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THE X-RAY PHOTOELECTRON SPECTRA OF METAL COMPLEXES OF SULFUR-CONTAINING LIGANDS: SULFUR 2*p* BINDING ENERGIES

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A. INTRODUCTION

The ability of X-ray photoelectron spectroscopy (XPS) to distinguish the various environments of halogen atoms in metal halides and their complexes is well documented [1—3]. Of particular significance have been the studies which have shown that in metal chlorides, bromides and iodides, outer-sphere halide may be differentiated from a variety of inner sphere environments which involve terminal and bridging M—X bonds.

The isoelectronic nature of Cl^- and S^{2-} together with the structural versatility of S^{2-} and its derivatives (RS^-, RSR, etc.) poses many important and interesting questions concerning the usefulness of the XPS technique in the structural characterization of metal complexes of sulfur-containing ligands. While there is a wide assortment of XPS data on the S 2*p* binding energies of such complexes in the literature, no attempt has yet been made to assess critically these data or to summarize the available information in a fashion which will be useful to anyone planning to utilize XPS in the characterization of sulfur-containing complexes. The present review addresses these points.

The one previous review which is of relevance to the present one was published in 1972 by Lindberg [4]. That article surveyed most of the electron spectroscopic data (UPS and XPS) available on organic sulfur compounds together with a few inorganics. Included among the latter group were several series of simple inorganic molecules in which there is a marked dependence of the S 2*p* chemical shift upon the sulfur oxidation state. The S 2*p* binding energies were found to decrease in the expected fashion in series such as $SF_6 > S_2F_{10} > SOF_2 > SO_2 > S_8$ [5] and $Na_2SO_4 > Na_2SO_3 > S_8 > Na_2S$ [6]. XPS data for an extensive series of organic sulfur compounds are available in an important paper by Lindberg et al. [5].

At the time of Lindberg's review [4], the S 2*p* binding energies of very few metal complexes had been investigated. Prior to 1972, such measurements had been restricted largely to studies on some thiocarbamate complexes of copper [7], the platinum complex $(Ph_3P)_2Pt(CS_2)$ [8] and certain non-heme iron proteins and iron complexes ($Fe(S_2CNEt_2)_2Br$, $Fe(S_2CNEt_2)_3$, $Fe_2(CO)_6(SMe)_2$ and $(\eta^5\text{-}C_5H_5)_4Fe_4S_4$) [9].

Any comparison of XPS data from different sources is complicated by the variety of different calibration techniques which have been used [10,11]. Of course, this is not a problem when measuring differences in binding energies within the same compound, but comparisons between binding energies reported by different groups can be a problem. Among the most commonly accepted references are a C 1*s* energy of 285.0 eV both for carbon contaminant and the carbon atoms of organic ligands *, a C 1*s* energy of 284.3 eV for graphite and a Au $4f_{7/2}$ energy of 83.8 eV for evaporated gold [11]. In the present review many of the S 2*p* binding energies which are discussed were referenced to these levels in the original literature and so are reported unchanged while others, when this seems appropriate, have been "corrected" to make them compatible with these calibration levels. Nonetheless, such a correction procedure is by no means always reliable because of the difficulty of ensuring good electrical contact between an external reference, such as evaporated gold, and the sample. Consequently, even the use of the same

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* Those aliphatic and aromatic carbon atoms not subject to marked inductive effects.

reference does not necessarily ensure consistency in the values of the measured binding energies although agreement is, more often than not, fairly satisfactory [12].

One additional calibration method which requires mention before we finally leave this subject is the use of adhesive tape ("Cellotape" or "Scotch tape"). This is a convenient backing material for powdered samples and its C 1*s* line has been used for calibration. Unfortunately, a variety of values have been ascribed to this level, namely, 290.0 eV [13], 285.5 eV [14] and 284.0 eV [15] and this has not always proved to be a very effective means of charge correction for samples mounted in this way [11—13].

The S $2p_{1/2,3/2}$ spin-orbit components differ in energy by ca. 1 eV. In many instances, these peaks are not well resolved and the S 2*p* binding energy is then often taken as the peak maximum of the overall band envelope, an energy which is usually close to that of the S $2p_{3/2}$ component. Alternatively, peak deconvolution procedures may be used to ascertain the S $2p_{1/2,3/2}$ binding energies. In other cases the spin-orbit components are well resolved and their energies readily measured.

B. LIGAND ABBREVIATIONS

bipy	2,2'-bipyridyl
CyNC	cyclohexylisocyanide
cystH$_2$	cysteine
cystH	monoanion of cysteine
cyst	dianion of cysteine
daes	bis(2-aminoethyl)sulfide
dbso	dibenzylsulfoxide
dith	dithiane
dmf	dimethylformamide
dmso	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dpso	diphenylsulfoxide
dtb	dithiobenzoate
dtbS	perthiobenzoate
dth	2,5-dithiahexane
dtpa	dithiophenylacetate
dtpv	dithiopivalate
dtpvS	perthiopivalate
en	ethylenediamine
HD	dimethylglyoximato
hist	L-histinyl
metH	methionine
met	anion of methionine
ndta	nitrodithioacetate

pdo	1,8-bis(2'-pyridyl)-3,6-dithiaoctane
$penH_2$	penicillamine
pen	dianion of penicillamine
phen	1 : 10-phenanthroline
py	pyridine
thiox	thioxane
tmtu	tetramethylthiourea
tren	tris(2-aminoethyl)amine
trien	triethylenetetramine
tsc	thiosemicarbazide
tu	thiourea

C. CHEMICAL SHIFTS IN METAL COMPLEXES CONTAINING HIGH OXIDATION STATE SULFUR

A few studies have been carried out on the S 2*p* binding energies of metal complexes containing high oxidation state sulfur but many of the data are fragmentary and in some instances it is difficult to reconcile differences in binding energies which have been obtained using different referencing procedures.

(i) Sulfates, sulfites and other sulfur-oxides

The observation of a chemical shift of 1.9 eV between the S 2*p* binding energies of Na_2SO_4 and Na_2SO_3 [6] leads to the expectation that a similar shift will be maintained in metal complexes containing these same anions. This appears to be the case as judged by the limited data available. However, this conclusion is complicated by the widely different referencing procedures which have been used [14—16]. The appropriate data are presented in Table 1. Within the different sets of data the S 2*p* energies are quite consistent, but it is not clear why Haraguchi et al. [16] find S 2*p* binding energies for the sulfite complexes of cobalt which are ca. 1 eV lower than those of the rhodium complexes reported by Nefedov et al. [17] since the referencing procedures they used (C 1*s* of 285.0 eV for carbon contaminant [17] and Au $4f_{7/2}$ of 84.0 eV for gold [16]) should give rather similar results. It may be that surface charging effects have not been eliminated in the case of the cobalt complexes (Table 1) [16], a conclusion which might go some way to explaining why the S 2*p* energy of $CoSO_4$ [16] is so much lower than that reported for $CuSO_4$ [14].

There is one additional source of S 2*p* binding energy data for metal sulfates and sulfites which has not been included in Table 1. Jørgensen and Berthou [13] have compiled an assortment of XPS data from measurements on over 600 compounds, including 98 which contain sulfur. We will refer to their data [13] since it pertains to both low and high oxidation state sul-

TABLE 1

Sulfur 2*p* binding energies (eV) of transition metal sulfates and sulfites

Compound	S 2*p*	B.E. [a]	Ref. [b]
$CuSO_4$	171.2	A	14
$CuSO_4 \cdot 5\ H_2O$ [c]	170.4	A	14
$CoSO_4$	169.1	B	16
$Cu(bipy)SO_4 \cdot 2\ H_2O$	169.1	A	14
$Cu(bipy)_3SO_4 \cdot 7\ H_2O$	169.9	A	14
$Cu(en)SO_4 \cdot H_2O$	170.3	A	14
$Cu(en)_2SO_4 \cdot H_2O$	169.4	A	14
$Cu(NH_3)_4SO_4 \cdot H_2O$	168.6	C	15
$Cu_2SO_3 \cdot CuSO_3 \cdot 2\ H_2O$	167.8	C	15
$K_3Rh(SO_3)_3 \cdot 2\ H_2O$	167.6	D	17
$NaRh(NH_3)_4(SO_3)_2 \cdot 2\ H_2O$	167.3	D	17
$NH_4[Co(en)(NH_3)_2(SO_3)_2]$	166.5	B	16
$NH_4[Co(NH_3)_4(SO_3)_2]$	166.2	B	16
$Co(NH_3)_4(SO_3)(CN)$	166.2	B	16

[a] Binding energy reference: A, C 1*s* of 285.5 eV for one-sided adhesive tape; B, Au $4f_{7/2}$ of 84.0 eV for evaporated gold; C, C 1*s* of 284.0 eV for one-sided adhesive tape; D, C 1*s* of 285.0 eV for carbon contaminant.

[b] Literature reference to the source of the binding energy data.

[c] The monohydrate and trihydrate have S 2*p* binding energies of 170.8 and 170.3 eV, respectively.

fur. * However, a problem arises in comparing these S 2*p* energies with the data of others because of the use by Jørgensen and Berthou [13] of a C 1*s* standard of 290.0 eV for the carbon atoms of one-sided Scotch tape. While a correction of their S 2*p* values by −5.0 eV might seem appropriate in order to make their data compatible with those of other workers, charging problems [13] prevent this from being a reliable procedure. This is illustrated by a comparison of data for $CuSO_4 \cdot 3\ H_2O$ reported by Jørgensen and Berthou [13] and Frost et al. [14]. The latter group used a value of 285.5 eV for the same reference level as that employed by Jørgensen and Berthou [13], so that the values of the S 2*p* binding energy for $CuSO_4 \cdot 3\ H_2O$ from these two sources [13,14] should differ by 4.5 eV. In fact, the values differ by 5.7 eV.

There is only one report on the S 2*p* binding energy of coordinated sulfur dioxide. This is for the Ir(I) complex $Ir(SO_2)(CO)Cl(PPh_3)_2$ for which a value of 166.8 eV was measured [18] for the S-bound form of the ligand. The absence of comparable data for other SO_2 complexes precludes any meaningful discussion of this result.

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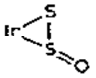
* Data for metal sulfates is mainly restricted to anhydrous and hydrated salts and does not include complex species. The only sulfite studied was the Au(I) complex $Na_3[Au(SO_3)_2]$. Other compounds of interest are the dithionates $BaS_2O_6 \cdot 2\ H_2O$ and $Na_2S_2O_6 \cdot 2\ H_2O$ and the peroxydisulfate salt $[Ag(py)_4]S_2O_8$, all of which reveal a single S $2p_{1/2,3/2}$ doublet [13].

Two sulfur-oxides of relevance to the present discussion are contained in the iridium complexes [Ir(dppe)$_2$(S$_2$O)]PF$_6$ and [Ir(dppe)$_2$(S$_2$O$_2$)]Cl. These complexes may be prepared by the oxidation of the complex [Ir(dppe)$_2$-(S$_2$)]Cl [19,20] and contain the [Ir(S$_2$O)] and [Ir(S$_2$O$_2$)] moieties (I and II below).



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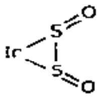

II

The S 2*p* XPS of the monoxide (I) reveals binding energies at 162.7 and 165.3 eV [21] in accord with the structure in which a singly oxidized disulfide unit (S_2^{2-}) contains two different sulfur environments in formal oxidation states of −1 and +1. The S 2*p* peak at 165.3 eV possesses a slightly lower intensity than that at 162.7 eV due to some loss of oxygen under the ultra high vacuum conditions within the spectrometer [21]. In the case of the S$_2$O$_2$ complex (II) a three peak S 2*p* spectrum (162.6, 165.1 and 168.3 eV of relative intensity 74 : 100 : 31) attests to the decomposition of a considerable portion of the complex (S 2*p* = 165.1 eV) to species containing the S$_2$ and SO$_3$ groups which have their S 2*p* binding energies at 162.6 and 168.3 eV, respectively [21]. The chemical shift between the two latter peaks (5.7 eV) is very close to that between the two sets of S 2*p* signals of Na$_2$S$_2$O$_3$ (6.0 eV) [5,10] and the complexes Na$_3$[Au(S$_2$O$_3$)$_2$] (5.5 eV) and [Co(NH$_3$)$_6$]-[Au(S$_2$O$_3$)$_2$] (5.3 eV) [13]. A somewhat smaller separation of 4.3 eV is characteristic of the $O_3SSSSO_3^{2-}$ anion in K$_2$S$_4$O$_6$ [13].

(ii) Dialkyl and diaryl sulfoxides

There have been three studies so far which report S 2*p* binding energies of metal complexes of sulfoxides [22—24], but only one of these reports [22] provides a substantiative body of data. Su and Faller [22] have reported S $2p_{3/2}$ and O 1*s* binding energies for a variety of metal complexes of dimethyl-, dibenzyl- and diphenylsulfoxide. Their data for the dmso complexes are shown in Table 2. Although they used a Au $4f_{7/2}$ reference energy of 83.0 eV, a value which is 0.8 eV lower than that usually employed [11], the data have not been corrected since it turns out that the most useful parameter is the energy difference ΔE(O 1*s* − S $2p_{3/2}$). It appears that within the group of complexes they studied, S-bound dmso is characterized by a value for ΔE(O 1*s* − S $2p_{3/2}$) of ca. 365.0 eV. This increases to ca. 365.8 eV for the O-bound form of the ligand [22]. A key compound in this investigation was the palladium complex [Pd(dmso)$_4$](BF$_4$)$_2$, which contains both O- and S-bound dmso. Two sets of S 2*p* peaks were clearly present [22] and their energies determined by a deconvolution procedure.

A similar trend is observed for several complexes of dibenzylsulfoxide (Sn(CH$_3$)$_2$Cl$_2$(dbso)$_2$, ZnCl$_2$(dbso)$_2$, SnCl$_2$(dbso)$_2$, PtCl$_2$(dbso)$_2$ and Pd$_2$Cl$_4$-

TABLE 2

Sulfur $2p$ binding energies (eV) of complexes of dimethylsulfoxide [a]

Compound	O 1s	S $2p_{3/2}$	ΔE(O 1s − S$p_{3/2}$)	Bonding mode
$NiCl_2(dmso)_3$	530.9	165.0	365.9	O
$CoCl_2(dmso)_3$	531.0	165.0	366.0	O
$MnCl_2(dmso)_3$	530.9	165.1	365.8	O
$ZnCl_2(dmso)_2$	531.1	165.4	365.7	O
$CuCl_2(dmso)_2$	530.4	164.7	365.7	O
$CdCl_2(dmso)$	530.7	165.1	365.6	O
$HgCl_2(dmso)$	531.4	165.6	365.8	O
$SnCl_2(dmso)_2$	531.0	165.3	365.7	O
$PtCl_2(dmso)_2$	530.5	165.6	364.9	S
$[Pd(dmso)_4](BF_4)_2$	530.9	165.9	365.0	S
	530.9	165.1	365.8	O
$PdCl_2(dmso)_2$	530.6	165.5	365.1	S
$AlCl_3(dmso)_6$	531.4	165.7	365.7	O
$FeCl_3(dmso)_2$	531.2	165.3	365.9	O
$RhCl_3(dmso)_3$	531.2	166.0	365.2	S
$SnCl_4(dmso)_2$	531.3	165.6	365.7	O
$Sn(CH_3)_2Cl_2(dmso)_2$	530.5	164.4	366.1	O
dmso	529.9	164.6 [b]	365.3	O

[a] All data taken from ref. 22; full-width half maximum (fwhm) values are 1.1—1.4 eV for S $2p_{3/2}$ and 1.3—1.6 eV for O 1s; binding energy reference, Au $4f_{7/2}$ = 83.0 eV.

[b] Other literature values reported for the S $2p$ binding energy of dmso are 165.7 [58] and 166.7 eV [5].

$(dbso)_2$). With the diphenylsulfoxide complexes $HgCl_2(dpso)$ and $CdCl_2(dpso)$, which contain O-bound dpso, the values of ΔE(O 1s − S $2p_{3/2}$) were unusually large (366.9 and 366.4 eV, respectively), in part due to a small decrease in the S $2p$ energies upon oxygen coordination [22]. It was suggested [22] that this might reflect the ability of the phenyl groups to compensate for loss in electron density at sulfur. A binding energy difference of 365.3 eV for $PdCl_2(dpso)_2$ is in accord [22] with the S-bound nature of dpso, whereas $SnCl_2(dpso)_2$ and $ZnCl_2(dpso)_2$, with values of 365.7 and 365.8 eV respectively, contain the O-bound ligand [22].

Baranovskii et al. [23] have reported a S $2p$ energy of 167.1 eV for $Na[RhCl_4(dmso)_2]$ and one of 166.1 eV in the dmso adduct of the thioacetate complex $Rh_2(OSCCH_3)_4$*, the S $2p$ energy of the thioacetate ligand being at 162.7 eV (see Sect. F(i)). In neither instance was a value for the O 1s energy

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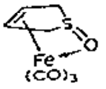
* S $2p$ binding energies of the dmso adducts of the related formate, acetate, benzoate and thiobenzoate Rh(II) complexes have recently been reported to be ca. 166.5 eV [58]. Free dmso has a S $2p$ binding energy of 165.7 eV [58], a value which is 1.0 eV lower than that reported by Lindberg et al. [5].

reported [23], so use cannot be made of the criterion for the mode of R_2SO bonding which was established by Su and Faller [22].

A complex containing the tricarbonyliron moiety π-bound to thiophene oxide

(S=O) * has O 1*s* and S $2p_{3/2}$ binding energies of 530.6 and 165.8 eV [24], thereby giving a value for $\Delta E(\text{O } 1s - \text{S } 2p_{3/2})$ of 364.8 eV, whereas the related complex with 2,5-dihydrothiophene oxide, which has a structure involving O-bound ligand (see III) [25], is characterized by O 1*s* = 532.0 eV,



III

S $2p_{3/2}$ = 167.0 eV and $\Delta E(\text{O } 1s - \text{S } 2p_{3/2})$ = 365.0 eV. Thus both complexes possess values for $\Delta E(\text{O } 1s - \text{S } 2p_{3/2})$ which Su and Faller [22] had proposed were likely to be characteristic of S-bound sulfoxides! Clearly this criterion is not valid in these instances since neither complex possesses this bonding mode. Accordingly, the bonding criteria of Su and Faller [22] should be viewed with caution when applied to systems other than those represented by the type of halide complexes listed in Table 2.

If the S $2p_{3/2}$ values in Table 2 are corrected by +0.8 eV to make them compatible with a Au $4f_{7/2}$ reference energy of 83.8 eV, then several of them become greater than the values for the cobalt sulfite complexes listed in Table 1. This is further support for the suggestion (see Sect. C(i)) that the latter values are ca. 1 eV too low due to charging effects.

D. CHEMICAL SHIFTS IN METAL COMPLEXES OF SULFIDES (S^{2-}), DISULPHIDES (RSSR), THIOLS (RSH) AND THIOETHERS (RSR)

(i) Sulfides

Most data on the XPS of metal sulfides pertain to binary sulfides and will not be considered in any detail here other than to mention that the available information relates to both stoichiometric (for example, see ref. 13) and defect phases (for example, $V_{0.92}S$ [26]). Some data on metal sulfides are available in the heterogeneous catalysis literature, where much interest has centered on the XPS of hydrodesulfurization catalysts and S 2*p* binding energies have been reported for phases such as MoS_2 [27].

S 2*p* binding energies have been reported for a variety of metal sulfide anions but it is not very profitable to compare data from different sources because of problems with the different referencing procedures used. Thus

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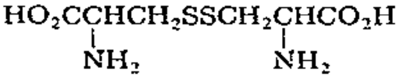
* Related iron carbonyl complexes of SO_2 and its 2,5-dimethyl derivative have also been isolated [24]. Neither involve coordination via the SO_2 function.

Rupp and Weser [15], using a C 1*s* reference of 284.0 eV for adhesive tape, report S 2*p* values for $(NH_4)_2CuS_4$ and $Na_2Cu_3S_3$ of 162.1 and 161.8 eV, respectively, while Kramer and Klein [9] who give a S 2*p* energy of 161.1 eV for $KFeS_2$, do not mention their referencing procedure. Jørgensen and Berthou [13] and Müller et al. [28] have studied various salts of sulfur-containing anions of the type MS_4^{3-} (M = Sb, V, Ta, Mo, W and Re). With the exception of Tl_3TaS_4 (S 2*p* = 170.1 eV), the binding energies occur in the range of 168.5—167.2 eV for Na_3SbS_4, $(NH_4)_3VS_4$, Tl_3VS_4, Tl_2MoS_4, Tl_2WS_4 and $(Me_4N)ReS_4$ upon using a C 1*s* Scotch tape reference energy of 290.0 eV [13,28]. Reducing these S 2*p* energies by 5 eV to make them more compatible with other referencing procedures gives values ranging from 163.5 to 162.2 eV.

In some instances oligomers containing bridging M—S—M bonds have been studied. Of particular interest have been iron complexes such as $(NH_4)[Fe_4S_3(NO)_7]$ [18] and $[(\eta^5\text{-}C_5H_5)_4FeS]_4$ [9] for which the S 2*p* energies of 162.7 and 162.1 eV, respectively, are in the ranges encountered for binary metal sulfides and metal sulfide anions (vide supra). A molecule of particular interest in this same context is the complex $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ which in spite of possessing two different sulfur environments displays only a single S 2*p* photoline at 161.8 eV [29]. However, its breadth (fwhm = 2.7 eV) indicates that the binding energies of the sulfide and thiol sulfurs are not coincident.

(ii) Disulfides

The only organic disulfide to have received much attention is cystine (IV), which is derived from the amino acid cysteine. Rupp and Weser [30]



$$HO_2C\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2SSCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2H$$

IV

have reported a value of 163.0 eV for the S 2*p* binding energy for cystine itself (relative to a C 1*s* energy of 284.0 eV for the carbon atoms of Scotch tape). Data are also available for Zn(II) and Cd(II) complexes which are formulated as Zn-cystine (1 : 1) and Cd-cystine (1 : 2) [31]. These complexes have S 2*p* energies of 163.0 and 162.8 eV [31], values which are similar to that reported for "Hg-cystine" (163.0 eV) [32]. On the other hand, the S 2*p* binding energy for the ligand bridged dimer di-*μ*-cystinato-di-copper(II), which unlike the Zn, Cd and Hg derivatives may actually involve weak M—S coordination [33] *, is located at 163.7 eV [34]. The reason for this chem-

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* Although the structure of this cystinate derivative of Cu(II) has not been determined, that of its penicillamine disulfide analog reveals some evidence for a very weak axial Cu—S interaction involving one of the sulfur atoms of the disulfide unit [33].

ical shift of +0.7 eV, relative to the Zn, Cd and Hg complexes, is not yet fully explained.

(iii) Thiols

A large number of complexes of various thiols have been the subject of XPS studies. These have included systems as varied as simple alkyl and aryl thiols, sulfur-containing amino acids, dithienes and ligands such as 2-mercaptobenzimidazole. In this section we will first discuss the simple thiols, then the amino acids and finally the remaining assortment of ligands.

Simple alkyl and aryl thiols

The only systematic XPS study devoted to complexes of simple thiols is that of Best et al. [18] which dealt with a series of Ni(II), Pd(II) and Pt(II) complexes of 1,2-ethanedithiol and benzenethiol. Table 3 lists the S 2*p* binding energies for the square-planar sulfur-bridged polymers $[Ni(SCH_2CH_2S)]_n$ and $[M(SPh)_2]_n$ (M = Ni, Pd or Pt) and square-planar monomers of the type $Ni(SCH_2CH_2S)L_2$ and $M(SPh)_2L_2$ (L = CyNC, PMe_2Ph or 1/2 dppe) [18]. The S 2*p* spectra of a pair of these complexes are shown in Fig. 1. These binding energies occur between 163.5 and 161.5 eV [18] and, in the case of the Pd(II) and Pt(II) derivatives, the S 2*p* binding energies of the bridging sulfur atoms in $[M(SPh)_2]_n$ are at least 0.5 eV higher than those of the sulfur atoms of the terminal thiol ligands in the square planar monomers. This same trend is not always exhibited for the analogous Ni(II) complexes (Table 3), where the S 2*p* energies of the polymers are indistinguishable from those of certain of the monomers [18]. However, one consistent result is the very low S 2*p* energies of all four dppe complexes [18]. One possible interpretation of this observation is that in these complexes dppe is a very effective σ-donor, thereby leading to a higher net electron density at the sulfur atoms in comparison to the situation with the other complexes.

TABLE 3

Sulfur 2*p* binding energies (eV) of complexes of 1,2-ethanedithiol and benzenethiol [a]

Compound	S $2p_{3/2}$	Compound	S $2p_{3/2}$
$[Ni(SCH_2CH_2S)]_n$	162.6	$[Pd(SPh)_2]_n$	163.4
$Ni(SCH_2CH_2S)(dppe)$	162.0	$Pd(SPh)_2(dppe)$	161.8
$Ni(SCH_2CH_2S)(PMe_2Ph)_2$	162.6	$Pd(SPh)_2(CyNC)_2$	162.9
$[Ni(SPh)_2]_n$	162.9	$[Pt(SPh)_2]_n$	163.5
$Ni(SPh)_2(dppe)$	161.5	$Pt(SPh)_2(dppe)$	161.9
$Ni(SPh)_2(PMe_2Ph)_2$	162.9	$Pt(SPh)_2(CyNC)_2$	162.2
$Ni(SPh)_2(CyNC)_2$	162.8		

[a] All data taken from ref. 18; binding energy reference, C 1s = 285.0 eV for carbon of the ligands.

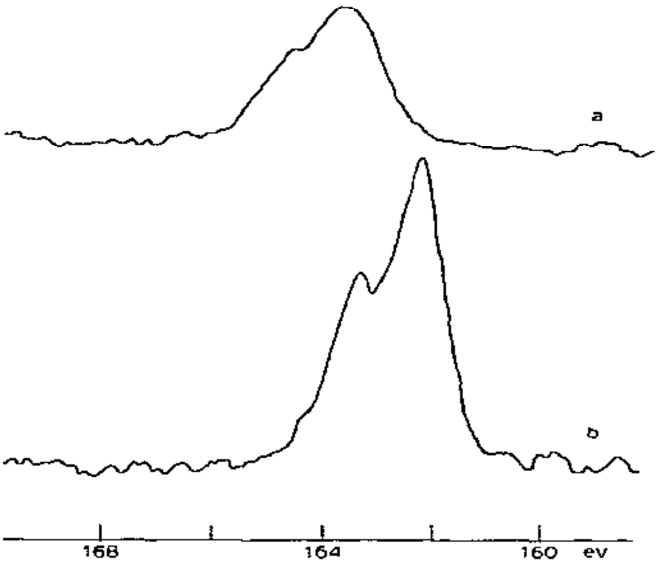


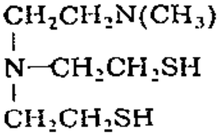
Fig. 1. Sulfur $2p$ binding energy spectra of (a) $[Pt(SPh)_2]_n$, and (b) *cis*-$Pt(SPh)_2(CyNC)_2$. (Reproduced with permission from ref. 18. Copyright by the American Chemical Society.)

From the above results [18], it is apparent that the binding energy order $R{-}S_b^- > R{-}S_t^-$ will not always hold since both the nature of the metal and the other ligands must be taken into account. In this respect, these results resemble those obtained previously for certain metal chlorides which contain both bridging and terminal M—Cl bonds [1,3]. In the latter systems, the binding energy order can be either $Cl_b > Cl_t$ or $Cl_b < Cl_t$ depending upon the particular system.

The observation that bridging thiol groups have S $2p$ energies close to 163 eV [18], is also borne out by data for the thiol-bridged dimers $Fe_2(SMe)_2(CO)_6$ and $Fe_2(SEt)_2(NO)_4$ for which S $2p$ = 163.5 eV [18]. Kramer and Klein [9] reported a S $2p$ energy of 162.3 eV for $Fe_2(SMe)_2(CO)_6$, 1.2 eV lower than the value measured by Best et al. [18]. However, since the former workers [9] did not give any information on the referencing procedure they used, any further consideration of this difference would seem to be unprofitable. We may note that a "correction" of ca. +1.2 eV to this and other data reported by Kramer and Klein [9] might be appropriate to make it compatible with the more commonly used referencing procedures. Thus a value of 161.4 eV for the S $2p$ binding energies of $(Bu_4N)[Fe(S_2C_6H_4)_2]$ and its pyridine adduct ($C_6H_4S_2^{2-}$ = benzenedithiolate) [9], if corrected to 162.6 eV, would bring it into line with the S 2*p* energies quoted in Table 3 for terminal M—SR units *.

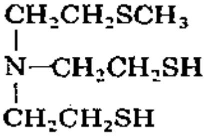
As mentioned previously (see Sect. D(i)), $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$, which contains two different sulfur environments, exhibits a broad S 2*p* photoline (fwhm = 2.7 eV) centered at 161.8 eV. Clearly, the S 2*p* energy of benzylthiol is contained within this band envelope, but its position has not been accurately determined by deconvolution procedures.

The XPS of Mo(VI) complexes of the two tripod ligands V and VI have recently been investigated [35]. These results are of particular significance since they permit us to establish the viability of using XPS to distinguish



$$\begin{array}{l} CH_2CH_2N(CH_3)_2 \\ | \\ N{-}CH_2CH_2SH \\ | \\ CH_2CH_2SH \end{array}$$

V



$$\begin{array}{l} CH_2CH_2SCH_3 \\ | \\ N{-}CH_2CH_2SH \\ | \\ CH_2CH_2SH \end{array}$$

VI

$Me_2NCH_2CH_2N(CH_2CH_2SH)_2$ $MeSCH_2CH_2N(CH_2CH_2SH)_2$

M—SR and M ← SR_2 binding. A discussion of this particular point will be deferred until after we have considered S 2*p* chemical shifts which are characteristic of the binding of thioethers to metal ions (see Sect. D(iv)).

To avoid the experimental problems associated with recording the XPS of the liquid ligands V and VI, they were converted into their crystalline chloride and/or oxalate salts in which the tertiary amine nitrogen atoms(s) had been protonated. Each of these salts exhibits a single well resolved S $2p_{1/2,3/2}$ doublet with a S $2p_{3/2}$ energy of 163.0 ± 0.1 eV [35]. This confirms that for VI the S 2*p* energies for the $—CH_2SH$ and $—CH_2SR$ moieties are essentially identical, a result which is in accord with the S 2*p* energies reported for cysteine, penicillamine and methionine ligands (vide infra). Upon complexation of the tripod ligand V to Mo(VI) in the complex $MoO_2[(SCH_2CH_2)_2NCH_2CH_2NMe_2]$, this S 2*p* doublet shifts by −1.5 eV to 161.5 eV [35] (Fig. 2). A negative chemical shift is also observed upon binding the thiol ligands cysteine and penicillamine to metal ions (vide infra).

The S 2*p* binding energy spectrum of the analogous Mo(VI) complex of VI, $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$, clearly shows evidence for the presence of two sets of S 2*p* peaks (Fig. 2) with S $2p_{3/2}$ energies of 163.3 and 161.7 eV. This result, coupled with the observation that the S 2*p* peak at 161.7 eV is essentially the same as the S 2*p* binding energy for the complex $MoO_2[(SCH_2CH_2)_2NCH_2CH_2NMe_2]$, which contains only thiol sulfur environments, confirms that in the XPS spectrum of $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$ the binding energy of the thiol sulfur atoms is much lower than that of the thioether sulfur atom.

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* A correction of ca. 1.2 eV is further supported by a comparison of the S 2*p* binding energies for Fe(III) dithiocarbamates quoted by Kramer and Klein [9] with comparable data of other workers (see Section F(ii)).

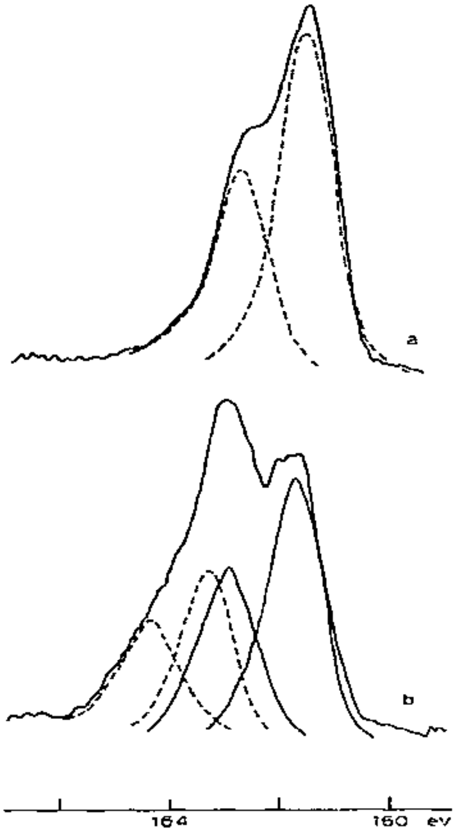
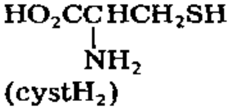


Fig. 2. Sulfur 2*p* binding energy spectra of (a) $MoO_2[(SCH_2CH_2)_2NCH_2CH_2NMe_2]$, and (b) $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$. Spectrum (b) has been deconvoluted into two sets of S $2p_{1/2,3/2}$ spin-orbit doublets. (Reproduced with permission from ref. 35. Copyright by the American Chemical Society.)

Sulfur-containing amino acids

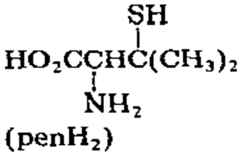
Studies on cysteine (VII) and penicillamine (VIII) and their metal complexes have been reported by Weser and co-workers [30—32,34,36—38] and



$$\underset{\displaystyle NH_2}{HO_2C\underset{|}{C}HCH_2SH}$$

VII

(cystH_2)



$$HO_2C\underset{\displaystyle NH_2}{\underset{|}{C}}H\overset{\displaystyle SH}{\overset{|}{C}}(CH_3)_2$$

VIII

(penH_2)

Walton and co-workers [35]. The S 2*p* binding energy for cysteine was reported to be 162.9 eV [30], close to that for its hydrochloride salt, L-cysteine · HCl · H_2O, which was 163.3 eV [35]. Penicillamine has its corre-

TABLE 4

Sulfur $2p$ binding energies (eV) of some cysteine and penicillamine complexes [a]

Compound	S $2p_{3/2}$	ΔE [b]
L-cysteine · HCl · H_2O	163.3	
$Na_2[Mo_2O_4(cyst)_2] \cdot 5\ H_2O$	161.9	−1.4
$K_4[Co(cyst)_3] \cdot 4\ H_2O$	162.5	−0.8
$K[Co(cyst)_2] \cdot 2\ H_2O$	162.7	−0.6
$H[Co(cyst)_2] \cdot 2\ H_2O$	162.6	−0.7
$K_3[Co(cyst)_3]$	162.6	−0.7
$Ni(cyst) \cdot 2\ H_2O$	162.5	−0.8
$[Pd(cystH)Cl]_2$	162.9	−0.4
$[Rh(cystH)_2Cl]_2$	162.7	−0.6
D-penicillamine	163.2	
$Na_2[Mo_2O_4(pen)_2] \cdot 3\ H_2O$	161.6	−1.6
$Co(pen)(hist) \cdot H_2O$ [c]	161.6	−1.6
$[Pb(pen)]_n$	161.3	−1.9
$Na_2Zn(pen)_2 \cdot 4\ H_2O$	162.4	−0.8
$[Ni(pen)]_n$	163.5	+0.3
$[Pd(penH)Cl] \cdot H_2O$	162.9	−0.3
$[Pt(penH)Cl] \cdot H_2O$	162.7	−0.5

[a] All data taken from ref. 35; binding energy reference, C $1s$ = 285.0 eV.

[b] Chemical shift between the free ligand and metal complex.

[c] This mixed ligand complex contains the L-histidinyl ligand (hist).

sponding binding energy at 163.2 eV [34,35]. These values are in turn very similar to those characteristic of the thiol (and thioether) sulfurs in the tripod ligands V and VI (vide supra). The similarity between the S $2p$ binding energies reported by these two different research groups is of interest in view of the different referencing procedures used (C 1s binding energy of 284.0 eV for Scotch tape in refs. 30 and 34 and a C 1s energy of 285.0 eV for the peak arising from carbon contaminants and the aliphatic carbon atoms of the ligands in ref. 35).

The first studies reported were those of Weser and co-workers [31,32] on the S $2p$ binding energies of the cysteine complexes of Zn(II), Cd(II) and Hg(II). These were found to have values between 161.6 and 162.2 eV, significantly lower than that of the free ligand [30,35]. A more thorough study of both cysteine and penicillamine complexes subsequently showed [35] that negative chemical shifts were the general rule. The data obtained by Walton and co-workers [35] are summarized in Table 4. For most of the complexes which are listed in this table, available spectroscopic and/or crystallographic evidence supports the presence of metal—thiol coordination.

At the present time it is not possible to account for the large variations in the magnitudes of the S $2p$ chemical shifts. While most complexes listed in Table 4 exhibit shifts of between −0.6 and −0.8 eV, two complexes, [Pd-

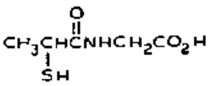
$\mathrm{(cystH)Cl]_2}$ and $\mathrm{[Pd(penH)Cl] \cdot H_2O}$, display smaller shifts, while for others ($\mathrm{Na_2[Mo_2O_4(cyst)_2] \cdot 5\ H_2O}$, $\mathrm{Na_2[Mo_2O_4(pen)_2] \cdot 3\ H_2O}$, $\mathrm{Co(pen)(hist) \cdot H_2O}$ and $\mathrm{[Pb(pen)]_n}$) the shifts are much larger. However, the absence of crystallographic data for most of these complexes precludes any attempt at present to interpret these trends in a meaningful fashion.

The one complex whose S 2*p* binding energy is at variance with the values reported for the other complexes in Table 4 is polymeric $\mathrm{[Ni(pen)]_n}$. The S 2*p* chemical shift of +0.3 eV for this Ni(II) complex supports the contention of Chow et al. [39] that it contains bridging sulfur donor atoms since it has been shown [18] that $\mathrm{M}\diagup\overset{\mathrm{R}}{\mathrm{S}}\diagdown\mathrm{M}$ bridges can exhibit higher S 2*p* binding energies than the sulfur atoms associated with terminal thiol ligands. The much lower S 2*p* binding energy (161.3 eV) which is characteristic of the polymeric Pb(II) complex $\mathrm{[Pb(pen)]_n}$ argues against it containing $\mathrm{M}\diagup\overset{\mathrm{R}}{\mathrm{S}}\diagdown\mathrm{M}$ bridges.

The large chemical shift associated with the binding of cysteine and penicillamine to Mo(V) in $\mathrm{Na_2[Mo_2O_4(cyst)_2] \cdot 5\ H_2O}$ and $\mathrm{Na_2[Mo_2O_4(pen)_2] \cdot 3\ H_2O}$ [35] seems to be characteristic of thiol binding to high oxidation state molybdenum since the Mo(VI) complexes of the tripod ligands V and VI show very similar S 2*p* chemical shifts (−1.5 and −1.3 eV) [35].

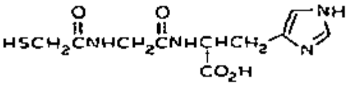
Another study which reports the XPS of a cysteine complex is that describing complexes between $\mathrm{Bu_3SnCl}$ and certain amino acids [40] *. S 2*p* data for the cysteine complex reveal a chemical shift of −0.7 eV, in accord with the results of others [31,32,35].

One final group of complexes relevant to our discussion on sulfur-containing amino acids, and best considered separately, are the various copper complexes of cysteine, penicillamine, α-mercaptopropionylglycine(IX) and N-mercaptoacetylglycyl-L-histidine(X). The complexes derived from ligands IX and X are believed to contain square planar copper and either $\mathrm{NO_2S}$ [41] or $\mathrm{N_3S}$ [42] donor sets, respectively; in the case of the copper complex of IX one of the oxygens arises from a coordinated water molecule. The abbreviations MPG and MAGH will be used for the anionic forms of the complexed ligands, so that the copper complexes of IX and X will be represented as $\mathrm{Na[Cu(MPG)] \cdot 2\ H_2O}$ and $\mathrm{Na_2[Cu(MAGH)] \cdot 2\ H_2O}$. The copper—cys-



$\mathrm{CH_3\underset{SH}{CH}\overset{O}{\overset{\|}{C}}NHCH_2CO_2H}$

IX



X

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* The S 2*p* binding energies reported in Table 2 of the paper by Limouzin and Llopiz [40] are incorrectly labelled. Binding energies quoted as S $2p_{1/2}$ and S $2p_{3/2}$ are in reality the S $2p_{3/2}$ and S $2s_{1/2}$ photolines, respectively.

teine complex [34] is of 1 : 1 stoichiometry, [Cu(cyst)]$_n$, while the two penicillamine species which were studied [34,37,38] comprise the well characterized complex $Tl_5[Cu_{14}(pen)_{12}Cl]$ and a violet colored material of poorly defined stoichiometry.

The features common to the XPS of these five complexes are (1), evidence that the copper is present as Cu(I) rather than Cu(II) *, and (2), S 2*p* binding energies in the range 163.0—163.9 eV [34,37,38,42,43] **,***. This has led Weser and co-workers [34,37,38,43] to propose that these complexes contain Cu(I) bound to sulfur radicals, i.e. Cu(I) (˙SR). In spite of some of these complexes possessing bulk properties which are characteristic of the presence of Cu(II), for example, the ESR Cu hyperfine structure associated with the paramagnetic complex $Na[Cu(MPG)] \cdot 2\ H_2O$ [41] and the crystal structure of $Tl_5[Cu_{14}(pen)_{12}Cl]$ which reveals eight Cu(I) and six Cu(II) sites [44], Weser and co-workers [34,37,38,43] have excluded the possibility that X-ray induced redox reactions of these copper complexes have occurred within the spectrometer. This conclusion was based upon the following observations [34,37,38,43]. (1) The XPS of the complex $Cu(en)_2(SCN)_2$, which contains Cu—S bonds, is purported to show [43] that this complex is not subject to photoreduction under these same experimental conditions. (2) Treatment of the violet Cu-penicillamine complex with 3% H_2O_2 produces a material whose XPS now shows the presence of Cu(II) and oxidized sulfur (S 2*p* = 169.2 eV) [34,37]. (3) If in the preparation of the violet colored Cu-penicillamine complex a three-fold excess of Cu(II) is used in the reaction, then the XPS of the resultant brown-green reaction mixture shows the presence of large quantities of Cu(II) in addition to Cu(I) [37] †.

In the opinion of this writer [44a], the preceding three points are not very convincing support for the contention that photoredox behavior can be excluded [34,37,38,43]. First, the contention of Weser [43] that the XPS of $Cu(en)_2(SCN)_2$ is typical of Cu(II) is incorrect. While satellite structure due to Cu(II) is apparently present [43], the energies of the primary Cu 2*p* photolines reported in his paper ($2p_{1/2}$ at 952.0 eV and $2p_{3/2}$ at 932.0 eV) [43] are in fact characteristic of Cu(I). Thus, in contrast to the belief of

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* Differences between the Cu 2*p* XPS of Cu(I) and Cu(II) species are quite striking (see for example, ref. 14 and D.A. Edwards, Inorg. Chim. Acta, 18 (1976) 65).

** Two different sets of Cu 2*p* and S 2*p* binding energies have been reported for $Na[Cu(MPG)] \cdot 2\ H_2O$ by Weser and co-workers [34,43]. On one occasion they reported a S 2*p* value of 163.7 eV [34] and on another it was quoted as 163.9 eV [43].

*** One puzzling feature of the published XPS data for the complex $Na_2[Cu(MAGH)] \cdot 2\ H_2O$, is that while the two sources [42,43] agree as to the values of the Cu $2p_{3/2}$ (932.1 eV) and S 2*p* (163.0 eV) binding energies, Weser and co-workers [43] report no Cu(II) satellite while Sugiura [42] observes such a feature at 943.5 eV (see Fig. 4 in ref. 42). The primary Cu $2p_{3/2}$ photoline due to Cu(II) must therefore be present within the broad high binding energy tail of the more intense Cu(I) Cu $2p_{3/2}$ peak at 932.1 eV.

† The presence of Cu(I) can be seen from the asymmetric shape of the Cu $2p_{3/2}$ photoline in the figure contained in ref. 37.

these workers [43], photoreduction has in fact occurred during their measurements. The XPS of unreduced $Cu(en)_2(SCN)_2$ had previously been described by Best and Walton [45] (see also Sect. G). Second, since treatment of the Cu-penicillamine complex with H_2O_2 would be expected to destroy the Cu—thiol bonding there is no reason to expect that the resulting material will be as readily photoreduced as the untreated complex. Finally, factor (3) can similarly be explained in terms of photoreduction. The excess Cu(II) present in the product obtained by mixing Cu(II) with penicillamine in a 3 : 1 mole ratio [43] is not reduced while that smaller portion of the Cu(II) complexed to the thiol group of penicillamine is converted to Cu(I) upon irradiation.

An additional observation which favors photoreduction as the most likely explanation of the results of Weser and co-workers is that the S 2*p* binding energies (163.0—163.9 eV) [34,37,38,42,43] can then be assigned to disulfide sulfur (RSSR) (Sect. D(ii)) rather than unstable ·SR radical species. In this event, photoreduction of Cu(II)—thiol complexes can be formally represented as $2[Cu(II){-}SR] \rightarrow [Cu(I)]_2(RSSR)$.

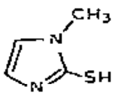
Other thiol-containing ligands

With one exception, namely complexes of dithienes, few other thiol-containing ligands have been the subject of XPS investigations.

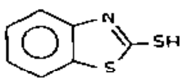
There is one report on a complex of thioglycolic acid (HO_2CCH_2SH). The Zn(II) derivative, which was given the erroneous formulation $Zn(HSCH_2CO_2H)_2$ [36], has a S 2*p* binding energy of 161.8 eV [36] which implies the presence of Zn—SR coordination.

For an assortment of dimeric Rh(II) complexes of thiosalicylic acid ($HO_2CC_6H_4SH$) the thiol groups are not coordinated [46]. These complexes contain four carboxylate groups bridging pairs of metal atoms and all contain the $Rh_2(O_2CC_6H_4SH)_4$ unit. However, in contrast to the S 2*p* binding energies of the free ligand and its sodium salt (164.2 eV), the complexes possess S 2*p* energies of ca. 163.5 eV [46]. Since the thiol group is not coordinated, it has been suggested [46] that this lowering in the S 2*p* binding energy can be attributed to hydrogen-bonding effects involving the —SH groups. This is certainly a very reasonable explanation.

Younes et al. [43] described XPS studies on copper complexes of 1-methyl-2-mercaptoimidazole (XI) and 2-mercaptobenzothiazol (XII). Derivatives of the former ligand comprised a 1 : 2 complex which is formally a derivative of Cu(II), and the mixed oxidation state species $[Cu_7(1\text{-methyl-2-mercaptoimidazole})_7](ClO_4)_2$. For both complexes, the Cu 2*p* spectra are characteristic of Cu(I) while their S 2*p* binding energies are reported to be



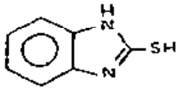
XI



XII

162.4 and 163.0 eV, respectively [43]. The difference of 0.6 eV between the S 2*p* values may in part be due to charging phenomena since the Cu 2*p* energies also differ by a similar value. Similar observations concerning the Cu 2*p* and S 2*p* binding energies were made [43] for the complex of ligand XII, Cu-(2-mercaptobenzothiazol)$_2$. Arguments in favor of all three complexes containing only Cu(I) in the pure complexes can be criticized along similar lines to those already discussed for copper complexes of the amino acids VII—X (vide supra).

The only other complex of relevance to this section is a complex of Bu_3SnCl with 2-mercaptobenzimidazole (XIII) [40]. However, the positive S 2*p* chemical shift (+1.9 eV) observed [40] upon complexation casts doubt as to the reliability of the data since there is no precedent for such a large positive shift upon forming a M--SR bond.


XIII

There have been three reports [18,47,48] on the XPS of metal complexes of dithienes (XIV). The data reported by Grim et al. [47,48] are summarized in Table 5. These studies were of particular interest since they permitted an assessment of charge changes within a series of structurally related neutral, anionic and dianionic complexes. Although it is not possible to determine the influence of changes in Madelung type potentials on the chemical shifts, it does appear that the metal charge is essentially constant within these series of complexes [47,48]. Thus the additional charge gained during the reduction from $[M(S_2C_2R_2)_2]^0$ to $[M(S_2C_2R_2)_2]^{2-}$ must reside principally on the

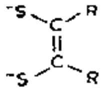

XIV
($R = C_6H_5$ or CN)

TABLE 5

Sulfur 2*p* binding energies (eV) of dithiene complexes of Ni(II), Pd(II) and Pt(II) [a]

Compound	Ni	Pd	Pt
$[M(S_2C_2Ph_2)_2]$	161.1	161.9	161.8
$(Et_4N)[M(S_2C_2Ph_2)_2]$	160.8	161.2	161.1
$(N_2H_5)_2[M(S_2C_2Ph_2)_2]$	160.5	161.3	161.3
$(Et_4N)[M(S_2C_2(CN)_2)_2]$	161.3	161.1	161.8
$(Et_4N)_2[M(S_2C_2(CN)_2)_2]$	161.4	161.2	161.8

[a] All data are taken from refs. 47 and 48; binding energy reference, Au $4f_{7/2}$ = 83.0 eV.

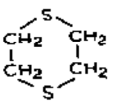
ligands, with some localization on the sulfur atoms in the phenyl derivatives since the S 2*p* energies of the anions are lower than those of the neutral complexes [47,48].

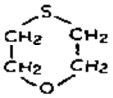
Other data for dithienes have been reported by Best et al. [18]. S 2*p* binding energies for $M[S_2C_2Ph_2)_2]$ (M=Fe or Ni), $(Ph_4P)[Fe(NO)(S_2C_2(CN)_2)_2]$, $Pt[S_2C_2(CN)_2]L_2$ (L=PPh_3 or $CNCH_8$) occur in the range 163.5—162.7 eV. When the S 2*p* energy for $Ni[(S_2C_2Ph_2)_2]$ reported by Grim et al. [47,48] is corrected by +0.8 eV, thereby changing the reference level to a Au $4f_{7/2}$ energy of 83.8 eV, the resulting value of 161.9 eV is still much lower than that published by Best et al. [18]. Clearly, in this instance the different referencing procedures used [18,47,48] cannot easily be interrelated.

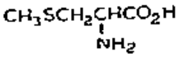
(iv) Thioethers

In the preceding section (D(iii)), devoted to the binding of thiol ligands to metal ions, mention was made of the S 2*p* binding energy spectrum of the Mo(VI) complex $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$ derived from the tripod ligand VI [35]. The spectrum of this complex is shown in Fig. 2 and reveals that the S 2*p* doublet associated with the thiol groups shifts by —1.3 eV upon complexation, whereas the corresponding doublet assigned to the thioether sulfur atom undergoes a very small positive (+0.3 eV) chemical shift [35]. These measurements [35] clearly show that the binding of thiol and thioether sulfur atoms can be differentiated by XPS.

The small chemical shift associated with the binding of the thioether sulfur in $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$ led to the suggestion [35] that the Mo—thioether bond might be very weak. This interpretation was supported by EXAFS studies on this complex [49] and, more recently, by a single crystal X-ray structure analysis [50]. However, in most instances it is by no means clear that the S 2*p* chemical shifts associated with the formation of thioether complexes show any simple correlation with the strength of the M—S bond. These doubts are based upon data for the S 2*p* binding energies of complexes derived from simple thioethers R_2S (R=Me or Et) [17], 1,4-dithiane (dith, XV) [51], 1,4-thioxane (thiox, XVI) [51] and 2,5-dithiahexane (dth) [51], the amino acid methionine ($metH_2$, XVII) [18,30,36]

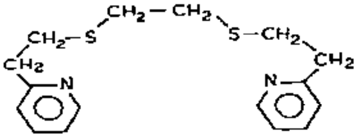

XV


XVI


$$CH_3SCH_2\underset{NH_2}{\underset{|}{C}}HCO_2H$$
($metH_2$)

XVII

and the mixed nitrogen-sulfur donor 1,8-bis(2′-pyridyl)-3,6-dithiaoctane (pdo, XVIII) [52]. While Jørgensen and Berthou [13] have reported the S


XVIII

$2p$ binding energies of $IrCl_3(SEt_2)_3$, $PtCl_2(SEt_2)_2$ and $[Ni(daes)_2](ClO_4)_2$ (daes = bis(2-aminoethyl)sulfide), those for the two diethylsulfide complexes differ by 2.5 eV [13] so it is clear that charging problems are associated with their Scotch tape referencing procedure. Consequently, these particular data [13] will not be considered further.

While the thioether complexes $RhCl_3(SMe_2)_3$, $RhCl_3(SEt_2)_3$, $RhCl_3(thiox)_3$, $[RhBr_2(dth)_2]ClO_4$ and $[PtCl_2(dith)]_n$ have been found to possess S $2p_{3/2}$ binding energies in the range 164.5—164.0 eV, relative to a C 1*s* energy of 285.0 eV for the organic ligands [17,51], the corresponding data for the free ligands were not recorded in these same studies. Accordingly, the chemical shifts associated with the binding of these particular thioether ligands were not determined. *

In the case of the Cu(II) complex of the tetradentate ligand XVIII, $[Cu(pdo)](ClO_4)_2$, its S $2p$ binding energy (164 eV) is little changed from that of the free ligand [52]. A comparison of the S $2p$ spectra of the rhenium complexes $Re_2Cl_5(dth)_2$ and $Re_2Cl_6(dth)_2$ [51] (the former complex contains two chelating dth molecules [53] while the latter is believed to possess two monodentate dth ligands [54]) reveals single S $2p_{1/2,3/2}$ doublets with S $2p_{3/2}$ components at 164.4 and 164.1 eV, respectively. The overall widths of the doublets are essentially the same (fwhm=2.1 eV). Accordingly, S $2p$ data for these copper and rhenium complexes provide examples where the chemical shifts between bound and free thioether sulfur are very small.

In contrast to these systems, there are others where a substantial positive chemical shift appears to occur. The binding of methionine sulfur to Pd(II) and Pt(II) in the complexes $M(metH)Cl_2$ causes S $2p$ chemical shifts of +1.2 and +0.9 eV, respectively, relative both to free methionine and complexes of the type $M(met)_2$ (M = Co, Ni, Cu and Zn) which do not involve sulfur coordination [18,35]. In these studies [18,35], the binding energy reference standard was a C 1*s* value of 285.0 eV for "contaminant" carbon. Actually, this peak is a composite of the C 1*s* energies arising from genuine carbon contaminants and the aliphatic carbon atoms of the ligand. Nonetheless, support for its usefulness as a referencing procedure in these particular studies [18,35] could be considered to be the close similarity of the metal binding energies of these complexes (Pd 3*d* or Pt 4*f*) [18,35] with those of other sulfur-containing complexes such as $[PtCl_2(dith)]_n$ [51], $[Pd(cystH)Cl]_2$ [35] and $[M(penH)Cl] \cdot H_2O$ (M=Pd or Pt) [35]. However, when this referencing procedure is used the C 1*s* binding energies of the methionine carboxylate carbon atoms occur over a much wider energy range (287.3—288.5 eV) than is the case with complexes of cysteine and penicillamine [35]. One explanation for this difference is that the contaminant carbon is not in good electrical contact with samples of certain of the methionine complexes and, therefore, is not altogether a satisfactory reference. If instead, the S $2p$ bind-

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* Lindberg et al. [5] report a S $2p$ binding energy for 1,4-dithiane of 163.4 eV, referenced to the C 1*s* energy of carbon contaminant.

ing energies are internally referenced to a constant C 1*s* value for the carboxylate carbons, then the S 2*p* energies of the Pd(II) and Pt(II) complexes are not much greater than those of the Co(II), Ni(II), Cu(II) and Zn(II) derivatives. The resolution of the problem as to which method constitutes the more satisfactory referencing procedure is not yet at hand.

E. CHEMICAL SHIFTS IN METAL COMPLEXES CONTAINING THE $>$C=S (THIONE) MOIETY

Any XPS study on metal complexes of multidentate ligands which contain a thione ($>$C=S) function first requires the appropriate data for simple thione ligands. Studies on thiourea complexes satisfy this requirement. The S 2*p* binding energy of thiourea has been variously reported [46,55,56] as 162.4, 162.3 and 162.2 eV. In two of these studies, the same referencing procedure was used, namely, a C 1*s* value of 285.0 eV for contaminant carbon [46,55], while in the other [56] a Au $4f_{7/2}$ value of 84.1 eV was chosen. Correction of the latter to 83.8 eV, the usual Au $4f_{7/2}$ reference value [11], gives a S 2*p* binding energy of 161.9 eV for thiourea, in excellent agreement with the value of 161.8 eV reported by Lee and Rabalais [57] using this same reference. Accordingly, it is apparent that these two referencing procedures give binding energies for thiourea which differ by approximately 0.5 eV.

In all instances where metal complexes of thiourea have been investigated [17,46,55,56,58], a positive chemical shift in the S 2*p* energies has been observed (see Table 6). However, in three instances ($NiCl_2(tu)_4$ [55], $Rh_2(O_2CH)_4(tu)_2$ and $Rh_2(O_2CCH_3)_4(tu)_2$ [58]) the shift is so small as to be effectively zero within experimental error. A similar result has been obtained for the Sn(IV) complex of tetramethylthiourea $SnCl_4(tmtu)_2$ (S 2*p* = 162.6 eV) where the S 2*p* chemical shift is +0.9 eV relative to the free ligand [59].

One further point of considerable interest concerns the complexes $[M(NCS)_2(tu)_2]_n$ (M=Co or Ni) and $[Cu(BF_4)(tu)_3]_2$, in which some or all of the thiourea ligands form M—S—M bridges. XPS measurements clearly show [55] that the S 2*p* binding energies associated with the bridging sulfur atoms are not significantly different from those of the thiourea ligands which are bound to one metal atom (Table 6). This behavior is in contrast to the binding energy differences which often exist between bridging and terminally bound thiol sulfur [18] and halide ligands [1—3].

S 2*p* binding energies of 163.1 and 163.5 eV were reported for the thiosemicarbazide complexes $RhCl_3(tsc)_3$ [17] and $Rh_2(O_2CH)_4(tsc)_2$ [46]. However, the corresponding data for the free ligand is not available [17,46].

The positive chemical shift which is more often than not characteristic of the binding of thione sulfur is clearly observed in XPS studies on more complex ligands containing this functional group. These studies [56,60,61] have been carried out on thiazole type ring systems, so that in addition to the presence of a thione sulfur atom there is also either a disulfide linkage [60]

TABLE 6

Sulfur 2*p* binding energies (eV) of thiourea complexes of the transition metals [a]

Compound	S 2*p*	ΔE [b]	Ref. [c]
Thiourea	162.4		55
$[Pr_4N]ReCl_5(tu)$	162.8	+0.4	55
$CoCl_2(tu)_2$	162.9	+0.5	55
$CoBr_2(tu)_2$	162.8	+0.4	55
$Co(NCS)_2(tu)_2$	162.8	+0.4	55
$Co(NO_3)_2(tu)_4$	162.9	+0.5	55
$Rh_2(O_2CH)_4(tu)_2$	162.4	+0.1 [d]	58
$Rh_2(O_2CCH_3)_4(tu)_2$	162.4 [e]	+0.1 [d]	58
$Rh_2(O_2CC_6H_5)_4(tu)_2$	162.6	+0.3 [d]	58
$RhCl_3(tu)_3$	163.2	+0.8	17
$[Rh(tu)_6]Cl(NO_3)_2$	163.0	+0.6	17
$[Rh(tu)_5Cl]Cl_2$	163.1	+0.7	17
$NiCl_2(tu)_4$	162.5	+0.1	55
$Ni(NCS)_2(tu)_2$	162.9	+0.5	55
$Ni(NO_3)_2(tu)_6$	162.8	+0.4	55
$CuCl(tu)_3$	162.7	+0.3	55
$[Cu(BF_4)(tu)_3]_2$	163.0	+0.6	55
$AgCl(tu)_2$	162.5	+0.3 [f]	56

[a] Data are taken from refs. 46, 55 and 56; binding energy references are C 1*s* = 285.0 eV for carbon contaminant or Au $4f_{7/2}$ = 84.1 eV.

[b] Chemical shift between the free ligand and metal complex.

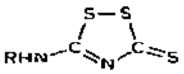
[c] Literature reference to the source of the binding energy data.

[d] This chemical shift is relative to a S 2*p* binding energy of 162.3 eV for thiourea [46, 58].

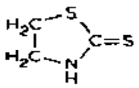
[e] This value conflicts with that reported earlier (163.0 eV) by this same group [46].

[f] This chemical shift is relative to a S 2*p* binding energy of 162.2 eV for thiourea [56].

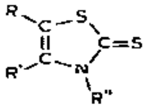
or a "thioether" sulfur [56,61]. The ligands of this type which have been studied are isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole, XIX) and several based upon the thionamide structure (XX and XXI).



XIX



XX



XXI

The S 2*p* spectrum of isoperthiocyanic acid reveals peaks at 164.3 and 162.3 eV assigned [60] to the endocyclic (disulfide) and exocyclic (thione) sulfur atoms (Fig. 3). Complexation of this ligand to Cu(I) and Pt(II), as in the complexes $CuCl(L)_2$ and $PtCl_2(L)_2$ [60], leaves the disulfide binding energies essentially unchanged but leads to a positive shift (+0.6 eV in the case of Cu(I) and +0.9 eV for Pt(II)) in the thione S 2*p* binding energies [60] (see Fig. 3). This observation is clearly in accord with coordination via the thione sulfur [60].

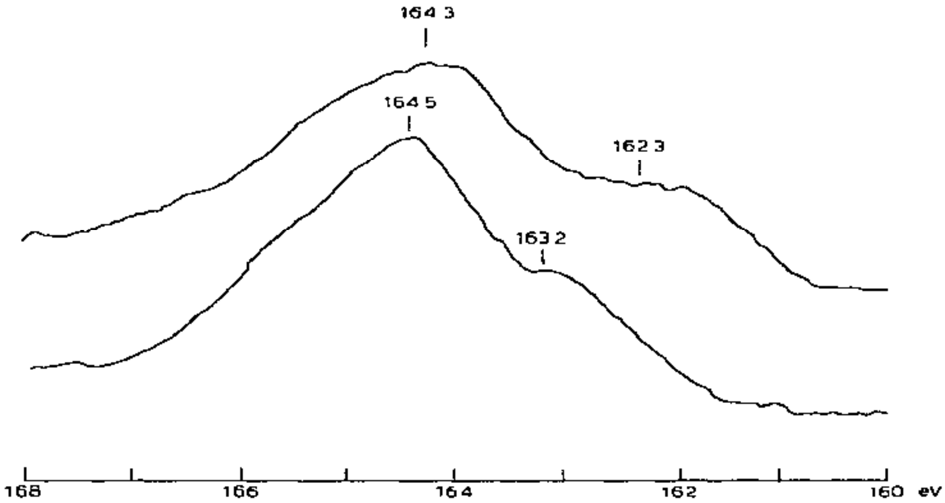


Fig. 3. Sulfur 2*p* binding energy spectra of (a) isoperthiocyanic acid, and (b) $PtCl_2(L)_2$. (Reproduced with permission from ref. 60.)

The thionamide ligand thiazolidine-2-thione (XX) exhibits S 2*p* binding energies at 163.8 and 162.2 eV, the lower of the two being assigned to thione sulfur [56]. Formation of the Ag(I) complex of this ligand leads to a shift of these S 2*p* binding energies to 163.6 and 162.5 eV, respectively, together with a substantial negative chemical shift of the N 1*s* binding energy, from 400.0 to 398.5 eV [56]. These observations, and analogous ones for the thionamide ligands 4-methyl-4-thiazoline-2-thione and benzothiazole-2-thione (derivatives of the type XXI in which R''=H) and their Ag(I) complexes (see Fig. 4), have been interpreted in terms of the stabilization of the mercaptide tautomeric form, i.e. $-N{=}\overset{|}{C}-S-Ag$. The interpretation of these binding energies was aided by CNDO and extended Hückel molecular orbital calculations [56].

The formation of a mercaptide derivative of the type $-N{=}\overset{|}{C}-S-Ag$ can be prevented by substitution of the secondary amine hydrogen. This has been accomplished [56] using a ligand of the type XXI, with R=H, $R'=CH_3$ and $R''=CH_2CH_2OH$, for which the S 2*p* energies are 164.1 and 161.7 eV. The formation of the Ag(I) complex does not affect the higher of these two binding energies but causes a +0.9 eV chemical shift of the 161.7 eV thione sulfur peak [56]. The N 1*s* binding energy at 400.5 eV shifts to 400.7 eV upon complex formation, an observation which is quite different from the situation where proton transfer from nitrogen to sulfur occurs (vide supra) [56]. Similar results have been observed for two other derivatives of the ligand type XXI. These are the 1 : 1 and 2 : 1 complexes of 3-(2-carboxyethyl)-4-

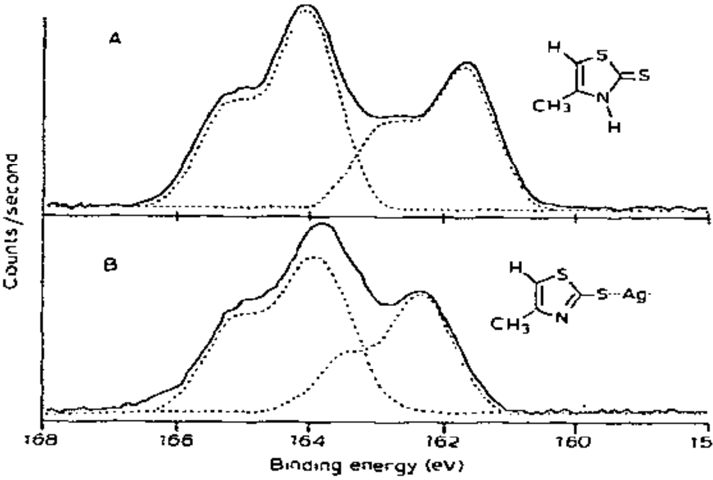


Fig. 4. Sulfur 2*p* binding energy spectra of (A) 4-methyl-4-thiazoline-2-thione, and (B) its Ag(I) complex. (Reproduced with permission from ref. 56. Copyright by the American Chemical Society.)

hydroxymethyl-4-thiazoline-2-thione (XXI, with R=H, R′=CH_2OH and R″=$CH_2CH_2CO_2H$) and the 1 : 1, 2 : 1 and 3 : 1 complexes of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione (XXI, with R=H, R′=CH_3 and R″=CH_2CO_2H). In both cases, complexation by Ag(I) causes the free ligand thione sulfur binding energy to shift from 161.6 eV to ca. 162.1 eV but leaves the S 2*p* binding energy peak at ca. 164.0 eV unchanged.

F. CHEMICAL SHIFTS IN METAL COMPLEXES CONTAINING THE $-\mathrm{C}\begin{array}{l}\scriptstyle\nearrow S\\ \scriptstyle\searrow O^-\end{array}$ (THIO) AND $-\mathrm{C}\begin{array}{l}\scriptstyle\nearrow S\\ \scriptstyle\searrow S^-\end{array}$ (DITHIO) MOIETIES

(i) Thiocarboxylates and perthiocarboxylates

There are only three reports [23,58,62] dealing with the S 2*p* XPS of derivatives of thioacetic acid (CH_3COSH) and thiobenzoic acid (PhCOSH). In all three instances, a C 1*s* reference of 285.0 eV was used. Stec et al. [62] report a S 2*p* binding energy of 162.5 ± 0.4 eV for $CH_3COS^-Na^+$, a value which decreases to 161.8 ± 0.3 eV in the Ag(I) salt CH_3COSAg. Baranovskii et al. [23,58] have studied the thioacetate and thiobenzoate dimers of Rh(II) together with an assortment of their adducts. In all instances, the S 2*p* binding energies fall in the narrow range 163.1—162.7 eV. A selection of these data [23,58] are presented in Table 7. Although the two types of sulfur present in $Rh_2(OSCR)_4(dmso)_2$ are readily distinguished (that due to the sulfur of dmso is at 166.4—166.1 eV), in the case of thiourea adducts $Rh_2(OSCR)_4(tu)_2$, the S 2*p* binding energies of the thiocarboxylate ligands

TABLE 7

Sulfur $2p$ binding energies (eV) of mono- and dithiocarboxylate complexes of the transition metals [a]

Compound	S $2p$	Ref. [b]
$Rh_2(OSCCH_3)_4$	162.9	23
$Rh_2(OSCCH_3)_4(tu)_2$	162.7	23
$Rh_2(OSCCH_3)_4(CH_3COSH)_2$	163.0	23
$Rh_2(OSCCH_3)_4(py)_2$	162.8	23
$Rh_2(OSCCH_3)_4(H_2O)_2$	162.8	23
$Rh_2(OSCCH_3)_4(CH_3CN)_2$	162.8	23
$Rh_2(OSCPh)_4$	162.9	58
$Rh_2(OSCPh)_4(tu)_2$	162.7	58
$Rh_2(OSCPh)_4(PhCOSH)_2$	162.9	58
$Rh_2(OSCPh)_4(dmf)_2$	163.0	58
$[Rh(NH_3)_5(OSCCH_3)]I_2$	163.1	23
$Ni(dtb)_2$	163.4	63
$Pd(dtb)_2$	163.5	63
$Cr(dtb)_3$	163.3	63
$Co(dtb)_3$	163.1	63
$Ni(dtpv)_2$	163.2	63
$Ni(dtpa)_2$	163.1	63
$Fe(dtpa)_3$	163.4	63
$Ni(ndta)_2$	163.5	63
$Pt(ndta)_2$	163.3	63

[a] Data taken from refs. 23, 58 and 63; binding energy references are C 1*s* = 285.0 eV for carbon contaminant or Au $4f_{7/2}$ of 84.0 eV for the underlying sample plate.

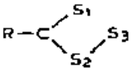
[b] Literature reference to the source of the binding energy data.

and thiourea (see Tables 6 and 7) are almost coincident [23,58]. Similarly, only a single S $2p$ binding energy is characteristic of $Rh_2(OSCR)_4(RCOSH)_2$ [23,58].

For a series of complexes of dithiocarboxylic acids (dithiobenzoate, dtb; dithiopivalate, dtpv; dithiophenylacetate, dtpa; and nitrodithioacetate, ndta) slightly higher S $2p$ energies were observed [63] than for the monothiocarboxylates we have discussed (Table 7). However, since a different referencing procedure was used in the study of the dithiocarboxylates (a Au $4f_{7/2}$ value of 84.0 eV) [63] it seems unlikely that any significant differences exist between these two sets of binding energy data. Note that the range of S $2p$ binding energies for the dithiocarboxylates (Table 7) changes from 163.5—163.1 eV to 163.3—162.9 eV when reference is made to the more usual Au $4f_{7/2}$ standard of 83.8 eV [11] rather than 84.0 eV.

One interesting observation concerning the data for the dithiocarboxylates is the insensitivity of the S $2p$ binding energies to variations in the metal and ligand substituents [63].

An extension of these studies [63] to include measurements on the metal complexes of perthiocarboxylates of benzoic and pivalic acids (abbreviated dtbS and dtpvS, respectively), shows the presence of inequivalent sulfur atoms. These ligands possess the framework shown in XXII.

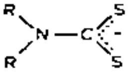


XXII

For free dtbS$^-$, CNDO/2 calculations suggest [63] that S_2 has a more positive charge than S_1 and S_3. S 2*p* binding energy measurements [63] on the mixed ligand complexes Ni(dtb)(dtbS) and Ni(dtpv)(dtpvS) and on Ni(dtbS)$_2$ and Ni(dtpvS)$_2$ show that they possess S 2*p* profiles which indicate two distinguishable sulfur atoms. Deconvolution of the S 2*p* profiles to give two sets of S $2p_{1/2,3/2}$ binding energies was accomplished [63]. Intensity ratios of 4 : 1 for the mixed ligand complexes and 2 : 1 for Ni(dtbS)$_2$ and Ni(dtpvS)$_2$ were in accord with the stoichiometries of these complexes [63], but the widely different chemical shifts between S_2 and S_1, S_3 (values of +1.8, +1.0, +2.4 and +1.2 eV were obtained for the four different complexes) raise questions as to the reliability of the deconvolution procedure.

(ii) Dithiocarbamates, xanthates and dithiophosphates

XPS data for a wide assortment of dithiocarbamate complexes (XXIII) are available from a variety of sources [4,9,13,16,18,23,64,65]. In most of these



XXIII

[4,16,18,23,64,65], the S 2*p* binding energies are reported to occur in the relatively narrow range of 162.9—161.7 eV and show no obvious correlation with the nature of the metal ion. * In some instances, data for the same compound are dependent on the source; for example, S 2*p* values of 162.0 [16] and 162.8 eV [65] have been reported for Co(S_2CNEt_2)$_3$. The values of these binding energies for dithiocarbamate complexes are very similar to those of other low oxidation state sulfur ligands and accordingly this binding energy range is of little diagnostic value.

There are two reports which give S 2*p* binding energies for dithiocarbamates which are outside the range 162.9—161.7 eV. Kramer and Klein [9] give S 2*p* binding energies for Fe(S_2CNEt_2)$_3$ and FeBr(S_2CNEt_2)$_2$ of 161.5

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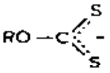
* Frost et al. have noted that the S 2*p* binding energies of diethyldithiocarbamate complexes are in the order Fe(III) < Co(III) < Ni(II) > Cu(II) > Zn(II), which is opposite to that of the "average metal—sulfur bond lengths for the first row transition metal complexes studied." However, the spread of S 2*p* binding energies within this series was only 0.4 eV and, since the structures of these complexes are of different types, it is difficult to judge how significant this trend really is.

and 161.4 eV, respectively, but report no details of their referencing procedure. Jϕrgensen and Berthou [13], using an adhesive tape reference with a C 1*s* value of 290.0 eV, report S 2*p* values between 168.3 and 166.8 eV for dithiocarbamates of Cu(II), Ag(I), Pb(II), As(III), Sb(III), Co(III), Te(IV), Cr(III) and Ni(II). Upon using a value of 285.0 eV for this same reference, these S 2*p* binding energies now occur between 163.3 and 161.8 eV.

One unexpected feature in the XPS studies of dithiocarbamates reported by Frost et al. [65], was the occurrence of "satellites" at ca. 6 eV above the S 2*p* primary photolines. It was suggested [65] that these features might be due to L → M or L → L * charge transfer shake-up processes. However, an alternative interpretation is that some of these "satellites" might be due to the formation of small amounts of high oxidation state sulfur contaminants. The S 2*p* binding energy of sulfate, for example, occurs in this region (ca. 190 eV) (see Sect. C(i)). This type of problem has previously plagued the interpretation of the S 2*p* XPS of certain sulfur-containing metalloproteins (see Sect. H).

The only XPS data on metal xanthates (XXIV) is that reported by Haraguchi et al. [16] for the Co(III) complexes $Co(S_2COEt)_3$ and $Co(S_2COPr^n)_3$,



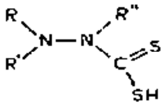
XXIV

both of which have a S 2*p* binding energy of 162.4 eV. For the dithiophosphates $Pb(S_2P(OEt)_2)_2$, $Rh(S_2P(OEt)_2)_3$, $Ni(S_2P(OPr)_2)_2$, and $M(S_2P(OPr)_2)_3$ (M=Co or Ir), the S 2*p* energies occur between 163.0 and 161.8 eV, when referenced to a C 1*s* value of 285.0 eV for adhesive tape rather than using the original value of 290.0 eV [13].

It is apparent from the foregoing discussion that the S 2*p* binding energies of metal dithiocarbamates, xanthates and dithiophosphates are very similar, so that S 2*p* XPS studies on complexes containing any combination of these ligands is unlikely to reveal more than a slightly broadened S $2p_{1/2,3/2}$ doublet.

(iii) Dithiocarbazates

Dithiocarbazic acids (XXV) form metal complexes in which coordination



XXV

to the metal can occur through N,S or S,S donor sets. It is for this reason that we consider dithiocarbazates separately from dithiocarbamates, xanthates and dithiophosphates.

So far, XPS studies on these systems have been restricted to their Ni(II) complexes, $(RR'NNR''CS_2)_2Ni$, and methyl esters [66]. Referencing to the Au $4f_{7/2}$ level at 84 eV gave S 2*p* binding energies for the complexes of between 162.8 and 162.3 eV [66]. These photolines possessed similar fwhm values [66] and there appeared to be no obvious correlation of the S 2*p* spectra with the ligand mode of coordination (N,S or S,S). The S 2*p* binding energies of the methyl esters (e.g. Me_2NNHCS_2Me at 163.0 eV) were higher than those of the complexes and the associated fwhm values greater by ca. 0.5 eV. It is apparent that in contrast to $(RR'NNR''CS_2)_2Ni$, the sulfur atoms in the esters possess markedly different charges. The S 2*p* photolines of the latter were deconvoluted to give two sets of S 2*p* binding energies differing by 1.5—2 eV, a procedure which was justified by some attendant semiempirical charge calculations [66].

(iv) Carbon disulfide

Whilst differing electronically from other ligands containing the $[CS_2]$ moiety, it is appropriate to consider the S 2*p* XPS of carbon disulfide complexes at this point. However, the available data are very sparse. Although the Pt 4*f* binding energies of $(Ph_3P)_2Pt(CS_2)$ were reported in an early XPS study on platinum complexes [8], the corresponding S 2*p* energies were not published. Nefedov et al. [17] have found that the S $2p_{3/2}$ energy is 162.9 eV in the Rh(I) complex $(Ph_3P)_3RhCl(CS_2)$, a value which is apparently 1 eV less than free CS_2 [17]. The Rh 3*d* binding energies are correspondingly high; a Rh $3d_{5/2}$ value of 309.6 eV versus 307.6 eV for $(Ph_3P)_3RhCl$ [17]. The significance of this result must await further studies on CS_2 complexes, for although a S 2*p* binding energy of 163.7 eV was measured for the ruthenium complex $[Ru(CS_2)Cl(PPh_3)_3]Cl$ [18], it is likely that this complex contains the triphenylphosphine—carbon disulfide zwitterion $Ph_3P^+—CS_2^-$ as a ligand rather than being a genuine η-CS_2 complex [67].

G. CHEMICAL SHIFTS IN METAL THIOCYANATES

The first paper specifically devoted to an assessment of the XPS technique as a means of differentiating the bonding modes of the thiocyanate ligand was that of Burger et al. [68]. This described the C 1*s*, N 1*s* and S 2*p* binding energies of several Co(III) and Ni(II) complexes containing bridging, N-bound or S-bound thiocyanate ligands. These workers used the relative magnitudes of the [C 1*s* — S 2*p*] and [N 1*s* — C 1*s*] binding energy differences as a guide to whether the M—SCN or M—NCS coordination modes could be differentiated. For example, [C 1*s* — S 2*p*] differences of 122.0 eV or more were characteristic of nickel(II) complexes containing N-bound thiocyanate or bridging thiocyanate whereas this value decreased to 121.4 eV or below for the cobalt(III) complexes of S-thiocyanate.

A later study by Best and Walton [45], which explored a much broader range of complexes, showed that the criteria established by Burger et al.

[68] were unreliable because the determination of the C 1*s* binding energy of the thiocyanate ligand in any series of complexes containing organic ligands or cations is invariably thwarted by overlap with the C 1*s* binding energies of the latter. Since most of the complexes which were studied by Burger et al. [68] (with the exception of $Ni(NH_3)_4(NCS)_2$) contained organic ligands (dimethylglyoxime, pyridine or γ-picoline), and in view of the sensitivity of the XPS technique to the detection of carbon-containing contaminants, it is unlikely that the C 1*s* energy which was used in determining the values of [C 1*s* — S 2*p*] and [N 1*s* — C 1*s*] was that due to thiocyanate. Accordingly, it was proposed [45] that the best way to analyze trends in the N 1*s* and S 2*p* binding energies was through variations in the [N 1*s* — S 2*p*] energy difference. Such a procedure also eliminates problems associated with the choice of different binding energy referencing procedures. By the careful choice of complexes of known structure, including molecules which contained two different thiocyanate environments, such as [Cu(tren)-(NCS)]SCN, [Cu(trien)(SCN)]SCN and Pd(dppe)(SCN)(NCS) *, it was concluded [45] that the S 2*p* energies of M—NCS, M—SCN, M—SCN—M and SCN^- differ at most by a few tenths of an electron volt, thereby preventing a ready distinction between these different bonding modes in most transition metal complexes.

More recently, Borghi et al. [69] reported their results on the XPS of coordination complexes containing the thiocyanate ligand. They concluded [69] that the [N 1*s* — S 2*p*] binding energy differences of ambidentate thiocyanate represent a means of distinguishing whether the thiocyanate ligands are bonded through their S or N atoms. Rather surprisingly, in the paper by Borghi et al. [69] no reference was made to the earlier work of Burger et al. [68] and Best and Walton [45], groups which had previously addressed the question of whether N 1*s* and S 2*p* binding could be used to deduce the mode of thiocyanate bonding. Their report [69] therefore prompted a further analysis of all the available literature data on metal thiocyanates [70], the essential features of which are summarized below.

Values of the [N 1*s* — S 2*p*] binding energy difference available from the literature [13,15,45,55,68—75] are presented in Table 8. The XPS data for the mixed N-bound/S-bound complex Pd(dppe)(SCN)(NCS) have been excluded from this table but its S 2*p* spectrum is shown in Fig. 5. As a result of analyzing these data [70], it can be established that the binding energy difference [N 1*s* — S 2*p*] is sometimes greater for M—NCS than M—SCN. For example, the value of [N 1*s*—S 2*p*] is 0.6 eV greater for $[M(NH_3)_5(NCS)]$-$(ClO_4)_2$ than $[M(NH_3)_5(SCN)](ClO_4)_2$ (M=Rh or Ir) [69], a conclusion which is similar to that which emerges from a careful comparison of the XPS of the series of Pd(II) complexes $K_2Pd(SCN)_4$, $Pd(bipy)(NCS)_2$ and Pd(dppe)(SCN)-

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* N-bound thiocyanate is represented as (NCS), S-bound as (SCN) and outer-sphere thiocyanate as SCN (without parentheses).

TABLE 8

[N 1*s* — S 2*p*] binding energy differences (eV) for some thiocyanate and isothiocyanate complexes of the transition metals.

Compound [a]	[N 1*s* — S 2*p*]	Ref. [b]	Mode of thiocyanate bonding
NaSCN	235.3	69	SCN^-
KSCN	235.1	68	SCN^-
	234.4	71	
$(NH_4)SCN$	235.3	71	SCN^-
$(Me_4N)SCN$	235.2	13	SCN^-
	235.3	71	
$(Ph_4As)SCN$	234.8	13	SCN^-
	234.8	72	
$[Cu(en)_2](SCN)_2$	235.8	45	SCN^-
$(NH_4)[Cr(NH_3)_2(NCS)_4]$	235.4	13	M—NCS
$K_3Cr(NCS)_6$	235.4	13	M—NCS
$[Cr(NH_3)_5(NCS)](ClO_4)_2$	236.2	69	M—NCS
$[Co(NH_3)_5(NCS)](ClO_4)_2$	236.3	69	M—NCS
$[Co(NCS)_2(tu)_2]_n$	235.6	55	M—NCS
$(Me_4N)_2Co(NCS)_4$	235.4	71	M—NCS
$(Et_4N)_2Co(NCS)_4$	235.5	71	M—NCS
$(Bu_4N)_2C$ [illegible] $CS)_4$	235.8	71	M—NCS
$[Ni(NCS)_2(tu)_2]_n$	235.7	55	M—NCS
$(Me_4N)_2Ni(NCS)_4$	235.6	71	M—NCS
$(Me_4N)_4Ni(NCS)_6$	235.4	71	M—NCS
$(Et_4N)_4Ni(NCS)_6$	235.4	71	M—NCS
$Ni(NH_3)_4(NCS)_2$	235.0	68	M—NCS
$Ni(tren)(NCS)_2$	236.4 [c]	13	M—NCS
$(Me_4N)_2Zn(NCS)_4$	235.6	71	M—NCS
$(Et_4N)_2Zn(NCS)_4$	235.2	71	M—NCS
$(Me_4N)_2MoO(NCS)_5$	236.0	45	M—NCS
$(Me_4N)_4Mo_2O_3(NCS)_8$	236.0	45	M—NCS
$Mo_2(NCS)_4(PEt_3)_4$	235.7	70	M—NCS
$(Bu_4N)_2Mo_2(NCS)_6(PEt_3)_2$	235.9	70	M—NCS
$Mo_2(NCS)_4(dppe)_2$	236.0	70	M—NCS
$Mo_2(NCS)_4(dppm)_2$	235.8	70	M—NCS
$Mo_2(NCS)_4(bipy)_2$	236.0	70	M—NCS
$Mo_2(NCS)_4(phen)_2$	235.9	70	M—NCS
$(Bu_4N)_2Re_2(NCS)_8$	236.2	45	M—NCS
	236.6	73	M—NCS
$(Bu_4N)_2$ [illegible] $)_6$	236.7	73	M—NCS
$(Bu_4N)Re(NCS)_4(dppe)$	236.2	74	M—NCS
$Re(NCS)_3(PEt_2Ph)(dppe)$	236.2	74	M—NCS
$Re(NCS)_3(PEt_2Ph)(bipy)$	236.2	74	M—NCS
$Re(NCS)_3(PEt_2Ph)(phen)$	236.3	74	M—NCS
$(Me_4N)_3Ru(NCS)_6$	235.2	13	M—NCS
$[Rh(NH_3)_5(NCS)](ClO_4)_2$	236.1	69	M—NCS
$[Ir(NH_3)_5(NCS)](ClO_4)_2$	236.1	69	M—NCS
$Pd(bipy)(NCS)_2$	236.1	45	M—NCS
$H[Co(HD)_2(SCN)_2]$	235.6	68	M—SCN
$(Ph_4As)_3Os(SCN)_6$	235.2	13	M—SCN

TABLE 8 (continued)

Compound [a]	[N 1*s* — S 2*p*]	Ref. [b]	Mode of thiocyanate bonding
$K_3Rh(SCN)_6$	235.0	13	M—SCN
$[Rh(NH_3)_5(SCN)](ClO_4)_2$ [d]	235.5	69	M—SCN
$(Me_4N)_3Ir(SCN)_6$	234.7	13	M—SCN
$[Ir(NH_3)_5(SCN)](ClO_4)_2$	235.5	69	M—SCN
$K_2Pd(SCN)_4$	235.4	45	M—SCN
$K_2Pt(SCN)_6$	234.3	13	M—SCN
$AuL(SCN)$ [e]	235.2	69	M—SCN
$AuL_2(SCN)$ [e]	235.4	69	M—SCN
$AuL_3(SCN)$ [e]	235.5	69	M—SCN
$HgCo(NCS)_4$	234.9	13	M—NCS—M′
	235.3	75	
$[Cu(SCN)]_n$	234.8	15	M—NCS—M
$[Cu(tren)(NCS)]SCN$	235.8	45	M—NCS and SCN^-
$[Rh(en)_2(NCS)_2]SCN$	236.2	69	M—NCS and SCN^-
$[Cu(trien)(SCN)]SCN$	235.7	45	M—SCN and SCN^-
$(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$	236.1	74	M—NCS and M—NCS—M
$(Bu_4N)_2Re_2(NCS)_8(PPr^n_3)_2$	236.3	74	M—NCS and M—NCS—M
$(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$	236.6	74	M—NCS and M—NCS—M
$(Bu_4N)_2Re_2(NCS)_8(dppm)_2$	236.2	74	M—NCS and M—NCS—M
$(Bu_4N)_2Re_2(NCS)_8(dppe)_2$	236.1	74	M—NCS and M—NCS—M

[a] See Sect. B for listing of ligand abbreviations.

[b] Literature reference to the source of the binding energy data.

[c] Only one N 1*s* binding energy is reported for this complex (see ref. 13) whereas two N 1*s* peaks (one due to amine nitrogen and the other to NCS) have been observed in the XPS of its copper(II) analogue (see ref. 45).

[d] This complex was erroneously formulated as the N-bound isomer $[Rh(NH_3)_5(NCS)](ClO_4)_2$ in the table of the binding energy data given in ref. 69.

[e] The nature of the tertiary phosphine (L) in these complexes was not specified (see ref. 69).

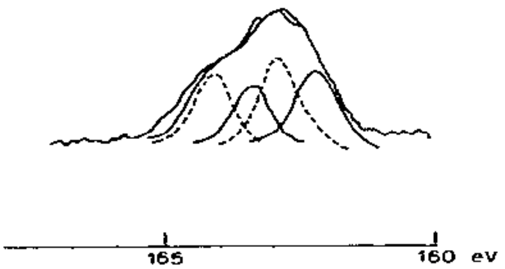

Fig. 5. Sulfur 2*p* binding energy spectrum of Pd(dppe)(SCN)(NCS) showing its deconvolution into two sets of S $2p_{1/2,3/2}$ doublets.

(NCS) [45,70]. The S 2*p* spectra of $K_2Pd(SCN)_4$ and $Pd(bipy)(NCS)_2$ reveal a well resolved S 2*p* doublet in each case (fwhm = 1.9 ± 0.1 eV) with [N 1*s* — S 2*p*] values of 236.1 and 235.4 eV, respectively. For the complex Pd(dppe)(SCN)(NCS), which possesses both N- and S-bound thiocyanate, the S 2*p* spectrum (Fig. 5) is significantly broader (fwhm = 2.6 eV). This spectrum may be deconvoluted to produce [70] two sets of doublets whose energies (S $2p_{3/2}$ at 162.3 and 162.9 eV) and associated [N 1*s* — S 2*p*] values (235.9 and 235.3 eV, based upon a N 1*s* binding energy of 398.2 eV [45]) are consistent with N- and S-bound thiocyanate, respectively.

The larger values of [N 1*s* — S 2*p*] for the N-bound thiocyanate complexes of Rh(III), Ir(III) and Pd(II) compared to their S-bound analogs, is borne out for many of the complexes listed in Table 8. However, there is a significant overlap in the range of [N 1*s* — S 2*p*] values for M—NCS compared to M—SCN, i.e. 236.7 — 235.0 eV versus 235.6 — 234.3 eV. A particularly striking illustration of this is the similarity of [N 1*s* — S 2*p*] for $(Me_4N)_3Ru(NCS)_6$ to the corresponding values for $(Ph_4As)_3Os(SCN)_6$ and $K_3Rh(SCN)_6$ (see Table 8). Accordingly, any attempt to correlate the value of [N 1*s* — S 2*p*] with the mode of thiocyanate bonding should be treated with caution, especially when the complex in question is one of unknown structure. This conclusion is supported by the following additional observations:
(1) The Cu(II) complexes [Cu(tren)(NCS)]SCN and [Cu(trien)(SCN)]SCN each contain two thiocyanate environments, yet both show only a single set of well resolved S $2p_{1/2,3/2}$ doublets [45] and give no evidence for the presence of both inner and outer sphere thiocyanate. This coincidence of the S 2*p* energies of SCN^- with those of Cu—NCS and Cu—SCN is supported by XPS measurements on $[Cu(en)_2](SCN)_2$ [45], a complex which contains outer sphere thiocyanate. Its S 2*p* energies [45] and [N 1*s* — S 2*p*] value (Table 8) are the same as those of [Cu(tren)(NCS)]SCN and [Cu(trien)(SCN)]SCN.
(2) The two complexes in Table 8 which contain only bridging thiocyanate ligands, $HgCo(NCS)_4$ and $[Cu(SCN)]_n$, have [N 1*s* — S 2*p*] ca. 235.0 eV, a value which is on the borderline between being characteristic of M—NCS and M—SCN.

The preceding discussion emphasizes the problems associated with distinguishing M—NCS, M—SCN, M—NCS—M and SCN^- environments, either on the basis of N 1*s* and S 2*p* binding energies or the binding energy difference [N 1*s* — S 2*p*], for complexes whose structures are unknown.

H. CHEMICAL SHIFTS IN SULFUR-CONTAINING METALLOPROTEINS

The preceding survey of the XPS of various classes of well-defined metal complexes of sulfur-containing ligands leads to the logical question of whether this information can be used in the characterization of more complicated molecules, such as metalloproteins. In fact there is now an appreciable body of XPS data available on such molecules, much of it having been obtained prior to some of the more important studies on the sulfur-containing coordination complexes. In this section we will consider briefly some of the more important XPS studies on sulfur-containing metalloproteins. In so doing we will take advantage of the hindsight provided by the availability of S 2*p* binding energy data for metal complexes of thiols, thioethers, disulfides, etc. (in particular see Sects. C and D).

One of the most interesting structural problems to which XPS has been applied is the characterization of the blue copper protein plastocyanin. The original study on this particular system [76] was carried out on French bean plastocyanin and also included S 2*p* measurements on the Co(II) and apo plastocyanins. The S 2*p* binding energy peak close to 164.0 eV (arising from the methionine and cysteine sulfur atoms) in the apo plastocyanin was also present in the Cu(II) and Co(II) plastocyanins, but an additional feature, shifted by ca. 5 eV to higher binding energy (relative to the 164 eV peak), was also observed [76]. This latter peak was approximately half as intense as the one at 164 eV, a result which led Solomon et al. [76] to propose that it was only the cysteine sulfur which was coordinated since the ratio of cysteine and methionine residues in this protein was known to be 1 : 2. However, a positive chemical shift of 5 eV or so upon complexation of cysteine sulfur was shown subsequently [35] to be inconsistent with the results of S 2*p* binding energy measurements on structurally characterized metal complexes of cysteine (see Sect. D(iii)). Furthermore, a recent structure determination on single crystals of Poplar plastocyanin has revealed [77] that the cysteine and one of the methionine sulfurs are bound to copper (together with two histidine nitrogens) thereby establishing that these S 2*p* binding energy measurements on plastocyanin [75] had not distinguished between the binding of cysteine and methionine sulfur.

A later study by Peeling et al. [78] of the S 2*p* binding energies of a number of plastocyanins together with the copper protein hemocyanin, led these workers to propose that the high binding energy sulfur peak (at ca. 169 eV) observed by Solomon et al. [76] was due to extraneous sulfate or some other form of oxidized sulfur introduced as a contaminant during the preparation of the metalloproteins. In response to this interpretation, Gray and co-workers [79] have shown that impurity theories are not consistent with their results since the high S 2*p* binding energy signal is lost upon generation of the apo plastocyanin and only reappears upon Co(II) reconstitution. Similar results are obtained for the copper proteins stellacyanin and azurin [79]. At the present time, the most favored interpretation for the appearance of the high binding energy peak is that it is caused by X-ray induced radiation damage which is metal-catalyzed [35,52]. An alternative explanation [80] invokes the need for trace amounts of oxygen to promote the gradual destruction of the native plastocyanin during X-irradiation. A suggestion by Larsson [81] that the high binding energy line could be due to satellites associated with inner-shell ionization from sulfur of the cysteine or methionine residues cannot be supported since no such satellites are seen in the S 2*p* XPS of metal complexes of cysteine, penicillamine or methionine [35].

In the light of the preceding XPS results for the plastocyanins and other copper proteins, the original interpretation of the S 2*p* binding energy spectrum of oxidized cytochrome *c* [82], an iron protein known to contain a iron—methionine sulfur bond, cannot be correct. An S 2*p* binding energy peak at 167.8 eV [82] must be due to oxidized sulfur rather than arising from a +5 eV chemical shift upon binding methionine to Fe(III). While on the subject of iron proteins, the XPS of several non-heme proteins have been recorded [9,83] and a significant difference observed between the S 2*p* energies of acid labile sulfur (as present in Fe—S—Fe bridges) and cysteine sulfur. Thus in the proteins reduced HIPIP *, oxidized clostridial ferredoxin and oxidized spinach ferredoxin, the S 2*p* energies of the cysteine residues are at ca. 163 eV while those characterizing the labile sulfur are ca. 1.5 eV lower. Similar results were reported independently by Liebfritz [83]. These observations are somewhat surprising when related S 2*p* binding energy measurements on the synthetic analog of bacterial iron—sulfur proteins $(Et_4N)_2$-$[Fe_4S_4(SCH_2Ph)_4]$ [29] did not produce evidence for two sets of S 2*p* peaks (see Sect. D (i)). Nonetheless, these studies on iron—sulfur proteins [9,83] once again reveal the effectiveness of the XPS technique in distinguishing different chemical environments within the same molecule.

An early XPS study on the metalloprotein bovine erythrocuprein (containing copper and zinc) [84] is of significance in that it was the first time a high binding energy S 2*p* peak (167.7 eV) was attributed to the presence of trace amounts of sulfate salts remaining bound to the enzyme even after extensive desalting procedures had been carried out. A lower energy peak at 163.0 eV was assigned [84] to sulfur atoms from cysteine, cystine and methionine residues.

Measurement of the S 2*p* binding energy of metallothionein, a high sulfur content protein containing Zn(II) and Cd(II), showed [36] that its value (161.7 eV) is characteristic of the binding of the cysteine residues to the Zn and Cd ions rather than the presence of cystine units (disulfides). A similar conclusion was drawn concerning chicken liver Cu-thionein [85] since its S 2*p* energy of 161.9 eV was found to be much lower than that of metal-free cystine-thionein (163.4 eV). However, in the case of an XPS study of Hg-thionein (prepared from rat liver metallothionein) [32], a much higher S 2*p* energy was recorded (162.7 eV), approaching the value which characterized the metal-free cystine-thionein. The greater polarization of sulfur by mercury (compared to zinc and cadmium) is a trend which Sokolowski et al. [32] had seen in other series of Zn, Cd and Hg complexes of sulfur ligands. Weser and co-workers [86,87] have recently extended their studies to Cu-thionein obtained from other sources. In one of these investigations, Cu-thionein

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* High potential iron protein.

from fetal bovine liver had a S 2*p* binding energy of 163.0 eV, a value which was attributed [87] to partial oxidation of the protein moiety and/or the presence of a different chemical environment near the Cu-thiolate chromophore. This ambiguity points out the occasional difficulty which is encountered in differentiating metal—thiol and metal—disulfide moieties by XPS although, more often than not,·measurement of the S 2*p* binding energies of such species provides a clear distinction between them.

A thiolate-rich Cu-thionein called cuprodoxin has been isolated by Prinz and Weser [88] and its S 2*p* binding energy of 161.8 eV found to be characteristic of copper coordinated to cysteine sulfur. However, in aged preparations mixed portions of cystine/cysteine residues were detected, while in completely "oxidized and deteriorated samples" the formation of RSO_3^- (S 2*p* = 168 eV) could be monitored.

I. CONCLUDING REMARKS

While there are many instances where the S 2*p* binding energies of sulfur-containing metal complexes vary very little (e.g. $(NH_2)_2CS \rightarrow M$ and $(CH_3COS)_xM$), there remain a variety of interesting structural problems in coordination chemistry which may be tackled using the XPS technique. The S 2*p* chemical shifts which exist between the different sulfur oxidation states (as in RSO_3^-, R_2SO, RSSR and RS^-, for example) are usually sufficiently large that there is little difficulty in differentiating such species. This has proved quite invaluable, for example, in establishing the presence of cysteine or cystine residues in metalloproteins.

When two different sulfur chemical environments are present within the same molecule, different S 2*p* signals are sometimes discerned even when the formal oxidation states of the different sulfur sites are the same. The distinction between acid labile sulfur and thiol sulfur in iron—sulfur chromophores of the type $[Fe_xS_x(SR)_y]$ is a good illustration of this, as is the distinction between thiol and thioether sulfur in the Mo(VI) complex $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SMe]$. Accordingly, with the large body of experimental data which now exists on the S 2*p* binding energies of metal complexes (as summarized in Sects. C—G) it is now much easier to select those structural problems which are most likely to be solved using this spectroscopic technique.

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