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X-ray Photoelectron Spectra of Inorganic Molecules [1]. XXIII. On the Question of the Usefulness of XPS in Studying the Ambidentate Nature of the Thiocyanate Ligand

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*As a result of analyzing the available data on the S 2p and N 1s binding energies of a large number of thiocyanate complexes, it can be demonstrated that the binding energy difference [N 1s–S 2p] is sometimes greater for M–NCS than M–SCN. However, as a means of deducing the mode of thiocyanate coordination in a complex of unknown structure, this procedure should be viewed with considerable caution. Not only are there cases where the value of this energy difference is the same for related series of complexes containing N- and S-bound thiocyanate (*e.g., *$(Me_4N)_3Ru(NCS)_6$* versus *$(Ph_4As)_3Os(SCN)_6$* and [Cu(tren)(NCS)]SCN* versus *[Cu(trien)(SCN)]-SCN), but [N 1s–S 2p] values for SCN^- and bridging M–NCS–M units may be very similar to those for M–NCS and M–SCN, making distinctions between these different bonding modes extremely difficult. Accordingly, in contrast to the recent conclusions of Borghi* et al., *we question the reliability of XPS in distinguishing between the different bonding modes of the thiocyanate ligand in molecules whose crystal structures are unknown.*

Introduction

Our investigations into the use of XPS to characterize structurally many transition metal chlorides, bromides and iodides [1–8] have been followed by studies of the S 2p binding energy spectra of a variety of metal complexes of sulfur containing ligands. Of particular interest were the complexes of ligands which contain thiol, thioether and thione sulfur donor atoms [9–12]. In addition, we explored the possibility that the mode of bonding of the ambidentate thiocyanate ligand may be established by the measurement of its C 1s, N 1s and S 2p binding energies [13], and concluded that the XPS technique does not usually permit a ready distinction between these different bonding modes in most transition metal complexes. Since the publication of our paper on this subject, Borghi *et al.* [14] have reported their results on the XPS of coordination complexes containing the thiocyanate ligand. They concluded [14] that differences between the N 1s and S 2p binding energies of ambidentate thiocyanate "represent an empirical regularity to distinguish whether the thiocyanate ligands are bonded through S or through N atoms." Since these workers were apparently unaware of our study and, in addition, we are not entirely in agreement with their conclusions, some further consideration of the XPS of thiocyanate complexes is clearly in order. This topic is discussed in the present paper.

Discussion

In the paper by Borghi *et al.* [14], no reference is made to other published work on the N 1s and S 2p binding energies of thiocyanate complexes. In fact, not only have there been studies by ourselves [13] and Burger *et al.* [15], both of which specifically addressed the question of whether N 1s and S 2p binding energies could be used to deduce the mode of thiocyanate bonding, but there have also been a variety of other occasions when the XPS of thiocyanate complexes have been reported [16–22], although in none of the latter were the N 1s and S 2p binding energies analyzed in this fashion. As we have discussed fully elsewhere [13], consideration of the C 1s binding energy of the thiocyanate ligand in any series of complexes containing organic ligands or cations is effectively thwarted by overlap with the C 1s energies of the latter. Accordingly, the best way of analyzing trends in the N 1s and S 2p binding energies is through variations in the [N 1s–S 2p] energy difference [13, 14].

The availability of such data for complexes containing N-bound, S-bound, bridging and ionic thiocyanate (including systems in which *two* such bonding modes are present within the same molecule) provides an adequate basis for considering the use of XPS in deducing the bonding mode. Values of the [N 1s–S 2p] energy differences available from the literature [11, 13–23], together with some new

TABLE I. [N 1s–S 2p] Binding Energy Differences (in eV) for Some Thiocyanato and Isothiocyanato Complexes of the Transition Metals.

Compound[a]	[N 1s–S 2p]	Ref.[b]	Mode of Thiocyanate Bonding	Compound	[N 1s–S 2p]	Ref.[b]	Mode of Thiocyanate Bonding
NaSCN	235.3	14	SCN^-	$(Bu_4N)_2Re_2(NCS)_8$	236.2	13	M–NCS
KSCN	235.1	15	SCN^-		236.6	16	M–NCS
	234.4	19		$(Bu_4N)_2Re(NCS)_6$	236.7	16	M–NCS
$(NH_4)SCN$	235.3	19	SCN^-	$(Bu_4N)Re(NCS)_4(dppe)$	236.2	22	M–NCS
$(Me_4N)SCN$	235.2	17	SCN^-	$Re(NCS)_3(PEt_2Ph)(dppe)$	236.2	22	M–NCS
	235.3	19		$Re(NCS)_3(PEt_2Ph)(bipy)$	236.2	22	M–NCS
$(Ph_4As)SCN$	234.8	17	SCN^-	$Re(NCS)_3(PEt_2Ph)(phen)$	236.3	22	M–NCS
	234.8	23		$(Me_4N)_3Ru(NCS)_6$	235.2	17	M–NCS
$[Cu(en)_2](SCN)_2$	235.8	13	SCN^-	$[Rh(NH_3)_5(NCS)](ClO_4)_2$	236.1	14	M–NCS
$(NH_4)[Cr(NH_3)_2(NCS)_4]$	235.4	17	M–NCS	$[Ir(NH_3)_5(NCS)](ClO_4)_2$	236.1	14	M–NCS
$K_3Cr(NCS)_6$	235.4	17	M–NCS	$Pd(bipy)(NCS)_2$	236.1	13	M–NCS
$[Cr(NH_3)_5(NCS)](ClO_4)_2$	236.2	14	M–NCS	$H[Co(HD)_2(SCN)_2]$	235.6	15	M–SCN
$[Co(NH_3)_5(NCS)](ClO_4)_2$	236.3	14	M–NCS	$(Ph_4As)_3Os(SCN)_6$	235.2	17	M–SCN
$[Co(tu)_2(NCS)_2]_n$	235.8	11	M–NCS	$K_3Rh(SCN)_6$	235.0	17	M–SCN
$(Me_4N)_2Co(NCS)_4$	235.4	19	M–NCS	$[Rh(NH_3)_5(SCN)](ClO_4)_2$[e]	235.5	14	M–SCN
$(Et_4N)_2Co(NCS)_4$	235.5	19	M–NCS	$(Me_4N)_3Ir(SCN)_6$	234.7	17	M–SCN
$(Bu_4N)_2Co(NCS)_4$	235.8	19	M–NCS	$[Ir(NH_3)_5(SCN)](ClO_4)_2$	235.5	14	M–SCN
$[Ni(tu)_2(NCS)_2]_n$	235.7	11	M–NCS	$K_2Pd(SCN)_4$	235.4	13	M–SCN
$(Me_4N)_2Ni(NCS)_4$	235.6	19	M–NCS	$K_2Pt(SCN)_6$	234.3	17	M–SCN
$(Me_4N)_4Ni(NCS)_6$	235.4	19	M–NCS	$AuL(SCN)$[f]	235.2	14	M–SCN
$(Et_4N)_4Ni(NCS)_6$	235.4	19	M–NCS	$AuL_2(SCN)$[f]	235.4	14	M–SCN
$Ni(NH_3)_4(NCS)_2$	235.0	15	M–NCS	$AuL_3(SCN)$[f]	235.5	14	M–SCN
$Ni(tren)(NCS)_2$	236.4[c]	17	M–NCS	$HgCo(NCS)_4$	234.9	17	M–NCS–M′
$(Me_4N)_2Zn(NCS)_4$	235.6	19	M–NCS		235.3	18	
$(Et_4N)_2Zn(NCS)_4$	235.2	19	M–NCS	$[Cu(SCN)]_n$	234.8	20	M–NCS–M
$(Me_4N)_2MoO(NCS)_5$	236.0	13	M–NCS	$[Cu(tren)(NCS)]SCN$	235.8	13	M–NCS and SCN^-
$(Me_4N)_4Mo_2O_3(NCS)_8$	236.0	13	M–NCS	$[Rh(en)_2(NCS)_2]SCN$	236.2	14	M–NCS and SCN^-
$Mo_2(NCS)_4(PEt_3)_4$	235.7	d	M–NCS	$[Cu(trien)(SCN)]SCN$	235.7	13	M–SCN and SCN^-
$(Bu_4N)_2Mo_2(NCS)_6(PEt_3)_2$	235.9	d	M–NCS	$(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$	236.1	22	M–NCS and M–NCS–M
$Mo_2(NCS)_4(dppe)_2$	236.0	d	M–NCS	$(Bu_4N)_2Re_2(NCS)_8(PPr^n_3)_2$	236.3	22	M–NCS and M–NCS–M
$Mo_2(NCS)_4(dppm)_2$	235.8	d	M–NCS	$(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$	236.6	22	M–NCS and M–NCS–M
$Mo_2(NCS)_4(bipy)_2$	236.0	d	M–NCS	$(Bu_4N)_2Re_2(NCS)_8(dppm)_2$	236.2	22	M–NCS and M–NCS–M
$Mo2(NCS)_4(phen)_2$	235.9	d	M–NCS	$(Bu_4N)_2Re_2(NCS)_8(dppe)_2$	236.1	22	M–NCS and M–NCS–M

[a] Ligand abbreviations are as follows: tren = tris(2-aminoethyl)amine; trien = triethylenetetramine; en = ethylenediamine; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; bipy = 2,2′-bipyridyl; phen = 1:10-phenanthroline; HD = dimethylglyoximato; L = tertiary phosphine. [b] Literature reference to the source of the binding energy data. [c] Only one N 1s binding energy reported for this complex (see ref. 17), whereas we observed two N 1s peaks (due to amine nitrogen and NCS) in the XPS of its copper(II) analogue (see ref. 13). [d] New data; recorded as described previously (see ref. 4). [e] This complex was erroneously formulated as the N-bound isomer $[Rh(NH_3)_5(NCS)](ClO_4)_2$ in the Table of binding energy data given in ref. 14. [f] The nature of the tertiary phosphine (L) in these complexes was not specified (see ref. 14).

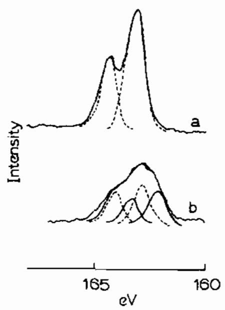

Fig. 1. Sulfur 2p binding energy spectra of (a) $K_2Pd(SCN)_4$ and (b) Pd(dppe)(SCN)(NCS). Deconvolutions were carried out using a DuPont 310 curve resolver employing a Gaussian-shape fit. For further details see text.

data for molybdenum(II) complexes containing N-bound thiocyanate, are presented in Table I. We have not included comparable data for complexes formulated by Borghi *et al.* [14] as '$NiL_2(NCS)$' and '$[NiL_2(C{\equiv}CPh)](NCS)$'; although L apparently represents a tertiary phosphine ligand no mention is made of the actual phosphine(s) used [24]. While XPS data for the mixed N-bound/S-bound complex Pd(dppe)(SCN)(NCS) are not given in the Table, the results for this important compound will be discussed fully. Finally, it should be mentioned that in most of the S 2p spectra recorded in our laboratory the $2p_{1/2}$ and $2p_{3/2}$ components are well resolved [13] so that [N 1s–S 2p] differences are quoted relative to the more intense S $2p_{3/2}$ peak. Other groups have taken the S 2p energy to be the maximum of the unresolved doublet.

The conclusion by Borghi *et al.* [14] that the [N 1s–S 2p] binding energy difference can be used to distinguish N-bound from S-bound thiocyanate was based upon a very limited set of binding energy data. Nonetheless, their observation [14] that [N 1s–S 2p] is 0.6 eV greater for $[M(NH_3)_5(NCS)](ClO_4)_2$ than $[M(NH_3)_5(SCN)](ClO_4)_2$, where M = Rh or Ir, is in accord with some data of ours on the series of palladium(II) complexes $Pd(bipy)(NCS)_2$, $K_2Pd(SCN)_4$ and Pd(dppe)(SCN)(NCS). The S 2p spectra of the latter two complexes are shown in Fig. 1. The spectra of $Pd(bipy)(NCS)_2$ and $K_2Pd(SCN)_4$ reveal a well resolved S 2p doublet (fwhm = 1.9 ± 0.1 eV in each case) with [N 1s–S 2p] values of 236.1 and 235.4 eV, respectively. For the complex Pd(dppe)(SCN)(NCS), which possesses both N- and S-bound thiocyanate [25] and is the only mixed complex of this type to have been investigated by XPS, the S 2p spectrum is significantly broader (fwhm = 2.6 eV). It can be deconvoluted (Fig. 1) using the following parameters: a separation of 1.1 (±0.1) eV between the individual sets of S $2p_{1/2}$ and S $2p_{3/2}$ levels, fwhm values of 1.0 ± 0.1 eV for the spin–orbit components and S $2p_{1/2}$:S $2p_{3/2}$ peak intensity ratios of approximately 1.0:1.7 [26]. This procedure affords two sets of doublets whose energies (S $2p_{3/2}$ at 162.3 and 162.9 eV) and [N 1s–S 2p] values (235.9 and 235.3 eV, based upon a N 1s binding energy of 398.2 eV [13]) are consistent with N- and S-bound thiocyanate, respectively. The relative intensities of the two sets of S $2p_{1/2,3/2}$ peaks are slightly different, the higher energy doublet, arising from the S-bound thiocyanate, being the most intense of the two.

The larger values of [N 1s–S 2p] for the N-bound thiocyanate complexes of Rh(III), Ir(III) and Pd(II) compared to their S-bound analogs, is borne out, in a general way, for most of the complexes listed in the Table. While there is some overlap in the range of [N 1s–S 2p] values for M–NCS compared to M–SCN, the former are usually higher, *i.e.*, 236.7–235.0 eV, *versus* 235.6–234.3 eV.

While the preceding discussion could be considered to support the notion that the mode of thiocyanate bonding can be deduced from XPS measurements, we do not believe that his will, in general, be a reliable method. In contrast to the conclusions of Borghi *et al.* [14], the binding energy differences [N 1s–S 2p] for M–NCS and M–SCN do not have "fairly constant" values. Each occurs over a range of about 1.5 eV and there is overlap between the two sets of data. A particularly striking illustration of this is the similarity of [N 1s–S 2p] for $(Me_4N)_3Ru(NCS)_6$ to the corresponding values for $(Ph_4As)_3Os(SCN)_6$ and $K_3Rh(SCN)_6$ (see Table). Accordingly, any attempt to correlate the value of [N 1s–S 2p] with the mode of thiocyanate bonding should be treated with caution, *especially when the complex in question is one of unknown structure.* This is further demonstrated by the following observations on a variety of thiocyanate complexes which possess structures different from those considered previously by Borghi *et al.* [14].

(1) The copper(II) complexes [Cu(tren)(NCS)]SCN and [Cu(trien)(SCN)]SCN each contain two thiocyanate environments, yet both show a *single set* of well resolved S $2p_{1/2,3/2}$ doublets [13] and give no evidence for the presence of both inner and outer sphere thiocyanate. Furthermore, these two complexes possess essentially identical [N 1s–S 2p] values, thereby demonstrating the inability of XPS to distinguish Cu–NCS from Cu–SCN in these particular complexes. The coincidence of the S 2p energies of SCN^- with those of Cu–NCS and Cu–SCN is supported by XPS measurements on $[Cu(en)_2](SCN)_2$ [13], a complex which contains outer sphere thiocyanate [27]. Its S 2p energies [13] and [N 1s–S 2p] value (see Table) are the same as those of [Cu(tren)(NCS)]SCN and [Cu(trien)(SCN)]SCN. While Borghi *et al.* [14] had measured the XPS of $[Rh(en)_2(NCS)_2]SCN$, and apparently observed only one set of S 2p binding energies, they did not comment

upon the similarity between the S 2p energies of Rh–NCS and SCN$^-$.

(2) The two complexes in the Table which contain only bridging thiocyanate ligands, HgCo(NCS)$_4$ and [Cu(SCN)]$_n$, have [N 1s–S 2p] ≈ 235.0 eV, a value which is on the borderline between being "characteristic" of M–NCS and M–SCN. This observation thereby raises the problem of how to distinguish M–NCS–M from M–NCS or M–SCN in a complex *whose structure is not already known.* With the current level of instrumental resolution, we suggest that this will not be an easy task, a point which is emphasized by our recent studies on tertiary phosphine complexes of the type $(Bu_4N)_2Re_2(NCS)_8(L)_2$ [22], which contain both bridging Re–NCS–Re and terminal Re–NCS units.

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