function of time (Laplace equation) and found a discontinuity in this function at a temperature between 22.3° and 25°C, interpretable either as a drastic increase in the diffusion coefficient of DPL through saline or as a greatly increased mobility of DPL at the air interface.

Gershenzon and Eknadiosyants (*7*) report that the rate of ultrasonic generation of aerosols from pure simple liquids at 200 khz (in grams per minute) is proportional to $\sqrt{P^0/\eta\sigma}$, where P^0 is vapor pressure, σ is surface tension, and η is viscosity. Having found that no aerosolization of DPL saline suspension occurs in the ultrasonic generator below 25°C, and that the rate approaches 60 percent of that for plain saline at 37°C, we postulate that, with DPL saline suspension, the effective surface viscosity below 25°C is very high, or that it is highly viscoelastic.

Our observations lead us to suggest the reinvestigation of the therapeutic administration of lecithin aerosols—a question apparently not pursued since Robillard *et al.* (*8*) reported the use of DPL in glycol and water, aerosolized by means of an air-jet (impingement) generator, for hyaline membrane disease (respiratory distress syndrome). Stable aerosol particles 0.1 to 0.6 micron in radius should easily reach the pulmonary alveoli and should act not only to supply DPL, if needed, to alveoli deficient in DPL, but also to convey agents such as penicillin, radioisotopes, and so forth. That the DPL aerosol particles do indeed reach the alveoli and deposit therein, when aerosolized ultrasonically at 30° to 45°C, is strongly supported by experiments on excised dog lung (*9*).

EDWARD W. MERRILL
DAVID J. GRAVES*
KENNETH A. SMITH
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge 02139
DANIEL C. SHANNON
HOMAYOUN KAZEMI
Pulmonary Unit, Massachusetts General Hospital and *Harvard Medical School, Boston, Massachusetts*

References and Notes

1. Standard in that the pure liquid is in equilibrium with pure vapor and the interface is flat.
2. An order-of-magnitude approximation is as follows: The flux I, (in grams per second) of a molecular species j undergoing steady-state evaporation from the surface of a sphere of radius r, where its concentration is C_{js} (in grams per cubic centimeter), into a quasi-infinite continuum, where its concentration is $C_{j\infty}$, is related to the diffusion coefficient D (in square centimeters per second) by the equation
$$I = 4\pi r D(C_{js} - C_{j\infty})$$
In the case at hand, the perfect gas law gives
$$C_s - C_\infty = (P^* - P^0)M/RT$$
where R is the gas constant. The solution for $P^0 = 47$ mm-Hg water vapor pressure at $T = 310°C$ and molecular weight $M = 18$ gives $I = 1.53 \times 10^{-11}$ g/sec for a sphere of radius 0.2 micron. Since the mass of the sphere at unit density $= 4\pi r^3/3 = 3.35 \times 10^{-14}$ g, this means that the sphere is losing 50 percent of its mass per millisecond at this instant.
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* Present address: U.S. Army Medical Corps, Fort Sam Houston, San Antonio, Texas.

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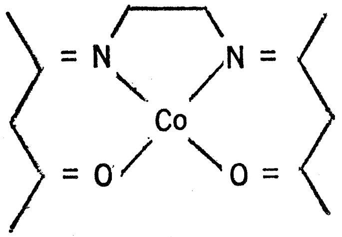
Monomeric Cobalt-Oxygen Complexes

Abstract. *Some Schiff base complexes of cobalt(II) form stable cobalt-oxygen species in solution instead of the usual cobalt-oxygen-cobalt bridged complexes. These one-to-one adducts were isolated as crystalline solids and characterized by means of elemental analysis, magnetic properties, and molecular weight determinations.*

Synthetic oxygen carriers of cobalt (II) complexes have been extensively studied (*1*). Unlike hemoglobin, in which one molecule of oxygen is bound to one iron atom, the oxygen adducts of cobalt(II) complexes generally contain two atoms of cobalt for every molecule of oxygen. The formation of 1 : 1 cobalt-oxygen adducts as active intermediates has been postulated (*2*). We report here on the formation and isolation of some 1 : 1 cobalt-oxygen adducts of the cobalt(II) Schiff base complex [**1**], bis-(acetylacetone)ethylenediiminecobalt(II) [Co(acac)$_2$en]. Floriana and Calderazzo (*3*) have investigated some corresponding salicylaldehyde (sa) Schiff base systems and found that all of these except one formed the usual peroxo-bridged compounds. The 3-methoxy derivative reacted with oxygen in the presence of pyridine to form the 1 : 1 cobalt-oxygen adduct.



[1]

Reversible oxygen absorption by complex [**1**] requires that it be dissolved in toluene in the presence of an appropriate Lewis base. The bases used were *N,N*-dimethylformamide (DMF), pyridine (py), 4-methylpyridine (CH$_3$-py), 4-cyanopyridine (CN-py), and 4-aminopyridine (NH$_2$-py). Oxygenation took place at approximately −10°C. Absence of the Lewis base or temperatures in solution above 0°C resulted in decomposition of the complexes as evidenced by a nonstoichiometric absorption of oxygen.

Complex [**1**] was prepared by a method similar to that of Everett and Holm (*4*). The five oxygen adducts (Table 1) were prepared by cooling a concentrated toluene solution of [**1**] and one of the five Lewis bases to below −10°C. Oxygen was then bubbled through the solution at this temperature. The crystalline product was isolated by cooling the solution to approximately −50°C and filtering at that temperature.

All of the crystalline oxygen adducts were found to be thermally unstable. The DMF adduct [**2**] decomposes quite dramatically on warming to room temperature. Controlled decomposition of a weighed sample in a vacuum chamber equipped with a Toepler pump results in the quantitative release of one mole of DMF (*5*) and one mole of oxygen (*6*) per mole of cobalt

$$\mathrm{Co(acac)_2en(DMF)O_2} \rightarrow \mathrm{Co(acac)_2en + DMF + O_2}$$

The other crystalline oxygen adducts containing coordinated pyridine and substituted pyridines ([**3**], [**4**], [**5**], [**6**]) did not release molecular oxygen on warming to room temperature in the solid state. However, if these solids are dissolved in an appropriate organic solvent in a vacuum, quantitative measurements (*6*) indicate that between 0.5 and 1.0 mole of oxygen are released per mole of cobalt. The lower than expected values for the release of oxygen by these 1 : 1 adducts is thought to be due to some decomposition associated with warming the solutions to room temperature. Other experiments show that some decomposition does take place at these conditions.

Table 1. Analytical and magnetic data for the monomeric oxygen adducts of bis(acetylacetone)-ethylenediiminecobalt(II).

Compound	Calculated percentage			Experimental percentage*			Magnetic moment† at 298°K (Bohr magneton)
	C	H	N	C	H	N	
Co(acac)$_2$en **[1]**	51.25	6.45	9.96	51.26	6.58	9.92	2.16
Co(acac)$_2$en(py)O$_2$ **[3]**	52.05	5.86	10.71	52.84	5.76	10.41	1.89
Co(acac)$_2$en(CH$_3$-py)O$_2$ **[4]**	53.15	6.15	10.34	54.40	6.28	10.34	1.54
Co(acac)$_2$en(NH$_2$-py)O$_2$ **[5]**	50.12	5.95	13.76	50.55	6.39	13.48	1.49
Co(acac)$_2$en(CN-py)O$_2$ **[6]**	51.75	5.27	13.42	52.54	5.50	13.36	1.71
Co(acac)$_2$en(DMF)O$_2$ **[2]**		See text					2.22

* Analyses performed by H. E. Beck. The oxygen adducts were analyzed immediately after removal from storage at temperatures below 0°C. † Corrected by the use of Pascal's constants.

Elemental analyses (Table 1) were carried out for the pyridine and substituted pyridine adducts; analysis was not possible for the DMF adduct because of its extreme instability.

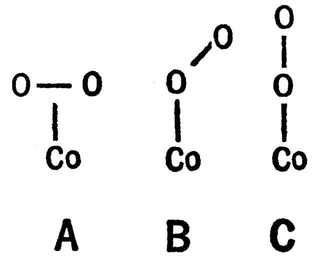
Molecular weight determinations of the crystalline pyridine adduct were made by measuring the freezing-point depression in pyridine solution. The apparatus was so designed that the determinations could be made in a controlled atmosphere of nitrogen or oxygen (*7*). The observed molecular weight of the pyridine adduct is 352, in good agreement with the calculated value of 392 for the monomeric species. The oxygen adducts containing the substituted pyridines give experimental molecular weights which indicate dissociation in solution, with the release of the substituted pyridine and coordination by the pyridine solvent present in large excess. Molecular weight determinations for the crystalline DMF adduct were not carried out because of its thermal instability.

Some information concerning the electronic nature of these crystalline oxygen adducts can be obtained from their magnetic properties. The paramagnetic moments of the five adducts were measured from liquid-nitrogen to room temperature by the Faraday method. The parent compound and each of the adducts obey the predicted Curie-Weiss behavior throughout this temperature range (Table 1.)

The moment found for the square planar parent complex is in the range of 2.2 to 2.9 Bohr magnetons, a value normally observed for square planar complexes containing the low-spin d^7 cobalt(II) ion (*8*). It is also in excellent agreement with the value reported by Everett and Holm for this complex (*4*). Low-spin cobalt(II) ions in an octahedral environment usually have a somewhat lower magnetic moment which has been attributed to spin-orbit coupling (*8*). The magnetic moments for the oxygen adducts reported here fall in the range normally observed for octahedral cobalt(II) complexes. The paramagnetism is an indication of the 1 : 1 stoichiometry of these adducts. Dimeric oxygen adducts of cobalt(II) Schiff base complexes containing bridging oxygen groups either are diamagnetic or have a small residual moment due to temperature-independent effects or incomplete oxygenation (*9*).

The presence of a single unpaired electron in these adducts can be explained equally well on the basis of one or other of the following electron pairing schemes. If we assume that the two unpaired electrons of the oxygen molecule are paired upon coordination, the odd electron in the complex is a result of the low-spin d^7 configuration of the cobalt(II) ion. Alternatively, upon coordination the odd electron on the cobalt can be thought of as being paired with one unpaired electron on the oxygen, leaving an odd electron on the oxygen ligand. Both explanations are equivalent, differing only in the degree of metal or oxygen character of the molecular orbital containing the unpaired electron.

The magnetic data can show that there is one oxygen molecule coordinated to each cobalt ion and can also be used to distinguish the three possible orientations of the coordinated oxygen with respect to the rest of the molecule. The three orientations (A, B, and C) are



The spin-only magnetic moment 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 structure C. Similar arguments have been used (*10*) to predict different orientations for the coordinated oxygen in oxyhemoglobin.

The last word on the orientation of the coordinated oxygen in these adducts must await analysis by x-ray diffraction. However, the infrared spectra of these oxygen adducts suggests that, of structures A and B, the latter is the probable orientation. All the pyridine adducts have strong absorption bands in the region from 1120 to 1140 cm^{-1}, which disappear or decrease when the compounds are warmed to room temperature. The tentative assignment of these bands to the O-O stretching vibrations of the oxygen ligand supports structure B, because of its low symmetry. The corresponding salicylaldehyde compound, 3-CH$_3$OCo(sa)$_2$en(py)-O$_2$, has a weak band at 1140 cm^{-1} and is thought (*11*) to have the more symmetrical structure A.

The reaction between oxygen and **[1]** in solution was also investigated. Oxygenation in undiluted DMF was completely reversible over ten oxygenation-deoxygenation cycles, provided the temperature of the solution was not allowed to exceed 0°C. This reaction was studied over a range of oxygen pressures from 130 to 720 mm-Hg. The equilibrium constant for the reaction

$$\mathrm{Co(acac)_2en(DMF)} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(acac)_2en(DMF)O_2}$$

was found to be $\log K = 2.11 \pm 0.10$ at −10°C. Attempts to make the data fit a reaction scheme resulting in the formation of a dimeric oxygenated species or the formation of a mixture of monomeric and dimeric species did not result in a constant value for the calculated equilibrium constant over the pressure range studied. We interpret this as further evidence for the formation of a 1 : 1 oxygen adduct.

Oxygenation at − 10°C of toluene solutions of **[1]** containing pyridine and the substituted pyridines, NH$_2$-py, CH$_3$-py, and CN-py, results in the absorption of 1 mole of oxygen per mole of cobalt; recycling through at least five oxygenation-deoxygenation cycles is possible. Equilibrium constants were not calculated for these reactions; however, a trend toward increasing formation of the oxygen adduct was noted with an increase in the base strength of the substituted pyridine.

Molecular weight measurements of the species formed on the oxygenation of [**1**] in pyridine were made by oxygenating the parent compound directly in the cryoscope cell. Complex [**1**] was dissolved in pyridine under a nitrogen atmosphere and the solution was cooled to below $-10°C$. The cell was then evacuated and filled with oxygen. After the solution was sufficiently agitated, the molecular weight (454) of the oxygenated species was calculated (molecular weight calculated for the pyridine adduct [**3**] was 392). Within the limits of experimental error, this indicates that a monomeric species is formed on oxygenation of [**1**] in pyridine solution.

On the basis of these data, we believe that the following equilibrium exists in solution

$$\mathrm{Co(acac)_2en} + \mathrm{B} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(acac)_2en(B)O_2}$$

(where B = DMF, py, CH_3-py, CN-py, NH_2-py) and that the oxygenated species formed in solution and the isolated crystalline solid are monomeric 1 : 1 oxygen adducts.

The similarity between the synthetic oxygen-carrying system described here and the naturally occurring iron-oxygen carrier, hemoglobin, is quite striking. The porphyrin-like heme group functions as a planar tetradentate ligand coordinated to the ferrous ion. This serves the same function as the $(acac)_2en$ ligand in the synthetic oxygen carrier. In oxyhemoglobin the iron is thought to achieve an octahedral environment through coordination of a histidine residue in a *trans* position to the coordinated oxygen. This is similar to the function of the Lewis base in the synthetic oxygen adducts described here.

ALVIN L. CRUMBLISS
FRED BASOLO

Department of Chemistry,
Northwestern University,
Evanston, Illinois 60201

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Sex Pheromone of the Queen Butterfly: Biology

Abstract. *Males of the queen butterfly* Danaus gilippus berenice, *deprived of the two extrusible brushlike "hairpencils" at the rear of their abdomen, are capable of courting females but incapable of seducing them. In normal courtship, an aphrodisiac secretion associated with the hairpencils is transferred by way of tiny cuticular "dust" particles to the antennae of the females. Of the two substances identified from the secretion, one (the ketone) acts as the chemical messenger that induces the females to mate. The only known function of the other compound (the diol) is to serve as a glue that sticks the dust to the female. Males were reared under conditions in which they produced subnormal amounts of ketone and showed reduced seductive capacity. Under certain experimental circumstances, the competence of these males was restored by addition of synthetic ketone.*

Many butterflies and moths possess extrusible brushlike structures which, because they are restricted to one sex and impregnated with secretion, are thought to serve for pheromone dissemination during courtship (*1*). In the queen butterfly *Danaus gilippus berenice* (Fig. 1A), whose mating behavior has been described (*2*), the brushes consist of a pair of tufted stalks ("hairpencils") present in the posterior abdomen of the male, where they are ordinarily tucked away within infoldings of the integument. When, during courtship, the male overtakes the female in flight, he everts the hairpencils (Fig. 1B) and brushes them against the female's antennae and head. She responds by alighting on herbage, whereupon he hovers closely above her and subjects her to further "hairpencilling." Eventually he too alights, and copulation takes place (Fig. 1C).

Hairpencils are glandular structures of considerable complexity. The surface of the individual hairs is irregularly covered with tiny cuticular spherules (Fig. 1D). This "dust" detaches readily and tends to stick to surfaces (including insect integument) against which hairpencils have been brushed. Stickiness of the dust is attributable to a coating of liquid secretion, stemming from specialized gland cells associated with the bases of the hairs. Extraction of hairpencils has led to identification of two components of the secretion (*3*)—a crystalline pyrrolizidinone (hereafter called the ketone), and a viscous terpenoid alcohol (the diol).

The importance of hairpencils for mating became apparent in preliminary tests carried out in the field. Individual males (112 specimens), captured on the wing at a site where queens of both sexes were persistently abundant, were experimentally deprived of their hairpencils (*4*), provided with identifying wing markings, and immediately released at the same site. Control males, captured and released together with the experimentals at the site, consisted of 112 individuals that were merely marked, and another 112 that were marked and subjected to the incidental preoperative manipulations undergone by the experimentals. The site was revisited at 2-day intervals for 16 days, and systematically sampled each time for marked males (captured individuals were noted and released again after each sampling). A high proportion of individuals of all samples (34 percent of experimentals; 40 and 45 percent of the two sets of controls) were recaptured at least once. Moreover, there appeared to be no difference in the viability of the samples (their frequency of recapture remained comparable on successive visits). However, there was a sharp difference in their frequency of recapture *in copula*. Whereas the two sets of controls were mating with simi-