Characterization of Isolable Dioxygen Cobalt Complexes Containing Linear Pentadentate Ligands

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Abstract: Cobalt(II) complexes with linear potentially pentadentate Schiff base ligands have been prepared and their reaction with dioxygen studied. The ligands were synthesized from salicylaldehyde and diamino compounds containing a central donor atom. Various derivatives were produced by using a substituted salicylaldehyde or by placing different hydrocarbon residues on a central nitrogen donor. Most of the cobalt(II) complexes are stable in the solid state, but all react with oxygen in solution to some extent. A monomeric superoxo adduct was isolated with one of the complexes containing an unsubstituted central nitrogen donor. Other cobalt(II) complexes of this type react with oxygen to form dimeric peroxo adducts. An unusual dimeric dioxygen complex was obtained with a compound in which the central nitrogen donor is substituted with the methyl group. This adduct is believed to incorporate both superoxo and precursor species. Comparison of the precursor structure to that of the dimeric peroxo adduct suggests a different mode of bonding than that which occurs in dioxygen complexes with other types of ligands. The significance of this observation is discussed with regard to the formation of monomeric vs. dimeric dioxygen adducts.

Investigations involving reversible dioxygen complexation to cobalt(II) Schiff base compounds employing tetradentate ligands have yielded numerous significant findings.[1-3] It has been observed[4] that an additional ligand must be present in order to isolate these dioxygen complexes. X-ray analyses[5] have shown that the additional ligand occupies a position trans to the dioxygen ligand. The fifth donor is necessary because the four-coordinate square-planar precursor is relatively unreactive. The type of additional ligand was shown to greatly influence the stability of the complex.[4] For solid state reactions in which there are no other ligands present, six-coordinate dioxygen adducts are produced by the mutual bridging of phenolic oxygen atoms between neighboring molecules. Thus, it is well established that in dioxygen adducts possessing Schiff base tetradentate ligands, six coordination positions must be occupied.

One might, therefore, expect pentadentate ligands to offer as much or more potential than would tetradentate ligands in this regard. Such complexes have received relatively little attention. Specifically only one compound, Co(SALDPT), has been studied[6] in any detail (SALDPT = bis(salicylideniminato-3-propyl)amine). Floriani and Calderazzo[4] reported the preparation of an irreversible 1:1 adduct, Co(SALDPT)(O_2), from tetrahydrofuran. The reaction of a benzene solution of Co(SALDPT) with dioxygen was found to yield a diamagnetic 2:1 adduct. An apparently similar 2:1 complex was isolated[8] from toluene, $[\mathrm{Co(SALDPT)}]_2(\mathrm{O_2})\cdot 2\mathrm{C_6H_5CH_3}$, and its molecular structure was determined. A comparison of the bonding parameters in this compound with that found in the more reversible $[\mathrm{Co(SALEN)}]_2(\mathrm{DMF})_2(\mathrm{O_2})$ reveals differences in the two systems (SALEN = bis(salicylideniminato)ethane). In the SALEN compound, dioxygen is trans to coordinated DMF with an O–O distance of 1.35 Å,[5] while in the SALDPT compound dioxygen is cis to the secondary nitrogen and has an O–O bond length of 1.45 Å.[8]

The present report concerns an in depth study of the reaction of dioxygen with cobalt(II) complexes containing different pentadentate ligands and the characterization of any isolable products. The structural formulas of the cobalt(II) starting compounds are shown in Figure 1. Characterization of these precursors[9,10] as well as two preliminary reports[11,12] dealing with dioxygen adducts of some of these compounds have already appeared.

Experimental Section

Materials. Salicylaldehyde, 5-chlorosalicylaldehyde, 5-methoxysalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-nitrosalicylaldehyde, 3-nitrosalicylaldehyde, and bis(3-aminopropyl)amine were obtained commercially and used without further purification. 3-Methoxysalicylaldehyde and 2-hydroxyacetophenone were purified by vacuum distillation prior to their use. Bis(3-aminopropyl)methylamine, bis(3-aminopropyl)-*n*-propylamine, bis(3-aminopropyl)phenylamine, bis(3-aminopropyl)isobutylamine, and bis(3-aminopropyl)benzylamine were prepared by catalytically reducing the corresponding cyano compound which was obtained via a published procedure.[13] Bis(3-aminopropyl)methylphosphine,[9,14] bis(3-aminopropyl) ether,[15] and bis(3-aminopropyl) sulfide[16] were synthesized as previously described. The addition of Br_2 to salicylaldehyde produced 5-bromosalicylaldehyde while 3-isopropylsalicylaldehyde was prepared by the Duff reaction.[17] All other chemicals used were reagent grade or equivalent. Oxygen was obtained from Airco Gas Products, Inc. and was not further purified.

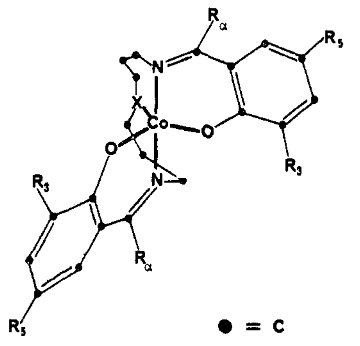
Preparation of Cobalt(II) Precursors. Co(SALDPT), Co(5-NO_2SALDPT), Co(5-ClSALDPT), Co(3-NO_2SALDPT), Co(3-CH_3OSALDPT), and Co(SALMeDPT) were prepared by the method of Calvin and co-workers.[2] The preparation of Co(SALMeDAPP), Co(SALPhDPT), Co(SALDAPS), and Co(SALDAPE) as well as various derivatives of the latter three compounds appeared in an earlier paper.[10] The same general preparative procedure was followed in making the other precursors. Anal. C, H, N.

Preparation of 2:1 Dioxygen Complexes from Solution. In a tubular flask equipped with bubbler and detachable frit, 50 mL of a previously filtered saturated solution (benzene, tetrahydrofuran, acetone, or acetonitrile) of the cobalt(II) complex was subjected to oxygen at atmospheric pressure. After a few minutes of bubbling, black or brown crystalline precipitates were formed. After 1–2 h, the contents of the flask were filtered (via the frit) and the product was dried by passing oxygen through the flask for an additional 10 min. Anal. C, H, N.

Preparation of Co(5-NO_2SALDPT)$O_2\cdot\frac{1}{2}(CH_3)_2CO$. Co(5-$NO_2$SALDPT) was dissolved in acetone and the solution (0.1 M) was filtered into the tubular flask. Oxygen at a pressure of 800 Torr was passed rapidly through the solution. No precipitate was observed but the solution became quite cold. Continued bubbling of oxygen resulted in almost complete solvent evaporation and the formation of a black crystalline precipitate. The product was isolated and dried under oxygen for 10 min as described above. Anal. Calcd for $(\mathrm{C_{20}H_{21}N_5O_8Co})(\mathrm{C_3H_6O})_{0.5}$: C, 47.16; H, 4.38; N, 12.79. Found: C, 47.56; H, 4.74; N, 12.56. $\mu_{\mathrm{eff}} = 1.51\ \mu_{\mathrm{B}}$; weight loss calcd for removal of O_2 and solvent = 11.56%; found 11.15% (90 °C).

Preparation of Co(α-CH_3SALDPT)O_2. Co(α-CH_3SALDPT) was exposed to oxygen for 48 h in the solid state. The light-brown precursor slowly changed color becoming very dark brown. The same reaction takes place in air but at a much slower rate. Anal. Calcd for $(\mathrm{C_{22}H_{27}N_3O_4})$: C, 57.89; H, 5.92; N, 9.21. Found: C, 57.68; H, 5.87; N, 9.33.

Physical Measurements. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240 elemental analyzer. Cobalt



Complex	X
Co(RSALDPT)	NH
Co(RSALMeDPT)	NCH_3
Co(RSALn-PrDPT)	$NCH_2CH_2CH_3$
Co(RSALi-BuDPT)	$NCH_2CH(CH_3)_2$
Co(RSALBzDPT)	$NCH_2C_6H_5$
Co(RSAL PhDPT)	NC_6H_5
Co(RSALMeDAPP)	PCH_3
Co(RSALDAPS)	S
CO(RSALDAPE)	O

R_3 = H, CH_3O, $CH(CH_3)_2$, NO_2
R_5 = H, Br, Cl, CH_3O, NO_2
R_α = H, CH_3

Figure 1. Structural representation and abbreviated names of the cobalt(II) precursors.

analysis and molecular weight measurements were conducted by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectral analyses were performed on a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer. Infrared spectra were taken as Nujol mulls between KBr plates on a Perkin-Elmer 621 grating spectrophotometer which was calibrated with polystyrene. Near-IR and visible spectra were measured on a Cary 14 spectrophotometer. Electron spin resonance spectra were obtained with a Varian E-12 electron spin resonance spectrometer. The field and frequency calibrations were made using Varian weak pitch and a Fluke frequency meter, Model 1953-A. Oxygen uptake measurements were obtained with a modified Warburg apparatus. Thermogravimetric analysis (TGA) data were obtained on a Tracor TGA-5 system. Sample weights were typically 10-20 mg and scanning rates were either 2 or 5 °C/min. Magnetic susceptibility measurements at four fields were made according to the Faraday method.

Results and Discussion

Cobalt(II) complexes of the type Co(RSALDPT) react with dioxygen in organic solvents. Products isolated from these reactions have the general formula $[Co(RSALDPt)]_2O_2$·solvent. These formulations are supported by elemental and thermogravimetric analyses. The presence of solvent is also substantiated by infrared and mass spectral analyses of the oxygenated materials.

The solvents used were chosen for their wide range in dielectric constants and their high vapor pressures which facilitate the isolation of oxygen complexes. Substituents (R) which differ in inductive and resonance effects were chosen in the belief that electron-donating groups should enhance the formation and stability of the oxygen complex and thereby provide a means of supporting the Co(III) nature of these compounds. This hypothesis was supported in that the reaction of dioxygen with $Co(3\text{-}CH_3OSALDPT)$ is considerably faster than the reaction with the 5-nitro derivative (Figure 2).

Thermogravimetric analyses (Figure 3) indicate both oxygen and solvent are lost at approximately the same temperature prior to sample decomposition (~250 °C). The absence of any well-defined separation between the removal of oxygen and the removal of solvent suggests that the oxygen is "locked in" by the solvent molecules and is removed only when the solvent is lost. The low percent weight loss observed in several cases can be attributed to some solvent loss on drying the sample.

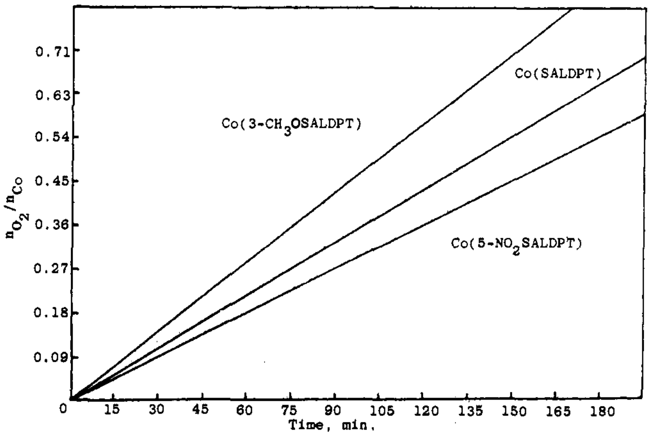


Figure 2. Oxygen uptake as a function of salicylaldehyde substitution. Reaction in diglyme solution at room temperature and 760 Torr of O_2 pressure.

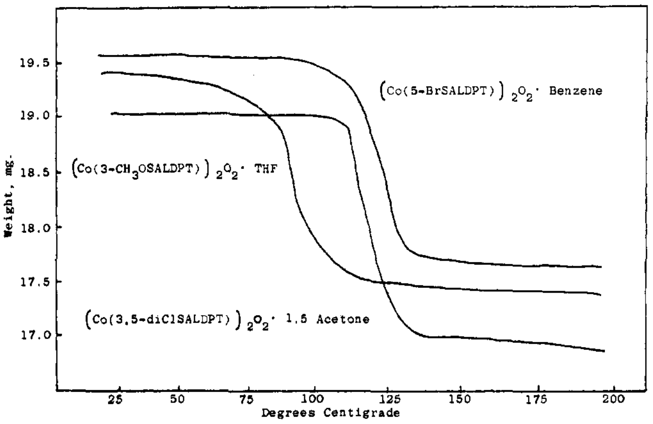


Figure 3. Thermogravimetric analyses of dioxygen complexes prepared in solution.

The formulation of these compounds as peroxo adducts is supported by their low magnetic moments. The complexes are essentially diamagnetic with slight paramagnetism which may arise from (1) the presence of a high-spin cobalt(II) impurity, (2) a superoxo impurity, and/or (3) temperature-independent paramagnetism. The diamagnetism arises as a result of a formal one-electron transfer from each cobalt(II) to the dioxygen molecule and a conversion from high- to low-spin behavior. This is consistent with what has been found for other postulated μ-peroxo adducts and with the x-ray structural analysis of $[Co(SALDPT)]_2O_2{\cdot}C_6H_5CH_3$.[8]

The dioxygen complexes are very stable in the solid state at room temperature and atmospheric pressure. They dissolve slowly in chlorinated solvents yielding dark solutions from which uncharacterized brown materials are produced. An ESR spectrum of the solutions just after the compounds are dissolved is that of a 1:1 adduct.[18] This indicates that the dimeric oxygen complexes are broken up upon interaction with solvent. The infrared spectra of the dioxygen adducts are similar to the precursors with only slight changes resulting from small shifts in some of the peaks. Additional peaks corresponding to the solvent are present in the adducts which are not present in the unoxygenated materials.

Even though O_2 and solvent are readily lost upon heating (~110 °C) in vacuo, the dioxygen adducts of Co(RSALDPT) are not completely reversible. This is indicated by the slightly low elemental analyses (~2% C) and magnetic moments (~3.5 μ_B) of the deoxygenated compounds relative to the cobalt(II) precursors. There is no evidence that the deoxygenated materials are air sensitive, so these results cannot be attributed to reoxygenation in the solid state.

Isolable and well-characterized 1:1 cobalt–dioxygen complexes incorporating a polydentate ligand are relatively rare. A consideration of the generally accepted mechanism for the reaction of dioxygen with cobalt(II) complexes may suggest why this is the case.

$$\mathrm{Co^{II}(RSALDPT) + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{III}(RSALDPT)O_2}$$

$$\mathrm{Co^{III}(RSALDPT)O_2 + Co^{II}(RSALDPT) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co^{III}(RSALDPT)]_2O_2}$$

If the concentration of starting material is very small in comparison to the concentration of oxygen, then the unreacted cobalt(II) complex should react preferentially with uncoordinated oxygen rather than coordinated oxygen. In order to obtain a very high concentration of oxygen, however, the precursor must be relatively unreactive. Taking these facts into consideration, it was possible to prepare a 1:1 adduct of Co(5-NO_2SALDPT).[11] A polar solvent, acetone, was used which should favor the formation of the more polar 1:1 adduct. The precursor concentration was kept less than 0.1 M in order to minimize dimerization and the pressure of oxygen was increased to 810 Torr to favor reaction with dioxygen.

Unlike the μ-peroxo complexes discussed previously, the reaction of dioxygen with Co(5-NO_2SALDPT) under these conditions did not produce an immediate precipitation. Only after prolonged exposure to oxygen and evaporation of the solvent to near dryness was a product obtained which we formulate as Co(5-NO_2SALDPT)O_2·½$(CH_3)_2CO$. Both oxygen and the solvent are lost at the same temperature (90 °C). These results correspond with what was found for the dimeric compounds in that a solvent effect is operating to increase the stability of the complex. Removal of oxygen and solvent resulted in a material with a magnetic susceptibility (μ = 3.83 μ_B) slightly less than the precursor which suggests a small amount of irreversible oxygenation.

The formulation of this compound as a 1:1 adduct does not necessarily mean it is a superoxo complex. The complex is considerably more paramagnetic than the μ-peroxo adducts, although the magnetic moment is slightly less than would be expected for one unpaired electron. The moment is consistent, however, with what has been found for other superoxo adducts.[19]

In order to define this compound more clearly as a superoxo adduct, the ESR spectrum of the solid-state material was obtained. This spectrum (Figure 4) is similar to the anisotropic spectra of other superoxo adducts.[18] The observation of this spectrum in the solid state at room temperature is unusual but is probably attributed to the solvent of crystallization which shields the paramagnetic centers from each other. The coupling constants are considerably smaller than those of low-spin cobalt(II) compounds,[20] and there is no nitrogen superhyperfine splitting. This indicates that most of the unpaired electron density has been removed from cobalt and now resides on the dioxygen ligand. Thus, the compound is correctly formulated as $Co^{III}O_2^-$.[21] The ESR parameters of Co(5-NO_2SALDPT)-O_2·½$(CH_3)_2CO$ associated with the spectrum are as follows: $g_\parallel$ = 2.086, $g_\perp$ = 2.012; $a_\parallel$ = 20.0 G, $a_\perp$ = 12.8 G. Attempts to prepare other 1:1 adducts in this fashion were unsuccessful, suggesting that the substituent plays an important role in the preparation of these compounds.

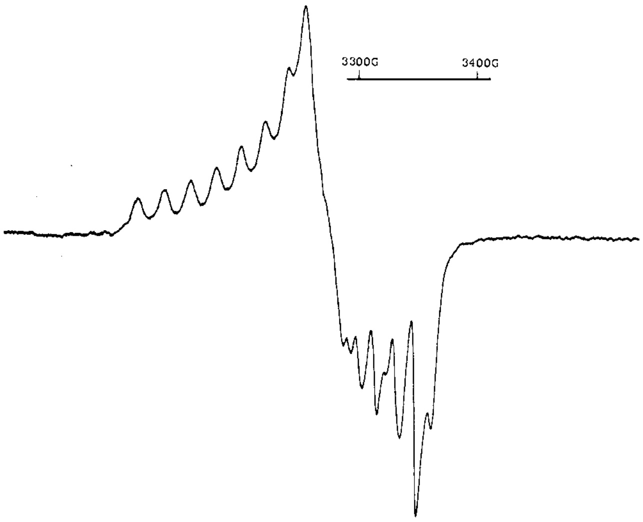


Figure 4. ESR x-band spectrum of Co(5-NO_2SALDPT)O_2·½$(CH_3)_2CO$; solid state; room temperature.

Two of the cobalt(II) complexes, Co(3-NO_2SALDPT) and Co(α-CH_3SALDPT), react with oxygen in the solid state. Both compounds darken on exposure to air but are completely reversible in that the color and precursor magnetic moment can be restored by heating the oxygenated compound in vacuo at 100 °C for 1 h. The α-CH_3SALDPT precursor was prepared in a cold reaction in which the temperature was maintained at 0 °C. Another form of this compound was obtained from a hot reaction, but this form was unreactive in the solid state. The preparation of active Co(3-NO_2SALDPT) was not dependent upon temperature.

The solid-state reaction of dioxygen with Co(3-NO_2-SALDPT) was previously studied by Calvin,[2] who reported a 2:1 Co/O_2 ratio based on O_2 uptake data. Elemental and thermogravimetric analyses (percent weight loss calculated for removal of weight equivalent to dioxygen, 3.18; found, 2.96) on the oxygenated complex also indicate the adduct should be formulated as [Co(3-NO_2SALDPT)]$_2O_2$. Magnetic susceptibility data, μ_{eff} = 1.44 μ_B, suggest a mixture of compounds. Although there is probably some 2:1 adduct present, there must also be some 1:1 complex. This is supported by ESR data on the solid-state compound which shows a spectrum of a 1:1 superoxo complex. The ESR parameters of the 1:1 adduct are as follows: $g_\parallel$ = 2.091, $g_\perp$ = 2.012; $a_\parallel$ = 21.4 G, $a_\perp$ = 13.6 G. It has been observed that Co(3-NO_2SALDPT) can be oxygenated–deoxygenated repeatedly without any noticeable irreversibility.

A compound which was not studied by Calvin is Co(α-CH_3SALDPT). This complex which is active only when prepared at low temperature reacts in the solid state with dioxygen in a 1:1 ratio. Elemental analyses support the formulation Co(α-CH_3SALDPT)O_2. Although TGA analysis was inconclusive due to the exceptional reversibility of the compound, oxygen uptake experiments support the 1:1 formulation (n_{O_2}/n_{Co} = 1.1). An ESR specturm of the 1:1 adduct was also obtained in the solid state, but it was not well-resolved ($g_\parallel$ = 2.097, $g_\perp$ = 2.016). The magnetic moment of 1.71 μ_B is consistent with a superoxo complex. There is no evidence of irreversibility and the precursor can be repeatedly oxygenated and deoxygenated.

In contrast to the exceptional reactivity of the Co(R-SALDPT) complexes, alkyl- and aryl-substituted compounds of the type Co(RSALR′DPT) are relatively unreactive toward oxygen. None of these cobalt complexes react with oxygen in the solid state, and only one dioxygen adduct was isolated from solution. This complex has the general formula [Co(SAL-MeDPT)]$_2O_2$·2C_6H_6 which is supported both by elemental

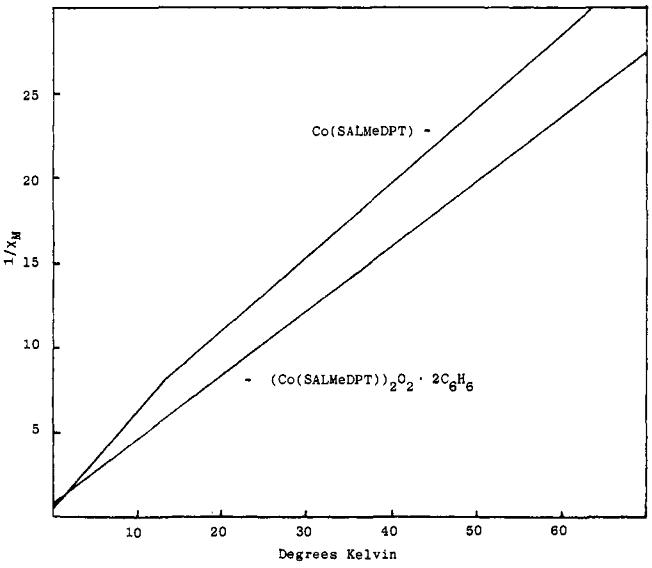


Figure 5. Low-temperature magnetic susceptibility data for Co(SALMeDPT) and $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$.

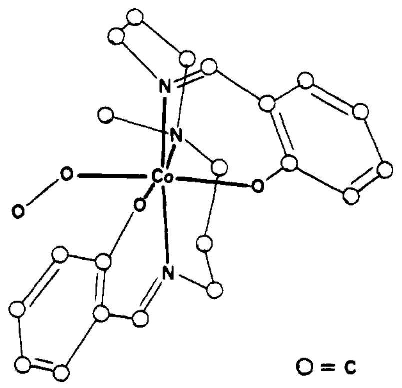


Figure 6. Probable conformation of the ligand in $Co(SALMeDPT)O_2$ based on ref 8. Note the position of the methyl group on the central nitrogen.

and thermogravimetric analyses.[12] Again both oxygen and solvent are lost simultaneously, but the temperature at which this loss occurs, 50 °C, is substantially less than that found for the Co(RSALDPT) adducts. Furthermore, elemental analyses and magnetic susceptibility of the deoxygenated compound are identical to that of the starting material. These results suggest the compound is considerably more reversible than the Co(RSALDPT) adducts prepared in solution. Deoxygenated species can be repeatedly oxygenated-deoxygenated with very little loss of compound due to irreversibility.

Volumetric O_2 uptake experiments in benzene solution at 810 Torr further support the 2:1 stoichiometry ($n_{O_2}/n_{Co} = 0.49$). Infrared analysis of the oxygenated complex via Nujol mull and KBr pellet techniques showed only one additional band in comparison with the precursor corresponding to benzene solvate. No vibrational modes involving coordinated oxygen were observed; however, the compound appears to deoxygenate upon crushing. Attempts to observe a laser Raman spectrum of the compound resulted in sample decomposition. $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ loses both oxygen and benzene within 48 h after placing the compound in vacuo (10^{-1} to 10^{-2} Torr) at room temperature. Deoxygenation proceeds more slowly at room temperature in the air. Heating the compound results in rapid deoxygenation. The volume of oxygen given off, corrected for benzene, corresponds again to a 2:1 adduct ($n_{O_2}/n_{Co} = 0.50$). The compound also vigorously evolves O_2 when placed in several noncoordinating organic solvents with precipitation of Co(SALMeDPT).

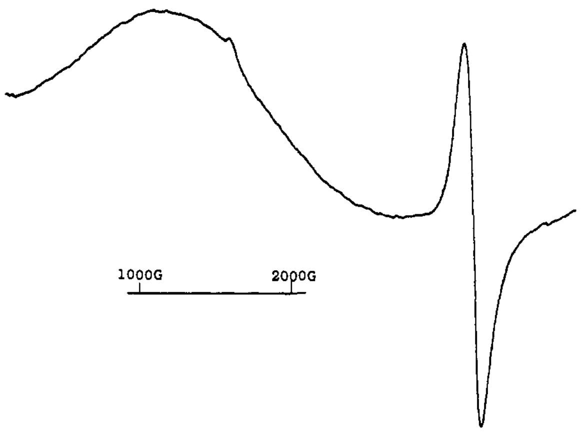


Figure 7. ESR x-band spectrum of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$; solid state; −150 °C.

One striking difference between the μ-peroxo adducts of Co(RSALDPT) and the dioxygen adduct of Co(SALMeDPT) concerns their magnetic properties. The former compounds are essentially diamagnetic whereas the latter compound is very paramagnetic with $\mu_{eff} = 3.26\ \mu_B$ for each cobalt atom at 25 °C. Low-temperature magnetic susceptibility measurements are consistent with those at room temperature. No spin pairing is observed down to 2.7 K (Figure 5). The magnetic moment of 3.26 μ_B is that of freshly prepared samples. Models show that a dimeric oxygen complex of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ may not have the same solid-state structure as μ-peroxo compounds of Co(RSALDPT). This is because of the steric crowding produced by the methyl groups (Figure 6). If this steric interaction were great enough, it could prevent dimerization of the type observed in $[Co(SALDPT)]_2O_2 \cdot C_6H_5CH_3$. The unusual magnetic moment can be explained in terms of magnetic exchange between the coordinated superoxide ligand and the high-spin cobalt(II) complex. The association of the superoxo compound and the cobalt(II) complex could be produced by a dipole–dipole or ion–dipole interaction Essentially, this could be thought of as a dimer with nonequivalent halves: $[(SALMeDPT)Co^{III}\text{-}O_2^{-}\text{---}Co^{II}(SALMeDPT)]$.

Although the above explanation is only tentative until a structural analysis is completed, an ESR spectrum of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ in the solid state can be interpreted in terms of a 1:1 adduct plus a high-spin cobalt(II) species (Figure 7). The broad signal at low field occurs at about 1000 G, consistent with the ESR signal of a high-spin cobalt(II) complex. The signal at about 3300 G corresponds to one unpaired electron but shows no cobalt hyperfine coupling. A physical mixture of 1:1 adduct and unreacted Co(II) is ruled out based on the homogeneous quality of the repeatedly obtained crystalline material and its consistent analyses which indicate no deoxygenation before or soon after the magnetic and spectral measurements are made. Furthermore, low-temperature magnetic data (Figure 5) on the starting compound, Co(SALMeDPT), show spin pairing starting to occur at 15 K. No spin state change is observed in $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ indicating that the high-spin cobalt(II) compound is not present as a discrete complex. A dipolar interaction could perturb the system enough to prevent spin pairing and also explain the lack of hyperfine coupling in the superoxo signal. It must be realized, however, that association could occur without involving the superoxo ligand.[22]

Surprisingly a dioxygen adduct of Co(SALMeDPT) could not be isolated from any other solvent, including toluene and pyridine. Attempts to isolate an oxygen complex with various derivatives (α-CH_3, 5-CH_3O, 3-CH_3O, and 5-NO_2) were unsuccessful even in benzene. Furthermore, no oxygen adducts of any of the other alkyl- or aryl-substituted compounds were obtained. These results indicate a very subtle solvent effect is operating in $[Co(SALMeDPT)]_2O_2\cdot 2C_6H_6$. The slightest variation in the steric requirements of the system is apparently not allowed. This also supports the idea of a weakly associated dimer, stabilized by the solvent which is present in the crystal lattice. The ultimate interpretation of the bonding in $[Co(SALMeDPT)]_2O_2\cdot 2C_6H_6$ will probably depend on an x-ray analysis. Small to medium size crystals have been obtained by slowly evaporating a benzene solution under 800 Torr of oxygen pressure. Preliminary data on the crystals indicate they are monoclinic but twinned. The cell constants are as follows: a = 12.74 Å, b = 68.34 Å, c = 11.70 Å, $\alpha = \gamma = 90.0°$, $\beta = 86.1°$. The calculated density is 1.34 g/cm^3 assuming eight dimers per unit cell (space group $C2/m$; one molecule per asymmetric unit). The twinned nature of the crystals has for the moment precluded a precise x-ray analysis.[23]

In relationship to the Co(RSALDPT) compounds, the amine substituted alkyl and aryl derivatives are considerably less reactive toward oxygen. It is believed the main reason for this is that the alkyl and aryl groups offer considerable steric blockage to the position of attack by dioxygen. Models show that the position cis to the central nitrogen is effectively blocked by large bulky groups on the amine nitrogen. However, there may be electronic effects operating in the N-substituted aryl compounds due to the substantially reduced basicity of this group. Nevertheless, the larger the substituent the less reactive the cobalt complex. This is indicated by oxygen uptake measurements which show that Co(SALDPT) reacts faster than Co(SALMeDPT) which reacts faster than Co(SALPrDPT) (Figure 8). They are what one would expect if steric hindrance was in fact responsible for the reduced reactivity of these compounds. Similar results have been obtained with similar nickel complexes in their reaction with pyridine. It was found that Ni(SALMeDPT) is considerably less reactive toward pyridine than Ni(SALDPT).[24] It was suggested that steric blockage by the methyl group was responsible for the reduced reactivity.

In order to compare complexes with similar pentadentate ligands, compounds with donors other than nitrogen and oxygen were synthesized. These ligands differed only in that the nitrogen in the central donor position was replaced by either phosphorus, sulfur, or oxygen. The complexes, Co(RSALMeDAPP), Co(RSALDAPS), and Co(RSALDAPE), were not reactive in the solid state, and solution reactions afforded only the original starting materials. Visually, there was no sign that oxygenation was taking place, but ESR investigations revealed that at least some 1:1 complex is formed.[25] There does not seem to be a substituent effect since the placement of electron-donating groups on the salicylaldehyde portion of the compounds does not increase their reactivity. We must assume then that the differences in reactivity of these compounds are related to differences in the donor properties of phosphorus, sulfur, and oxygen, relative to nitrogen. However, other aspects must be considered since ligands with these type donors do produce stable adducts in other systems.[26] Perhaps the arrangement of the chelate ligand about the metal is an important factor.

In summary, the reaction of dioxygen with cobalt(II) complexes containing pentadentate Schiff base ligands is quite varied. Both stable and unstable adducts are formed and in some cases dioxygen complexes could be isolated. As a group, compounds of the type Co(RSALDPT) appear to be the most reactive. It is with these complexes that stable adducts are obtained. The compounds from solution reactions are somewhat irreversible but not completely irreversible as had previously been reported. The products from solid-state reactions are much more reversible and exemplify the type of oxygen carrier worthy of further study. An exception to this occurs with Co(SALMeDPT). This complex forms a very reversible isolable dioxygen adduct in benzene. Its properties can be attributed to an unusual type of bonding caused by steric crowding. It is believed that this type of pentadentate complex may offer a possible route to the preparation of 1:1 adducts by preventing dimerization. However, attempts to prove this by placing larger groups on the central amine donor failed as a result of the reduced reactivity of these compounds.

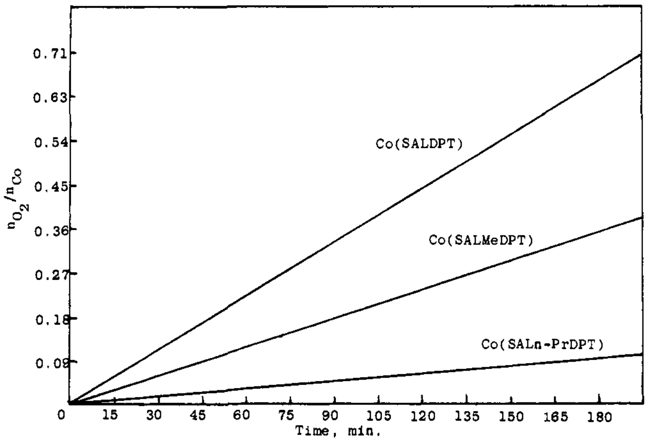


Figure 8. Oxygen uptake as a function of amine substitution. Reaction in diglyme solution at room temperature and 760 Torr of O_2 pressure.

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