An X-Ray Photoelectron Spectroscopic Study of Cobalt(II) Schiff Base Complexes and Their Oxygenation Products[1,2]

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Abstract: A series of μ-peroxo and superoxo complexes of cobalt Schiff base compounds has been studied by X-ray photoelectron spectroscopy. The binding energies of cobalt core electrons have been shown to be dependent on the nature of the Schiff base ligand which is coordinated to the cobalt ion. Co $2p_{3/2}$ binding energies increased by 0.9-1.9 eV when the Co(II) complexes were oxygenated, indicating that the oxygenation process can be described by an oxidative addition type of interaction between oxygen and cobalt. This description is also supported by a comparison between the Co $2p_{3/2}$ binding energies in the cobalt-oxygen complexes and in some structurally similar cobalt(III) complexes. Deconvolution of the O $1s_{1/2}$ peak from the dioxygen complexes has shown that superoxo oxygen atoms exhibit a $1s_{1/2}$ binding energy approximately 1 eV higher than that found for μ-peroxo oxygen atoms.

The oxygenation of cobalt(II) complexes has yielded to date reversible and irreversible 1:1 and 2:1 (Co:O_2) dioxygen adducts.[3] The reaction whereby these materials are formed is generally believed to be an oxidative addition wherein the cobalt ion is oxidized to a certain extent which is dependent on the electronic nature of a given cobalt(II) precursor.[4-8] Since the technique of X-ray photoelectron spectroscopy (XPS) has been used to describe the electronic environment in a large number of transition metal complexes,[9] an investigation using XPS seemed appropriate for the study of charge distribution in cobalt complexes and their corresponding dioxygen adducts. It was expected that correlations could be made between cobalt and oxygen core-electron binding energies and parameters such as the extent of electron delocalization between cobalt and oxygen, reversible vs. irreversible behavior, and the differences, if any, between μ-peroxo and superoxo complexes. The only previously reported[10] XPS study of cobalt-dioxygen complexes has dealt with the binding energies of Co(bzacacen)[11] and Co(bzacacen)O_2py evaporated from methanol and pyridine, respectively. The investigators noted a binding energy increase accompanying oxygenation but it was pointed out that the Co(bzacacen) probably contained a Co(III) impurity.

We have undertaken a systematic study of the electronic charge distribution in a series of four-coordinate and five-coordinate cobalt(II) complexes and their oxygenation products, as well as some structurally similar cobalt(III) complexes. The results of this investigation present unambiguous evidence that the cobalt(II) ion is oxidized during the oxygenation process. Although the transfer of an electron from cobalt to dioxygen might not be 100% complete in the adducts which have been investigated, our results clearly show that the dioxygen adducts should *not* be formulated as complexes in which a cobalt(II) ion is bound to singlet oxygen.[12]

Experimental Section

The cobalt(II) complexes were prepared by previously reported[13-19] procedures and were characterized by means of elemental analyses, infrared spectra, and magnetic susceptibility determinations. Agreement with literature data was good.

The cobalt-oxygen complexes were prepared by the methods of Floriani and Calderazzo[20] for the unsubstituted salen compounds and Landels and Rodley[18] for [Co(bzacacen)]O_2py. The purity of each sample was confirmed by repeated elemental analyses, infrared spectra, and magnetic susceptibility measurements. Co(3-CH_3O-saldpt)O_2 was obtained as a solid material by oxygenating Co(3-CH_3O-saldpt) in the same manner as that used by Floriani and Calderazzo[20] to prepare Co(saldpt)O_2. The very dark brown solid material gave an elemental analysis consistent with the formulation as a 1:1 adduct (calculated for $C_{22}H_{27}N_3O_6Co$: C, 54.10; H, 5.57; N, 8.60. Found: C, 53.98, H, 5.57; N, 8.51), and exhibited a magnetic moment of 1.56 μ_B (22.5°C). The ESR spectrum of this material was also in agreement with the formulation as a superoxide.[21]

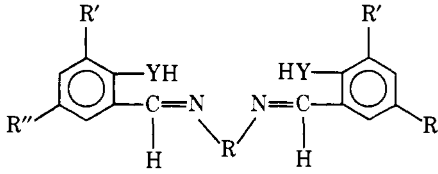
Cobalt(III)-iodide complexes of the Schiff base compounds were prepared by treating the cobalt(II) complexes with molecular iodine in CH_2Cl_2 solution. These complexes were also characterized[22] by means of elemental analyses, infrared spectra, and magnetic susceptibility determinations.

XPS spectra were determined using an AEI ES-100 photoelectron spectrometer according to published procedures.[23,24] The previously described technique[24] of mixing graphite with the sample to account for charging effects was used for the oxygen complexes, as well as the cobalt(III) iodide compounds. The more thermally stable unoxygenated cobalt(II) precursors were sublimed as thin films onto a gold-plated probe[23] and the Au $4f_{5/2}$ and Au $4f_{7/2}$ levels were used for calibration of the spectrometer.

XPS spectra were deconvoluted using the GASCAP IV[25] program in conjunction with a PDP/8I computer. The program requires input for the number of peaks and the height, half-width, and position for each peak suspected of comprising the multiplet. Based on these parameters, a spectrum is calculated which can be compared to the experimental spectrum. The program contains a routine which performs a point-by-point subtraction of the calculated spectrum from the experimental spectrum. In all of the deconvoluted spectra presented in this paper such a subtraction was nearly a straight line, thus indicating a good fit between calculated and experimental spectra. All of the spectra to be discussed in the deconvolution section were deconvoluted at least twice (once each for two different runs of the same sample). Agreement between these two deconvolutions for all of the complexes was excellent.

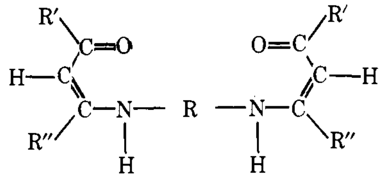
Results and Discussion

Effect of Coordination on the Ligand Donor Atoms. The donor atom (N and O) $1s_{1/2}$ binding energies for the free ligands are presented in Table I. These data were collected on samples which had been sublimed onto a gold-plated probe, except for H_2(bzacacen), which was run as a 2:1 (sample to graphite) mixture on double-stick tape. For H_2(salen), H_2(salophen), and H_2(saltm), the O $1s_{1/2}$ binding energies are quite similar. By referring to structure I, it can be seen that the oxygen atoms in these three ligands are in approximately the same electronic environment; i.e., all are phenolic oxygen atoms. Thus, the expectation that their binding energies should be similar is supported experimentally. The O $1s_{1/2}$ binding energies in H_2(bae) and H_2(bza-



Ia, $Y = O$; $R = C_2H_4$; $R' = R'' = H$	H_2(salen)
b, $Y = O$; $R = C_2H_4$; $R' = H$; $R'' = Cl$	$H_2$5-Cl-salen
c, $Y = O$; $R = C_2H_4$; $R' = OCH_3$; $R'' = H$	$H_2$3-CH_3O-salen
d, $Y = O$; $R = (CH_2)_3NH(CH_2)_3$; $R' = R'' = H$	H_2(saldpt)
e, $Y = O$; $R = (CH_2)_3NH(CH_2)_3$; $R' = OCH_3$; $R'' = H$	$H_2$3-CH_3O-saldpt
f, $Y = O$; $R = C_6H_4$; $R' = R'' = H$	H_2(salophen)
g, $Y = NH$; $R = C_2H_4$; $R' = R'' = H$	H_2(oaben)

cacen) (structure II) are also similar, but quite different



IIa, $R = C_2H_4$; $R' = R'' = CH_3$	H_2(bae) (or H_2(acacen)
b, $R = C_2H_4$; $R' = C_6H_5$; $R'' = CH_3$	H_2(bzacacen)

(approximately 2 eV) from those of the ligands derived from salicylaldehyde. The oxygen atoms in H_2(bae) and H_2(bzacacen) are ketone oxygens and not phenolic oxygens. Thus, the conclusion of Dudek and Holm[26] that Schiff base ligands derived from β-diketones and diamines exist mainly in the ketamine form is supported by the XPS data.

The donor atom core-electron binding energies have also been measured for the cobalt(II) Schiff base complexes, and these are listed in Table II. Positive binding energy shifts for nitrogen and negative shifts for oxygen are observed (relative to the free ligand) for the ligands derived from aryl aldehydes. A positive shift for nitrogen is consistent with a decrease in electron density on the nitrogen upon donation of its lone pair of electrons to the metal. A negative shift for oxygen can be rationalized on the grounds that two protons neutralize more of the electronic charge on the phenolic oxygen atom in the free ligand than a cobalt(II) ion in the complex because of a higher charge density for the proton relative to the Co(II) ion. In the Schiff base ligands derived from β-diketones, the proton resides primarily on the imine nitrogen, not the oxygen, in the free ligand. Upon complexation, therefore, the electron density on the oxygen is reduced and the binding energy increases. It should be emphasized that the magnitude of the binding energy shifts may be considerably reduced over their real value because of the potential for hydrogen bonding between donor atom pairs in the free ligand.

Effect of Ligands on the Cobalt Ion. In order to calculate chemical shifts for cobalt core (2p) electrons in the Schiff base complexes, the cobalt 2p binding energies in cobalt metal were determined. This was done by electroplating cobalt metal onto half of a rectangular piece of gold. Since the cobalt metal was in electrical contact with the conducting piece of gold, charging problems did not arise. However, it was necessary to argon ion etch the sample to remove any oxidized species from the surface. Replicate measurements on samples of cobalt metal cleaned in this manner showed that the Co 2p$_{1/2}$ and 2p$_{3/2}$ binding energies are 793.0 ± 0.1 and 778.0 ± 0.1 eV, respectively. These values are tabulated in Table III, along with the cobalt 2p binding energies in some of the Co(II) complexes.

Table I. Nitrogen and Oxygen Core-Electron Binding Energies in Schiff Base Ligands (eV)[a]

Ligand	N 1s$_{1/2}$	O 1s$_{1/2}$[b]
H_2(salen)	398.3 ± 0.1	532.2 ± 0.1
H_2(salophen)	398.6 ± 0.1	532.4 ± 0.1
H_2(saltm)	398.3 ± 0.1	532.1 ± 0.1
H_2(bae)	398.9 ± 0.1	530.2 ± 0.1
H_2(bzacacen)	399.0 ± 0.1	530.4 ± 0.1
H_2(oaben)	398.2 ± 0.1	

[a] Uncertainty corresponds to one standard deviation from the mean. Values less than 0.1 eV have been rounded off to 0.1 eV. [b] These values represent a composite O 1s$_{1/2}$ binding energy since the oxygen peaks have not been deconvoluted.

Table II. Nitrogen and Oxygen Core-Electron Binding Energies in Co(II) Schiff Base Complexes (eV)[a,b]

Complex	N 1s$_{1/2}$	O 1s$_{1/2}$[c]
Co(oaben)	398.2 ± 0.1 (0.0)	
Co(salen)	398.9 ± 0.2 (+0.6)	530.9 ± 0.2 (−1.3)
Co(salophen)	398.9 ± 0.3 (+0.3)	531.2 ± 0.1 (−1.2)
Co(bae)	399.1 ± 0.1 (+0.2)	531.8 ± 0.1 (+1.6)
Co(bzacacen)		530.9 ± 0.1 (+0.5)
Co(saldpt)·H_2O	399.0 ± 0.1	530.8 ± 0.1

[a] Uncertainty corresponds to one standard deviation from the mean. [b] Binding energy shifts relative to the values for the free ligands. [c] These values represent a composite O 1s$_{1/2}$binding energy. See Table VIII for the deconvoluted values.

Table III. Cobalt 2p Binding Energies for Cobalt Metal and Co(II) Schiff Base Complexes (eV)[a,b]

Compound	Main Co 2p$_{1/2}$	Satellite Co 2p$_{1/2}$	Co 2p$_{3/2}$
Co metal	793.0 ± 0.1 (794)[c]		778.0 ± 0.1 (779)[c]
Co(oaben)	794.2 ± 0.2 (+1.2)	796.2 ± 0.3 (+3.2)	779.3 ± 0.1 (+1.3)
Co(salen)	794.8 ± 0.2 (+1.8)	796.0 ± 0.1 (+3.0)	779.9 ± 0.1 (+1.9)
Co(salophen)	794.9 ± 0.2 (+1.9)	796.1 ± 0.2 (+3.1)	779.8 ± 0.2 (+1.8)
Co(bae)	795.2 ± 0.1 (+2.2)	796.8 ± 0.2 (+3.8)	780.1 ± 0.1 (+2.1)

[a] Number in parentheses is chemical shift, where chemical shift = B.E. shift relative to Co metal. [b] Uncertainty corresponds to one standard deviation from the mean of no fewer than four independent measurements. [c] Values reported in ref 41.

The Co 2p$_{1/2}$ level is split into two peaks in the complexes. An example of this splitting is shown in Figure 1. The satellite structure is also present in the 2p$_{3/2}$ level, but the main peak is considerably more intense than the satellite peak. This probably occurs because the process which causes the satellite structure is a secondary process. Consequently, the satellite peak would appear to be more important in the 2p$_{1/2}$ level because the 2p$_{1/2}$ peak is only one-half as intense as the main photopeak arising from the 2p$_{3/2}$ level. The possibility of an Auger electron excitation as a source of the satellite peak can be either confirmed or ruled out by changing the energy of the incident radiation. By scanning a sample of Co(oaben) with the Mg Kα X-ray (E = 1253.6 eV) as the incident radiation, a spectrum showing satellite structure similar to that in Figure 1 was obtained.

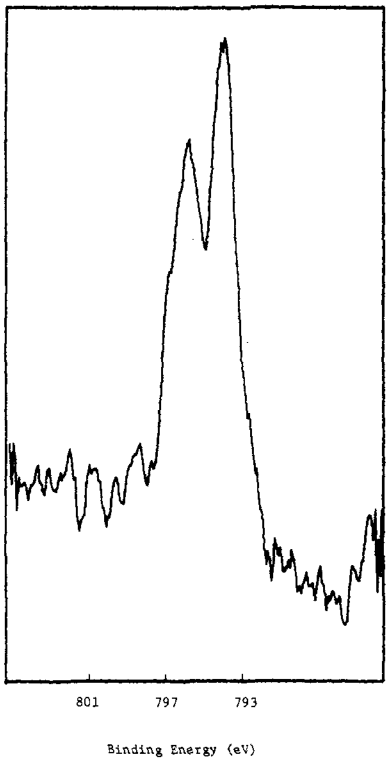


Figure 1. Splitting of the Co $2p_{1/2}$ level in Co(oaben).

The satellite structure has been attributed to a multielectron excitation ("shake-up" or "shake-off") process, whereby photoionization of the core (2p) electron causes simultaneous excitation or ionization of a valence electron. Satellite peaks in a large number of paramagnetic cobalt(II) complexes have also been attributed[27,28] to multielectron excitation phenomena.

The complexes in Table III are listed in the order of increasing binding energy, and the chemical shift is consistent with an increase in the oxidation number of cobalt from 0 to +2. More important, however, is the fact that the binding energy and thus the chemical shift appears to be dependent on the nature of the ligand. From visible spectral data,[29-31] the order of decreasing ligand field strength is given by oaben > salen $\simeq$ salophen > bae. Thus, in Co(oaben) the smallest chemical shift was observed because of greater charge donation to the metal by the ligand. On the other hand, bae is the weakest ligand of the series and thus Co(bae) exhibited the largest chemical shift. Since the ligand field strengths of salen and salophen are very similar, it would be expected that the cobalt binding energies in these Schiff base complexes would be similar. The data in Table III support this argument. It should be noted, however, that these data run counter to the "cis effect" series recently proposed[32] for these types of ligands.

The cobalt $2p_{3/2}$ binding energies for some additional Co(II) Schiff base complexes are summarized in Table IV. These complexes are the Co(II) precursors for the oxygen complexes. The effect of substitution on the sal or acac ligand system can be examined by comparing the binding energies of the complexes in Table IV with those of the unsubstituted compounds (Table III). For example, the chemical shift for Co(3-CH_3O-salen) and Co(5-Cl-salen) is 0.5 eV less than that for Co(salen). This is presumably due to the +M resonance ("electron donating") effect of -OCH_3 and -Cl.[33] The importance of substitution on the ligand can also be seen in the case of Co(bzacacen). In this case, the Co $2p_{3/2}$ chemical shift is considerably less (approximately 1 eV) than the shift for the unsubstituted Co(bae) complex.

Table IV. Cobalt $2p_{3/2}$ Binding Energies for Cobalt(II) Schiff Base Complexes[a,b]

Compound	Co $2p_{3/2}$ B.E. (eV)	Ligand type
Co(saldpt)·H_2O	780.8 ± 0.1 (+2.8)	Pentadentate
Co(3-CH_3O-saldpt)	781.2 ± 0.1 (+3.2)	Pentadentate
Co(3-CH_3O-salen)	779.4 ± 0.1 (+1.4)	Tetradentate
Co(5-Cl-salen)	779.4 ± 0.1 (+1.4)	Tetradentate
Co(bzacacen)	779.2 ± 0.1 (+1.2)	Tetradentate

[a] Uncertainty corresponds to one standard deviation from the mean of no fewer than three independent measurements. [b] Number in parentheses is chemical shift relative to Co metal.

An examination of Table IV shows that the pentadentate ligands saldpt and 3-CH_3O-saldpt produce higher Co $2p_{3/2}$ binding energies than any of the four-coordinate complexes listed in Tables III or IV. The secondary (dpt) nitrogen in these two complexes is coordinated to the metal and would be expected to increase the electron density on the metal by donation of the lone electron pair. This donation of electron density would result in a lower metal binding energy, not a higher one. The apparent contradiction can be explained by the fact that Co(saldpt)·H_2O and Co(3-CH_3O-saldpt) are high-spin complexes, whereas the four-coordinate materials are low spin.[34] Because of metal-ligand electron-electron repulsion, the nucleus of the metal is more "shielded' from some of the electron density of the ligand in the high-spin form than in the low-spin form. Consequently, the positive charge on the metal ion is not reduced as much as it would be if the complex were low spin, and the binding energies for the metal core electrons are higher. A determination of the metal binding energies in Cu(saldpt) affords an excellent test for the validity of this hypothesis. Since copper(II) is a d^9 ion, there is no possibility for the existence of high-spin and low-spin forms. Thus, the additional nitrogen (dpt) atom should increase the electron density on the metal ion (relative to Cu(salen)) and result in a lower binding energy for copper core electrons. The Cu $2p_{3/2}$ binding energies for Cu(salen) and Cu(saldpt) are 934.5 ± 0.1 and 933.9 ± 0.1 eV, respectively.[35] Thus the five-coordinate complex, in the absence of spin-state changes, exhibits a lower metal $2p_{3/2}$ binding energy than the four-coordinate complex.

XPS Study of Cobalt-Oxygen Complexes. It was found that some dioxygen complexes could not be studied because they lost O_2 under the vacuum conditions of the instrument. In fact, the Co $2p_{1/2}$ and $2p_{3/2}$ binding energies for $[Co(salen)]_2O_2$ were determined and found to be identical with those for Co(salen). An independent experiment showed that when the oxygenated sample was placed under a vacuum of approximately 10^{-6} Torr, the color changed from black to the maroon color of Co(salen). Similar experiments demonstrated that $[Co(salen)]_2O_2(DMF)_2$ and $[Co(3\text{-}CH_3O\text{-salen}]_2O_2(H_2O)_2$[36] also changed color and, thus, could not be studied under the high-vacuum (10^{-7} to 10^{-8} Torr) conditions in the instrument. All of the complexes whose binding energies are reported here, however, did not change color at 10^{-6} Torr (at room temperature). The magnetic moments were also the same at both 10^{-3} Torr and atmospheric pressure.

The experimentally determined Co $2p_{3/2}$ and O $1s_{1/2}$ binding energies for the dioxygen complexes are listed in Table V. For the tetradentate Schiff base complexes, the binding energy shift[37] is positive and ranges from 0.9 to 1.9

Table V. Co $2p_{3/2}$ and O $1s_{1/2}$ Binding Energies for Cobalt–Dioxygen Complexes (eV)^{a,b}

Complex	Co $2p_{3/2}$	O $1s_{1/2}$^{c}
[Co(3-CH_3O-salen)]O_2py	781.3 ± 0.1 (+1.9)	532.1 ± 0.1 [3.6]
[Co(3-CH_3O-salen)]$_2O_2$(DMSO)	781.0 ± 0.1 (+1.6)	532.0 ± 0.1 [3.6]
[Co(5-Cl-salen)]$_2O_2$(DMSO)$_2$	780.3 ± 0.1 (+0.9)	531.2 ± 0.2 [3.1]
[Co(bzacacen)]O_2py	780.8 ± 0.1 (+1.6) (781.4 ± 0.1)^{d}	531.4 ± 0.3 [3.0]
[Co(saldpt)]O_2	781.0 ± 0.1 (+0.2)	531.2 ± 0.1 [2.8]
[Co(3-CH_3O-saldpt)]O_2	781.3 ± 0.1 (+0.1)	532.0 ± 0.1 [3.9]

[a] Number in parentheses is B.E. shift relative to unoxygenated Co(II) complex. [b] Uncertainty corresponds to one standard deviation from the mean. [c] Number in brackets is average full-width at half-maximum (FWHM). These values represent a composite O $1s_{1/2}$ binding energy. See Table IX for the deconvoluted values. [d] Value reported in ref 10.

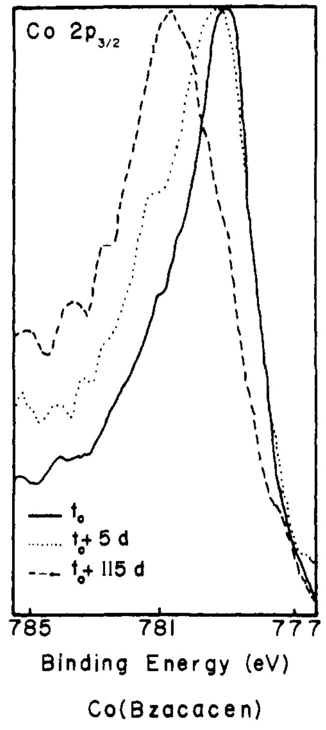


Figure 2. Solid-state decomposition of Co(bzacacen). t_0 = time of purification.

eV. The positive increase in binding energy is consistent with an increase in oxidation state for the cobalt ion. It appears, therefore, that the increase in binding energy is consistent with the oxidative addition description of the oxygenation process. The binding energy increase accompanying the oxygenation process for the pentadentate Schiff base complexes is, within experimental error, equal to zero. At first the logical conclusion would seem to be that the Co(II) ion is not oxidized during the formation of these oxygen adducts. However, it must be remembered that these two complexes are formed from high-spin precursors, and it has already been shown that the metal core-electron binding energies are dependent on the spin state of the metal ion. Thus, a direct comparison between binding energies of the high-spin precursor and the low-spin dioxygen complex is not meaningful or informative. The important point to note is that the [Co(saldpt)]O_2 and [Co(3-CH_3O-saldpt)]O_2 complexes yield Co $2p_{3/2}$ binding energies which are in the same range as the other cobalt Schiff base oxygenation products. Furthermore, it should be noted that while the binding energy shifts are positive upon oxygenation, they are perhaps reduced somewhat because of the increase in coordination number accompanying oxygenation.

Floriani and Calderazzo[20] suggested that the Co(II) complexes were more easily oxygenated in donor solvents because the coordinated solvent trans to the oxygen was able to compensate for the electronic charge which was transferred from cobalt to oxygen. Since the donation of negative charge to the cobalt ion by a ligand is equivalent to a reduction in binding energy for cobalt core electrons, it might be expected that complexes in which cobalt core electrons have lower binding energies would form more stable oxygen complexes. The data for Co(3-CH_3O-salen) and Co(5-Cl-salen) (Table IV) support this argument. The Co $2p_{3/2}$ binding energy is 0.5 eV lower in these two complexes than in Co(salen). Accordingly, the μ-peroxo complexes, [Co(3-CH_3O-salen)]$_2O_2$(DMSO) and [Co(5-Cl-salen)]$_2$-O_2(DMSO)$_2$, are more stable with respect to loss of O_2 under vacuum than [Co(salen)]$_2O_2L_2$.

The only previously reported XPS study of cobalt-dioxygen complexes has dealt with the binding energies of Co(bzacacen) and Co(bzacacen)O_2py.[10] Since the results of this study could have been complicated by a Co(III) impurity (the Co $2p_{3/2}$ photoelectron peak for Co(bzacacen) was abnormally wide, ~4.0 eV),[10] we have determined the XPS spectra of these particular complexes again. In accord with the previously reported results, the Co $2p_{3/2}$ peak of Co(bzacacen) (mixed in a sample to graphite ratio of 2:1 and run on double-stick tape) was examined and a binding energy of 780.2 ± 0.3 eV was obtained. The average full-width at half-maximum (FWHM) for the peak was ~3.8 eV. The large FWHM associated with the peak, as well as the large standard deviation, suggested that the compound might have been impure. The complex was purified by boiling the red-orange compound in ethanol and filtering the suspension while hot. The slightly yellow filtrate was discarded, and the red-orange crystals were dried in a vacuum desiccator. Sublimation of this compound onto a gold-plated copper probe gave a Co $2p_{3/2}$ binding energy of 779.2 eV, and the FWHM had decreased to 2.6 eV (a value typical of the other Co(II) Schiff base complexes). In order to determine whether the purification treatment or the sublimation procedure was responsible for the removal of the impurity, the "purified" complex was mixed with graphite in a sample to graphite ratio of 2:1. The XPS spectrum of this material revealed a binding energy which was identical with that found by the sublimation procedure, and the FWHM was still 2.6 eV. From this information, it was concluded that some type of impurity (in which the cobalt ion has a $2p_{3/2}$ binding energy of approximately 780 eV) was removed by the purification procedure. When the spectrum was taken 3 days later on the same mixture, the FWHM had increased to 3.6 eV. It was suspected that Co(bzacacen) was undergoing oxidation in the solid state without an accompanying color change.[38] In order to confirm this suspicion, the XPS spectrum on the same mixture was taken again, almost 4 months after the purification procedure. The results of this time-dependent decomposition study are shown in Figure 2. The large shift to higher binding energy clearly indicated that solid-state decomposition has taken place in the complex. Although the decomposition product has not been identified, the spectrum suggests that oxidation to a Co(III) species has taken place.

Table VI. Co $2p_{3/2}$, O $1s_{1/2}$, and I $3d_{5/2}$ Binding Energies in Iodocobalt(III) Complexes (eV)[a-c]

Complex	Co $2p_{3/2}$	O $1s_{1/2}$[d]	I $3d_{5/2}$
Co(3-CH_3O-salen)I(H_2O)	781.3 ± 0.1	532.7 ± 0.1	619.7 ± 0.1
	(+1.9) [2.5]	[3.7]	[2.4]
Co(3-CH_3O-salen)Ipy	781.6 ± 0.1	532.5 ± 0.1	618.9 ± 0.2
	(+2.2) [3.4]	[4.0]	[2.7]
Co(5-Cl-salen)I	781.2 ± 0.1	531.9 ± 0.1	619.8 ± 0.1
	(+1.8) [2.6]	[2.9]	[2.5]
Co(bzacacen)I	781.9 ± 0.2	532.5 ± 0.2	619.7 ± 0.2
	(+2.7) [3.0]	[2.9]	[2.5]
Co(saldpt)I·H_2O	781.6 ± 0.2	531.9 ± 0.1	619.6 ± 0.2
	(+0.8) [2.4]	[3.1]	[2.4]
Co(3-CH_3O-saldpt)I	781.7 ± 0.2	532.7 ± 0.2	619.8 ± 0.1
	(+0.5) [2.5]	[4.2]	[2.3]

[a] Number in parentheses is B.E. shift relative to Co(II) precursor. [b] Number in brackets is average FWHM. [c] Uncertainty corresponds to one standard deviation from the mean. [d] These values represent a composite O $1s_{1/2}$ binding energy since the oxygen peaks have not been deconvoluted.

Table VII. Extent of Electron Transfer between Cobalt and Oxygen in Some Dioxygen Complexes

Complex	Extent of electron transfer from Co to O (%)
[Co(3-CH_3O-salen)]O_2py	69–100
[Co(3-CH_3O-salen)]$_2O_2$(DMSO)	65–100[a]
[Co(5-Cl-salen)]$_2O_2$(DMSO)$_2$	32–62[a]
[Co(bzacacen)]O_2py	47–71[a]

[a] These values are only estimates. Direct comparisons with the iodo complexes are not possible because all of the ligands are not the same. See text.

XPS Study of Co(III) Complexes. A series of cobalt(III) Schiff base complexes has also been investigated by XPS. The reason for this study was twofold: (1) although a binding energy increase accompanied the oxygenation process, it could be argued that this was due to factors other than oxidation of the cobalt atom—particularly electron withdrawal by the dioxygen group; (2) a comparison between the oxygen complexes and the cobalt(III) complexes will give an estimate of the extent of electron transfer between cobalt and oxygen. If it is assumed that electron transfer between cobalt and iodine in the iodide complexes is 100%, i.e., the complex can be represented as $Co^{3+}\cdots I^-$, then the Co $2p_{3/2}$ binding energies in these complexes can be used to determine whether the cobalt ion is, in fact, completely oxidized during the oxygenation process. The binding energies in these complexes are presented in Table VI. A comparison of the Co $2p_{3/2}$ binding energy shifts in Table VI with the Co $2p_{3/2}$ binding energy shifts for the corresponding oxygen complexes (Table V) shows that they are similar. The comparison between the iodo complexes and the dioxygen complexes is not a rigorous one because not all of the ligands which are present in the oxygen complexes are present in the iodo complexes. The complex Co(3-CH_3O-salen)Ipy, however, affords a direct comparison between the oxygen complex and the iodo complex because a pyridine ligand is present in both. If the per cent electron transfer in the cobalt(II) compound is assigned a value of zero, and a value of 100 is assigned to the Co(III) iodo complex, then the per cent electron transfer in the oxygen complexes can be calculated by eq 1

$$\%\text{ electron transfer} = \frac{\text{B.E.S. for oxygen complex}}{\text{B.E.S. for iodo complex}} \times 100 \quad (1)$$

where B.E.S. is the binding energy shift relative to the appropriate Co(II) compound. The result of this calculation for [Co(3-CH_3O-salen)]O_2py yields 86 ± 17% for the extent of electron transfer between cobalt and oxygen. The large error is a result of the comparatively large uncertainty (±0.2 eV) associated with each binding energy shift. Similar calculations for the other oxygen adducts of the tetradentate Schiff base complexes lead to the results summarized in Table VII. It is interesting to note that the per cent electron transfer calculated is in reasonable agreement with ESR studies.[4]

A calculation of this sort cannot be carried out with the cobalt complexes of saldpt and 3-CH_3O-saldpt because of the spin state changes already discussed. However, an examination of the absolute Co $2p_{3/2}$ binding energies in [Co(saldpt)]O_2 and [Co(3-CH_3O-saldpt)]O_2 can provide some insight as to whether the cobalt ion should be formulated as Co(II) or Co(III). For example, the Co $2p_{3/2}$ binding energy range for the low-spin cobalt(II) Schiff base complexes listed in Tables III and IV is 779.2–780.1 eV. Similarly, the Co $2p_{3/2}$ binding energy range for the iodocobalt(III) complexes (Table VI) is 781.2–781.9 eV. The Co $2p_{3/2}$ binding energies for [Co(saldpt)]O_2 and [Co(3-CH_3O-saldpt)]O_2 (781.0 and 781.3 eV, respectively) clearly fall in the binding energy range associated with cobalt(III) complexes of these Schiff base ligands. Although the calculations of per cent electron transfer are crude and contain a sizeable uncertainty, the comparison of cobalt-oxygen complexes with the corresponding iodo complexes presents unambiguous evidence that the cobalt ion is oxidized during the oxygenation process.

Deconvolution of Oxygen Peaks. The O $1s_{1/2}$ signal from the oxygen complexes was complicated by the presence of several different types of oxygen in the compounds. The complexity of the signal is evidenced by the large FWHM associated with the O $1s_{1/2}$ peak (Table V). In order to separate the individual peaks comprising the broad signal, the oxygen peaks from the dioxygen complexes have been deconvoluted. It was felt that because of the inherent assumptions and approximations present in any deconvolution procedure, a preliminary set of deconvolutions should be carried out to show not only that a broad peak could be deconvoluted into several narrower peaks, but also that each of the narrower peaks could be identified with a certain part of the complex under consideration.

Assuming that the Schiff base oxygen donor atoms were not changed significantly during the oxygenation process, their binding energies in the Co(II) complex and the dioxygen complex should be quite similar. Thus, the first step in the deconvolution procedure was to determine the binding energy of the oxygen atoms of the Schiff base ligand. Figure 3 shows the deconvolution of the O $1s_{1/2}$ peak from a sample of Co(salen) sublimed onto a gold-plated probe. The agreement between experimental and calculated spectra is very good (the baselines do not coincide because there is always a finite number of "background" electrons at a given binding energy). The more intense peak, of course, corresponds to the phenolic oxygen atom of the Schiff base ligand. The peak to higher binding energy has been attributed to contamination. The source of the contamination is not known, but it arises in (or from) the instrument and is not an impurity in the sample. This was easily shown by deconvoluting another sample of Co(salen) run on a different day but under the same conditions as the sample whose spectrum is shown in Figure 3. The binding energies of the O $1s_{1/2}$ peaks in both deconvolutions were essentially the same, even though the overall appearance of the two spectra was quite different. This shows that the appearance of the spectrum can be changed quite drastically simply by chang-

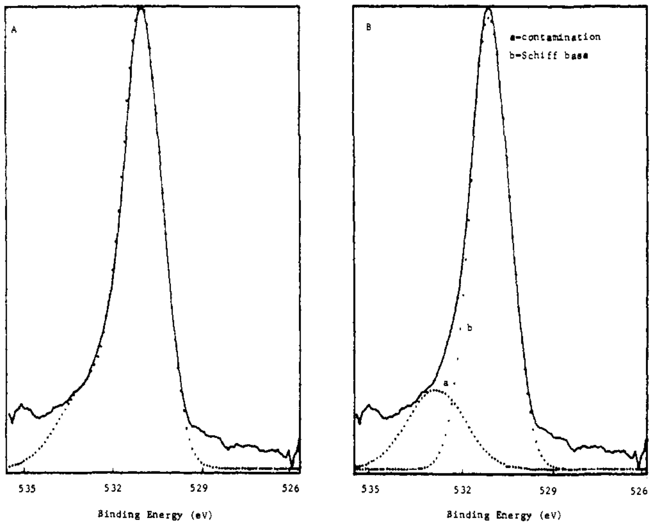


Figure 3. Deconvolution of the O $1s_{1/2}$ peak from Co(salen) sublimed onto a gold-plated probe: (A) comparison between experimental (—) and calculated (···) peaks; (B) deconvoluted peaks which make up the calculated spectrum.

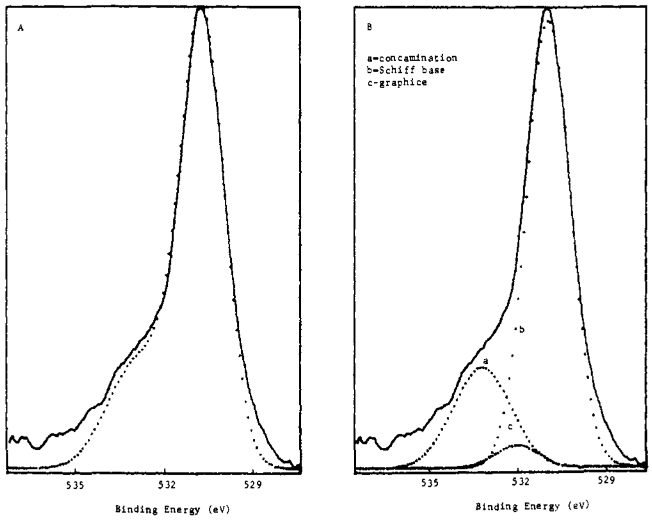


Figure 4. Deconvolution of the O $1s_{1/2}$ peak from Co(bzacacen) mixed with graphite and run on double-stick tape: (A) comparison between experimental (—) and calculated (···) peaks; (B) deconvoluted peaks which make up the calculated spectrum.

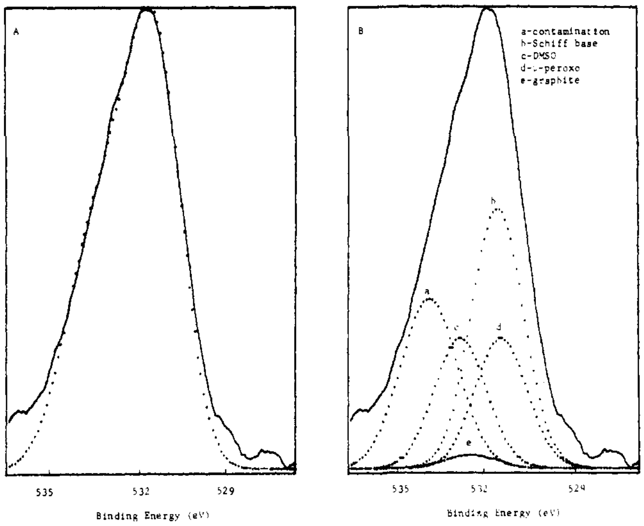


Figure 5. Deconvolution of the O $1s_{1/2}$ peak from $[Co(5\text{-}Cl\text{-}salen)]_2O_2(DMSO)_2$ mixed with graphite and run on double-stick tape: (A) comparison between experimental (—) and calculated (···) peaks; (B) deconvoluted peaks which make up the calculated spectrum.

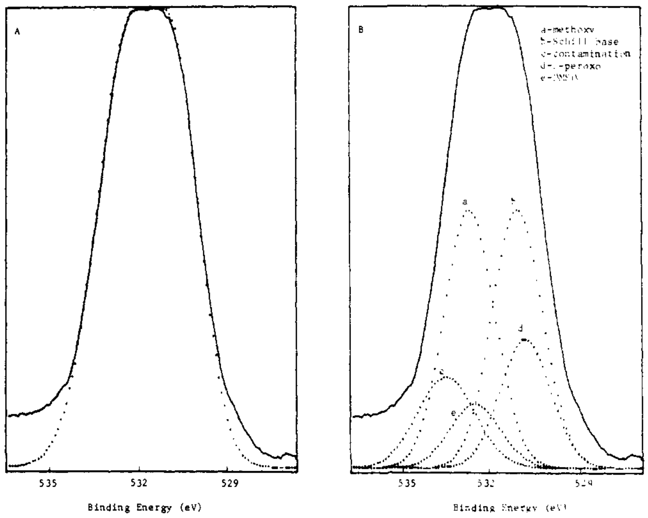


Figure 6. Deconvolution of the O $1s_{1/2}$ peak from $[Co(3\text{-}CH_3O\text{-}salen)]_2O_2(DMSO)$ mixed with graphite and run on double-stick tape: (A) comparisons between experimental (—) and calculated (···) peaks; (B) deconvoluted peaks which make up the calculated spectrum.

ing the intensity of the O $1s_{1/2}$ peak attributed to "contamination". Furthermore, the fact that the intensity ratio of the two peaks (i.e., Schiff base oxygen and "contamination" oxygen) does not remain constant rules out the possibility that the anomalous peak arises from an impurity in the sample. The probable source of this contamination is H_2O. For example, Carver et al.[39] have obtained O $1s_{1/2}$ data for ZnO and Cr_2O_3, and attribute peaks at 533.2 (for ZnO) and 532.7 eV (for Cr_2O_3) to H_2O.

To show that the deconvolution procedure is valid for samples which have been mixed with graphite as well as those which were sublimed, the O $1s_{1/2}$ peak from a spectrum of Co(bzacacen) (freshly purified, mixed with graphite and run on double-stick tape) was deconvoluted (Figure 4). The deconvolution results show that no signal arising from the oxygen in the double-stick tape was observed, and that the contribution to the total signal by the oxygen in graphite was negligible. The binding energy values for the deconvoluted O $1s_{1/2}$ peaks from Co(II) Schiff base complexes have been summarized in Table VIII. The FWHM associated with the Schiff base oxygen atoms is in good agreement with the value of 1.8 eV expected for the O $1s_{1/2}$ signal where there is only one type of oxygen.[40] This fact,

Table VIII. Binding Energies of Deconvoluted O $1s_{1/2}$ Peaks from Co(II) Schiff Base Complexes (eV)[a]

		Oxygen type		
Complex	$-OCH_3$	Contamination	Graphite	Schiff base
Co(salen) (1)		533.0 [2.4]		531.0 [1.6]
(2)		532.4 [2.4]		530.8 [1.6]
$Co(3\text{-}CH_3O\text{-}salen)$ (1)	532.3 [1.5]	532.7 [2.4]		530.6 [1.5]
(2)	532.5 [1.5]	533.1 [2.4]		530.7 [1.5]
Co(bzacacen)		533.0 [2.4]	531.8 [1.6]	530.6 [1.6]

[a] Number in brackets is FWHM.

Table IX. Binding Energies of Deconvoluted O $1s_{1/2}$ Peaks from Cobalt(III)-Dioxygen Complexes (eV)[a]

	Oxygen type[b]						
Complex	a	b	c	d	e	f	g
$[Co(5\text{-}Cl\text{-}salen)]_2O_2(DMSO)_2$							
Run no. 122373	533.1	531.8	530.8		530.7		532.1
	[2.4]	[1.9]	[1.9]		[1.9]		[1.9]
Run no. 121473	533.3	531.9	531.0		530.8		532.3
	[2.4]	[2.1]	[2.1]		[2.1]		[2.1]
$[Co(3\text{-}CH_3O\text{-}salen)]_2O_2(DMSO)$	533.3		530.8	532.5	530.6		532.3
	[2.4]		[2.1]	[2.1]	[2.1]		[2.1]
$[Co(bzacacen)]O_2py$							
Run no. 123173A	533.1	531.8	530.7			531.4	
	[2.4]	[2.1]	[2.1]			[2.1]	
Run no. 12874B	532.9	531.9	530.7			531.6	
	[2.4]	[1.9]	[1.9]			[1.9]	
Run no. 12974	532.9	531.8	530.6			531.6	
	[2.4]	[2.0]	[2.0]			[2.0]	
$[Co(3\text{-}CH_3O\text{-}salen)]O_2py$	533.4	531.8	530.8	532.5		531.7	
	[2.4]	[2.1]	[2.1]	[2.1]		[2.1]	
$[Co(saldpt)]O_2$	533.0	531.8	530.5			531.5	
	[2.4]	[1.9]	[1.9]			[1.9]	
$[Co(3\text{-}CH_3O\text{-}saldpt)]O_2$	533.4	531.9	530.7	532.7		531.4	
	[2.4]	[2.1]	[2.1]	[2.1]		[1.9]	

[a] Number in brackets is FWHM. [b] Legend: a = "contamination" oxygen; b = graphite oxygen; c = Schiff base oxygen; d = $-OCH_3$ oxygen; e = μ-peroxo oxygen; f = superoxo oxygen; g = DMSO oxygen.

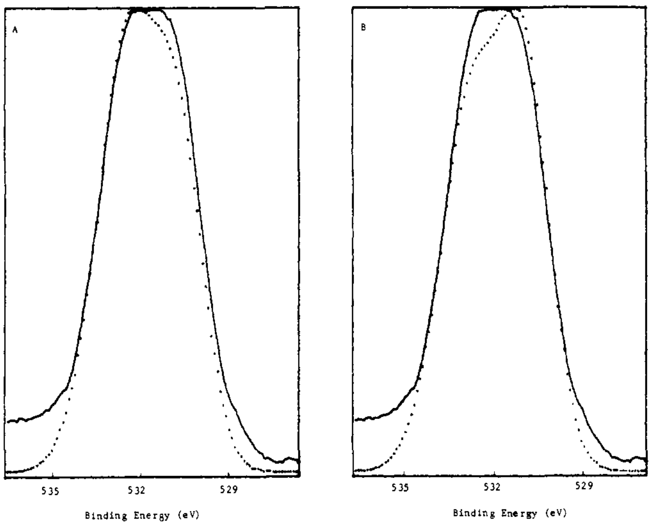


Figure 7. Deconvolution of the O $1s_{1/2}$ peak in Figure 6 assuming that the intensity of the DMSO oxygen peak (e) in Figure 6 is twice the intensity (A) shown in Figure 6 or zero (B).

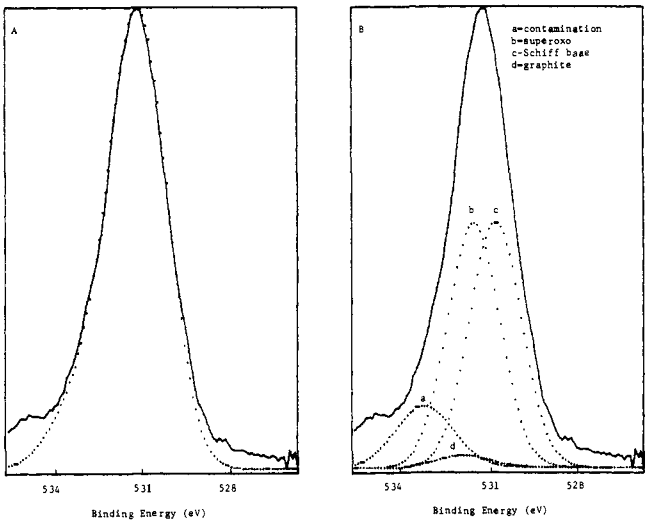


Figure 8. Deconvolution of the O $1s_{1/2}$ peak from $Co(bzacacen)O_2py$ mixed with graphite and run on double-stick tape: (A) comparison between experimental (—) and calculated (···) peaks; (B) deconvoluted peaks which make up the calculated spectrum.

together with the good agreement between binding energies for different spectra, indicates that the deconvolution procedure is a reliable one for use with XPS peaks.

The O $1s_{1/2}$ spectra of the oxygen complexes were deconvoluted by fixing the position of the graphite oxygen, the Schiff base (including $-OCH_3$) oxygen, and the oxygen peak due to contamination. The height (intensity) of the contamination oxygen peak was variable, as were the heights and positions of the additional oxygen peaks (e.g., DMSO, μ-peroxo, superoxo). The spectrum was calculated from a specific set of peak parameters. The parameters were then changed until the calculated spectrum gave a good fit to the experimental spectrum and point-by-point subtraction yielded a nearly straight line.

The deconvolution of the O $1s_{1/2}$ peak from $[Co(5\text{-}Cl\text{-}salen)]_2O_2(DMSO)_2$ is shown in Figure 5. The fit between calculated and experimental peaks is quite good. The peaks which comprise the calculated spectrum were plotted individually in Figure 5B, and the binding energies associated with these peaks are listed in Table IX.

The μ-peroxo bridge contains oxygen atoms which are each formally uninegative, as are the oxygens in the Schiff base ligand. Furthermore, there is one μ-peroxo oxygen atom per two phenolic ligand oxygens. For these reasons, the peak at 530.7 eV was assigned to the μ-peroxo oxygen atoms. At higher binding energy than, but with the same intensity as, the μ-peroxo oxygen atoms is the DMSO oxygen (532.1 eV). The assignment of the DMSO and μ-peroxo oxygen peaks can be confirmed by a comparison with the deconvolution results of other oxygen complexes. For example, deconvolution of the O $1s_{1/2}$ peak in $[Co(3\text{-}CH_3O\text{-}salen)]_2O_2(DMSO)$ should give rise to μ-peroxo and DMSO oxygen peaks with binding energies which are quite similar to those found for the μ-peroxo analog with the 5-Cl-substituted ligand. Such a deconvolution is shown in Figure 6, and the binding energies are tabulated in Table IX.

Because of the large number of deconvoluted peaks, the O $1s_{1/2}$ peak arising from graphite was omitted. The fit between calculated and experimental peaks is very good. The agreement between the binding energies for μ-peroxo and DMSO oxygen in $[Co(5\text{-}Cl\text{-}salen)]_2O_2(DMSO)_2$ and $[Co(3\text{-}CH_3O\text{-}salen)]_2O_2(DMSO)$ is excellent (Table IX). This indicates that the assignment of peaks to the μ-peroxo and DMSO oxygens is correct. It is interesting to note that the μ-peroxo adduct of the 3-methoxy complex is formulated as having *one* DMSO molecule per two molecules of the cobalt complex, whereas the corresponding 5-chloro compound has *two* molecules of DMSO per two molecules of the cobalt complex. Aside from confirmation by elemental analysis results, the formulation for $[Co\text{-}3\text{-}CH_3O\text{-}salen)]_2O_2(DMSO)$ is also confirmed by the deconvolution results. For example, if the DMSO peak is removed completely, or is given an intensity corresponding to the DMSO in $[Co(5\text{-}Cl\text{-}salen)]_2O_2(DMSO)_2$, the calculated spectrum no longer fits the experimental peak (Figure 7).

The superoxide complexes were deconvoluted in a manner similar to that used for the μ-peroxo adducts. The positions and intensities of all oxygen atoms except the superoxo oxygens were fixed. The parameters of the superoxo peak were then changed until a good fit was obtained. The O $1s_{1/2}$ deconvolution for $[Co(bzacacen)]O_2py$ is shown in Figure 8. The resulting binding energies are listed in Table IX (values for the deconvolution of three different runs on the same sample are listed). The superoxide peak was given an intensity equal to that of the Schiff base oxygens. Such an assignment presupposes that the two oxygen atoms in the superoxide group are equivalent. It is probable that the peaks are not, in fact, exactly equivalent. However, XPS might not be a sufficiently sensitive technique to differentiate between the two. If the peak attributed to the superoxo oxygen atoms (Figure 8) is broken up into two peaks (each with half the intensity of the original peak), the two peaks can be separated by as much as 0.4 eV without a serious alteration in the fit between calculated and experimental spectra. If they are separated by 0.6 eV, however, the calculated spectrum begins to fall outside the experimental peak. The only conclusion which can be reached from these observations is that XPS (or, more precisely, the deconvolution procedure as applied in this work) is not capable of establishing whether the peaks are equivalent or nonequivalent. In any case, if the two superoxo oxygen atoms are not electronically equivalent, they probably do not differ in binding energy by more than 0.5 eV.

The assignment of the superoxo oxygen binding energy can be verified by examining the deconvoluted O $1s_{1/2}$ spectrum from $[Co(3\text{-}CH_3O\text{-}salen)]O_2py$. As with the other deconvoluted spectra, the agreement between the calculated and experimental peaks was very good. The superoxide, Schiff base, and $-OCH_3$ oxygens can all be nicely separated from one another and from the (ever-present) contamination peak. The binding energy of the superoxide oxygen atoms in this complex (Table IX) is in good agreement with the superoxide binding energy in $[Co(bzacacen)]O_2py$, thereby confirming the assignment of the peak at 531.6 eV to the superoxide oxygens.

Now that the binding energies of the μ-peroxo and superoxo oxygen atoms have been determined, a comparison between the two values is informative. The average binding energy for μ-peroxo oxygen atoms is 530.7 eV; that for superoxo oxygen atoms (assuming equivalence) is 531.6 eV. These values are what one would expect to find based solely on the formal charge of the oxygens in each group. For example, each oxygen atom in a μ-peroxo bridge (O_2^{2-}) is formally uninegative, while each oxygen atom in a superoxide group (O_2^-) carries only one-half of a negative charge. This means that the oxygens in a superoxide group are more positive than those in a μ-peroxo group and should exhibit a higher binding energy. This notion is supported by the deconvolution binding energies of the two types of oxygens.

Thus, the formulation of dioxygen adducts of Co(II) Schiff base complexes as $Co(III)\text{-}O_2^{2-}\text{-}Co(III)$ or $Co(III)\text{-}O_2^-$ complexes is supported not only by the cobalt 2p binding energies but by the O $1s_{1/2}$ binding energies obtained by deconvolution of the oxygen peaks from the dioxygen complexes.

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Chemical Evolution of a Nitrogenase Model. IX. Concerning the Effects of Adenosine 5′-Triphosphate and of Acids in the Model System and the Adenosine 5′-Triphosphate Requirement of Nitrogenase

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Abstract: The stimulatory effect of ATP in molybdothiol model systems of nitrogenase is compared to that of simple protic acids at similar ionic strength with four different substrates, i.e., c-$C_6H_{11}NC$, CN^-, $CH_2{=}CH{-}CN$, and C_2H_2. The activation of molybdothiol catalyst systems by ATP is attributed to its tendency to form intermediate protonated complexes with oxomolybdate ion and its molybdenum-catalyzed hydrolysis to ADP and inorganic phosphate. The net effect consists in facilitating the removal of molybdenum-bound OH group(s) which enhances the rate of conversion of oxidized forms of the catalyst into the active reduced form. The ATP effect of nitrogenase is interpreted on the basis of these observations. Stimulation of catalytic activity by protic acids is as a rule weaker than that by ATP and interpreted as an anion-assisted protonation of the molybdothiol catalyst. ATP as well as each of the acids studied also specifically influence the product distribution and electron transfer efficiency in the model system employed.

One of the remarkable features of molybdothiol model systems of nitrogenase (N_2-ase) is their activation by substrate amounts of ATP and of other nucleoside phosphates under nonenzymatic conditions.[1] This activation was previously postulated to occur via protonated ATP or nucleoside phosphate complexes of the molybdothiol catalyst. In the case of ATP, this interaction is accompanied by a molybdenum-catalyzed hydrolysis of ATP to ADP and inorganic phosphate (P_i).[2] The ATP requirement of N_2-ase was accordingly interpreted to involve the interaction of ATP with the molybdenum active site, causing the removal of kinetically inert OH group(s) with the simultaneous hydrolysis of ATP into ADP and P_i. The net effect of ATP in N_2-ase as well as in the model systems was postulated to consist in the acceleration of the conversion of oxidized forms of the molybdenum catalyst into the active reduced form, a process which is slow in the absence of ATP. Although this interpretation of the ATP effect is supported by a considerable body of experimental evidence, it was recently challenged by Shilov et al.[3] who argued that the ATP addition causes merely a nonspecific, anion-independent protonation of the molybdothiol catalyst and acceleration of $NaBH_4$ decomposition. Using C_2H_2 as the substrate, Shilov et al. produced a similar stimulation of catalytic activity with H_2SO_4 as with ATP and consequently considered the ATP effect in the model systems as nonspecific and irrelevant to the action of ATP in N_2-ase holoenzyme. The authors of ref 3 also raised a number of other objections against our previous work, but only their critique of the ATP effect deserves comment at this time. In the present paper we shall therefore show that the ATP effect in N_2-ase model systems is real and different from that of simple protic acids. We will also demonstrate that the stimulatory effects of protic acids are weaker than those of ATP and dependent upon the nature of the acid anion. We shall finally draw attention to previously published observations of other authors on the molybdate-catalyzed hydrolysis of ATP and other organic phosphates which indirectly reaffirm our own conclusions on the role of ATP in nitrogenase models.

Model System and Reaction Conditions Employed

The N_2-ase model system employed consisted of the Mo^{5+} complex of L-(+)-cysteine (complex I) as the source of the mononuclear catalytically active species designated Mo^{ox} in the oxidized and Mo^{red} in the reduced form.[2] The reducing agent $NaBH_4$ was used in the absence of added iron cocatalysts. To compare the stimulatory effects of ATP with those of simple protic acids, experiments were performed not only with ATP but also in the presence of H_3PO_4, CH_3COOH, H_2SO_4, HCl, and $HClO_4$ under identical conditions and at the same initial pH. Contrary to the conditions employed by the authors of ref 3, who added ATP or H_2SO_4 to their reaction solutions last, we studied the effects of ATP and of the other acids by adding them prior to $NaBH_4$, as described in ref 2. In this manner, sudden or uncontrollable drops of the solution pH were avoided. We shall show that the pH of the reaction solutions increases when $NaBH_4$ is injected at $t = 0$ and that it continues to rise until the $NaBH_4$ is consumed. The substrates employed were cyclohexylisocyanide (c-$C_6H_{11}NC$), CN^-, $CH_2{=}CH{-}CN$, and C_2H_2. A number of experiments were also performed with ADP and AMP instead of ATP. The principal aim of this study was to demonstrate existing differences in the effects of ATP and of simple protic acids and to obtain further information on the nature of the stimulatory action of these agents in the N_2-ase model system. The reduction of the above-mentioned substrates by molybdothiol catalysts has already been described in previous publications of this series.