Application of Electron Spectroscopy for Chemical Analysis to the Study of Ambidentate Binding in Sulfoxide Complexes

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A reliable method for determining the mode of binding of ambidentate sulfoxide ligands to metals has been developed based upon a novel application of ESCA. Relative differences between S $2p_{3/2}$ and O 1s ionization potentials show a characteristic separation for oxygen-bound and sulfur-bound sulfoxides.

Introduction

In the formation of metal–dialkyl sulfoxide complexes, the shift of the S–O stretching frequency to lower values on binding to oxygen and to higher values on binding to sulfur has been well established.[1-3] Although the S–O stretching mode generally gives rise to a distinct intense peak in the infrared spectrum, its location is often obscured or complicated by overlap or mixing with other bands such as C–H rocking modes.[4] This complication may become severe with large organic substituents. Moreover, when sulfoxides have a phenyl group bound directly to sulfur, the shift of the S–O stretch on complexation becomes so small that the determination of the binding site by infrared analysis is difficult or impossible.[5] We have measured the ionization potentials of electrons from inner shells of sulfur and oxygen in a series of sulfoxide complexes and found that they provide a straightforward means of distinguishing the mode of binding.

Results and Discussion

The ionization potentials of sulfur and oxygen electrons of some DMSO (dimethyl sulfoxide), DPSO (diphenyl sulfoxide), and DBSO (dibenzyl sulfoxide) complexes and their corresponding S–O stretching frequencies from infrared measurements are given in Table I. Infrared and X-ray crystallographic results have shown that most neutral platinum, palladium, and rhodium dialkyl sulfoxide complexes contain metal–sulfur, rather than metal–oxygen bonds. First-row transition metals favor oxygen-bonded sulfoxide. These complexes serve as models for known modes of binding and as such they may be used to test the method developed for analysis of the ESCA results.

Major factors affecting the ionization potentials of the inner orbitals of the ligand are (1) the mode of binding to the metal, *i.e.*, metal–sulfur or metal–oxygen binding, (2) the valence of the metal ion, and (3) the molecular geometry. Determination of the bonding site by directly comparing shifts of the S $2p_{3/2}$ ionization potentials is complicated by contributions from the latter two factors (as well as possible charging effects[6]), which mask straightforward correlations.

It is therefore convenient to simplify the interpretation of the shifts by considering the metal ion as a positive point

charge. The ionization potentials of orbitals in the ligand atoms nearest the metal will be most strongly influenced by the charge on the metal. On this basis, one should observe increasing positive shifts in inner shell ionization potentials with increasing oxidation state of the metal. Comparison of our observed shifts relative to the free ligand agree with this assumption, except for certain Cu(II) compounds, the results of which will be discussed in detail subsequently.

In order to obtain a parameter which would be independent of metal oxidation state but which would reflect the proximity to the metal atom, we have considered relative differences. The difference (O 1s – S $2p_{3/2}$) between the O 1s and the S $2p_{3/2}$ ionization potential of each compound appears to be the most characteristic parameter of the binding mode. This follows from

$$(\text{O } 1s - \text{S } 2p_{3/2}) = (\text{O } 1s_c - \text{O } 1s_f) + (\text{O } 1s_f - \text{S } 2p_{3/2f}) +$$
$$(\text{S } 2p_{3/2f} - \text{S } 2p_{3/2c})$$

where c refers to the complex and f to the free ligand. Since (O $1s_f$ – S $2p_{3/2f}$) is constant for a given sulfoxide, the observed value for (O 1s – S $2p_{3/2}$) depends upon the mode of binding of the ligand to metal. It is clearly shown in Table I that a sulfur-bound complex has a (O 1s – S $2p_{3/2}$) relative shift of ~365.0 eV while an oxygen-bound complex has a relative shift ~365.8 eV. These characteristic values generally hold for the dialkyl sulfoxide complex and are also observed in the Pd(DMSO)$_4{}^{2+}$ cation, which contains both oxygen-bound and sulfur-bound sulfoxides. Figure 1 further illustrates the deviations with sulfur IP but correlation with relative shift.

Similarly, both benzyl and phenyl analogs have been subjected to the same method of analysis. The benzyl derivatives follow the methyl analogs closely; whereas the phenyl derivatives HgCl$_2$·DPSO and CdCl$_2$·DPSO show some unusual features. The O 1s ionization potential is shifted significantly to higher values compared to the free ligand indicating a substantial decrease in charge on the oxygen, whereas the sulfur IP is shifted to slightly lower values on complexation, indicating a slightly more negative sulfur atom. This possibly reflects the ability of the phenyl groups to compensate for loss of electron density at sulfur. As a result, the relative shifts for HgCl$_2$·DPSO and CdCl$_2$·DPSO are exceptionally large.[7] Because of the substantially large difference it would appear that oxygen binding could be assigned with confidence.

(1) F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, **82**, 2986 (1960).

(2) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Amer. Chem. Soc.*, **82**, 6013 (1960).

(3) For a review, see J. Gopalakrishnan and C. C. Patel, *J. Sci. Ind. Res.*, **27**, 475 (1968); W. L. Reynolds, *Progr. Inorg. Chem.*, **12**, 1 (1970).

(4) R. S. Drago and D. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

(5) For example, see J. Gopalakrishnan and C. C. Patel, *Inorg. Chim. Acta*, **1**, 165 (1967). Previous attempts to examine effects on other ligands bound to metals by ESCA have appeared. For example, see W. E. Morgan, W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971), and references therein.

(6) Since the sample is an insulator which is in contact with a conducting support, a charge can develop due to the loss of electrons from the sample which may produce an offset in the measured potential. The observed ionization potential of each element should be shifted the same amount; hence the relative shifts between two elements in the same molecule should not be significantly affected by the charging phenomena. The use of an electron flood gun, however, appears to minimize the charging problem.

Table I

	S $2p_{3/2}$, eV	O 1s, eV	(O 1s – S $2p_{3/2}$), eV	Mode	$\nu(SO)$,[m] cm^{-1}
$NiCl_2 \cdot 3DMSO$	165.0	530.9	365.9	O	(940)[a] (992, *1037, 1000*)[b] (1004, 999)[c]
$CoCl_2 \cdot 3DMSO$	165.0	531.0	366.0	O	(950)[a] (1002, *994*)[b] (999)[c]
$MnCl_2 \cdot 3DMSO$	165.1	530.9	365.8	O	(950)[a] (1004)[b]
$ZnCl_2 \cdot 2DMSO$	165.4	531.1	365.7	O	(952)[a]
$CuCl_2 \cdot 2DMSO$	164.7	530.4	365.7	O	(923)[a] (980, 987)[c]
$CdCl_2 \cdot DMSO$	165.1	530.7	365.6	O	(950)[a] (991)[c]
$HgCl_2 \cdot DMSO$	165.6	531.4	365.8	O	(1005, 1030)[c]
$SnCl_2 \cdot 2DMSO$	165.3	531.0	365.7	O	(920)[d]
$PtCl_2 \cdot 2DMSO$	165.6	530.5	364.9	S	(1157, 1134)[a] (~1110)[c] (1135, 1160)[e]
$Pd(DMSO)_4(BF_4)_2$	165.9	530.9	365.0	S	(1150, 1140, 920, 905)[f]
	165.1	530.9	365.8	O	(1150, 1140, 920, 905)[f]
$PdCl_2 \cdot 2DMSO$	165.5	530.6	365.1	S	(1120)[a] (1118)[c] (1116)[e] (1115)[g]
$AlCl_3 \cdot 6DMSO$	165.7	531.4	365.7	O	(1009)[c]
$FeCl_3 \cdot 2DMSO$	165.3	531.2	365.9	O	(933)[a] (981, 988)[c]
$RhCl_3 \cdot 3DMSO$	166.0	531.2	365.2	S	(1130, 1145)[g]
$SnCl_4 \cdot 2DMSO$	165.6	531.3	365.7	O	(915)[a] (907, 919)[h] (920, 905)[g]
$Sn(CH_3)_2Cl_2 \cdot 2DMSO$	164.4[h]	530.5[h]	366.1	O	(945) (944)[h]
DMSO	164.6[h]	529.9[h]	365.3		(1060)[j] (1055)[e]
$Sn(CH_3)_2Cl_2 \cdot DBSO$	164.6	530.8	366.2	O	(985)[e] (996, *986*)[i]
$ZnCl_2 \cdot 2DBSO$	165.0	530.8	365.8	O	(955, 966, 987)[g]
$SnCl_2 \cdot 2DBSO$	164.8	530.6	365.8	O	(1027, 1031)[g]
$PtCl_2 \cdot 2DBSO$	165.0	529.9	364.9	S	(1133, *1123*) (1150)[e]
$Pd_2Cl_4(DBSO)_2$	165.5	530.6	365.1	S	(1120, 1130, 1177)[e]
DBSO	163.7[h]	529.2[h]	365.5		(1026) (1030)[e] (*1038, 1028*)[g]
$SnCl_2 \cdot 2DPSO$	165.0	530.7	365.7	O	(934, 925) (975, 950)[d]
$ZnCl_2 \cdot 2DPSO$	165.4	531.2	365.8	O	(995)[g]
$CdCl_2 \cdot DPSO$	164.4[h]	530.8[h]	366.4	O	(1045–1050)[l]
$HgCl_2 \cdot DPSO$	164.2[h]	531.1[h]	366.9	O	(1045–1050)[l]
$PdCl_2 \cdot 2DPSO$	165.5	530.8	365.3	S	(1050)[l]
DPSO	164.6[h]	529.9[h]	365.3		(1045)[l]

[a] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, 64, 1534 (1960). [b] D. W. Meek, D. K. Straub, and R. S. Drago, *J. Amer. Chem. Soc.*, 82, 6013 (1960). [c] J. Selbin, W. E. Bull, and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, 16, 219 (1961). [d] J. S. Morrison and H. M. Heandle, *ibid.*, 29, 393 (1967). [e] W. Kitching, C. J. Moore, and D. Doddrell, *Inorg. Chem.*, 9, 541 (1970). [f] B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 8, 971 (1969). [g] This work. [h] H. G. Langer and A. H. Blut, *J. Organometal. Chem.*, 5, 288 (1966). [i] M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 3224 (1961). [j] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 82, 2986 (1960). [k] Low-temperature spectra. [l] J. Gopalakrishnan and C. C. Patel, *Inorg. Chim. Acta*, 1, 165 (1967). [m] Italic values of SO stretching frequencies are solution values. All others are for Nujol mulls.
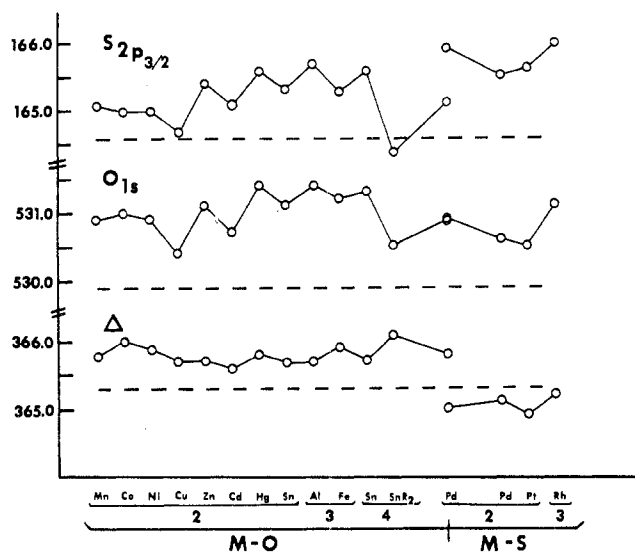

Figure 1. Ionization potentials of some sulfoxide complexes. Formulas for the complexes may be found in Table I.

However, this assignment differs from that based on infrared data.[5]

The SO stretching frequency of diphenyl sulfoxide shows very little change upon coordination with palladium. The

(O 1s – S $2p_{3/2}$) relative shift in $PdCl_2 \cdot 2DPSO$ is smaller than that of $HgCl_2 \cdot DPSO$, $CdCl_2 \cdot DPSO$, and other oxygen bound complexes; thus, the ESCA results suggest that it is sulfur bound. This small shift for the palladium complex also provides further complementary support for assigning the oxygen-bound mode to the mercury and cadmium complexes.

Conclusion

We have generally considered only two modes of binding and have shown that the ESCA data can be used to distinguish between these alternatives; however, other alternatives such as polymeric species or special cases should be considered.[8] The ESCA results for $Sn(CH_3)_2Cl_2 \cdot 2DMSO$ and $CuCl_2 \cdot$ 2DMSO indicate oxygen binding in agreement with the implications of infrared spectra. The ionization potentials of the sulfur and oxygen in these compounds are lower than in other oxygen-bound compounds when one considers their oxidation states. An X-ray study has indicated that the Sn–O distance in the tin complex is 2.36 Å and the structure is a distorted cis octahedral monomer.[9] This Sn–O distance is considerably longer than that in similar tin compounds (*i.e.*, 2.10 Å[10]) and longer than the Fe–O of $FeCl_3 \cdot 2DMSO$ (*i.e.*,

(7) These complexes sublime readily, such that low temperatures are required to obtain the ESCA spectra. Samples were prepared by sublimation onto a cold probe (appropriate metal to ligand intensities were observed); however, we suspect that the data may be less accurate.

(8) One might speculate that octahedra sharing oxygen atoms could be responsible for similar relative shifts. We have noted that sulfur-bonded sulfoxide complexes can be distinguished by the interaction of the free oxygen with a lanthanide metal ion in shift reagents; thus, in certain circumstances one may observe sulfur binding to one metal and oxygen binding to another.

(9) N. W. Isaacs, C. H. Kennard, and W. Kitching, *Chem. Commun.*, 820 (1968).

(10) E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967).

2.00 Å[11]). The longer metal–oxygen distance reflects the decreasing effect of the charge on the metal implied by the ionization potentials. Holah and Fackler[12] have suggested that coordination about the copper atom in CuCl$_2$·2DMSO is octahedral in the solid on the basis of reflectance spectra and X-ray powder data. The unusual ionization potentials might suggest polymerization involving the sulfoxide, but probably reflect the long Cu–O bonds expected for Jahn–Teller distortions in octahedral copper complexes.[13]

We believe the analysis of relative shifts in ionization potential provides a viable method for distinguishing the mode of binding in ambidentate sulfoxides. The great advantage of the ESCA method lies in its theoretical simplicity and absence of ambiguity in peak assignments found with infrared spectra. We anticipate that this method will be widely applicable in the determination of binding mode with other ambidentate ligands.

Experimental Section

All of the compounds were prepared as described in the references indicated in Table I, with the exception of ZnCl$_2$·2DBSO and SnCl$_2$·2DBSO, which were prepared in the same manner as the DPSO analogs. Peak ratios of Cl 2p to S 2p IP's were measured in most compounds to confirm their stoichiometry. A Perkin-Elmer 421 infrared spectrophotometer was used to record and check the ir spectra for the compounds to ensure their identity and purity.

The ionization potentials (IP's) were recorded using a Hewlett-Packard 5950A ESCA spectrometer equipped with a monochromatized aluminum X-ray source, a variable-temperature probe, and an electron flood gun. Methylene chloride solutions of the compound were sprayed onto a gold-plated sample holder evaporated to leave a thin layer. The IP values were generally recorded at room temperature and calibrated relative to the Au 4f$_{7/2}$ of the sample holder assumed

to be at 83.0 eV.[14] The spectrometer is capable of a precision and reproducibility of ±0.01 eV. The use of relative shifts avoids the problems with uncertainties in absolute accuracy (±0.1 eV). Full widths at half-height were between 1.1 and 1.4 eV for S 2p$_{3/2}$ and between 1.3 and 1.6 eV for O 1s. All IP's were determined with at least two separate samples. Those showing unusual features were checked with at least four samples. Certain volatile compounds as indicated in Table I were maintained at temperatures below −100° during the recording of the spectra. The flood gun, which compensates for the charging of the sample by neutralizing the charge with a stream of electrons, was operated between 0.1 and 0.3 mA. In most cases the IP's shifted less than 0.2 eV to smaller values when applying the flood gun. The relative shifts from atoms in the same molecule did not change.

Although the approximate separation was evident in the spectrum of Pd(DMSO)$_4$(BF$_4$)$_2$, accurate IP's were obtained by deconvolution of the two S 2p$_{3/2}$ and two S 2p$_{1/2}$ peaks using the program CATACALE and a PDP-12 computer.

(11) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Crystallogr.*, **23**, 581 (1967).

(12) D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, **4**, 1721 (1965).

(13) We are currently pursuing the possibility that "long" bonds may be conveniently characterized by analysis of ESCA spectra.

(14) A value of 82.8 eV has been used by some workers based upon the studies of J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 125 (1967).

Nucleophilic Substitution on Nitrogen. Kinetics of Reactions of Hydroxylamine-*O*-sulfonic Acid in Dimethyl Sulfoxide–Water Solvents
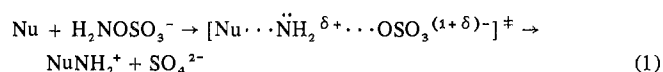
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The kinetics of reactions of iodide and triphenylphosphine with hydroxylamine-*O*-sulfonic acid have been examined in dimethyl sulfoxide–water solvents. The reactions involve nucleophilic substitution on nitrogen with sulfate as the leaving group. For triphenylphosphine, rate = k_2[H$_2$NOSO$_3$$^-$][(C$_6H_5$)$_3$P] and for iodide, rate = k_{OS}[H$_2$NOSO$_3$$^-$][I$^-$] + k_{HOS}·[H$_3$NOSO$_3$][I$^-$], with the observed second-order rate constants decreasing markedly on going from 0 to 1.00 mole fraction of dimethyl sulfoxide in the solvent. This solvent effect on rate suggests that, for reaction of H$_3$NOSO$_3$, protonation occurs on nitrogen, with SO$_4$$^{2-}$ rather than HSO$_4$$^-$ as the leaving group. In 0.96 mole fraction of dimethyl sulfoxide, the reaction of H$_3$NOSO$_3$ with iodide is accelerated by added perchloric acid. The iodide dependence of the hydrogen ion dependent pathway is interpreted in terms of a dissociative process, involving either NH$_3$$^{2+}$ or an NH$_3$$^{2+}$,OSO$_3H^-$ ion pair as an intermediate, which occurs in competition with direct attack on H$_3$NOSO$_3$H$^+$.

Introduction

As part of a study of nucleophilic substitution at trivalent nitrogen, we have reported the kinetics of reactions of a variety of soft-base nucleophiles with hydroxylamine-*O*-sulfonate ion, H$_2$NOSO$_3$$^-$, in water.[2,3] These reactions are thought to proceed by direct attack on the nitrogen center

$$\text{Nu} + \text{H}_2\text{NOSO}_3^- \rightarrow [\text{Nu}\cdots\overset{..}{\text{N}}\text{H}_2{}^{\delta+}\cdots\text{OSO}_3{}^{(1+\delta)-}]^{\ddagger} \rightarrow$$
$$\text{NuNH}_2^+ + \text{SO}_4{}^{2-} \qquad (1)$$

(2) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973).

(3) P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, **13**, 719 (1974).

(1) NDEA Fellow 1971–1973.