

An X-ray Photoelectron Spectroscopy Study of a Series of Manganese Complexes Containing Schiff Base Ligands

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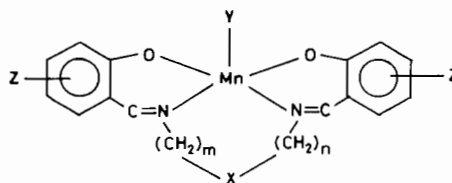
Core binding energies for a series of manganese complexes derived from Schiff-base ligands prepared by condensing various salicylaldehyde derivatives with a variety of polyamines have been measured. The Mn $2p_{1/2,3/2}$ binding energies are relatively insensitive to changes in ligand substituent, ligand donor groups and oxidation state of Mn. Pentadentate and tetradentate ligands have been employed. Formal oxidation states for manganese range from +1 to +4. Manganese $3s_{1/2}$ multiplet splitting gives good agreement with expected trends caused by changes in manganese oxidation state.

Introduction

The involvement of manganese and oxygen in a variety of chemical [1–3] and biochemical [4, 5] processes has been widely theorized. As a consequence of these predictions, considerable interest [6–11] has been generated concerning the nature of the products produced upon allowing simple manganese(II) complexes to react with molecular oxygen. The large number of obtainable oxidation states of manganese and oxygen (*i.e.* singlet and triplet O_2 , superoxide, peroxide and oxide) coupled with numerous modes of Mn–O interaction (*i.e.* mononuclear, dinuclear monobridged and dibridged, polymeric, *etc.*) create enormous problems concerning characterizing these interesting materials. Since most of the compounds [12] prepared to date are powders and have the same Mn:O ratio, X-ray photoelectron spectroscopy (XPS) offers much potential toward gaining a better understanding of the manganese-oxygen interaction in that the electronic environment at the manganese and oxygen can be monitored before and after oxygenation.

We wish to describe the results of a XPS study regarding the oxygen complexes of manganese

chelates derived from salicylaldehyde and its derivatives with ethylenediamine [13–17] and various triamines [18–20], Structure I. A preliminary account of these findings has been previously reported [21]. Electrochemical studies via cyclic voltammetry have shown the reduction potentials for manganese to be quite sensitive to changes in substituents on the aromatic portion of the ligand and number of donor groups. The present study will describe the sensitivity of manganese binding energies to these changes as well as to changes in oxidation states of manganese with a common ligand environment.



R	m	n	X	Name
H	1	1	not present	SALEN
H	3	3	not present	SALHXDA
H	1	2	not present	SALTM
H	3	3	N–H	ZSALDPT
CH ₃	3	3	N–CH ₃	ZSALMeDPT

Y = NCS⁻; Z = H, 5-NO₂, 3-NO₂, 5-CH₃O, 3-CH₃O

Structure I

Experimental

Manganese(I), manganese(II), manganese(III) and manganese(IV) complexes were synthesized and characterized by methods which have been described [22–24].

Samples for XPS were prepared by mounting the solid sample in powder form to the probe by means of double stick tape. The binding energies of all electrons are reported relative to the instrumental

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TABLE I. Manganese 2p Binding Energies.

Oxidation State	Complex	Binding Energy (eV)	
		2p _{1/2}	2p _{3/2}
IV	[Mn(SALHXDA)] ₂ O ₂	652.8	641.4
	[Mn(SALTM)] ₂ O ₂	652.8	641.0
	[Mn(SALEN)] ₂ O ₂	652.6	641.4
III	[Mn(3-CH ₃ OSALDPT)]NCS	652.6	640.7
	[Mn(5-CH ₃ OSALDPT)]NCS	652.8	640.5
	[Mn(3-NO ₂ SALDPT)]NCS	652.4	640.7
	[Mn(5-NO ₂ SALDPT)]NCS	652.8	640.6
	[Mn(5-NO ₂ SALDPT)] ₂ O ₂	652.9	640.8
II	Mn(5-NO ₂ SALDPT)	652.4	640.3
	Mn(3-NO ₂ SALDPT)	652.4	640.3
	Mn(SALEN)	652.0	641.4
	Mn(SALHXDA)	653.2	641.3
I	[Mn(5-NO ₂ SALDPT)]NO	652.4	640.5
	[Mn(5-NO ₂ SALDPT)]NO	652.6	640.2

background carbon (1s_{1/2}) photopeak taken to have a value of 284.0 eV. Each level reported was measured at least twice. Reported values have a standard deviation of 0.2 eV or less.

XPS spectra were measured on a DuPont Model 650B electron spectrometer utilizing a magnesium anode (MgK_α = 1253.6 eV). The pressure in the analyzer region was less than 10⁻⁶ torr during all measurements.

Results and Discussion

XPS of Manganese(II) and Manganese(III) Complexes

Manganese binding energies for both the 2p_{1/2} and 2p_{3/2} levels in each complex are tabulated in Table I. The complexes are grouped according to formal oxidation states of the metal. Several authors [25, 26], have observed that a one electron oxidation of many metal complexes has often resulted in an increase in metal BE of approximately 1 eV. Most metals have been observed to exhibit this trend. Table I, however, offers the ready assessment that over a range of ligands as well as formal oxidation states there is little change in the 2p binding energies of manganese. The only exception is found within the Mn(II) complexes. A decrease of about 1 eV is observed in going from a 4-coordinate complex to a 5-coordinate complex. This is consistent with the

idea that an increase in coordination number of manganese increases the electron density at the metal lowering the binding energy of core electrons. Other than this single case there is little evidence that (1) changes in electron donating or withdrawing groups on the ligand, (2) changes in coordinated anion in the case of Mn(III) (O₂²⁻ or NCS⁻), or (3) changes in oxidation state of the metal result in changes in the binding energy of 2p electrons on manganese. This strongly suggests that there exists a very efficient mechanism for the redistribution of electron density through the ligand-metal system of this type of compound or an interpretation based on ground state charge distributions is not valid. This finding is in marked contrast to the findings of electrochemical studies [18–20] on both Mn(II) and Mn(III) complexes of the same and related types. For instance, using Mn(SALDPT)NCS and its substituted derivatives, Coleman *et al.* [20] showed that electron withdrawing groups such as -NO₂ or -Cl exhibited peak potential (E_p) values significantly anodic to those with electron-donating (ΔE_p = +0.389 V) groups such as CH₃ or OCH₃. The differences in the XPS binding energy and electrochemical data very likely lie in the fact that the XPS data were obtained on solid state samples while the electrochemistry was of necessity performed in solution. One would infer that a highly associated structure in the solid state allows 'communication' between individual

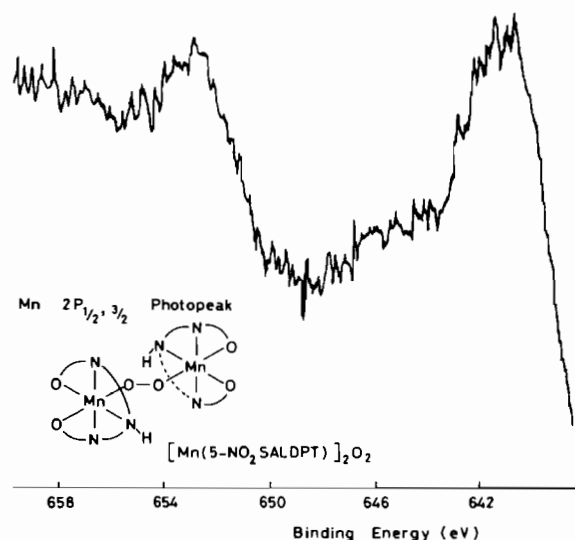


Fig. 1. Mn2p Photopeak Region for $[\text{Mn}(5\text{-NO}_2\text{-SALDPT})]_2\text{O}_2$.

molecules; whereas, in solution each complex molecule is surrounded by its own solvated domain.

Satellite structure is present but not well resolved in the Mn $2p_{3/2,1/2}$ spectra (Fig. 1) and appears as high energy shoulders on each photopeak. The separation between the $2p_{3/2}$ and $2p_{1/2}$ levels varies among the complexes by about 2 eV, however, there is no consistent trend indicating that while multiplet splitting may be present there is no consistent variation with formal oxidation state of manganese.

Manganese(IV) Complexes

Manganese $2p_{1/2,3/2}$ binding energies for the Mn(IV) compounds are of the same magnitude as for the Mn(II) and Mn(III) complexes. Structural changes do not cause any significant variation in the Mn 2p binding energies and again contrasts with trends observed in previous studies. Titus *et al.* [16] have shown that increasing the length of the methylene chain joining the imine donors in the ligand increases the general reactivity of these complexes toward oxygen. Addition of an electron withdrawing group to the aryl part of the ligand decreased the reactivity with O_2 . These authors have proposed a polymeric structure with di- μ -oxo bridges between Mn(IV) centers. This high degree of association would certainly provide an adequate mechanism for charge equalization (hence binding energy equalization) within the polymer lattice. XPS support for this view comes from the fact that there is no evidence for the presence of O_2^{2-} ions in the O 1s spectra but rather a broad (FWHM 3.5 V) emission envelope (with maximum at about 531 eV) characteristic of all the complexes. In the case of $[\text{Mn}(\text{SALEN})]_2\text{O}_2$, attempts to deconvolute the O $1s_{1/2}$

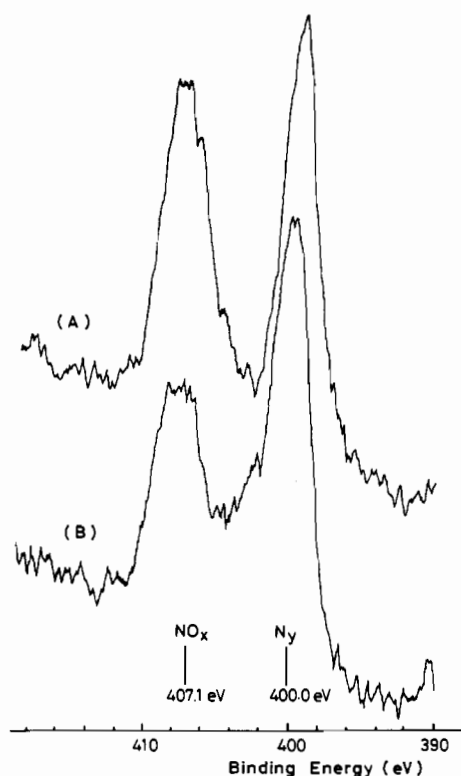


Fig. 2. Nitrogen Photopeak Region for $[\text{Mn}(\text{SALMeDPT})]\text{-NO}$: a) Initial Spectrum. b) After Exposure to X-Rays for 15 minutes.

peak were unsuccessful. In particular, assigning peaks for each kind of oxygen as in the cobalt-oxygen complexes [13] did not produce a good (or even reasonable) fit to the experimental peak. Attempts to deconvolute the peak by assuming a poly catenaxo structure or a di- μ -oxo structure were also unsuccessful.

Manganese(I) Complexes

Two manganese(I)-nitrosyl complexes are included in this study. $[\text{Mn}(5\text{-NO}_2\text{SALDPT})]\text{NO}$ is much less stable with respect to photodecomposition in the X-ray beam than in $[\text{Mn}(5\text{-NO}_2\text{SALMeDPT})]\text{NO}$. Both of the complexes extensively decompose presumably by the evolution of NO gas under the high vacuum of the spectrometer [22]. This is evidenced by the observation that both compounds revert to a yellow color characteristic of the Mn(II) complexes after a time at high vacuum. Mn $2p_{1/2,3/2}$ binding energies do not change with time during the decomposition process and have values which are very nearly the same as for the other complexes in this study.

The decomposition process is best monitored by observing the N $1s_{1/2}$ photopeak area for $[\text{Mn}$ -

TABLE II. Mn 3s Binding Energy (eV) vs. Manganese Oxidation State.

Oxidation State	Complex	Binding Energy	Δ BE
IV	[Mn(SALHXDA)] ₂ O ₂	88.4, 82.6	5.8
	[Mn(SALTM)] ₂ O ₂	88.3, 83.0	5.3
	[Mn(3-CH ₃ OSALDPT)] ₂ O ₂	88.7, 82.6	6.1
	[Mn(SALEN)] ₂ O ₂		
III	[Mn(5-NO ₂ SALDPT)]NCS	88.0, 82.4	5.6
	[Mn(5-NO ₂ SALDPT)] ₂ O ₂	87.7, 81.9	5.8
II	Mn(5-NO ₂ SALDPT)	87.9, 81.5	6.4
	Mn(3-NO ₂ SALDPT)	88.1, 82.1	6.0
	Mn(SALEN)	88.7, 82.3	6.6
	Mn(SALHXDA)	88.6, 82.5	
I	[Mn(5-NO ₂ SALDPT)]NO	82.0	0
	[Mn(5-NO ₂ SALMeDPT)]NO	82.4	0

Fig. 3. Manganese 2p Photopeak Region for KMnO₄.

(SALMeDPT)]NO over a period of time. The N 1s_{1/2} emission lines consist of a peak at 407.1 eV and one at 400.0 eV. The high energy peak may be assigned to the nitro portion (NO_x) of the complex consisting of the NO₂ moiety and (NO)⁺. The low energy line may be attributed to the other nitrogen (N_y) donors in the ligand, *i.e.*, -C=N- and -N(CH₃)-. Initially (Fig. 2a) the ratio of the areas of these two photo-

peaks, A_{N_y}:A_{NO_x}, is 1.13:1.00. This is in close agreement with the stoichiometric 1 to 1 ratio for the nitrosyl complex. After 15 minutes exposure to X-rays (Fig. 2b), this ratio has risen to 1.9 to 1 indicating a loss of NO_x nitrogen. This 1.9:1 ratio remains constant during further irradiation. It is possible to observe this sort of decomposition in the spectrometer for other manganese compounds. Figure 3 shows the Mn 2p_{3/2} region for KMnO₄ shortly after the sample has been exposed to X-rays. The photopeak at 645 eV which is due to the MnO₄⁻ ion can be observed to decrease with exposure time coupled with a simultaneous increase in the intensity of the photopeak at 642 eV which is due to manganese in a lower oxidation state (unidentified at the present time).

An increase in oxidation state as indicated previously was expected to increase the binding energy for manganese. In fact, Oky and Hirokawa [27] observed about 1 eV increases in the 2p binding energies in various manganese oxides for each unit increase in formal oxidation state of the metal. This suggests that one or more factors in the case of the substituted salicylaldehyde ligands tends to offset the expected changes in binding energy. For instance high spin Mn(II) would be expected to be more ionic than high spin Mn(III), *e.g.* the higher metal charge results in greater ligand to metal covalency. The process of going from Mn(II) to Mn(III) involves removal of an electron from a sigma antibonding molecular orbital. This allows the ligands to draw in closer to the metal thereby neutralizing the increase in charge arising from oxidation. In the case of the Mn(I)-nitrosyl com-

plex, accessibility of empty antibonding orbitals on the NO^+ moiety greatly facilitates the flow of charge away from Mn(I) thus raising the apparent Mn binding energy.

Multiplet Splitting of the Mn 3s Level

Paramagnetic atoms, in particular the transition metals, exhibit multiplet splitting caused by interaction of unpaired electrons in outer shells with an unpaired electron left behind after the ejection of a photoelectron. This interaction should, of course, be approximately zero for diamagnetic compounds. For first row transition metals the 3s level is usually studied because (1) there are only 2 possible states (neglecting configuration interaction) and (2) the splitting is greatest when the two subshells are in the same principal quantum shell. For a given ligand the variation in experimental values for multiplet splitting follows closely the number of unpaired 3d electrons with the greatest splitting occurring with 5 unpaired electrons [28].

Mn $3s_{1/2}$ binding energies and splitting values are found in Table II. It is not possible to follow one ligand through all four oxidation levels, however, it is easily seen that the expected trend is present. For instance the splitting for $[\text{Mn}(\text{SALHXDA})]_2\text{O}_2$ (Mn(IV) d^3 , 3 unpaired electrons) is 5.8 eV; while, for $[\text{Mn}(\text{SALHXDA})]$ (d^5 , 5 unpaired electrons) the value is 6.1 eV. $[\text{Mn}(5\text{-NO}_2\text{SALDPT})]\text{NCS}$ (d^4 , 4 unpaired electrons) is 5.6 eV; while, for $[\text{Mn}(5\text{-NO}_2\text{-SALDPT})]$ (d^5 , 5 unpaired electrons) the splitting is 6.4 eV. It would be difficult to rationalize differences in compounds where ligand and oxidation state have both changed; however, there is observed a general increase of about 1–1.5 eV as oxidation state of Mn decreases from four to two. In $[\text{Mn}(5\text{-NO}_2\text{-SALDPT})]\text{NO}$ and $[\text{Mn}(5\text{-NO}_2\text{SALMeDPT})]\text{NO}$ the Mn has a formal +1 (d^6) oxidation state. Complexes of this type have been shown to be diamagnetic ($\mu_{\text{eff}} < 0.2$ B.M.) [22]. XPS of this compound produces initially an unsplit $3s_{1/2}$ photopeak which upon prolonged exposure to X-ray and/or vacuum splits into a doublet of 6.0 eV separation. This suggests that the complex loses coordinated NO with time and the compound reverts to the paramagnetic Mn(II) precursor complex.

In conclusion, interpretation of the $2p_{1/2,3/2}$ electron binding energies of manganese in complexes using SALEN and related chelates is not as straightforward as for similar cobalt complexes [29]. Aside from an approximate 1 eV change in going from 4-coordinate to 5-coordinate Mn(II), the BE values are insensitive to changes in ligand substituent and manganese oxidation state. Multiplet splitting of the Mn $3s_{1/2}$ level agrees with expected trends in oxidation state as observed in other transition metal systems.

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