XPS Studies of Some Heterometallic Complexes of Pt with Bridging Sulphido

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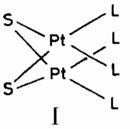
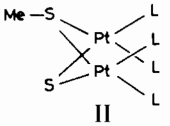
The synthesis and X-ray structural data of some heterometallic complexes containing platinum has recently been described in the literature [1].

This class of compounds contain compact aggregates of up to six co-ordinatively unsaturated metal atoms, and are interesting because of their relevance to heterometallic complexes, showing multiple metal sites, in homogeneous catalytic processes [8].

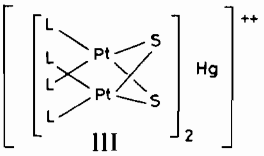
By X-ray photoelectron spectroscopy we intend to give additional information on the electronic and steric structure $[Pt_2(\mu S)_2L_4]$ (I), $[Pt_2(\mu S_1\mu SMe)L_4]$ (II), in which the (μS) bridge is able to act as a bidentate thioether ligand to give the $[[Pt_2(\mu S)_2L_4]_2H_8](BPh_4)_2$ (III) tetrahedral compound.



I



II



III

X-ray photoelectron spectra were recorded using a VG ESCA III MK 2 spectrometer equipped with $Al_{K\alpha}$ source (1486.6 eV) according to the usual technique [5].

The samples were dusted as a thin film onto double-sided adhesive tape. The Cl_s line b.e. (285.0 eV) from residual pump-line oil contamination was used as an internal standard for spectral calibration.

The reported binding energies were measured at the half width of the half-maxima of the bands. Peak deconvolution was performed by means of a DuPont curve resolver using Gaussian fits.

X-ray crystallographic studies on I show that the geometry of this compound is distorted from planarity and the very large sulphur–sulphur separation (~3 Å) allows the sulphur atom to act as a ligand [2].

Table I lists the Pt $4f_{7/2}$, The $P2_p$, $S2_p$ and Hg 4f binding energies (eV). All the Pt $4f_{7/2}$ binding energy values lie in the range accepted for the bivalent compounds (Pt^{+2}) and they are very similar in all of the compounds.

The $P2_p$ binding energy values (132, 0–132.2 eV) lie in the range found for the compounds in which the phosphines act as ligands.

These values are higher than those for the free molecule (131.1 eV). This means that the phosphines are σ-coordinated to the platinum atoms and that there is only a very small degree of Me → L back-donation.

$S2_p$ b.e. values and the FWHM differ considerably between I and II (162.4 eV and 162.8 eV; 2.3 and 3.0 eV). In the second compound the larger FWHM is indicative of the presence of two components. By deconvolution of the $S2_p$ peak of this compound it is possible to find two components with b.e. values at 162.2 eV and 163.5 eV (in intensity ratio 1:1) attributable to the mercapto and tio-groups, respectively.

It is known from the literature [3] that the Me–S bond in the fragment M–S–M is less covalent than the M–SMe bond of the mercapto-groups. The value of the $S2_p$ (163.5 eV) attributed to the mercapto-group Me–S reflects the decrease of the charge

TABLE I. Pt $4f_{7/2}$, $S2_p$, $P2_p$ and Hg Binding Energies (eV).

Compound	Pt $4f_{7/2}$	$S2_p$	$P2_p$	Hg $4f_{7/2}$
$[Pt_2(\mu S)_2L_4]$	73.0	162.4	132.0	
$[Pt_2(\mu S\mu SMe)L_4]$	73.2	162.2–163.5	132.2	
$[(Pt_2(\mu S)_2L_4)_2Hg](BPh_4)_2$	73.3	162.4	132.2	101.5
L = PPh_3			131.1	

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TABLE II. Pt $4f_{7/2}$, Ni $2p_{3/2}$ and $S2_p$ binding energies (eV).

Compound	S2p	Pt $4f_{7/2}$	Ni $2p_{3/2}$	References
$[Pt_2(\mu S)_2L_4]$	162.4	73.0	–	This work
$[Ni_3(\mu S)_2L_6]$	161.5	–	855.4	3
$[Pt(S_4C_4Ph_4)]^{-2}$	161.3	71.1	–	6
$[Ni(S_4C_4Ph_4)]^{-2}$	160.3	–	852.8	6
$[Pt(R_2NCS_2)_2]$	163.3	72.5	–	7
$Ni(R_2NCS_2)_2]$	162.4	–	854.9	3

density on the sulphur atom as a consequence of the decrease in covalency of the S–Me bond.

The value of the other sulphur (162.2 eV) lies in the range found in the literature [4] for ionic sulphide groups.

The coordination of two molecules of I to Hg results in a tetrahedral complex $[(Pt_2(\mu S)_2L_4)_2Hg](BPh_4)_2$.

The ability of the bridge sulphur ligands to act as a bidentate thioether is confirmed by the $S2_p$ b.e. values of 162.4 eV in this compound (III), which is very close to that of compound (I). By comparing the b.e. values of compounds I and III it can be shown that there is a small increase of the b.e. values for Pt 4f and $P2_p$.

This fact, together with the constancy of the b.e. value for the $S2_p$, can be tentatively interpreted in terms of an electron-withdrawal from the phosphine ligands, and through the Pt–S bond, to compensate for the decrease of the charge owed to the additional Hg–S bond.

As a general point the $S2_p$ b.e. values for Pt–S bonds are higher than for Pd–S and Ni–S bonds.

Table II reports the values referrring to the present paper together with some literature data which show, for Ni and Pt compounds with the same ligands, a difference in $S2_p$ b.e. of about 1 eV. Differences of the same magnitude also hold for compounds of the two metals with different ligands, provided the S atom is in a similar electronic configuration. As an example, one can compare b.e. data for the S 4f b.e. values of the compounds reported here and those of Ni dithiocarbazates and dithiocarbamates, in which a formal charge of –1 is delocalized over the two sulphur atoms of the ligand.

The explanation of this finding may lie in the different character of the Ni and Pt atoms bonded to the sulphur. Indeed, S and Pt are considered as having a 'soft' character and this could result in a higher covalency of the Pt–S bond (with respect to the Ni–S bond) with a consequent withdrawal of the electronic charge from sulphur.

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