general properties of such electron-deficient species may be rationalized as follows. The species involved are electron deficient and will therefore seek the site where electrons are most readily available. This is to be found at multiple π bonds, and these are therefore preferentially attacked. With C–H bonds, the highest electron density is present between the carbon and the hydrogen and accordingly insertion will occur. In the case of C–F bonds, however, the unbonded side of the fluorine atom presents a high electron density due to nonbonding electrons. It is quite plausible that the incoming carbon atom finds this side to be a more readily available source of electrons than the C–F bond itself. Steric factors may also contribute to making insertion to give a C–C–F transition state less favorable than simple attachment to give a C–F–C configuration. The CF₄ molecule presents mostly the electron-rich unbonded "backside" of the fluorine atom to an impinging C atom, while with CH₄ there is relatively little peripheral electron density to prevent an approach to the C–H bond. The hypothesis that at C–F bonds abstraction is favored over insertion thus becomes reasonable. The same consideration can also account for the apparent unreactivity of single C–C bonds toward electron-deficient species.[1,4]

Monomeric Oxygen Adducts of N,N'-Ethylenebis(acetylacetoniminato)ligandcobalt(II). Preparation and Properties[1]

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Abstract: A series of monomeric molecular oxygen carriers of the general formula Co(acacen)(B)O₂ (acacen = (CH₃C(O⁻)=CHC(CH₃)=NCH₂–)₂; B = N,N-dimethylformamide, pyridine, 4-aminopyridine, 4-methylpyridine, and 4-cyanopyridine) were prepared in nonaqueous solvents. These adducts are reversibly formed in solution and are shown to be monomeric by oxygen uptake and molecular weight experiments. The equilibrium constant for the reaction in N,N-dimethylformamide was measured at $-10°$ and found to be $\log K_{eq} = 2.11 \pm 0.10$. Crystalline adducts were isolated and characterized by means of elemental analysis, oxygen evolution measurements, molecular weight, magnetic measurements, and electronic and infrared spectra. These oxygen adducts are formulated as monomeric octahedral complexes of low-spin cobalt(III), because epr measurements[3] show that the unpaired electron is largely associated with the coordinated oxygen.

Schiff base complexes of cobalt(II) have long been known to bind molecular oxygen.[4] Following the discovery of Tsumaki[5] that crystals of N,N'-ethylenebis(salicylideneiminato)cobalt(II) darken when exposed to the atmosphere, Calvin and his coworkers[6] conducted an exhaustive study of the oxygen-carrying capabilities of this complex and some of its ring-substituted derivatives in the solid state. They discovered that reversible coordination with oxygen was only possible with an "active" crystalline modification of the solid complex. Solution oxygenation reactions of these complexes would preclude the necessity of preparing an active form of the crystal. Calvin makes only a brief reference to the oxygenation of N,N'-ethylenebis(salicylideneiminato)cobalt(II) in pyridine solution.[7] This reaction in pyridine and other solvents has recently been rein-

vestigated by Calderazzo and coworkers.[8,9] Fritz and Gretner[10] have investigated the reaction of oxygen with a pentadentate cobalt(II) Schiff base complex, N,N'-dipropylenaminebis(salicylideneiminato)cobalt(II).

Although the initial formation of a monomeric 1:1 oxygen adduct in solution has been postulated on the basis of kinetic evidence,[11] thus far practically all of the oxygen adducts of cobalt(II) complexes have been dimeric oxygen-bridged species. The first well-defined example of a monomeric oxygen adduct of cobalt(II) prepared in solution and isolated as a crystalline solid was recently reported by Floriani and Calderazzo.[9] We wish to report here in detail results given in an earlier communication[12] on the reaction of molecular oxy-

(1) Abstracted from the Ph.D. Thesis of A. L. Crumbliss, Northwestern University, 1968.

(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

(3) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).

(4) L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963).

(5) T. Tsumaki, *Bull. Chem. Soc. Jap.*, **13**, 252 (1938).

(6) M. Calvin, *et al., J. Am. Chem. Soc.*, **68**, 2254 (1946).

(7) R. H. Bailes and M. Calvin, *ibid.*, **69**, 1886 (1947).

(8) F. Calderazzo, C. Floriani, and J. F. Salzman, *Inorg. Nucl. Chem. Lett.*, **2**, 379 (1966).

(9) C. Floriani and F. Calderazzo, *J. Chem. Soc., A*, 946 (1969).

(10) H. P. Fritz and W Gretner, *Inorg. Nucl. Chem. Lett.*, **3**, 141 (1967).

(11) C. Tanford, D. C. Kirk, Jr., and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **76**, 5325 (1954); J. Simplicio and R. G. Wilkins, *ibid.*, **89**, 6092 (1967); F. Miller, J. Simplicio, and R. G. Wilkins, *ibid.*, **91**, 1962 (1969). It should be noted that evidence has just been presented for monomeric oxygen adducts of vitamin B₁₂ᵣ by J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *ibid.*, **91**, 2775 (1969).

(12) A. L. Crumbliss and F. Basolo, *Science*, **164**, 1168 (1969).

gen and N,N'-ethylenebis(acetylacetoniminato)cobalt-(II), Co(acacen), in nonaqueous solvents containing

Co(acacen)
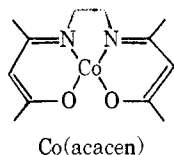
added base to form a series of monomeric oxygen adducts.

Experimental Section

Materials. All solvents were carefully dried and stored under nitrogen. Particular care was taken with N,N-dimethylformamide, which was distilled *in vacuo* from BaO and stored over molecular sieves in a nitrogen atmosphere. Pyridine was refluxed over and distilled from CaH.

The reagents 2,4-pentanedione, ethylenediamine, and anhydrous cobalt(II) iodide were obtained commercially and used without further purification. 4-Methylpyridine was obtained commercially, but was vacuum distilled prior to use. 4-Cyanopyridine (Aldrich Chemical Co.) was recrystallized from hexane, mp 78.5°. 4-Aminopyridine (Aldrich Chemical Co.) was recrystallized twice from benzene, mp 161.5°.

Analyses. C, H, and N analyses were performed by H. Beck of this department. Analyses of the thermally unstable oxygen adducts were performed immediately upon removal from sealed tubes stored below −20°. The elemental analyses of the compounds isolated were reported previously.[12]

Molecular oxygen was identified by its mass spectrum. These spectra were obtained by R. M. Sherrill of this department, using a Consolidated Electrodynamics 21-130 mass spectrometer.

N,N-Dimethylformamide (DMF) was identified by means of an F and M Model 720 gas chromatograph, using a column filled with 15% Versamid 900 on 60-80 meshs upport washed with acid and base.

Preparation of Complexes.[13] All preparations and manipulation of the cobalt complexes were carried out under an atmosphere of prepurified nitrogen. Oxygen used for the preparation of the oxygen adducts was dried over P_4O_{10}.

Co(acacen). The Schiff base, N,N'-ethylenebis(acetylacetonimine), was prepared by the literature method of Martell, Belford, and Calvin.[14] The cobalt complex was prepared by a modification of the method of Everett and Holm.[15]

The oxygen adducts were all prepared in a similar manner using an apparatus specially designed so that oxygenation, crystallization, and isolation of the adduct could all take place in the same reaction chamber while maintaining a controlled temperature below 0°.

Co(acacen)(DMF)O₂. In a typical preparation 0.90 g (3.2 mmoles) of Co(acacen) was dissolved in 40 ml of DMF to give a red-orange solution, which was oxygenated at −20° to yield an opaque black colored solution. While still in an oxygen atmosphere, the solution was cooled to *ca.* −50° while the product crystallized. The reaction solution was filtered at this temperature to isolate a dark, almost black product which was washed three times with dry ether. The solid product was dried briefly in an oxygen stream and then *in vacuo*. A temperature of less than −20° was maintained during the work-up of the reaction. The product was stored in sealed tubes below −20°.

Co(acacen)(py)O₂. In a typical preparation 0.55 g (2.0 mmoles) of Co(acacen) was dissolved in 39 ml of toluene with 13 ml of pyridine (165 mmoles) to give a deep red solution, which, when oxygenated at −20°, turned to an opaque black color. While still in an oxygen atmosphere, the solution was cooled to *ca.* −50° while the product crystallized. The reaction solution was then filtered at this temperature to isolate red-brown crystals which were washed with one 5-ml portion of precooled toluene followed by two 5-ml portions of precooled pentane. The crystals were dried *in vacuo*

and stored in sealed tubes below −20°. The same product can be isolated from neat pyridine in a similar manner.

Co(acacen)(CH₃-py)O₂. In a typical preparation 0.69 g (2.5 mmoles) of Co(acacen) was dissolved in 13 ml of toluene and 7 ml (72.0 mmoles) of 4-methylpyridie to give a deep red solution, which turned an opaque black color upon oxygenation at −20°. Precooled toluene, 22 ml, was added to the reaction solution to ensure complete precipitation of the product. While still in an oxygen atmosphere, the solution was cooled to *ca.* −50° while the product crystallized. The solution was filtered at this temperature to isolate a carmine red product which was washed once with 5 ml of precooled toluene and five times with 10-ml portions of precooled pentane. The solid was dried *in vacuo* and stored in sealed tubes below −20°.

Co(acacen)(CN-py)O₂. In a typical preparation 0.21 g (2.0 mmoles) of 4-cyanopyridine was added to a solution of 0.56 g (2.0 mmoles) of Co(acacen) in 60 ml of toluene in a nitrogen atmosphere. Oxygenation at −20° changed the deep red solution to an opaque black color. The oxygen adduct was crystallized by cooling to *ca.* −50° and isolated by filtration at that temperature. The solid was washed twice with 15-ml portions of precooled pentane. The reddish black solid was dried *in vacuo* and stored in sealed tubes below −20°.

Co(acacen)(NH₂-py)O₂. In a typical preparation 0.35 g (3.7 mmoles) of 4-aminopyridine was added to a solution of 0.97 g (3.5 mmoles) of Co(acacen) in 50 ml of DMF in a nitrogen atmosphere. The solution was oxygenated at −20° to give an opaque reddish black colored solution. The adduct was crystallized by adding 100 ml of precooled toluene and cooling to *ca.* −50°. After filtration at this temperature in an oxygen atmosphere, the brown product was washed twice with 10 ml of precooled toluene followed by two washings with 15 ml of precooled pentane. The solid was dried *in vacuo* and stored in sealed tubes below −20°.

Physical Measurements. Infrared spectra were recorded using a Perkin-Elmer 337 spectrophotometer. Nujol mulls of the oxygen adducts were prepared immediately after removal from sealed tubes at low temperatures and after the samples had been warmed to room temperature (see text).

Electronic spectra were obtained on a Cary Model 14 recording spectrophotometer using Nujol mulls.

Oxygen absorption by solutions of Co(acacen) was determined by *PVT* measurements at constant pressure or constant volume. Solutions of the unoxygenated complex were prepared in an inert atmosphere in a specially designed creased reaction flask. This flask was connected to the vacuum line where its contents could be exposed to oxygen, an inert gas, or high vacuum. The reaction flask bottom was designed to fit into a rubber cup and was agitated by an eccentric attached to the shaft of a $^1/_8$-hp electric motor. Agitation was sufficient so that oxygenation or deoxygenation was completed in less than 5 min. The flask was jacketed so that the reaction solution could be maintained at a constant temperature.

A standard vacuum line equipped with an automatic toepler pump was used for the quantitative measurement of oxygen released from the solid adducts. DMF was quantitatively measured by trapping at liquid nitrogen temperature, removing the trap from the line and weighing on an analytical balance.

Weight loss measurements on 20-mg crystalline samples of Co(acacen)(DMF)O₂ were made by loading the complex on a Cahn Model G electrobalance under a purge of cold helium. Samples were accurately weighed below 0° and then allowed to warm to 25° under a helium purge. The weight loss was then recorded.

Molecular weight measurements were made in pyridine by freezing point depression as described by Dilts and Shriver.[16]

Magnetic measurements were made by the Faraday method using a Varian 6-in. electromagnet with truncated pole pieces powered by a Sorensen Nobatron DCR 300-8A power supply. Deflections were measured by means of a Cahn Model G electrobalance equipped with external controls. An open quartz sample bucket was suspended in a double-walled dewar which permitted temperature control and which also allowed a helium flow to be passed through the sample cavity. The apparatus was calibrated using HgCo(SCN)₄.[17,18] Temperature control was achieved by passing a liquid nitrogen boil-off through the outer jacket of the dewar. Susceptibility determinations were made on at least two and sometimes five different samples of each complex. For all samples,

(13) The following abbreviations will be used throughout this paper: N,N-dimethylformamide, DMF; pyridine, py; 4-methylpyridine, CH₃-py; 4-aminopyridine, NH₂-py; 4-cyanopyridine, CN-py; N,N'-ethylenebis(acetylacetoniminato)cobalt(II), Co(acacen).

(14) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).

(15) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966).

(16) J. A. Dilts and D. F. Shriver, *ibid.*, **90**, 5769 (1968).

(17) F. A. Cotton, D. M. L. Goodgame, and A. Sacco, *ibid.*, **83**, 4157 (1961).

(18) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

Table I. Reversible Oxygen Uptake by Solutions of N,N'-Ethylenebis(acetylacetoniminato)cobalt(II) at $-6°$

Co(acacen), mmole	Solvent, ml	Additional ligand, mmole	O_2 absorbed,[a] mmole	$Co:O_2$
3.81×10^{-1} [b]	DMF (10)		3.63×10^{-1}	1.05
7.40×10^{-2}	Py (15)		7.39×10^{-2}	1.00
1.60×10^{-1}	Toluene (10)	CH_3-py (103.0×10^{-1})	1.67×10^{-1}	0.96
1.01×10^{-1}	Toluene (10)	NH_2-py (3.54×10^{-1})	9.90×10^{-2}	1.02
6.55×10^{-2}	Toluene (10)	CN-py (6.86×10^{-1})	7.20×10^{-2}	0.91

[a] Corrected for oxygen solubility in solvent. [b] Insufficient volume of solvent used to completely dissolve Co(acacen). All other determinations made with no undissolved solid present (see text).
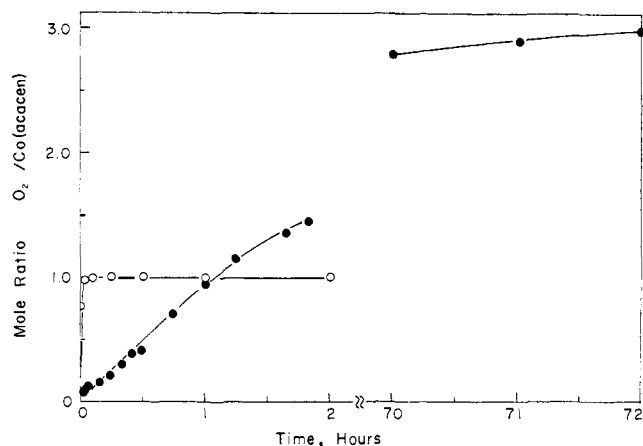

Figure 1. Oxygen absorption by DMF solutions of Co(acacen): O, data collected/at 6° and 760 mm of O_2 pressure; ●, data collected at 25° and 480 mm of O_2 pressure.
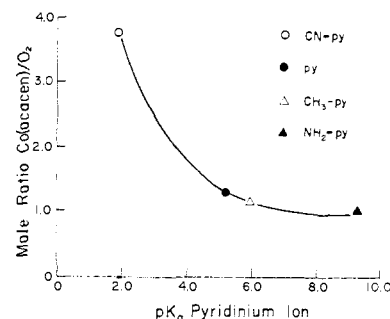

Figure 2. Oxygen adduct formation as a function of the base strength of the ligand in the axial position. A plot of the oxygen absorbed expressed in terms of the mole ratio Co(acacen)B/O_2 vs. the pK_a values of BH⁺. Data were collected for toluene solutions at $-10°$ and 300 mm of O_2 pressure.

deflections were measured at a minimum of ten temperatures over a temperature range from -196 to $25°$ (except for Co(acacen)-(DMF)O_2, where the upper temperature limit was $0°$). Data on each sample were collected at two field strengths to check for ferromagnetic and antiferromagnetic effects. In all cases the magnetic moment was found not be dependent on field strength. Curie-Weiss law parameters were obtained from the least squares plot of $1/\chi_g$ vs. T. Susceptibilities were corrected for diamagnetic contributions by the use of Pascal's constants.[19]

X-Ray powder patterns were obtained using a 57.3-mm radius Debye–Scherrer camera, and a vanadium foil filtered Cr $K\alpha$ X-ray source (λ 2.2909 Å). The powdered samples were sealed in 0.01-mm thin-walled capillary tubes.

Results

Solution Studies. The reaction of oxygen with Co-(acacen) in noncoordinating organic solvents (e.g., benzene or toluene) or weakly coordinating solvents (e.g., methanol or ethanol) results in a nonstoichiometric gas uptake by these solutions. Similar behavior is observed in coordinating solvents such as DMF or pyridine when the reaction is carried out at room temperature (Figure 1). Since at room temperature there is a continuous slow uptake of oxygen over a period of days, it appears that cobalt(II) must be catalyzing the oxidation of the organic ligand. However, at temperatures below $0°$ toluene solutions of Co(acacen) containing DMF, pyridine, or a substituted pyridine were found to react reversibly with molecular oxygen in a well-defined manner.

The substituted pyridine bases used in this investigation and the pK_a values[20] of the protonated bases are as

(19) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 400.
(20) K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967, p 146.

follows: NH$_2$-py, 9.3; CH$_3$-py, 6.00; py, 5.27; CN-py, 1.86. These particular choices were made because of their wide range of base strength and the absence of complicating steric factors.

Table I summarizes the results of oxygen uptake by Co(acacen) in solutions containing these substituted pyridines. These data show 1 mole of oxygen being absorbed per mole of cobalt complex, indicating the formation of a monomeric oxygen adduct. The oxygen absorption is reversible in that the solutions can be deoxygenated, by shaking in a vacuum, and then reoxygenated. This process can be carried out over 3–5 cycles without any apparent loss in oxygen-carrying capabilities.

At low oxygen pressures, the unoxygenated cobalt complex is in equilibrium with the oxygenated species. At a given pressure of oxygen we find that the relative amounts of oxygenated species formed increase with the base strength of the substituted pyridine present in solution (Figure 2). At a given oxygen pressure the degree of oxygenation of Co(acacen) in solutions containing DMF is less than in solutions containing a substituted pyridine.

Oxygenation in DMF at $-10°$ is rapid and completely reversible. For example, the oxygen absorption is greater than 90% complete in less than 30 sec at an oxygen pressure of 400 mm, and levels off to zero after 2–3 min; further absorption of oxygen by the solution is not observed, even on shaking in an oxygen atmosphere for up to 60 min. The reverse reaction, brought about by shaking the solution under vacuum, is complete in the order of minutes. These oxygenation–deoxygenation experiments can be carried out over at least 10 cycles without any apparent loss of oxygen-carrying ability.

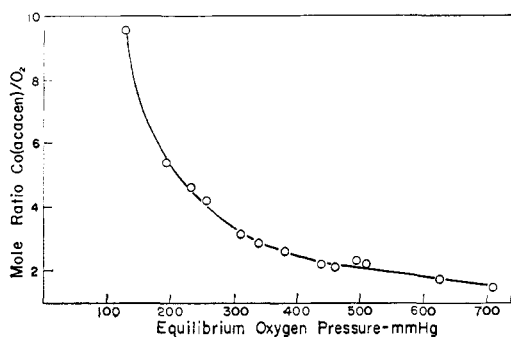Oxygen absorption data in DMF over an oxygen pressure range from 130 to 760 mm (Figure 3) is in

Figure 3. Oxygen absorption by DMF solutions of Co(acacen) as a function of oxygen pressure, at −10°.

Table II. Analytical Data. Oxygenated DMF Adduct of N,N′-Ethylenebis(acetylacetoniminato)cobalt(II)

		Calcd, %	Exptl, %
O₂[a]		8.28	6.6 ± 1.4
DMF[b]		18.92	18.0 ± 1.9
% wt loss[c]		27.20	27.3 ± 0.8
	C	51.25	50.79
Co(acacen)	H	6.45	6.42
residue	N	9.96	9.97

[a] Oxygen identified by mass spectroscopy. Value given is an average of four determinations. [b] DMF identified by vapor phase chromatography. Value given is an average of five determinations. [c] Calculated for the loss of 1 mole of O₂ and 1 mole of DMF per mole of complex. Value given is an average of four determinations.

agreement with that expected for equilibrium reaction 1. The calculated equilibrium constant for reaction

$$Co(acacen) + DMF + O_2 \rightleftharpoons Co(acacen)(DMF)O_2 \quad (1)$$
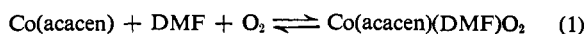
1 in DMF solution at −10° is log K_{eq} = 2.11 ± 0.10. Attempts to make the data fit an equilibrium expression for a reaction producing a dimeric oxygen-bridged species, or a combination of monomeric and dimeric species, did not result in a constant value for the calculated equilibrium constant over the pressure range studied.

Additional evidence for the formation of a monomeric oxygen adduct in pyridine solution is obtained from molecular weight measurements. A 3.80 × 10⁻² M solution of Co(acacen) in pyridine was oxygenated directly in the cryoscope cell at −20°. The molecular weight of the oxygen adduct prepared in this manner was then determined by freezing point depression and found to be 454 (calcd for Co(acacen)(py)O₂: 392).

When solutions of the oxygen adduct prepared in this manner are allowed to warm above 0°, the observed freezing point depression indicates the presence of many lower molecular weight species in solution. These could presumably be due to an oxidation of the ligand by the bound oxygen, as has been observed in other oxygen-carrying systems.[21] This behavior is the probable reason for the nonstoichiometric uptake of oxygen by solutions of Co(acacen) at temperatures above 0°, as noted above.

Characterization of the Crystalline Adducts. A crystalline oxygen adduct was isolated from a DMF solution of Co(acacen) oxygenated at −20°. When the dark, almost black, crystals were allowed to warm above 0°, they turned a bright orange color, reminiscent of Co(acacen). Controlled decomposition of this nature using vacuum line techniques shows that the following reaction is occurring in the solid state.

$$Co(acacen)(DMF)O_2 \longrightarrow Co(acacen) + DMF + O_2 \quad (2)$$
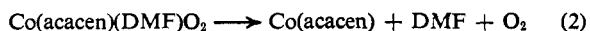
The Co(acacen) residue was identified by its infrared spectrum and elemental analysis. The condensable gas evolved was identified by vapor phase chromatography as DMF and the noncondensable gas as oxygen, by mass spectral analysis. These results are shown in Table II. The slightly low values for the condensable and noncondensable gas evolution are thought to be due to the extreme difficulty in handling this thermally unstable compound.

This adduct was further characterized by loading samples on an electrobalance under a helium purge

maintained below 0° and weighing accurately. When the sample was allowed to warm above 0° a weight change corresponding to the loss of 1 mole of DMF and 1 mole of O₂ per mole of complex was recorded (see reaction 2 and Table II).

The oxygenated substituted pyridine adducts of Co(acacen) were prepared and isolated in a similar manner to that of the DMF adduct at temperatures below 0°. The oxygen is more tightly bound in these complexes as is shown by the fact that upon warming to room temperature they do not release molecular oxygen. Consequently, C, H, and N analyses were obtained directly on the oxygen adducts.[12]

Certain organic solvents (e.g., CHCl₃, DMF, and THF) were found to dissolve the oxygenated substituted pyridine adducts while simultaneously causing them to evolve molecular oxygen. The ability of these solids to release molecular oxygen is strong evidence that the crystalline compounds contain oxygen bound as molecular oxygen; in particular it precludes formulating these adducts as substituted pyridine N-oxide complexes.

Molecular weights of the crystalline substituted pyridine oxygen adducts were determined by freezing point depression. (The extreme thermal instability of the DMF adduct precludes obtaining molecular weight data on this complex.) The crystalline adducts were dissolved in pyridine and cooled below −10° in an oxygen atmosphere to prevent decomposition and/or deoxygenation. The oxygenated pyridine adduct, Co(acacen)(py)O₂, gave an experimental molecular weight of 352 (calcd for Co(acacen)(py)O₂: 392). The experimental values obtained for the molecular weights of the oxygenated substituted pyridine complexes indicate that they dissociate in solution. Presumably the substituted pyridine is released in favor of coordination by the pyridine solvent present in large excess.

Magnetic susceptibilities of all the oxygen adducts and the parent complex were measured. These complexes all exhibit a temperature dependent bulk susceptibility for 80 to 298°K, as predicted by the Curie–Weiss law. The results of these measurements are summarized in Table III.[22] These data indicate that the parent

(21) L. J. Zompa, C. S. Sokol, and C. H. Brubaker, *Chem. Commun.*, 701 (1967).

(22) Temperature dependent magnetic measurements were made on Co(acacen) residues after the solid state deoxygenation of Co(acacen)-(DMF)O₂. The calculated magnetic moment (μ_{eff} = 2.43 BM at 298°K) is slightly higher than that observed for Co(acacen) prior to oxygenation in solution (see Table III). Powder pattern data indicate that samples of Co(acacen) prior to oxygenation in DMF and after deoxygenation are isomorphous. This indicates that this slight change in magnetic moment is probably not due to any large difference in crystal packing. This very small change in magnetic moment is not understood, but could be due to the formation of a small amount of high spin cobalt(II) impurity which would not show up in the elemental analysis.

compound, Co(acacen), and its monomeric oxygen adducts may be described as containing a cobalt(II) ion in a low-spin d^7 electronic configuration, and oxygen in a singlet state. However recent epr studies[3] suggest the systems more nearly approximate $Co(III)-O_2^-$.

Table III. Magnetic Properties of N,N'-Ethylenebis(acetylacetoniminato)cobalt(II) and Its Ligand + Oxygen Adducts (298 °K)[a]

Compound	$\chi_G \times 10^{6}$ [b]	μ_{eff}, BM	θ
Co(acacen)	6.52 ± 0.07	2.16 ± 0.01	25
Co(acacen)(DMF)O₂	4.94 ± 0.5	2.22 ± 0.10	30
Co(acacen)(py)O₂	3.40 ± 0.15	1.89 ± 0.04	6
Co(acacen)(CH₃-py)O₂	2.00 ± 0.20	1.54 ± 0.06	8
Co(acacen)(CN-py)O₂	2.54 ± 0.20	1.71 ± 0.05	6
Co(acacen)(NH₂-py)O₂	1.85 ± 0.05	1.49 ± 0.02	20

[a] Results are an average of two to five independent determinations. [b] Cgs units.

Table IV lists the infrared absorptions of the substituted pyridine oxygen adducts. These are absorptions which are not present in the parent cobalt complex, or the substituted pyridine. It was not possible to obtain

Table IV. Infrared Spectra of Oxygenated Substituted Pyridine Adducts of N,N'-Ethylenebis(acetylacetoniminato)cobalt(II)

	A[a]	B[b]
Co(acacen)(py)O₂	1123 (vvs)	
	878 (w)	
	800 (vw)	825 (vw)
	603 (vw)	615 (vw)
	578 (vvw)	580 (vvw)
	555 (vvw)	555 (vvw)
Co(acacen)(CH₃-py)O₂	1195 (s)	
	1137 (vvs)	1137 (m)
	1098 (w)	1098 (vvw)
	1055 (s)	1062 (m)
	880 (vw)	895 (m)
	665 (vw)	665 (vw)
	580 (vvw)	
	555 (vvw)	
Co(acacen)(NH₂-py)O₂	1132 (vvs)	
	1095 (vw)	1095 (vw)
	1068 (w)	
	1055 (s)	1050 (m)
	1045 (w)	
	880 (w)	885 (w)
	668 (w)	
	580 (w)	
	560 (w)	
Co(acacen)(CN-py)O₂	1140 (vvs)	1140 (vvw)
	1090 (vw)	1090 (vvw)
	1055 (m)	1055 (m)
	1045 (w)	1045 (w)
	890 (vw)	890 (vw)
	600 (vvw)	600 (vvw)

[a] Spectra obtained immediately after sample removed from sealed tube stored at low temperature. [b] Spectra obtained after drying at room temperature.

the infrared spectrum of Co(acacen)(DMF)O₂ due to its extreme thermal instability. Particular note should be made of the region from 1120 to 1140 cm⁻¹. All four complexes exhibit an intense absorption band in this region when the mull is prepared immediately after removal of the solid from a sealed tube stored at low temperatures. This intense band is either absent or greatly reduced in intensity when the mull is prepared

after the solid has been allowed to warm to room temperature for a period of time. On this basis we would like to tentatively assign the absorption between 1120 and 1140 cm⁻¹ to a vibration of coordinated molecular oxygen.

Additional support for this assignment comes from the observation that gaseous O_2 has a Raman active absorption at 1555 cm⁻¹ and that the O–O stretch in solid H_2O_2 occurs at 1380 cm⁻¹.[23] This makes our assignment at 1140–1120 cm⁻¹ a reasonable one, since we would expect the O–O stretching frequency to be shifted to lower energy upon coordination.

The weak intensity electronic absorption at 1180 mμ found for the parent compound, Co(acacen), is not present in the mull spectra of the substituted pyridine oxygen adducts or in spectra of oxygenated DMF solutions of Co(acacen). This is in agreement with the results of Yamada and coworkers,[24] who report that a low intensity absorption in the region near 1200 mμ is diagnostic of cobalt in a square-planar ligand field. This absorption band disappears on formation of an octahedral complex.

Discussion

The results of our investigation show that the reaction of Co(acacen) and molecular oxygen can be described by the scheme in eq 3.

$$(3)$$

B = DMF, py, CH₃-py, NH₂-py, and CN-py
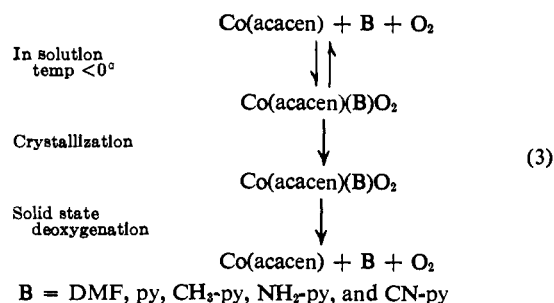
Oxygen uptake data by solutions of Co(acacen)B substantiate the claim of a monomeric oxygen adduct being formed reversibly in solution. This is further supported by recent epr studies.[3] The purpose of the Lewis base, B, undoubtedly is to stabilize the cobalt–oxygen bond by enabling octahedral coordination around the metal to be achieved upon oxygenation in solution. Stable adduct formation is not possible in the absence of B. The stabilizing effect seems to increase with an increase in the base strength of B (see Figure 2). Further evidence for the formation of the monomeric species, Co-(acacen)(B)O₂, in solution is obtained from molecular weight measurements in pyridine.

Analytical evidence for formulating the crystalline adducts as having the same monomeric stoichiometry as those initially formed in solution comes from elemental analysis, oxygen evolution, and molecular weight experiments.

The magnetic data on the oxygenated adducts provide strong support for formulating these complexes as monomeric 1:1 oxygen carriers. The observed magnetic moments all fall in the range normally found for

(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 72.
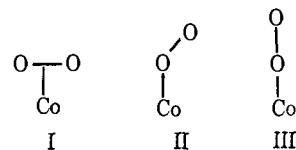(24) S. Yamada, Coord. Chem. Rev., 1, 415 (1966); H. Nishikawa and S. Yamada, Bull. Chem. Soc. Jap., 37, 8 (1964); S. Yamada and H. Nishikawa, ibid., 38, 683 (1965).

octahedral low-spin cobalt(II) complexes.[25] Oxygen, in the free gaseous state, exhibits two unpaired electrons. Upon coordination the symmetry of the molecule is lowered, thus removing its orbital degeneracy and allowing the two unpaired electron to pair. If the cobalt(II) is not formally oxidized, we would thus expect the monomeric oxygen adduct, Co(acacen)(B)O_2, to exhibit a magnetic moment similar to other low-spin octahedral cobalt(II) complexes. The close adherence to the Curie–Weiss law, the low values for the Weiss constant, θ, and the absence of a field dependence exhibited by the oxygen adducts prepared in this study are indications that the paramagnetism of these complexes is not due to temperature-independent, ferromagnetic, or antiferromagnetic effects. Therefore, we can formulate these compounds as being monomeric octahedral low-spin cobalt(II) complexes. However, the epr results reported[3] in the paper that follows this one show that the unpaired electron is largely associated with the coordinated oxygen in accord with the approximate representation Co(III)–O_2^-.

Other 1:1 oxygen adducts prepared by oxygenation in the solid state exhibit similar magnetic moments. The oxygen adduct of bis(dimethylglyoximato)cobalt-(II) exhibits a room temperature magnetic moment of 1.20 BM.[26] N,N'-Dipropylenaminebis(salicylidene-iminato)cobalt(II), when oxygenated, exhibits a magnetic moment of 1.69 BM.[27] Floriani and Calderazzo[9] report a magnetic moment of 1.65 BM for the crystalline monomeric oxygen adduct of N,N-ethylenebis-(3-methoxysalicylideneiminato)cobalt(II) prepared in pyridine solution.

Those cobalt(II) oxygen carriers reported in the literature as oxygen-bridged dimeric species all exhibit little or no paramagnetism. The solid state oxygenation of N,N'-ethylenebis(salicylideneiminato)cobalt(II) yields a peroxy-bridged product which has only a small residual paramagnetic moment, which may be due to incomplete oxygenation.[9,27] Floriani and Calderazzo[9] report that the oxygenation product of this complex and some of its ring-substituted derivatives in solution yield a peroxo-bridged species containing no unpaired electrons. When N,N'-dipropylenaminebis(salicylidene-iminato)cobalt(II) is oxygenated in benzene, the solid dimeric adduct is diamagnetic.[10] The crystalline oxygen-bridged dimer of bis(histidinato)cobalt(II) has also been reported to be diamagnetic.[28]
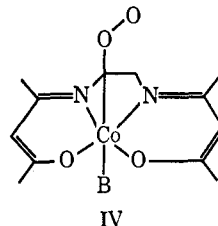
Thus far we have only commented on the formulation of these adducts as monomeric octahedral cobalt reversible oxygen carriers, and have implied nothing about the nature of the cobalt–oxygen linkage, except that it is easily cleaved. Three geometries are shown below for the cobalt–oxygen linkage.

(25) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).
(26) G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).
(27) M. Calvin and C. Barkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1948).
(28) C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963); L. Michaelis, *Arch. Biochem.*, **14**, 17 (1967).

The spin-only magnetic moment of the oxygen adduct indicates that the symmetry around the O_2 axis in the complex has been sufficiently reduced to remove the degeneracy of the oxygen antibonding orbitals, thus ruling out linear structure III. Similar arguments have been made by Griffith[29] and Pauling[30] to rule out III and support I and II, respectively, for the geometry of the iron–oxygen linkage in oxyhemoglobin on the basis of its observed magnetic properties.

The infrared spectra of these oxygen adducts lead us to suggest the possibility that the cobalt–oxygen linkage in these complexes may possess a linear (III) or angular (II) geometry. The low symmetry of the coordinated oxygen in these configurations should produce an intense infrared absorption, as is observed in the adducts obtained. However, as already mentioned, the spin-only magnetic moment of the oxygen adduct does not permit structure III. This means that the most probable geometry is that of angular structure II. The corresponding salicylaldehyde compound, Co(3-CH_3O-salen)pyO_2, has a weak ir band at 1140 cm^{-1} and is suggested[9] to have the more symmetrical structure I.

In conclusion, the results of our investigation indicate that Co(acacen) reacts reversibly with oxygen in solution containing a base to form IV, which can be isolated as a crystalline solid.

IV

(29) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).
(30) L. Pauling, *Nature*, **203**, 182 (1964).