPh) ₂ (CyNC) ₂	162.9	338.0 (1.2)	A	XXI	Pt(MetH)Cl ₂	164.2	72.4 (1.4)	A
XI	[Pt(SPh) ₂] _n	163.5	73.0 (1.7)	A	XXII	[NH ₄][Fe ₄ S ₃ (NO) ₇]	162.7		B

^a Ligand abbreviations are as follows: dppe, 1,2-bis(diphenylphosphino)ethane; CyNC, cyclohexyl isocyanide; MetH, methionine. ^b 2p_{3/2} for Co, Ni, Cu, and Zn, 3d_{5/2} for Pd, and 4f_{7/2} for Pt; full-width half-maximum values (fwhm) given in parentheses. ^c Spectra recorded using either a Hewlett-Packard 5950A ESCA spectrometer (A) or a McPherson ESCA-36 photoelectron spectrometer (B). ^d Spectrum recorded using a cold probe. ^e Kramer and Klein³² reported a value of 162.3 eV for this binding energy but did not give any information on the referencing procedure which they used. ^f These values are in good agreement with those reported previously by Weser et al.^{29,30}

Table II. Sulfur 2p Binding Energies of Dithiocarbamate and Dithiene Derivatives and Other Sulfur-Containing Complexes of the Transition Metals^a

No.	Compd	Energy, eV	No.	Compd	Energy, eV
XXIII	Fe[S ₂ CN(C ₂ H ₅) ₂] ₂	162.3	XXX	Fe[S ₂ C ₂ (C ₆ H ₅) ₂] ₂	163.5
XXIV	Fe(NO)[S ₂ CN(CH ₃) ₂] ₂	162.5	XXXI	Ni[S ₂ C ₂ (C ₆ H ₅) ₂] ₂	163.3 ^e
XXV	Fe(NO)I[S ₂ CN(C ₂ H ₅) ₂] ₂	162.3	XXXII	[(C ₆ H ₅) ₃ P][Fe(NO)(S ₂ C ₂ (CN) ₂) ₂]	162.7
XXVI	Co[S ₂ CN(CH ₃) ₂] ₃	162.6 ^b	XXXIII	Pt[S ₂ C ₂ (CN) ₂](PPh ₃) ₂	162.7
XXVII	Mo(NO) ₂ [S ₂ CN(C ₂ H ₅) ₂] ₂	162.3	XXXIV	Pt[S ₂ C ₂ (CN) ₂](CNCH ₃) ₂	162.8
XXVIII	Mo(NO)[S ₂ CN(C ₂ H ₅) ₂] ₃	161.7	XXXV	Ir(SO ₂)(CO)Cl(PPh ₃) ₂ ^d	166.8
XXIX	Mo ₂ O ₄ [S ₂ CN(C ₂ H ₅) ₂] ₂	163.1	XXXVI	[Ru(CS ₂)Cl(PPh ₃) ₃]Cl ^{d,e}	163.7

^a All spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer. ^b Good agreement with the value reported previously (162.8 eV) by Frost et al.¹⁹ ^c This value differs from that reported (162.1 eV after correction to a Au 4f_{7/2} standard of 84.0 eV) by Grim et al.³¹ ^d Spectrum recorded using a cold probe. ^e This complex probably contains the triphenylphosphine-carbon disulfide zwitterion, Ph₃P⁺-CS₂⁻, as a ligand rather than being a η-CS₂ complex (see G. R. Clark, T. J. Collins, S. M. James, W. R. Roper, and K. G. Town, *J. Chem. Soc., Chem. Commun.*, 475 (1976)).

platinum(II) thiolate complexes of the types [M(SPh)₂]_n, [M(SCH₂CH₂S)]_n, M(SPh)₂L₂, and M(SCH₂CH₂S)L₂, where L = cyclohexyl isocyanide, dimethylphenylphosphine, or 1/2 1,2-bis(diphenylphosphino)ethane, were available from previous investigations,⁹ while the isoelectronic dimers [Fe(SCH₃)(CO)₃]₂ and [Fe(SC₂H₅)(NO)₂]₂ were obtained using recommended procedures.^{10,11} The platinum(II) complex with DL-methionine, Pt(DL-MetH)Cl₂, and the bis(methioninato) complexes of the type M(Met)₂, where M = Co, Ni, Cu, or Zn, were prepared by the standard literature methods.^{12,13}

The complexes [NH₄][Fe₄S₃(NO)₇], [Ru(CS₂)Cl(PPh₃)₃]Cl, and Ir(SO₂)(CO)Cl(PPh₃)₂ together with a wide variety of dialkyldithiocarbamate and dithiene derivatives (see Results and Discussion) were synthesized, purified, and characterized using published procedures.¹⁴⁻²⁵

Spectral Measurements. X-ray photoelectron spectra were recorded using either a Hewlett-Packard 5950A ESCA spectrometer (Al Kα radiation) at Purdue University or a McPherson ESCA-36 photoelectron spectrometer (Mg Kα radiation) at the University of Arizona. Experimental procedures are described fully elsewhere.^{3,26-28} The measured binding energies were standardized using a Au 4f_{7/2} binding energy of 84.0 eV or a C 1s binding energy of 285.0 eV for double-stick tape or the aromatic carbon atoms of the organic ligands or a value of 285.3 eV for the complexes with dithiocarbamate ligands. An electron "floodgun" was used in conjunction with the Hewlett-Packard instrument to eliminate differential surface-charging effects.^{3a} The spectra of those complexes which were susceptible to sublimation or decomposition under normal experimental conditions were recorded using a cold probe (ca. -95 °C). For spectra obtained with the McPherson instrument, the S 2p_{1/2} and 2p_{3/2} peaks were either deconvoluted or resolved using a du Pont 310 curve resolver, or the curves were simulated using a curve-generation subroutine which is part of the McPherson ESCA-36 program package (S 2p_{1/2}, fwhm 2.1-2.3 eV; S 2p_{3/2}, fwhm 1.9-2.2 eV). In the case of spectra recorded using the Hewlett-Packard spectrometer, the S 2p_{1/2} and 2p_{3/2} peaks were usually well resolved with a spin-orbit separation ΔE(S 2p_{1/2}-S 2p_{3/2}) of 1.0 ± 0.1 eV. These peaks were consistently narrower (fwhm 1.2-1.4 eV) than those obtained using the McPherson instrument.

Results and Discussion

The data obtained in the present study are summarized in Tables I and II. To our knowledge only five of the compounds which are the subject of this investigation have previously had details of their XPS reported. The S 2p binding energies of methionine (XVI) and its zinc(II) complex (XX) and Co[S₂CN(CH₃)₂]₃ (XXVI) are found to be in good agreement with literature data,^{6,19,29,30} after making any necessary corrections for differences in referencing procedures. However, the S 2p energies for the nickel(II)-dithiene complex Ni[S₂C₂(C₆H₅)₂]₂ (XXXI) do not agree with the results of an earlier study by Grim et al.³¹ While there is no obvious explanation for this discrepancy, the internal consistency of the S 2p energies reported in Table II for several such dithiene complexes leads us to conclude that the value we report is a reasonable one. Finally, although the S 2p_{3/2} energy of the dimeric complex [Fe(SCH₃)(CO)₃]₂ (XIV) is different from that reported previously by Kramer and Klein,³² we have no information on the referencing procedure these latter workers used. Thus we do not know whether the difference (1.2 eV) between the S 2p_{3/2} energy they report and that given in Table I is entirely due to the different referencing procedures which were used.

The results of our S 2p binding energy measurements on complexes of thiol ligands are summarized in Table I and some representative spectra are shown in Figure 1. The group of complexes I-XIII enable a comparison to be made between the S 2p energies of the polymeric square-planar complexes [M(SR)₂]_n, where M = Ni, Pd, or Pt, which contain M-SR-M bridges, and the monomeric square-planar derivatives of the type M(SR)₂L₂, where L = 1/2 dppe, PMe₂Ph, or CyNC.⁹ For the palladium(II) and platinum(II) derivatives, the S 2p binding energies of the bridging sulfur atoms

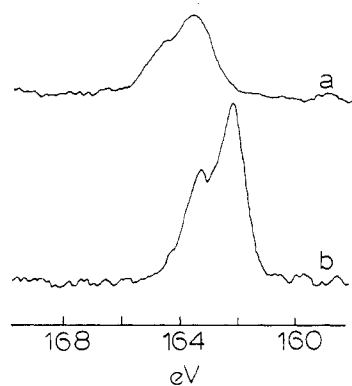


Figure 1. S 2p binding energy spectra of (a) $[\text{Pt}(\text{SPh})_2]_n$ and (b) $\text{cis-Pt}(\text{SPh})_2(\text{CyNC})_2$.

(complexes VIII and XI) are higher (by at least 0.5 eV) than those of the sulfur atoms of the terminal thiol ligands in the square-planar monomers IX, X, XII, and XIII. This same trend is not exhibited in the series of nickel(II) complexes (I–VII) where the S 2p energies of the polymers I and IV are in certain instances indistinguishable from those of monomeric complexes containing terminal thiol groups (complexes III, VI, and VII). Thus it is apparent that the binding energy order $\text{R-S}_b^- > \text{R-S}_t^-$ will not always hold since both the nature of the metal and the other ligands which are coordinated must be taken into account. In this respect, these results resemble those observed previously for certain metal chlorides which contain both bridging and terminal M–Cl bonds.⁴ For these systems, the binding energy order can either be $\text{Cl}_b > \text{Cl}_t$ or $\text{Cl}_b < \text{Cl}_t$ depending upon the particular system.⁴ The observation that the bridging thiol groups generally have S 2p energies close to 163 eV is also borne out for the thiol-bridged dimers XIV and XV.^{33,34}

An indication of the magnitude of the S 2p chemical shift which can be expected upon complexing a thiol or thioether group to a metal ion is shown by our measurements on methionine and its derivatives (Table I and Figure 2). The S 2p energies of the cobalt(II), nickel(II), copper(II), and zinc(II) derivatives (XVII–XX) are unchanged from that of uncomplexed methionine. This result is in accord with the observation^{35,36} that the sulfur atoms are not coordinated to the metal ions. In contrast to this situation, the platinum(II) complex $\text{Pt}(\text{MetH})\text{Cl}_2$, which does contain coordinated sulfur,³⁷ exhibits S 2p binding energies which are shifted by +1.2 eV relative to the free ligand. This latter result is relevant to the results of a recent study of the x-ray absorption spectra³⁸ of alanyl-methionine complexes of platinum(II), in which the K-absorption edges of the sulfur atom were displaced by $\sim +0.8$ eV relative to the uncomplexed ligand.

Our results on the XPS of coordinated thiol and methionine ligands clearly show that the S 2p binding energies occur below 164 eV. This upper binding energy limit is at least 3.3 eV below where the S 2p binding energies of complexed thiol and thioether groups in plastocyanins and cytochrome *c* have previously been assigned.^{5,6} Thus Isaacson et al.⁶ have proposed that the S 2p binding energy difference between bound and unbound methionine groups in oxidized cytochrome *c* is 4.8 eV, whereas our results indicate that a chemical shift in the neighborhood of +1.2 eV is more realistic. A variety of other data also supports our contention. Thus Weser and co-workers^{30,39,40} have shown that the S 2p binding energies of zinc(II), cadmium(II), and mercury(II) complexes of cysteine occur below 163 eV. These complexes all contain M–S bonds.^{36,41} Similar results have been found for Cd–thionein,³⁰ Cu–thionein,⁴² Hg–thionein,⁴⁰ and a mercury(II) complex of glutathione.⁴⁰ In addition, although non-heme iron proteins which contain labile sulfur (S^{2-}) and

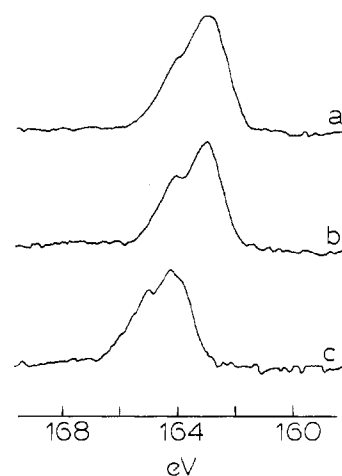


Figure 2. S 2p binding energy spectra of (a) methionine, (b) $\text{Co}(\text{Met})_2$, and (c) $\text{Pt}(\text{MetH})\text{Cl}_2$.

cysteine sulfur exhibit two S 2p peaks separated by between 1.2 and 2.0 eV^{32,43} (the one at higher energy is assigned to labile sulfur), neither of these peaks is located above ~ 164 eV. Finally, we note that even with more complicated sulfur-containing ligands such as dialkyldithiocarbamates (complexes XXIII–XXIX), dithienes (complexes XXXI–XXXIV), thioacetates,⁴⁴ and dithiocarbazates⁴⁵ the S 2p peaks occur within the relatively narrow energy range of 163.6–161.7 eV. Our results on the dithiocarbamate systems are in good agreement with other literature data,^{19,32} and conform to the belief that ligands containing “reduced” sulfur (i.e., formally S^{2-} , $-\text{C}-\text{S}^-$, $-\text{C}-\text{S}-\text{C}-$, or $\text{C}=\text{S}$) will not exhibit S 2p binding energies much above 164 eV.⁴⁶

It seems most likely that the occurrence of S 2p peaks close to 168 eV can only be attributed to the presence of some type of oxidized sulfur. Indeed, the detection by XPS of sulfate impurities in such metalloproteins as erythrocyte has already been documented in the biochemistry literature.⁴⁷ With the S 2p energies of both coordinated sulfoxides^{44,48} and coordinated SO_2 , as in $\text{Ir}(\text{SO}_2)(\text{CO})\text{Cl}(\text{PPh}_3)_2$ (XXXV), at ~ 166 eV, there is little doubt that the S 2p energies of coordinated thiol and thioether ligands will be located below 165 eV.⁴⁹

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Thermally Induced Spin Transition in Tris(2-methoxy-1,10-phenanthroline)iron(II) Perchlorate. Variable-Temperature Mössbauer, Magnetic Susceptibility, and Far-Infrared Measurements

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Tris(2-methoxy-1,10-phenanthroline)iron(II) perchlorate, $[\text{Fe}(2\text{-CH}_3\text{Ophen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, has been prepared in polycrystalline form and studied by variable-temperature ^{57}Fe Mössbauer spectroscopy (293–15 K), magnetic susceptibility (300–2 K), and far-IR (298 and 108 K) measurements. The compound shows a temperature-dependent $^5\text{T}_2(\text{O}_h) \rightleftharpoons ^1\text{A}_1(\text{O}_h)$ transition with $T_c \approx 205$ K (T_c is temperature of 50% conversion). The magnetic crossover is clearly reflected in the Mössbauer spectra as well as in the effective magnetic moment. The far-IR spectra at 298 and 108 K exhibit distinct absorption lines which are characteristic of high-spin and low-spin Fe-N vibrations. The Debye-Waller factors of the different spin states differ in a factor of nearly 2. Two high-spin iron(II) quadrupole doublets are observed in the Mössbauer spectra. From a theoretical analysis of the temperature dependence of the quadrupole splitting in conjunction with a ligand field calculation, with trigonal distortion, spin-orbit coupling, and covalency effects taken into account, these high-spin doublets have been found to be consistent with $^5\text{E}(\text{D}_3)$ and $^5\text{A}_1(\text{D}_3)$ ground states. The magnetic properties of this compound and other $[\text{Fe}(2\text{-Xphen})_3](\text{ClO}_4)_2$ complexes are discussed in terms of electronic and steric influences of the substituent X.

Introduction

The nature of the substituent X in the 2 position of 1,10-phenanthroline (phen) exerts a marked influence on the magnetic properties of the ferrous complexes $[\text{Fe}(2\text{-Xphen})_3](\text{ClO}_4)_2$. For X = H (abbreviated here as phen complex) the compound is diamagnetic with iron being in the $^1\text{A}_1(\text{O}_h)$ electronic ground state. For X = CH₃ (abbreviated as the 2-CH₃phen complex) it has been shown by magnetic^{1,2} and Mössbauer effect measurements^{2,3} that a temperature-dependent high-spin $^5\text{T}_{2g}(\text{O}_h) \rightleftharpoons$ low-spin $^1\text{A}_{1g}(\text{O}_h)$ transition takes place. In the case of X = Cl (abbreviated as the 2-Cl(phen) complex) the iron(II) compound is paramagnetic with the electronic ground state of iron being $^5\text{A}_1(^5\text{T}_{2g})$ under

D_3 symmetry in the temperature range 300–4.2 K,^{4,5} the complex does not exhibit thermally induced spin crossover as originally believed by Halbert et al.⁶ One methyl group each in the 2 and 9 positions of 1,10-phenanthroline causes the complex $[\text{Fe}(2,9\text{-(CH}_3)_2\text{phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (abbreviated as 2,9-(CH₃)₂phen complex) to exhibit high-spin behavior in the temperature range 300–79 K.⁷

A combined steric and electronic effect of the substituent X appears to play a dominating role in the magnetic behavior of these complex compounds. To gain more insight into these effects we have investigated the electronic structure of iron in $[\text{Fe}(2\text{-CH}_3\text{Ophen})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, where the methoxy group next to the nitrogen atom is bigger and therefore likely to be