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XPS Studies of some Metal Thionitrosyl Complexes: Correlation of the Binding Energies with Simple M. O. Theory

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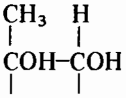
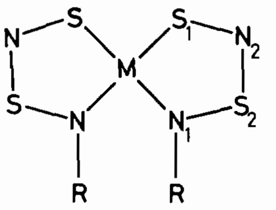
The X-ray photoelectron spectra of some transition metal thionitrosyl complexes have been measured. The binding energies of the metal core electrons confirm the expected formal oxidation state of +2 for the metal. The N(1s) and S(2p) binding energies are shown to correlate well with the calculated charge on the atom in question corrected by the effect of the Coulombic potential of the whole molecule upon the ionising electron.

Introduction

As part of an investigation of the preparation and physical properties of metal thionitrosyl complexes I* we have measured the X-ray photoelectron spectra (XPS) of four of these compounds, Ia–Id, which have been prepared [1] and characterized [2] in our laboratory. The platinum polysulphide complex, $(NH_4)_2PtS_{15}$, has also been included in our study. Bossa *et al.* [3] have recently reported the XPS of three similar complexes Ib, Ie and If.

	M	R
a.	Co	H
b.	Ni	H
c.	Pd	H
d.	Pt	H
e.	Ni	$Si(CH_3)_3$
f.	Ni	bridging  $-\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}OH-\overset{H}{\underset{\vert}{\overset{\vert}{C}}}OH$



I

Experimental

Details of the preparation, purification and characterization of the compounds will be reported elsewhere [1, 2].

XPS spectra were obtained by means of a Vacuum Generators VG-3 instrument equipped with an AlK_α source (1486.6 eV), at a resolution of 1 eV. The spectra were calibrated using the C(1s) peak of the pump oil (285.0 eV).

The spectra were digitised by means of a cartographic table and, after subtraction of the slopping baselines, they were deconvoluted using programmes written in this department.

Theoretical Considerations

The results obtained for the binding energies of the metal core, N(1s) and S(2p) electrons are recorded in Tables I, II and III respectively. The energies for the metal core electrons (Table I) are in good agreement with those previously reported [4] for these metals in a formal oxidation state of +2 (or +4 in the case of Pt^{IV}) and no further comment seems necessary.

TABLE I. The Metal Core Binding Energies (B.E.).

Compound	Orbital	B.E./eV
$Co(S_2N_2H)_2$	2p (1/2)	796.2
	2p (3/2)	781.0
$Ni(S_2N_2H)_2$	2p (1/2)	872.0
	2p (3/2)	854.8
$Pd(S_2N_2H)_2$	3d (3/2)	343.7
	3d (5/2)	337.6
$Pt(S_2N_2H)_2$	4f (5/2)	76.8
	4f (7/2)	73.7
$(NH_4)_2PtS_{15}$	4f (5/2)	77.9
	4f (7/2)	74.7

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*These complexes have also been termed thiazenes or dithiazenes. The IUPAC requirements are not satisfied by either of these names. Indeed, there seems to be no simple systematic name for these complexes.

TABLE II. The Ligand N(1s) Binding Energies (B.E.) and the Calculated Values of the Charge Density, q, and the Coulombic Energy, V.

No.	Compound		B.E./eV	$q/\lvert\text{electrons}\rvert$	V/eV	(kq + V)/eV^{a}
1	$Ni(S_2N_2H)_2$	N(1)	398.6	−0.52	10.11	−1.886
2		N(2)	400.0	−0.15	3.98	0.383
3	$Pd(S_2N_2H)_2$	N(1)	399.3	−0.52	11.46	−0.582
4		N(2)	401.3	−0.13	4.75	1.734
5	$Pt(S_2N_2H)_2$	N(1)	399.6	−0.54	11.06	−1.377
6		N(2)	401.4	−0.10	3.79	1.376
7	$PhNH_2$^{c}		398.6	−0.31	4.58	−2.613
8	$PhNO_2$^{c}		405.1	0.51	−7.29	4.543
–	$Co(S_2N_2H)_2$	N(1)	399.0	b	b	b
–		N(2)	400.6	b	b	b

^{a}k = 23.203 volts. ^{b}No calculations were possible for this complex since its geometry is unknown. ^{c}Literature data taken from references 6 and 8.

TABLE III. The Ligand S(2p) Binding Energies (B.E.) and the Calculated Values of the Charge Density, q, and the Coulombic Energy, V.

No.	Compound		B.E./Ev	$q/\lvert\text{electrons}\rvert$	V/eV	(kq + V)/eV^{a}	(k′q + V)/eV^{b}
1	$Ni(S_2N_2H)_2$	S(1)	163.7	−0.39	10.13	3.898	1.195
2		S(2)	166.1	0.15	0.57	2.960	3.994
3	$Pd(S_2N_2H)_2$	S(1)	164.5	−0.46	9.70	2.417	−0.741
4		S(2)	169.1	0.18	0.87	3.738	4.979
5	$Pt(S_2N_2H)_2$	S(1)	165.1	−0.34	9.30	3.923	1.592
6		S(2)	169.2	0.07	1.36	2.473	2.956
7	$(NH_4)_2PtS_{15}$	S(1)	164.8	−0.66	17.73	7.247	2.703
8		S(2)	164.8	−0.24	5.79	1.982	0.329
9		S(3)	164.8	−0.20	5.67	2.393	0.972
10	Sulphur		163.6	0.0	0.0	0.0	0.0
11	SOF_2^{d}		170.2	1.15	−11.08	7.213	15.143
12	SO_2^{d}		168.3	0.89	−8.93	5.227	11.365
–	$Co(S_2N_2H)_2$	S(1)	164.2	c	c	c	c
–			166.7	c	c	c	c

^{a}k = 15.907 volts. ^{b} k′ = 22.803 volts. ^{c}No calculations were possible for this complex since its geometry is unknown. ^{d}Literature data taken from references 6 and 11.

The N(1s) and S(2p) spectra, on the other hand, invite analysis in terms of the charge distribution in the various complexes, not only because this type of correlation has been widely reported in the literature [4] but, more importantly, on account of the light which such studies might throw upon the electronic structure and bonding of these compounds. However, although many such correlations have been reported they have been largely concerned with organic or simple, non-metal inorganic compounds and, by comparison, few attempts have been made to apply similar methods to the XPS of ligands attached to highly charged metal atoms in inorganic complexes.

The reasons for the lack of such studies are quite clear. The simplest of the literature methods for calculating charge density, q, is probably the use of Pauling's ionicity function [5]. For metal complexes difficulties arise because the metal electronegativities are not well defined. Furthermore, with thionitrosyl ligands numerous resonance forms are possible and a knowledge of the relative contributions of these structures is required for a successful application of this method [6].

The direct approach of a molecular orbital calculation founders upon the fact that the most well established semi-empirical methods, CNDO and INDO [7], are not parameterised for metal atoms whilst *ab initio* methods are not sufficiently widely available and/or too costly.

With these difficulties in mind, and in the light of the fact that the XPS of the metal core electrons indicate a formal charge of +2 on the thionitrosyl metal atoms, we have adopted the following approach to the correlation of our spectra with charge densities. Siegbahn *et al.* [8] have proposed that the binding energy B.E. of a core electron can be expressed in the form of equation (1). q is the charge on the atom from which the electron is removed, V is

$$\text{B.E.} = kq + V \qquad (1)$$

the Coulombic energy of the ionising electron in the field of the molecule and k is an empirical constant. Clearly, a very important part of B.E. will arise from the contribution to V of the highly charged metal atom and we have calculated this term assuming a charge of +2 (or +4 in the case of Pt^{IV}) on the metal atom. Values ranging from 9 to 15 eV are found. Values of q and contributions to V from the ligands were determined by means of a CNDO [7] calculation on the appropriate free ligand using geometries as found by X-ray crystallography [9]. In the case of the platinum thionitrosyl, where there appear to be substantial differences in the geometry of the two ligands [9b], calculations were carried out using both geometries. Interestingly, these calculations did not converge but a calculation using an average geometry did converge and those are the results used here. Indeed, for all complexes the average ligand geometry has been used.

It should be noted that, in principle, there will be contributions to V from other nearby molecules. Previous applications of equation (1) have been confined to gas phase samples for which neglect of such inter-molecular terms in V would seem to be quite justified. For our solid state samples the position is not quite so clear. However, calculations of the inter-molecular terms indicate that the total contribution to V from adjacent molecules is less than 0.5 eV, a figure comparable in magnitude with the overall accuracy of XPS measurements. We have therefore neglected these effects.

Results for Nitrogen (1s)

The results for N(1s) binding energies are summarized in Table II and Fig. 1. Data from the literature for aniline and nitrobenzene have been included in order to link our work with correlations involving organic molecules. Calculations of q, and hence V, for the cobalt complex could not be made because no crystal structure is available. However, it is clear from the measured binding energies that the compound is very similar to the nickel complex and the points for the two compounds would undoubtedly lie very close together on the graph.

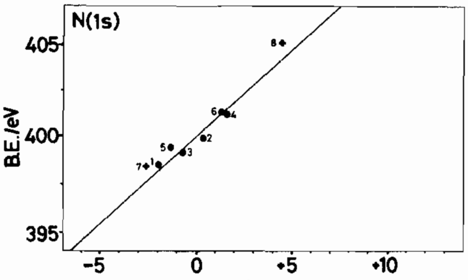

Fig. 1. The measured N(1s) binding energies plotted against kq + V. The numbers correspond to those given in Table II.

The excellent correlation of theory and experiment shown in Fig. 1 appears to justify our approach and it is particularly gratifying that the points for aniline and nitrobenzene fit on the line so well. Further discussion is postponed until the S(2p) results have been described.

Results for Sulphur (2p)

The case of the sulphur (2p) binding energies is not so clear cut. In order to obtain the parameter k a plot of B.E. – V against q was first made and in this case data for S_8, SOF_2 and SO_2, three compounds which fit well on a wide-ranging correlation constructed by Siegbahn [11], were included. It was at once apparent that there is considerable scatter of the points on this plot and that two straight lines might be drawn through them; one including all the points in Table III and one in which the thionitrosyls and S_8 only were included, and the points for SO_2 and SOF neglected. We denote the k value obtained from the second of these lines k′. The resulting plots of B.E. versus kq + V and versus k′q + V are shown in Figs. 2 and 3 respectively.

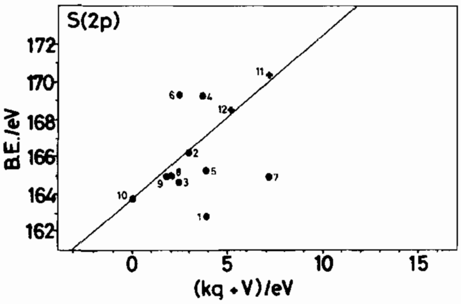

Fig. 2. The measured S(2p) binding energies plotted against kq + V. The numbers correspond to those given in Table III.

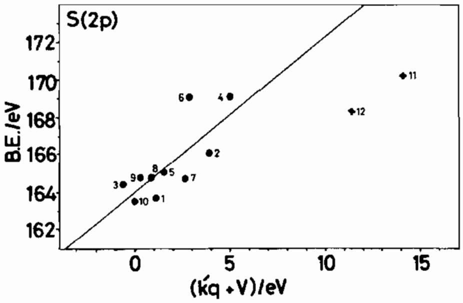

Fig. 3. The measured S(2p) binding energies plotted against k′q + V. The numbers correspond to those given in Table III. The points 11 and 12 are not included in the least squares fit (see text for the difference between k and k′).

Discussion

In Fig. 2 the points for S_8, SOF_2 and SO_2 lie on the least-squares line and it may therefore be said that this figure represents a correlation which would link up with that for a much wider range of sulphur compounds. However, the scatter of the points is large – standard deviation = 2.1 eV. In Fig. 3, on the other hand, the scatter of the thionitrosyl points is considerably reduced (standard deviation = 1.6 eV) but the least-squares line clearly deviates from that of a general S(2p) correlation. This is scarcely surprising in view of the great differences in the types of compound involved and, indeed, one might feel that the remarkable correlation in the case of the N(1s) data is the more surprising result.

Comparison of our results for N(1s) and S(2p) seems to indicate that where as the bonding of nitrogen in the thionitrosyl complexes does not differ markedly from that in simple organic and inorganic molecules, the bonding of sulphur is significantly different in the various types of compound. One might speculate that the presence of the metal and the essentially planar structure of the thionitrosyl complexes are much more favourable to sulphur 3d orbital involvement in bonding than are small molecules such as SO_2 and SOF_2 with their highly electronegative substituents. Such suggestions must, however, be considered very tentative.

On a more specific problem, it is of interest to compare our assignments of the N(1) and N(2) signals (Table II) with that proposed by Boassa *et al.* [3]. Our assignment arises naturally from our theoretical treatment while theirs is based upon the effect upon the binding energies of the substituents on the ligands. The two assignments disagree and clearly indicate the need for further work in this area.

In considering, in this context, the validity of our calculations we note that ours is essentially an ionic model; a point which has been made strongly by a referee and with which we agree. In adopting this over-simplified approach we were, of course, aware of its implications but thought it worthwhile on two grounds. Firstly, it is not uncommon for discussions of the electronic properties of transition metal complexes to be based upon calculations involving only the free ligands. Secondly, as we have already pointed out, it is very difficult to allow for covalency quantitatively in the absence of M.O. parameters for the metal atoms in question.

We believe that Figs. 1 and 3 demonstrate that useful correlations of experimental B.E.'s with theoretical parameters, calculated in the simple way which we have described, can be made, and that these relationships enable semi-quantitative conclusions about electronic structure and bonding in ligands to be drawn from their XPS spectra. Nevertheless, it is clear from the problem with the N(1s) spectra that our assignments cannot be considered as firmly established until more sophisticated calculations have been made.

Acknowledgements

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