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Core Electron Binding Energies of Platinum and Rhodium Polysulfides*

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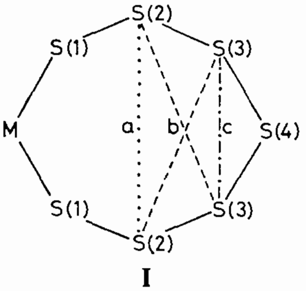
Abstract

The X-ray photoelectron spectra for $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$ and $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ are consistent with those previously reported for $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$, where different electron binding energies were observed for the structurally distinct sulfur atoms in the polysulfido ligands. The 4f binding energies for the platinum polysulfides are lower than those for platinum(IV) bonded to elements other than sulfur, and the 3d binding energies for the rhodium complex are lower than most values for rhodium(III) bonded to oxygen or nitrogen.

Introduction

X-ray photoelectron spectra for the polysulfido complexes $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ and $(Ph_4P)_3[Cu_3(S_4)_3]$ were reported recently [1]. The primary interest in studying these materials was as model compounds to help identify the sulfur species present on the surface of sulfide minerals under certain processing conditions [2]. The 2p binding energies observed for the sulfur atoms S(1) in **I** nearest to the metal atom were comparable with those for sulfur atoms in mineral sulfides, whereas sulfur atoms further from the metal had 2p binding energies at least 1 eV greater but still less than the value for elemental sulfur. We assume (in line with all available evidence) that branching (–S–S(S)$_x$–S–; $x \geqslant 1$) will not be present in oligosulfido ligands, that is that direct links from S(1) to S(3) in MS_5 or MS_6 or from S(2) to S(4) in MS_7 are not present (though from Steudel's elegant work [3], it is clearly possible to generate elements of structure like –S–S(O)–S–). A difference in the S(2p) binding energies for the structurally distinct sulfur atoms (S(1), S(2) and so on) within the polysulfido ligands is consistent with calculations of the charge distribution in S_4^{2-} and S_5^{2-} [4] and $(NH_4)_2[Pt(S_5)_3]$ [5].



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Numbering system for chelated oligosulfide: in S_4^{2-} species, the two atoms marked S(2) are linked (line a); in S_5^{2-} species, line b links S(2) with S(3); and so on. Lines a, b and c may represent S–S bonds only for S_4^{2-}, S_5^{2-} and S_6^{2-} species respectively.

In our previous study, care was taken to minimize the possibility of decomposition of the polysulfides during the determination of the electron spectra [1]. Specimens were cooled to lower their vapour pressure before being subjected to the vacuum of the spectrometer, and maintained at 190 K while under X-irradiation. Nevertheless it could be argued that the observed $Pt(4f)_{7/2}$ binding energy of 73 eV was too low to be consistent with platinum(IV), as most values for platinum(IV) recorded in the literature are greater than 74 eV. For example, the $Pt(4f)_{7/2}$ binding energy for $Pt(OH)_4$ is 74.2 eV [6] whereas that for $Pt(OH)_2$ is 72.8 eV [7] with respect to 70.9 eV for platinum(0). However it is common for the metal core electron binding energies in sulfides to be lower than those in oxides and hydroxides for the same formal oxidation state of the metal. In fact the values for some sulfides and arsenosulfides are comparable with those for the corresponding metal; for example the Fe(2p) binding energies for FeS_2 [8] and iron(0) are essentially the same, as are the Co(2p) binding energies for CoAsS [9] and cobalt(0), but they are of the order of 2 eV less than the values for FeO [10] and CoO [11]. Thus low binding energies for the metal atom in a sulfide do not necessarily mean a low formal oxidation state.

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*In common with others, we use the generic word polysulfide to denote S_n^{2-}, with $2 \leqslant n \leqslant 10$, but since all our systems involve $5 \leqslant n \leqslant 7$, we might more properly speak of oligosulfides.

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Furthermore synthetic PtS_2, a stable platinum(IV) sulfide, has been examined by electron spectroscopy recently and the $Pt(4f)_{7/2}$ binding energies for freshly cleaved and air-exposed surfaces found to be 73.3 and 73.0 eV respectively [12]. These values agree well with the $Pt(4f)_{7/2}$ binding energy for the platinum(IV) polysulfide. The corresponding $S(2p)_{3/2}$ binding energies of 161.8 and 161.7 eV for the two PtS_2 surfaces are also close to the binding energy of 161.8 eV obtained for sulfur atoms S(1) in the polysulfide.

If the $[Pt(S_5)_3]^{2-}$ complex had decomposed either on sample preparation (by evaporation of solvent from a solution of the complex) or on X-irradiation, then the expected decomposition products would have been $[Pt(S_5)_2]^{2-}$, which has been isolated by Wickenden and Krause [13] as a tetrapropylammonium salt, and elemental sulfur. In this case, a component at 163.5 eV due to elemental sulfur should have been present in the S(2p) photoelectron spectrum, together with the contributions from the pentasulfido ligands. The fact that a component at 163.5 eV was not observed in the S(2p) spectrum from the specimen of platinum(IV) complex examined, is evidence that decomposition had not occurred. Moreover the binding energies determined from powdered material and from thin layers deposited from solution were the same so that decomposition during sample preparation would have been unlikely. Nevertheless it was of interest to determine the electron spectra for related polysulfides to ascertain whether their metal binding energies were also low and whether the S(2p) spectra were consistent with that observed for $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ [1]. Accordingly, X-ray photoelectron spectra have been obtained for $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$, which has recently been shown [14] to be similar in structure to the tris-pentasulfidoplatinate(IV) complex, and $(NH_4)_2[PtS_{17}]\cdot 2H_2O$, for which the crystal structure has yet to be determined and it is not known whether the anion is $[Pt(S_5)_2S_7]^{2-}$ or $[Pt(S_6)_2S_5]^{2-}$. $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ was re-examined under the same spectrometer conditions to facilitate comparison with spectra from the other two complexes.

The evidence that the oxidation state of platinum is indeed IV for the dihydrated solids $(NH_4)_2[PtS_{15}]$ and $(NH_4)_2[PtS_{17}]$ rests in both cases in their optical activity (indicating a tris-chelated, *i.e.* six coordinated, structure) and in the cases of both dimorphs of $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ on crystal structures.

Experimental

Dark red crystals of $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$ were prepared and the crystal structure determined as described by Cartwright *et al.* [14]. The crystals of this compound are sparingly soluble in ethanol and very soluble in water. Ethanolic solutions appear to be stable for many hours; however, some cloudiness becomes evident in aqueous solutions after one hour. Maroon crystals of $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ were prepared and characterized as described by Gillard *et al.* [15]. These crystals are sparingly soluble in water but freely soluble in polar organic solvents. Aqueous solutions are stable in the dark, but slowly deposit sulfur and form platinum(II) species on exposure to light [15]. Brick-red crystals of $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ were also prepared as described by Gillard *et al.* [15]. Samples for electron spectroscopic examination were prepared by rapid evaporation of solvent from both aqueous and ethanolic solutions on to metallic gold or platinum substrates under nitrogen, as well as by pressing the powdered materials into indium foil or on to double-sided adhesive tape.

X-ray photoelectron spectra were obtained with a Vacuum Generators ESCA3 spectrometer at an operating pressure of 10^{-7} Pa. Unmonochromatized X-rays from a magnesium anode and an analyzer pass energy of 20 eV and slit width of 2 mm were used. Under these conditions, the $4f_{7/2}$ peak from gold had a width of 1.05 eV and a binding energy of 83.8 eV. Specimens were cooled to 180 K under nitrogen before evacuation, and maintained at this temperature while in the analyzer. S(2p) spectra were fitted with doublets having Gaussian-shaped (1/2, 3/2)-components constrained to an intensity ratio of 1:2 and to a separation of 1.19 eV.

Results and Discussion

The S(2p) spectrum from a thin film of $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$ evaporated under nitrogen from a freshly-prepared aqueous solution on to a gold substrate is shown in Fig. 1 with background subtracted and fitted approximately with three doublets. Results are given in Table I, with some related quantities. The

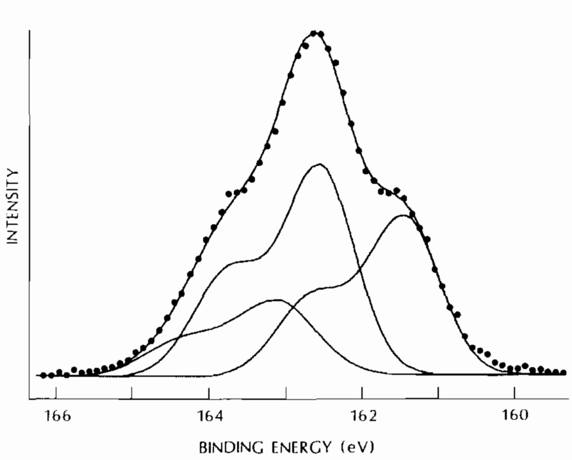

Fig. 1. S(2p) photoelectron spectrum for $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$ fitted with three doublets.

TABLE I. $2p_{3/2}$ Binding Energies[a] (eV) and Relative Intensities (I) for Sulfur in $(NH_4)_x[MS_n]\cdot yH_2O$ (M = Rh, $x = 3$, or Pt, $x = 2$; $n = 15$ or 17) and Related Compounds and Substances

Compound	y	S(1)	I(1)	S(2)	I(2)	S(3)	I(3)	I(4)	Other	Reference
S_8									163.5	1, 5
$[M(S_5)_3]^{x-}$[b]			6		6		3			
$(NH_4)_3[Rh(S_5)_3]$	2	161.5	6	162.6	7	163.2	3			this work
$(NH_4)_2[Pt(S_5)_3]$	0	164.8		164.8		164.8				5
$(NH_4)_2[Pt(S_5)_3]$	2	161.8	6	162.7	6	163.1	3			1
$[M(S_5)_2(S_7)]^{x-}$[b]			6		6		4	1		
$[M(S_5)(S_6)_2]^{x-}$[b]			6		6		5	0		
$(NH_4)_2[PtS_{17}]$	2	161.9	6	162.8	6	163.2	5	0		this work
PtS_q[c]		161.7							163.2	1
PtS_2		161.7								12
AuS_p[c]		161.3							163.0	17

[a] S(1) refers to atoms nearest to the metal and 'other' to S remote from the metal. [b] Relative intensities calculated. [c] Measured for sulfur deposited electrochemically on the particular metal; $1 < p, q < 10$.

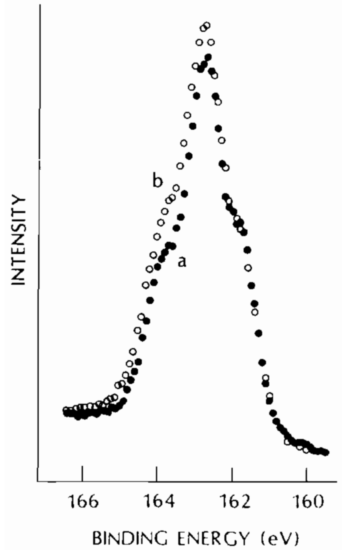

Fig. 2. S(2p) photoelectron spectra for (a) $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ (●) and (b) $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ (○).

$2p_{3/2}$ binding energies of 161.5, 162.6 and 163.2 eV for the fitted doublets are similar to those obtained previously for $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ [1], *viz.* 161.8, 162.7 and 163.1 eV relative to $Au(4f)_{7/2} = 83.8$ eV. Nevertheless the value for the component at lowest binding energy being 0.3 eV less for the rhodium complex would be largely responsible for the difference in the appearance of the spectrum from the rhodium complex and that from the platinum(IV) analogue (a in Fig. 2). A N(1s) binding energy of 400.5 eV, a symmetrical $Rh(3d)_{5/2}$ peak at 308.2 eV and S(2p) binding energies within the expected range indicate that charging was minimal. While the fit to the S(2p) spectrum would not be unique and is no more than adequate, it is consistent with the structurally distinct sulfur atoms within the polysulfido ligand having significantly different electronic environments. The lowest binding energy is comparable with values for metal sulfides as in sulfide minerals, and would arise from the six sulfur atoms S(1) of **I** in each molecule nearest to the metal. The highest binding energy has a value approaching, but still less than, that for elemental sulfur, and would arise from the three sulfur atoms S(3) of **I** in each molecule furthest from the metal. The intermediate binding energy would arise from the intermediate sulfur atoms S(2) of **I**. The corresponding intensity ratio for the three fitted doublets was approximately 6:7:3 rather than 6:6:3 as expected. This discrepancy could arise from uncertainties in the curve fitting (such as lineshape and background). It does not appear to be the result of decomposition of the rhodium complex, as the presence of a significant amount of elemental sulfur was precluded by the absence of a component at 163.5 eV and the absence of any change in the S(2p) spectrum after the specimen was subjected to several hours of ultra high vacuum at ambient temperature, conditions under which elemental sulfur should volatilize. Futhermore, spectra from the polysulfide evaporated on to platinum or from ethanolic solution were essentially the same. Spectra from rhodium polysulfide powder were broadened and shifted 1 to 2 eV to higher binding energy due to charging, but the Rh(3d)–S(2p) energy separation was the same. No variation in the spectra with irradiation time was observed.

The $Rh(3d)_{5/2}$ binding energy of 308.2 eV is 1.1 eV greater than that for rhodium metal and 0.5 eV less than that for Rh_2O_3 [16]. While the value for the polysulfide might have been expected to be slightly closer to that of the metal, it is at the low end of the range observed for rhodium(III) [8].

The S(2p) spectrum from a thin film of $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ evaporated from aqueous solution on to a gold substrate is shown in Fig. 2 together with the spectrum from $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$. The two spectra have been normalized so that the intensities of the shoulders near 162 eV are approximately equal. The intensity of this shoulder should be determined by the number of sulfur atoms S(1) bonded to platinum, and should be the same for both complexes, that is six, since both are readily resolved into stable enantiomers. It can be seen that for the PtS_{17} complex, the shoulder near 164 eV and to a lesser extent the peak maximum, are larger than those for the PtS_{15} complex. Indeed the spectrum from the former complex can be fitted adequately on the same basis as for the tris-pentasulfidoplatinate-(IV) but with an intensity ratio closer to 6:6:5 than 6:6:3. If the curve fitting were reliable, this result would indicate that the two additional sulfur atoms in each molecule are most probably two atoms remote, S(3) of **I**, from the platinum atom. Therefore as shown in Table I it is more likely that the anion structure is $[Pt(S_6)_2S_5]^{2-}$ than $[Pt(S_5)_2S_7]^{2-}$. In the latter case, the ratio of sulfur atoms S(1), S(2), S(3) and S(4) would be 6:6:4:1, and the binding energy for the most remote sulfur atom, S(4), might be expected to be another one or two tenths of an eV closer to the binding energy 163.5 eV for elemental sulfur. There is no obvious sign in the experimental spectrum of extra intensity at such a slightly higher binding energy expected for S(4); for the $[Pt(S_5)_2(S_7)]^{2-}$ structure, this would amount to about 6% of the whole S(2p) intensity. It would be one quarter the intensity of the component due to S(3), and should give rise to a change of shape at the high binding energy base of the spectrum. No such change appears. While this finding supports the $[Pt(S_6)_2(S_5)]^{2-}$ isomer, the uncertainty in fitting the spectra is too great to make that support definitive.

The $Pt(4f)_{7/2}$ binding energy for the $[PtS_{17}]^{2-}$ complex was the same as that for the tris-pentasulfidoplatinate(IV), *viz.* 73.0 eV. The Pt(4f) peaks were symmetrical, so that if decomposition to platinum(II) had occurred, the entire surface layer would have been affected. Specimens prepared by pressing the powdered material into indium foil gave rise to charge shifting of approximately 0.6 eV; however as in the case of the $PtS_{15}{}^{2-}$ complex, the S(2p)–Pt(4f) separation was the same as for specimens prepared by solvent evaporation. If X-ray photo-decomposition of the platinum(IV) to platinum(II) indeed occurred, then it must have taken place in a time less than that required to determine one electron spectrum, whether the exciting X-rays were monochromatized as in our earlier work [1] or unmonochromatized. The observed platinum binding energies and S(2p) spectra are therefore those for the complexes as prepared and characterized. The formal oxidation state for the platinum in the polysulfides examined is definitely IV, as the anions can be optically resolved [15], therefore not all 4f binding energies for platinum(IV) are greater than 74 eV as is often assumed.

Conclusions

The X-ray photoelectron spectra for $(NH_4)_3[Rh(S_5)_3]\cdot 2H_2O$ and $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ are consistent with those previously reported for $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$, where different electron binding energies were observed for the structurally distinct sulfur atoms in the polysulfido ligands. Although the $4f_{7/2}$ binding energies for the two platinum complexes are lower than those for platinum(IV) bonded to elements other than sulfur, the electron spectra did not indicate decomposition to platinum(II) and elemental sulfur. The $3d_{5/2}$ binding energy for the rhodium complex was also lower than most values for rhodium(III) bonded to oxygen or nitrogen.

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