X-ray Photoelectron Spectra of Inorganic Molecules. 21.[1] Sulfur 2p Chemical Shifts Associated with the Binding of Thiol and Thioether Groups to Transition Metal Ions

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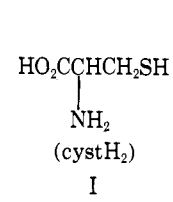
Abstract: The S $2p_{3/2}$ binding energies of a series of metal complexes of cysteine and penicillamine occur over the relatively wide energy range of 163.5–161.3 eV. In most instances these energies are appreciably lower than those of the free ligands (~163.2 eV), a result which contrasts with earlier S 2p chemical shift data for metal complexes of methionine. These results lead to the possibility of using X-ray photoelectron spectroscopy (XPS) to distinguish metal binding to thiol and thioether sulfur when these two coordination modes exist within the same molecule. Measurements of the XPS of molybdenum(VI) complexes of the tripod ligands $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$ and $CH_3SCH_2CH_2N(CH_2CH_2SH)_2$ have demonstrated that such distinctions can be made using this technique.

Introduction

The possibility that X-ray photoelectron spectroscopy (XPS or ESCA) could provide a means of monitoring the binding of metal ions to different sulfur sites in sulfur-containing metalloproteins has prompted several such investigations.[3-13] One group of molecules which has attracted more than the usual amount of interest and also generated considerable controversy are the copper proteins, plastocyanin, oxyhemocyanin, stellacyanin, and azurin.[10,12,13] This controversy has centered on the question of whether a chemical shift of ~+5 eV between the S 2p binding energies of the apoproteins (~164 eV) and the metalloproteins (~169 eV) is evidence for cysteine sulfur coordination to the metal ions,[10,13] or is attributable entirely to the presence of extraneous high oxidation state sulfur.[12] These conflicting interpretations have led Larsson[14] to offer an alternative explanation of these results, namely, that the high binding energy line (HBE) at ~169 eV could be due to satellites associated with inner-shell ionization from sulfur of the cysteine or methionine residues.

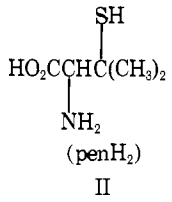
In spite of the interest in these systems, there is a dearth of information on the XPS of well-defined metal complexes containing cysteine, methionine, and related ligands. Rather surprisingly, such systematic investigations did not precede the XPS studies on the more complicated copper proteins.[10,12-14] During our recent investigation of the S 2p binding energy spectra of metal complexes of 1,2-ethanedithiol and benzenethiol,[15] we also observed that for methionine (metH), which contains a thioether moiety, coordination of the sulfur atom to Pt(II), in the complex $Pt(metH)Cl_2$, causes a positive S 2p chemical shift. For methionine complexes of the type $M(met)_2$, M = Co(II), Ni(II), Cu(II), or Zn(II), in which the sulfur atoms are not coordinated, the S 2p binding energies (S $2p_{3/2}$ = 163.0 eV) are unchanged from that of the free ligand.[15] These studies[15] and those by Weser and co-workers,[6,8,16,17] who measured the S 2p binding energies of Cu(I), Zn(II), Cd(II), and Hg(II) complexes of cysteine, constitute the only reports dealing with the S 2p XPS of methionine and cysteine complexes of the transition and nontransition metals. Furthermore, this paucity of data hinders any attempts to judge the usefulness of the XPS technique in differentiating the binding of metal ions to methionine and cysteine sulfur.

In order to assess the interpretations which have been previously advanced to explain the S 2p binding energy spectra of copper proteins,[10,12-14] we have investigated the XPS of an extensive series of metal complexes of cysteine (I) and its closely related derivative, penicillamine (II). These measurements, together with a comparison study on the XPS of derivatives of the tripod ligands III and IV, establish the viability of using XPS to distinguish M–SR and M ← SR_2 binding.



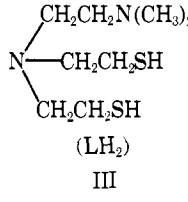
($cystH_2$)

I



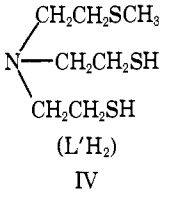
($penH_2$)

II



(LH_2)

III



($L'H_2$)

IV

Details of these results are now reported and are compared with other pertinent literature data.

Experimental Section

Preparation of Metal Complexes. DL-Methionine, DL-penicillamine, and L-cysteine hydrochloride monohydrate were obtained from the Aldrich Chemical Co. Most of the metal complexes were synthesized, purified, and characterized using published procedures.[18-30] The dark brown-green nickel(II) cysteine complex $[Ni(cyst)\cdot 2H_2O]_n$ was prepared using the same procedure as that purported to give $K_2Ni(cyst)_2$.[22] Anal. Calcd for $C_3H_9NNiO_4S$: C, 16.85; H, 4.24. Found: C, 16.22; H, 4.41. In contrast to $K_2Ni(cyst)_2$, which is diamagnetic, $[Ni(cyst)\cdot 2H_2O]_n$ is paramagnetic (μ_{eff} = 2.7 μB) and possesses an absorption maximum at 580 nm in its diffuse reflectance spectrum. Its IR spectrum displays broad intense absorption band envelopes centered at ~3300 (ν(O–H) and ν(N–H)) and 1590 cm^{-1} ($\nu(COO^-)$, ν(O–H), and ν(N–H)). The symmetric $\nu(COO^-)$ mode is located at 1395 cm^{-1}.

Derivatives of the tripod ligands $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$, abbreviated LH_2, and $CH_3SCH_2CH_2N(CH_2CH_2SH)_2$, abbreviated $L'H_2$, were prepared using the following procedures.

$(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2\cdot 2HCl$. To 0.1 mL (~0.5 mmol) of $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$[31] in absolute ethanol (0.5 mL) was slowly added 0.8 mL (~1 mmol) of concentrated HCl. The solution was filtered yielding a white precipitate. Dissolution in hot ethanol followed by cooling produced a white, crystalline solid which was washed with ethanol and ethyl ether and dried under vacuum, yield 44%. Anal. Calcd for $C_8H_{22}Cl_2N_2S_2$: C, 34.18; H, 7.83; N, 9.97.

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Table I. Core Electron Binding Energies of Metal Complexes of Cysteine and Penicillamine[a]

compd	S $2p_{3/2}$	N 1s	metal	others
L-cysteine hydrochloride monohydrate	163.3 (1.4)	401.4 (1.6)		
$Na_2[Mo_2O_4(cyst)_2]\cdot 5H_2O$	161.9 (1.4)	399.6 (2.0)	Mo $3d_{5/2}$ 231.1 (1.3)	
$K_4[Co(cyst)_3]\cdot 4H_2O$	162.5 (1.3)	399.5 (1.6)	Co $2p_{3/2}$ 780.1 (1.4)	K $2p_{1/2,3/2}$ 295.6,292.8 (1.5)
$K[Co(cyst)_2]\cdot 2H_2O$	162.7 (1.5)	400.0 (1.6)	Co $2p_{3/2}$ 780.8 (1.9)	K $2p_{1/2,3/2}$ 295.7,293.0 (1.5)
$H[Co(cyst)_2]\cdot 2H_2O$	162.6 (1.4)		Co $2p_{3/2}$ 780.3 (1.9)	
$K_3[Co(cyst)_3]$	162.6 (1.1)	399.7 (1.4)	Co $2p_{3/2}$ 780.6 (1.4)	K $2p_{1/2,3/2}$ 295.6,292.9 (1.4)
$Ni(cyst)\cdot 2H_2O$	162.5 (2.0)	399.7 (1.7)	Ni $2p_{3/2}$ 854.9 (3.0)	
$[Pd(cystH)Cl]_2$	162.9 (1.5)	400.0 (1.7)	Pd $3d_{5/2}$ 337.7 (1.5)	Cl $2p_{1/2,3/2}$ 199.5,198.2 (1.6)
$[Rh(cystH)_2Cl]_2$	162.7 (1.6)		Rh $3d_{5/2}$ 309.2 (1.3)	Co $2p_{1/2,3/2}$ 199.4,198.0 (1.5)
D-penicillamine	163.2 (1.6)	401.2 (2.0)		
$Na_2[Mo_2O_4(pen)_2]\cdot 3H_2O$	161.6 (1.4)	399.8 (1.7)	Mo $3d_{5/2}$ 231.0 (1.2)	
$Co(pen)(hist)\cdot H_2O$[b]	161.6 (1.6)	400.1 (1.9)	Co $2p_{3/2}$ 781.4 (1.7)	
$[Pb(pen)]_n$	161.3 (1.4)	399.1 (1.4)	Pb $4f_{7/2}$ 137.7 (1.2)	
$Na_2Zn(pen)_2\cdot 4H_2O$	162.4 (2.0)	400.0 (1.9)	Zn $2p_{3/2}$ 1022.6 (2.0)	
$[Ni(pen)]_n$	163.5 (1.6)	399.8 (1.7)	Ni $2p_{3/2}$ 855.9(2.6)	
$[Pd(penH)Cl]\cdot H_2O$	162.9 (1.8)	400.0 (1.5)	Pd $3d_{5/2}$ 337.7 (1.8)	Cl $2p_{1/2,3/2}$ 199.6,198.2 (1.5)
$[Pt(penH)Cl]\cdot H_2O$	162.7 (1.8)	400.2 (1.9)	Pt $4f_{7/2}$ 72.3 (1.5)	Cl $2p_{1/2,3/2}$ 199.5,198.1 (1.6)

[a] Relevant full-width half-maximum values (fwhm) given in parentheses. [b] This mixed ligand complex contains the L-histidinyl ligand (abbreviated hist); see ref 24.

Table II. Core Electron Binding Energies of Derivatives of the Tripod Ligands $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2(LH_2)$ and $CH_3SCH_2CH_2N(CH_2CH_2SH)_2(L'H_2)$[a]

compd	S $2p_{3/2}$	N 1s	Mo $3d_{5/2}$
$(LH_4)^{2+}2Cl^-$	163.0 (1.4)	398.8 (1.5)	
		401.2 (1.6)	
$(LH_4)^{2+}2HC_2O_4^-$	162.9 (1.8)	398.5 (2.0)	
		400.9 (2.0)	
$MoO_2(L)$	161.5 (1.1)	399.4 (1.6)	231.2 (1.1)
$(L'H_3)^+HC_2O_4^-$	163.0 (1.1)	398.7 (1.1)	
		401.1 (1.5)	
$MoO_2(L')$	163.3 (1.1)[b]	399.6 (2.0)	231.4 (1.3)
	161.7 (1.1)[b]		

[a] Relevant full-width half-maximum values (fwhm) given in parentheses. [b] These binding energies and fwhm values were obtained by the deconvolution of the spectrum shown in Figure 1.

Found: C, 33.51; H, 7.80; N, 9.71. Thiol titration: 1.74 thiols per mol wt 281.12.

$(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2\cdot 2HO_2CCO_2H$. To a solution of 0.086 g (0.68 mmol) of $(COOH)_2\cdot 2H_2O$ in 1.5 mL of ethanol was added slowly 0.07 mL (0.34 mmol) of $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$.[31] The solution was refrigerated for 1 h and filtered and the white, crystalline precipitate was washed with ethanol and ethyl ether and dried under vacuum, yield 84%. Anal. Calcd for $C_{12}H_{24}N_2O_8S_2$: C, 37.12; H, 6.18; N, 7.22. Found: C, 37.84; H, 6.76; N, 7.85. Thiol titration: 1.84 thiols per mol wt 388.26.

$CH_3SCH_2CH_2N(CH_2CH_2SH)_2\cdot HO_2CCO_2H$. This salt was prepared as described above from $CH_3SCH_2CH_2N(CH_2CH_2SH)_2$[32] except that a 1:1 ratio of oxalic acid and ligand was used, yield 71%. Anal. Calcd for $C_9H_{19}NO_4S_3$: C, 35.88; H, 6.31; N, 4.65. Found: C, 36.97; H, 6.89; N, 5.60. Thiol titration: 1.6 thiols per mol wt 301.28.

The complexes $MoO_2(L)$ and $MoO_2(L')$ were prepared as described in ref 31 and 32, respectively.

Spectra Measurements. A Hewlett-Packard Model 5950A ESCA spectrometer was used to record the X-ray photoelectron spectra. An electron "floodgun" was used to reduce to a minimum differential surface-charging effects. Full details of the experimental procedures are described elsewhere.[33,34]

Results and Discussion

XPS data for metal complexes of cysteine and penicillamine are summarized in Table I. These ligands will be abbreviated as $cystH_2$ and $penH_2$, respectively, in all subsequent discussions. The notation $cystH^-$, $cyst^{2-}$, $penH^-$, and pen^{2-} will be used for their appropriate anionic formulations as present in the various metal complexes. Related XPS data for derivatives of the mixed nitrogen–sulfur tripod ligands III and IV are presented in Table II. These ligands will subsequently be abbreviated LH_2 and $L'H_2$, respectively.

The binding energies in Tables I and II have been referenced to a C 1s energy of 285.0 eV for "contaminant" carbon.[35] Actually, this peak is a composite of C 1s energies arising from genuine carbon contaminants and the aliphatic carbon atoms of the ligands. However, since this peak was generally quite narrow (fwhm values in the range 1.5–2.2 eV) and its position well defined, it still served as a convenient reference. This procedure was the same as that used previously in reporting the XPS of methionine and several of its complexes.[15] In the case of the ligands and complexes listed in Table I, the C 1s peak at 285 eV was accompanied by a fairly weak carboxylate carbon C 1s peak centered between 287.8 and 288.4 eV. The similarity of the latter binding energy for different complexes, together with the internal consistency of the results presented in Tables I and II, assured us that this referencing procedure was quite satisfactory. Furthermore, the N 1s and S $2p_{3/2}$ energies obtained for both $cystH_3^+Cl^-\cdot H_2O$ and $penH_2$ (see Table I) are in excellent agreement with related data reported by others.[17,36]

The K 2p and Cl 2p binding energies associated with several of the complexes listed in Table I fall into very narrow energy ranges and are in good agreement with literature values for these binding energies in other metal complexes.[37-39] Likewise, the metal core electron binding energies (2p, 3d, and 4f) are characteristic of the metal oxidation states represented by the complexes in Table I and further support the consistency of our referencing procedure. Thus the Co $2p_{3/2}$, Ni $2p_{3/2}$, Pd $3d_{5/2}$, and Pt $4f_{7/2}$ binding energies in Table I are in excellent agreement with comparable data we have reported previously[15] for other complexes of these metal ions with sulfur-containing ligands.

Having established that the K 2p, Cl 2p, and metal binding energy spectra reveal no unusual features, we are now in a position to consider the S 2p chemical shifts associated with binding of thiol sulfur. These data together with the corresponding N 1s binding energies are discussed in subsequent sections.

S 2p and N 1s Binding Energies. In Tables I and II, only the S $2p_{3/2}$ component of the S $2p_{1/2,3/2}$ doublet is listed. The less intense S $2p_{1/2}$ peak is located at ~1.0 eV to the high binding energy side of S $2p_{3/2}$. In some systems it is well resolved from the S $2p_{3/2}$ peak, but in others it appears as a shoulder.

Cysteine and Penicillamine Complexes. With one exception,

namely, polymeric $[Ni(pen)]_n$, the S 2p binding energies of the cysteine and penicillamine complexes (Table I) are lower than those of the free ligands. This result is in accord with the previous reports of Weser and co-workers[8,17] who observed S 2p chemical shifts of up to −1.3 eV for metal complexes of cysteine (Cu(I), Zn(II), Cd(II), and Hg(II)) and penicillamine (Cu(I)). For most of the complexes which were the subjects of the present study, available spectroscopic[22,25,40] and crystallographic[24,41] evidence supports the presence of metal–thiol coordination (M–S). Only in the case of the nickel(II)–cysteine complex $Ni(cyst)\cdot 2H_2O$, which we isolated during our attempts to synthesize $K_2Ni(cyst)_2$,[22] are there no previous literature reports on its spectroscopic properties. However, the IR spectrum of this complex (see Experimental Section) does not display a ν(SH) vibration and, accordingly, it most likely contains M–S coordination.

The S 2p chemical shift of +0.3 eV for the nickel(II) complex $[Ni(pen)]_n$ supports the contention of Chow et al.[25] that it contains bridging sulfur donor atoms since we have previously shown[15] that M–S(R)–M bridges can exhibit higher S 2p binding energies than the sulfur atoms associated with terminal thiol ligands. The much lower S 2p binding energy (161.3 eV) which is characteristic of the polymeric lead(II) complex $[Pb(pen)]_n$ argues against it containing M–S(R)–M bridging units.

At the present time we are unable to account for the large variations in the magnitudes of the S 2p chemical shifts. While most complexes listed in Table I exhibit shifts of between −0.6 and −0.8 eV, two complexes, $[Pd(cystH)Cl]_2$ and $[Pd(penH)Cl]\cdot H_2O$, display smaller shifts, while for others ($Na_2[Mo_2O_4(cyst)_2]\cdot 5H_2O$, $Na_2[Mo_2O_4(pen)_2]\cdot 3H_2O$, $Co(pen)(hist)\cdot H_2O$, and $[Pb(pen)]_n$) 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.

Only in the case of one complex, namely, $K_3Co(cyst)_3$, did we find any evidence for high binding energy (HBE) sulfur. The S $2p_{1/2,3/2}$ peaks at 162.6 and 163.6 eV were accompanied by a very weak doublet at 169.2 and 168.1 eV due to high oxidation state sulfur contaminants.[12,15,17] Accordingly, we can provide no experimental evidence in support of the contention of Larsson[14] that the HBE S 2p lines which are present in the XPS of copper(II) and cobalt(II) plastocyanin[10,13] could be due to charge-transfer satellites. There seems no doubt, on the basis of the present work and previous studies,[12,13,15,17] that the S 2p peaks in the neighborhood of 168 eV, which have been observed in metal complexes of thioether and thiol ligands, are due to the presence of "oxidized" sulfur. While Peeling et al.[12] have claimed that the HBE S 2p peaks originally observed by Solomon et al.[10] in the plastocyanines are due to impurities, Gray and co-workers[13] have shown this not to be the case. A resolution of these conflicting interpretations is clearly desirable. Since Gray and co-workers[13] have demonstrated that their pure samples of the apoproteins are essentially free of the HBE S 2p signals, the reappearance of these signals upon copper(II) or cobalt(II) reconstitution[10,13] may be a consequence of a metal ion catalyzed oxidation of a small proportion of the cysteine and/or methionine residues in these metalloproteins.[42] Thus the presence of "sulfur impurities" as proposed by Peeling et al.[12] does not have to be invoked to explain the results of Gray and co-workers.[10,13]

The negative S 2p chemical shifts which are observed for all the cysteine and penicillamine complexes, except $[Ni(pen)]_n$, are accordingly characteristic of thiol coordination to the metal ions and the formation of terminal M–SR units. These results contrast with our previous observation[15] that the binding of methionine sulfur to platinum(II) in the complex $Pt(metH)Cl_2$ causes a S 2p chemical shift of +1.2 eV relative to free methionine and complexes of the type $M(met)_2$, where M = Co, Ni, Cu, and Zn, which do not involve sulfur coordination. Measurements on the palladium(II) complex $Pd(metH)Cl_2$ show that its S 2p binding energies (S $2p_{3/2}$ at 163.9 eV) closely resemble those of its platinum analogue when the same binding energy reference standard is used (a C 1s value of 285.0 eV for "contaminant" carbon).[43] Accordingly, the different chemical shift characteristics associated with the binding of thioether and thiol groups to a metal ion clearly lead to the possibility that these bonding modes may be differentiated in complexes containing both. As we will discuss shortly, measurements of the XPS of the molybdenum(VI) complexes of tripod ligands III and IV demonstrate the feasibility of using this technique to make such distinctions.

The N 1s binding energies of the metal complexes of cysteine and penicillamine are, as expected,[44] lower than those of $cystH_3^+Cl^-$ and $penH_2$ in which the amino groups are protonated. With the exception of the N 1s binding energy of $[Pb(pen)]_n$, they all fall within the range of 400.1–399.5 eV. In the case of the lead(II) complex, the low N 1s energy may reflect a problem in our binding energy referencing procedure, a possibility which is perhaps supported by the low value of the S 2p binding energy. However, if we "correct" both the N 1s and S 2p energies by an amount which would place the N 1s energy within the 400.1–399.5-eV range, the S 2p energy is still at least 1.0 eV lower than that of $penH_2$ itself.

Mixed Tripod Ligands LH_2 and $L'H_2$. To avoid the experimental problems associated with recording the XPS of the liquid ligands III (LH_2) and IV ($L'H_2$), we converted them to their crystalline chloride and/or oxalate salts. In these compounds, the tertiary amine nitrogen atom(s) have been protonated. The appropriate XPS data and that for the molybdenum(VI) complexes $MoO_2(L)$ and $MoO_2(L')$ are given in Table II. The S 2p binding energies of ~163.0 eV for the chloride and oxalate salts are very similar to those of the ligands metH, $cystH_2$, and $penH_2$. Furthermore, the appearance of a *single* S $2p_{1/2,3/2}$ doublet for the oxalate salt of $L'H_2$, which contains both thiol and thioether sulfurs, confirms that the S 2p energies for the $-CH_2SH$ and $RSCH_2-$ moieties are essentially identical. The presence of two N 1s peaks in the XPS for these same salts (Table II) shows that, under the high-vacuum conditions present in the XPS spectrometer, deprotonation of the quaternary nitrogen atoms to produce the "free" tertiary amine function has begun to occur. The peaks at ~401 eV are due to the protonated amine groups[44] while the lower energy peak close to 399 eV may be assigned to any "uncomplexed" tertiary amine nitrogens. In addition to a C 1s peak at 285.0 eV, to which all other binding energies in Table II have been referenced, a weaker, higher energy peak at ~288 eV, in the spectra of the oxalate salts, is assigned to the carbon atoms of the oxalate anion.

The S 2p binding energy spectrum of the molybdenum(VI) complex of $L'H_2$ clearly shows evidence for the presence of two sets of S 2p peaks (Figure 1). Using our standard deconvolution procedure for the resolution of spectra containing overlapping $2p_{1/2,3/2}$ doublets,[45] we obtained the results shown in Figure 1 in which the lower energy doublet is twice as intense as the higher energy doublet. This result, coupled with the observation that the energy of the lowest energy S $2p_{1/2,3/2}$ doublet agrees with the S 2p binding energies for the complex $MoO_2(L)$, which contains only thiol sulfur environments, confirms that in the spectrum of $MoO_2(L')$ the binding energies of the thiol sulfur atoms are much lower than those of the thioether sulfur atom. A further observation of note concerns the absence of any significant chemical shift between the S 2p energies of the thioether sulfur atom in $MoO_2(L')$ and that in the oxalate salt $(L'H_3)^+HC_2O_4^-$ (Table II). One interpretation of this result is that the binding of this sulfur atom to molybdenum must, at most, be very weak. This conclusion is supported by some very recent EXAFS studies of this complex.[46] This spectro-

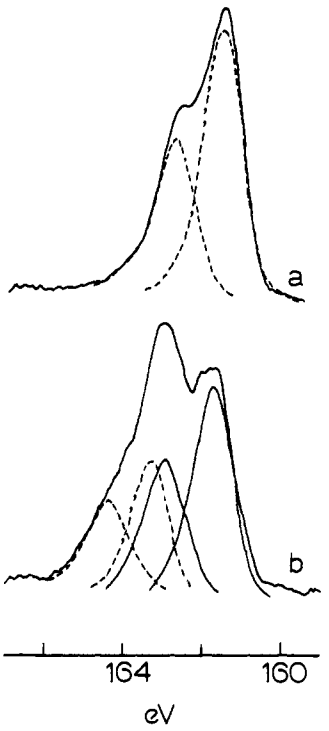

Figure 1. The S 2p binding energy spectra of (a) $MoO_2(L)$ and (b) $MoO_2(L')$, where $LH_2 = (CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$ and $L'H_2 = CH_3SCH_2CH_2N(CH_2CH_2SH)_2$.

scopic technique indicates the existence of two different Mo-S distances in this complex, the longer of the two (2.80 vs. 2.40 Å) being associated with the Mo-thioether linkage.[47] The present study demonstrates the first instance of the use of XPS to unambiguously distinguish between M-S-CH_2-R and M ← S(CH_3)-CH_2-R coordination.

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References and Notes

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