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2p Electron Binding Energies for the Sulfur Atoms in Metal Polysulfides

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Abstract

Different electron binding energies have been observed for the structurally-distinct sulfur atoms in $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ and the tetraphenylphosphonium salt of $[Cu_3(S_4)_3]^{3-}$. The sulfur atoms nearest to the metal are similar in character to those in mineral sulfides, whereas sulfur atoms further from the metal have 2p-binding energies at least 1 eV greater.

Introduction

The Bureau of Mines has been using X-ray photoelectron spectroscopy (XPS) to identify surface species leading to or inhibiting the flotation of sulfide minerals. Different surface sulfur entities have been suggested as responsible for the hydrophobicity that enables the collectorless flotation of sulfide minerals with or without pretreatment with sodium sulfide [1–3]. One proposed entity is a polysulfide-like species [1]; however, sufficient data on polysulfides have not been available to distinguish the presence of such a species at a mineral surface from an appreciably metal-deficient lattice or from the presence of very thin layers of deposited sulfur.

In recent years, several metal polysulfido complexes and clusters have been synthesized and characterized (for a review, see ref. 4 and pertinent refs. therein). Therefore, these materials were envisaged as suitable models to help identify polysulfide species on mineral surfaces by electron spectroscopic techniques. In a polysulfido ligand, at least two different kinds of sulfur might be expected: those directly bonded to the metal and those away from the metal, the latter forming sulfur-to-sulfur bonds. While the sulfurs involved in bonding with the metal should be more sulfide-like, and give rise to core electron binding energies significantly lower than for elemental sulfur, those not directly bonded to the metal should approach the characteristics for elemental sulfur, but still have binding energies not greater than those of elemental sulfur. However, Grinter and Woollins [5] have reported that all the sulfurs in $[Pt(S_5)_3]^{2-}$ have 2p binding energies of 164.8 eV, which is higher than their reported value of 163.6 eV for elemental sulfur.

Two metal polysulfido complexes were examined in the present study: the ammonium salt of $[Pt^{IV}(S_5)_3]^{2-}$ and the tetraphenylphosphonium salt of $[Cu_3{}^{I}(S_4)_3]^{3-}$. The structure of the $[Pt(S_5)_3]^{2-}$ ion has been shown to consist of three bidentate (chelating) five-membered sulfur chains octahedrally coordinated to a central platinum atom; the three six-membered rings formed by the five sulfur atoms and the platinum are in chair configurations [6, 7].

The $[Cu_3(S_4)_3]^{3-}$ complex has almost C_3 symmetry [8]. It consists of three CuS_4 five-membered rings with half-chair conformation, each ring projecting outward from a puckered central Cu_3S_3 ring. This central ring has a chair conformation and is made up of a triangle of nonbonded Cu(I) atoms, each one bridged by a sulfur atom and showing alternating short and long Cu–S lengths. The coordination at each Cu is trigonal.

Experimental

Brick-red crystals of the form of $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ characterized crystallographically by Jones and Katz [7] were prepared as described by Gillard, Wimmer, and Richards [9]. The tetraphenylphos-

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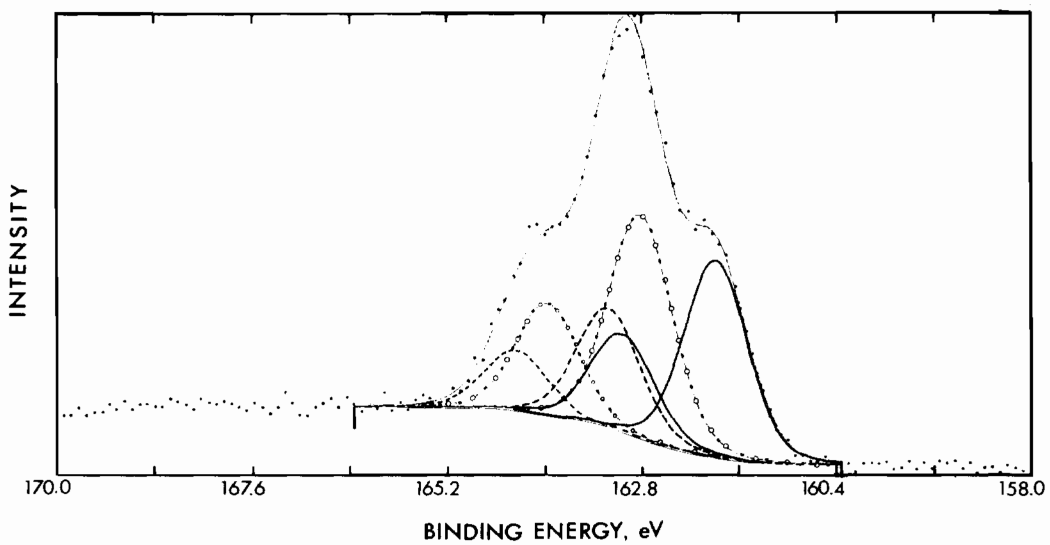

Fig. 1. Sulfur (2p) spectrum for $[Pt(S_5)_3]^{2-}$.

phonium salt of $[Cu_3(S_4)_3]^{3-}$ was synthesized following the method of Müller *et al.* [8]. IR and UV–Vis spectroscopy confirmed the identity of the materials.

Samples for XPS experiments were prepared by the following methods: (a) depositing thin films of the materials on Au foil by solvent evaporation (ethanol for $[Pt(S_5)_3]^{2-}$ and acetonitrile for $[Cu_3(S_4)_3]^{3-}$), (b) pressing pellets of the materials (3 mm in diameter and less than 0.5 mm in thickness), and (c) pressing the powdered materials into indium foil.

X-ray photoelectron spectra were obtained with a Surface Science Laboratories SSX-100* spectrometer equipped with a monochromatized Al Kα source. The spectrometer was operated at a pressure of less than 10^{-7} Pa, with an X-ray beam diameter of 0.3 mm and an analyzer pass energy of 50 eV. Under these conditions, the $(4f)_{7/2}$ peak from metallic gold had a width of 0.95 eV and a binding energy of 83.9 eV. Specimens were cooled to 180 K before being subjected to a pressure of less than 130 Pa and were maintained at this temperature while in the analyzer. When pelletized or indium-mounted material was being examined, a nickel grid 2 mm above the specimen surface was employed in conjunction with a low-energy electron flood gun in order to minimize differential charging. After the subtraction of a sigmoidal background [10], S(2p) spectra were fitted with doublets having (1/2, 3/2)-components constrained to an intensity ratio of 1:2, to a separation of 1.15 eV, and to a 20% Lorentzian, 80% Gaussian lineshape.

Results and Discussion

In Fig. 1, the S(2p) spectrum from a thin film of $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ resulting from the evaporation of an ethanolic solution on metallic gold is shown fitted with three doublets having $2p_{3/2}$ binding energies of 161.9, 162.8, and 163.2 eV and with a corresponding intensity ratio of approximately 2:2:1. A low-energy electron flood gun was not used in the determination of this spectrum, as the relatively good resolution together with a symmetrical $Pt(4f)_{7/2}$ peak at 73.1 eV indicated that the effects of charging were minimal. To eliminate the possibility that the S(2p) spectrum might have been an artefact of the method of sample preparation, a pellet of the material was examined also. In this case, a flood gun had to be used. While the resulting S(2p) spectrum was slightly broader than that shown in Fig. 1, the overall shape was similar and the Pt(4f)–S(2p) energy separation was the same.

The fit to the spectrum shown in Fig. 1 is not unique and would depend, *inter alia*, on the shape of the background assumed. However, the fit is statistically acceptable and is consistent with the S(2p) binding energies observed for sulfide minerals and related model systems. In particular, the $2p_{3/2}$ binding energies for layers of sulfur electrochemically deposited on gold are *ca.* 161.4 eV for the sulfur atoms nearest to the gold and 163.0 eV for the outermost atoms in thick layers of sulfur [11]. Preliminary results suggest that the corresponding values for layers of sulfur deposited electrochemically on platinum are 161.8 eV and 163.2 eV [12]. Bulk elemental sulfur (S_8) has a binding energy of 163.6 eV relative to $Au(4f)_{7/2}$ = 83.9 eV, in agreement with Grinter and Woollins [5].

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*Reference to specific trade names does not imply endorsement by the Bureau of Mines.

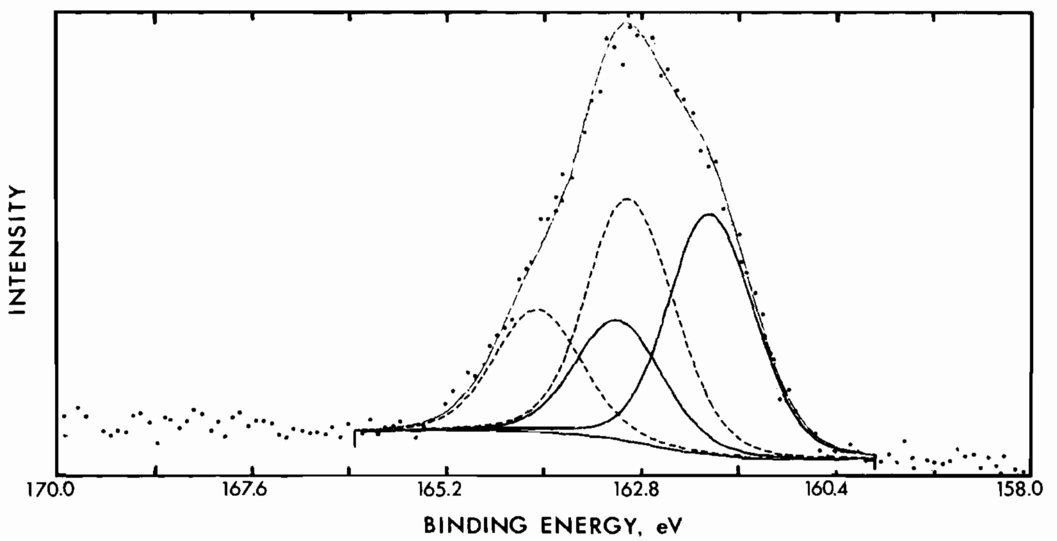

Fig. 2. Sulfur (2p) spectrum for $[Cu_3(S_4)_3]^{3-}$.

The relative intensities of the fitted components are also consistent with the three pairs of sulfur atoms nearest to the platinum atom being sulfide-like, the three pairs of next-nearest sulfur atoms having an electronic environment intermediate between the sulfur in sulfur-rich sulfides such as pyrite (FeS_2) and elemental sulfur, and the three most remote sulfur atoms being close to elemental sulfur in character. By contrast, it is difficult to rationalize a binding energy 1.2 eV greater than that for elemental sulfur for each of the sulfur atoms, as reported by Grinter and Woollins [5].

The S(2p) spectrum from the tetraphenylphosphonium salt of $[Cu_3(S_4)_3]^{3-}$ mounted on indium foil is shown in Fig. 2 fitted with two doublets having $2p_{3/2}$ binding energies of 162.0 eV and 163.0 eV and having approximately equal intensities. The binding energy scale has been corrected to take account of *ca.* 3 eV overcompensation produced by the flood gun concomitant with the minimization of differential charging. The S(2p) spectrum obtained from a thin film of the copper complex salt deposited on gold by evaporation from an acetonitrile solution was qualitatively similar. The latter spectrum could be fitted with two equal-intensity doublets having $2p_{3/2}$ binding energies of 161.85 eV and 163.05 eV. No binding energy correction was required for this spectrum as charging was not evident and a flood gun was not used. The $Cu(2p)_{3/2}$ binding energy was 932.4 eV, close to the value of 932.3 eV observed for chalcocite (Cu_2S) under the same spectrometer conditions [13]. The absence of excited final-state satellites in the Cu(2p) spectrum confirms that the copper in the polysulfido complex was present as Cu(I). The fitted S(2p) binding energies and intensities are consistent with three pairs of sulfur atoms in each anion being bonded to copper atoms and three pairs of sulfur atoms being bonded to the former six. The electron binding energies for sulfur in the two different environments nearest to the metal atoms are not expected to be significantly different. The $S(2p)_{3/2}$ binding energy observed for the sulfur atoms in Cu_2S is 161.6 eV and that for the sulfur atoms in the S_2 groups in covellite (CuS) is 161.8 eV [13]. The binding energies are also consistent with those observed for the sulfur atoms nearest and next nearest to the metal atom in $[Pt(S_5)_3]^{2-}$.

Conclusions

Different electron binding energies have been observed for the structurally distinct sulfur atoms in the metal polysulfido complexes studied. The sulfur atoms nearest to the metal are similar in character to those in mineral sulfides. Sulfur atoms adjacent to those bonded to the metal are appreciably different, with 2p binding energies approximately 1 eV greater, while those one atom more remote from the metal have a 2p binding energy approaching, but still less than, that for bulk elemental sulfur. These binding energies are of relevance to the identification of sulfur species present at the surface of sulfide minerals under flotation conditions.

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