Inorganica Chimica Acta, 25 (1977) L85–L86
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X-ray Photoelectron Spectra of Inorganic Molecules. XX.* Observations Concerning the Sulfur 2p Binding Energies in Metal Complexes of Thiourea

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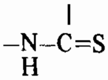
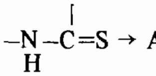
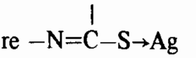
Received October 4, 1977

Following our detailed investigations of the core electron binding energies associated with different halogen environments in transition metal halides [1–3], we have recently turned our attention to several problems which involve using X-ray photoelectron spectroscopy (XPS) to identify the nature of the metal–sulfur binding in metal complexes derived from sulfur containing amino-acids [4] and thiazole type ring systems [5]. In our investigations of isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole) [5], we showed, from S 2p binding energy measurements, that this molecule utilizes its exocyclic thione sulfur atom in forming complexes with $PdCl_2$, $PtCl_2$ and CuCl. Other workers have used XPS to probe the nature of the bonding between silver(I) and a variety of thionamide ligands [6, 7]. In the latter molecules, which contain the  $-\overset{|}{\underset{H}{N}}-C=S$ unit, the interesting question arises as to whether the thione group remains intact (*i.e.*,  $-\overset{|}{\underset{H}{N}}-C=S \rightarrow Ag$), or whether silver forms mercaptide complexes of the structure  $-N=\overset{|}{C}-S\rightarrow Ag$ [6, 7]. These previous studies [5–7] 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 [5] or a thioether sulfur [6, 7]. This situation permits the S 2p binding energy shifts associated with the two different types of sulfur to be internally referenced one to the other. For both isoperthiocyanic acid [5] and the thionamides [6, 7], the free ligands exhibit S 2p binding energies for the exocyclic thione sulfur which are 2.4 to 1.4 eV lower than for the endocyclic sulfur atoms. Coordination of the thione sulfur atom leads to an increase in its S 2p binding energies *relative to those of the endocyclic sulfur atoms.*

In spite of these XPS studies on the five membered thiazole type ring systems, little attention has been paid to the XPS of metal complexes of the much simpler thiourea ligand. Although a few reports have appeared on the S 2p binding energies of metal complexes of thiourea [8–10], the present evidence concerning the magnitude of the chemical shifts which occur upon coordination of this ligand to transition metal ions is fragmentary. The need for a systematic study of the XPS of such complexes is obvious, and accordingly we now report preliminary details of such an investigation which has been carried out in our laboratory.

The C 1s, N 1s and S 2p binding energies of a variety of thiourea complexes were recorded with a Hewlett–Packard 5950A ESCA spectrometer using the experimental procedure we have described fully elsewhere [11, 12]. The appropriate data are presented in Table I. In all instances, the complexes we studied are species which are known to contain S-bonded thiourea [13–17].

Our data for thiourea (N 1s and S 2p binding energies) are in satisfactory agreement with that reported by Nefedov *et al.* [9], who used a different instrument but the same referencing procedure, and Gerenser *et al.* [6], who used a HP 5950A instrument and a referencing procedure† which should not give results which differ very much from those obtained using carbon contaminant as the reference [18].

Nefedov *et al.* [9, 10] have indicated that the coordination of thiourea through its sulfur atom leads to a S2p chemical shift of +0.8 eV. Although there is no indication as to the source of the data upon which this conclusion was based, Nefedov and co-workers had earlier reported [8] that the rhodium(III) complexes $Rh(tu)_3Cl_3$, $[Rh(tu)_6]Cl(NO_3)_2$ and $[Rh(tu)_5Cl]Cl_2$ exhibit S2p energies of 163.2, 163.0 and 163.1 eV, respectively. However, from the results of our study it is clear that the thiourea S 2p chemical shifts can be much less than +0.8 eV (see Table I). Thus, for the six coordinate nickel(II) complex $NiCl_2(tu)_4$ we find that the S $2p_{1/2,3/2}$ binding energies are not significantly different from those of the free ligand and for the remainder of the complexes listed in Table I this shift is between +0.3 and +0.6 eV.

In view of the small magnitudes of the thiourea S 2p chemical shifts, it is clearly important to eliminate any differences in charging effects which might exist between the various complexes. This is difficult to do either by utilizing the electron floodgun attachment [12] associated with the HP instrument or by use of an 'external' reference (*e.g.*, the C 1s binding energy of carbon contaminant or the Au $4f_{7/2}$ energy of an evaporated gold film). Unfortunately, the alternative approach of 'internally' referencing the S2p energies to either the C 1s or N 1s level of thiourea

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*Part XIX: S. A. Best and R. A. Walton, *Isr. J. Chem.*, in press.

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†Au $4f_{7/2}$ B.E. of 84.1 eV for an evaporated thin film of the metal or admixture with graphite.

TABLE I. X-ray Photoelectron Spectra of Transition Metal Complexes of Thiourea.[a]

Complex	C 1s		N 1s		$S\ 2p_{3/2}$[b]	Halogen (Cl $2p_{3/2}$, Br $3p_{3/2}$ or F 1s
	Thiourea	–NCS	Thiourea	Other		
Thiourea	288.1	–	400.1	–	162.4(1.0)	–
$CoCl_2(tu)_2$	288.5	–	400.3	–	162.9(1.1)	198.8
$CoBr_2(tu)_2$	288.5	–	400.2	–	162.8(1.0)	182.5
$Co(NCS)_2(tu)_2$	288.3	286.4	400.1	398.6(*N*CS)	162.8(1.2)	–
$Co(NO_3)_2(tu)_4$	288.5	–	400.3	407.1(*N*O_3)	162.9(1.2)	–
$NiCl_2(tu)_4$	288.2	–	400.0	–	162.5(1.1)	198.4
$Ni(NCS)_2(tu)_2$	288.2	~286.0	400.0	398.6(*N*CS)	162.9[c]	–
$Ni(NO_3)_2(tu)_6$	288.4	–	400.2	407.1(*N*O_3)	162.8(1.3)	–
$CuCl(tu)_3$	288.1	–	400.1	–	162.7(1.2)	198.0
$[Cu(BF_4)(tu)_3]_2$	288.1	–	400.2	–	163.0(1.4)	686.4
$[Pr_4N]ReCl_5(tu)$	288.3	–	399.8	401.7(*N*Pr_4)	162.8(1.4)	198.3

[a] Recorded using Al-$K_{\alpha 1,2}$ radiation; binding energies (in eV) are quoted relative to a carbon 1s value of 285.0 eV for carbon contaminant and are considered accurate to ± 0.1 eV. [b] $2p_{1/2}$ component at ~ 1.0 eV to higher energy; fwhm value given in parentheses. [c] Peak shape different from that encountered in the case of the isostructural cobalt(II) analog $Co(NCS)_2(tu)_2$ due to a slight mismatch in the S 2p energies of the tu and NCS ligands.

cannot be used with any confidence since there is no justification in assuming that the charge at the carbon atom of thiourea is independent of the nature of the metal salt or that the N 1s binding energy remains constant when the amine protons may be subject to hydrogen bonding interactions in certain salts. Nonetheless, it is apparent from the data reported in Table I that in sulfur bonded thiourea the S 2p chemical shifts relative to the free ligand are *usually* greater than the related N 1s chemical shifts associated with the unbound amine nitrogen atoms.

One further point of considerable interest concerns the complexes $[M(NCS)_2(tu)_2]_n$, where M = Co or Ni, and $[Cu(BF_4)(tu)_3]_2$, in which all or some, respectively, of the thiourea ligands form M–S–M bridges. XPS measurements clearly show that the S 2p 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. This behavior is in contrast to the binding energy differences which may often exist between bridging and terminally bound thiol sulfur [4] and halide ligands [1–3].

Acknowledgments

Support from the National Science Foundation (Grant CHE74-12788A02) is gratefully acknowledged.

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