

ence solution was 0.10M NaHCO₃. The electrode was conditioned overnight in an external solution of the same strength. Both internal and external solutions were changed the next morning, and the system was allowed to equilibrate for 4 hours prior to use.

The response time for both systems ranged from 2 to 5 minutes, the longer time being required for the more dilute solutions. The data are summarized in Table 1. Both systems responded with an essentially Nernstian slope. The chloride salts of these amines showed greater selectivity and sensitivity for divalent phosphate than the corresponding phosphate salts.

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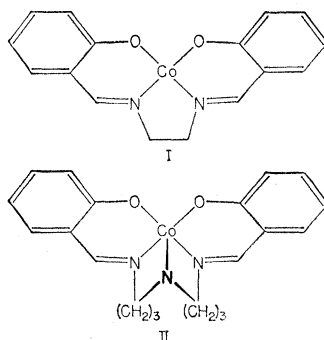
12 August 1969

Structure of an Oxygen-Carrying Cobalt Complex

Abstract. *Bis(3-fluorosalicylaldehyde) ethylenediimine cobalt(II), a reversible oxygen-carrying compound, has been crystallized as a tetramer with two oxygen molecules bound to the four cobalt atoms, each oxygen molecule bridging between two metal atoms. These dimers are further linked by two bonds between the oxygen atom of the salicylaldehyde and the cobalt atom. The oxygen-to-oxygen distance, 1.21 angstroms in molecular oxygen, has increased to 1.308(28) angstroms (where the number in parentheses is the estimated standard deviation) in this compound, the shortest distance yet observed in such a bridging arrangement.*

In recent years much effort has been expended in the determination of the structures of compounds containing molecular oxygen, in the expectation that knowledge will be gained concerning the mechanism of oxygen transport in biological systems. Several reversible

oxygen carriers have been crystallized, notably Vaska's compound (I) and its derivatives; the structures of these iridium and rhodium oxygen carriers have been determined by Ibers and his co-workers (2). Another group of reversible oxygen carriers was discovered by Pfeiffer *et al.* (3) and investigated by Calvin and his co-workers (4). These are cobalt compounds of the Schiff base formed from salicylaldehyde and either ethylenediamine or 3,3'-diamino di-*n*-propylamine (structures I and II).

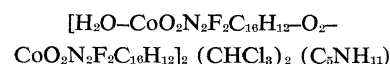


The ethylenediamine compound is able to absorb and desorb oxygen reversibly in the solid state with the metal:O₂ ratio being 2:1. This ratio implies a bridging arrangement of an oxygen molecule between two cobalt atoms; such bridges are well known in μ -peroxo- and μ -superoxodicobalt systems (5). (These latter are not reversible oxygen carriers, however.)

The possibility existed that the bonding in the reversible oxygen carriers was of a different nature from that in the cobalt-ammonia complexes; thus we have prepared and attempted to crystallize many varieties of this 2:1 oxygen complex, bis(salicylaldehyde)ethylenediimine cobalt(II). We report here the structure of the oxygenated form of bis(3-fluorosalicylaldehyde) ethylenediimine cobalt(II), a tetrameric species which contains two O₂ groups. The tetramer can be formulated as a dimer of bis(3-fluorosalicylaldehyde) ethylenediimine cobalt(III)- μ -superoxo-bis(3-fluorosalicylaldehyde) ethylenediimine cobalt(II)·H₂O, but the precise electron distribution in the compound cannot be inferred from this (or any other equivalent) systematic name. We chose the name to be as descriptive as possible of the bond distances and geometry we found. Alternate formulations [such as Co(III)-O₂²⁻-Co(III) or Co(II)-O₂⁰-Co(II)] are less satisfactory on account of the O-O distance.

During the solution of the structure we found that the tetramer had crystallized with two moles of solvent chloro-

form and one mole of piperidine (from the original material); thus the formula of the compound we studied is



The crystals have a deep red-purple color, and they turn darker on slight heating. At 95°C or so they lighten to a red-orange color; the dark color reappears as they cool. These color changes are those that have been observed for the reversible oxygenation and deoxygenation of this compound, and thus we believe that the crystal we have studied contains a reversibly bound O₂ group.

The crystals were prepared from a sample originally made by Calvin's group in 1943 and given to us by Dr. E. W. Hughes. The compound had been crystallized (as a powder) from piperidine. A few tenths of a gram were dissolved in boiling chloroform in a 100-ml flask; the flask was covered with a serum cap, pumped full of N₂, and placed in a refrigerator at 2°C. After 1 day the serum cap was punctured with a 15-cm hypodermic needle which was left in place to permit entry of oxygen from the air. Crystals appeared after 1½ to 2 weeks, and they were removed after 9 weeks. At that time the crystals were still exceedingly small: the largest measured 0.033 by 0.035 by 0.085 mm and contained about 0.15 μ g of material.

The compound crystallizes in the triclinic space group $P\bar{1}$, with one tetramer in a cell of dimensions $a = 12.937(4)$ Å, $b = 14.806(3)$ Å, $c = 14.866(9)$ Å, $\alpha = 118.42(9)^\circ$, $\beta = 112.28(15)^\circ$, and $\gamma = 107.89(4)^\circ$ (numbers in parentheses represent the estimated standard deviations). The centric space group $P\bar{1}$ was chosen because there was more than one molecule of bis(3-fluorosalicylaldehyde) ethylenediimine cobalt(II) in the unit cell. This choice of space group was confirmed by the successful solution of the structure. The one molecule of piperidine in the cell is disordered about a center of symmetry. The observed density, 1.72 ± 0.05 g/cm³, is in good agreement with the calculated value of 1.67 g/cm³. A total of 1902 independent reflections were measured with cobalt radiation on a Datex-automated General Electric diffractometer. Because of the small size of the crystal, only 530 of these were greater than 5 times their standard deviations; thus we did not expect to be able to obtain highly accurate atomic parameters. The structure was solved

by Patterson and Fourier techniques and refined by three-dimensional least-squares analysis to a final R -index

$$R = \frac{\sum \|F_o| - |F_c\|}{\sum F_o}$$

of 0.15. The weighted R -index however,

$$\frac{\sum w(F_o^2 - F_c^2)}{\sum w F_o^4}$$

is 0.03. A total of 268 parameters were refined. This large number was needed even though only the heavy atoms—the cobalt atoms, three chlorine atoms, and the bridging oxygen atoms—were allowed to vibrate anisotropically. The goodness of fit

$$\sqrt{\frac{\sum w(\Delta F)^2}{(n-p)}}$$

(where w is the weight, n represents the number of data, and p is the number of parameters) is 1.67; this indicates that the model fits the data reasonably well.

Figure 1 is a drawing prepared by ORTEP (6) which shows the oxygen-carrying portion of the structure. The O—O distance, 1.21 Å in O₂, has increased to 1.308(28) Å, a distance typical of a superoxide ion. This is the shortest O—O distance that has been found for any O₂ group bridging two cobalt atoms. The O₂ bridge is not a symmetric one: the distance between Co(2) and O(5) is 1.93(3) Å, whereas the distance between Co(1) and O(4) is 2.00(3) Å. This difference is also evident in the thermal motion of the two oxygen atoms. Although both atoms are vibrating anisotropically (see Fig. 1), the less tightly bound O(4) exhibits a much larger vibration. The root-mean-square amplitudes along the axes of the thermal ellipsoids for these atoms are: for O(5), 0.08, 0.18, and 0.20 Å; for O(4), 0.15, 0.21, and 0.32 Å. These features of the bonding indicate that the Co—O bonds are rather weak and that the bridging group is a different O₂ species from the one found in the ammine μ -superoxidocobalt compounds (5), in which the Co—O distances are 1.895 Å and the bridging atoms are symmetrically disposed about the Co—Co axis.

An even more striking difference is the departure from planarity of the group Co—O—O—Co in the oxygen-carrying complex. A superoxo bridge requires these four atoms to be coplanar, and a peroxo bridge would be expected to have a significant torsion angle about the O—O bond (5); such a geometry has been observed in previously determined structures. In this compound,

however, the O—O distance corresponds even more closely to that of a superoxide ion, and yet the torsion angle is 122° rather than 180°.

There are some significant differences in bond lengths between corresponding cobalt-ligand bonds around Co(1) and Co(2). Around Co(1) are four short bonds to ligands in a plane and two longer bonds, one to a water molecule and one to an oxygen atom of the O₂ group. This cobalt atom has an environment similar to that of a typical planar Co(II) complex (7). On the other hand, Co(2) has longer in-plane metal-ligand bonds and one shorter and one longer Co—O bond. This cobalt atom looks more like a Co(III) atom (8). However, with this designation of oxidation state to the cobalt atoms, one must call the bridging O₂ group a μ -superoxide ion in order to account for all the electrons in this compound.

The bonding between the bridging O₂ species and the cobalt atom in this

reversibly oxygenated complex can be better described as weak π -bonding with partial charge transfer from the filled 3d_{xz} or 3d_{yz} orbitals of Co(II) to the π^* orbital of O₂, and the electronic state of the π complex lies somewhere between a “no bond” limiting case and a complete charge-transfer bond (9). The asymmetry of the O₂ bridging group and the difference in thermal motion of the two oxygen atoms indicate that the O₂ group bonds to Co(1) and Co(2) with different bonding strength. The formation of a bond between the cobalt atom and the O₂ molecule is extremely sensitive to the change of environment, and thus to electron density, at the cobalt atoms. The compound reported here demonstrates that too strong or too weak a metal donor easily causes the bonding of O₂ to be irreversible (10) or nonexistent and that only a delicate balance in the properties of metal and ligand can produce a reversible oxygen-carrying compound.

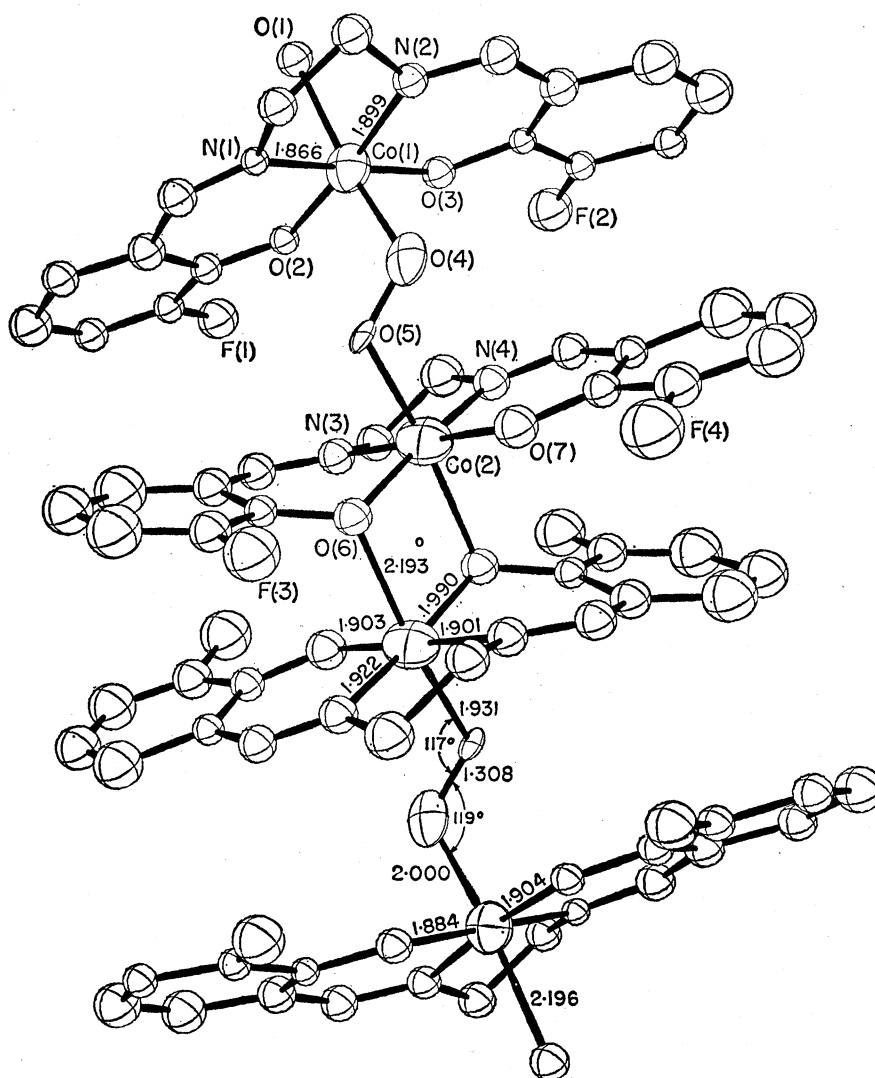


Fig. 1. Perspective view of the tetrameric oxygen-carrying cobalt compound showing important distances (in angstroms) and angles.

Note added in proof: After this paper was submitted, a paper (11) reported the structure of another oxygen-carrying bis(salicylaldehyde) ethylenediimine cobalt(II) compound. This compound crystallized as a dimer, the O₂ group bridging between the cobalt atoms, with dimethylformamide molecules occupying the sixth position around the cobalt atoms.

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Benzene Complexes with Copper(II)montmorillonite

Abstract. Benzene formed a stable complex through its π electrons to the copper ion in copper(II)montmorillonite. Copper(II) was the only exchangeable metal cation in montmorillonite to form a complex with benzene. Only those clay minerals whose charge arises in the octahedral layer produced the complex.

The adsorption of organic molecules on clay surfaces is highly dependent on the cationic species (exchangeable cation) satisfying the negative charge site of the clay (1). Organic molecules commonly are bonded to the exchangeable cation either by formation of a complex or by hydrogen bonding. Empty *d* orbitals of certain metal ions provide coordination sites for electrons

of Lewis base organic molecules. Benzene has only electrons in π orbitals available for such bonding.

Benzene adsorption was studied on thin self-supporting films (2 mg of clay per square centimeter) of homoionic Wyoming montmorillonite (API No. 25) with the following exchange cations: Na, Ca, Al, Cr(III), Cu(II), Fe(II), Fe(III), Ag(I), Mn(II), Ni(II), Co(II),

and Zn. For preparation of the films, clay suspensions were dried on a flat polyethylene surface and then peeled away. The clay films were dried in a vacuum desiccator containing P₂O₅ (24 hours) and, while still in a partial vacuum, exposed to benzene vapor over a free benzene surface for a few minutes. A period of at least another 24 hours was allowed for equilibrium to be reached. The color of the Cu(II)-montmorillonite film changed from a very pale blue to dark red within a few minutes after it was exposed to benzene. Exposing the Cu(II)montmorillonite film to room conditions caused the color to change from dark red to green or gray. The original dark red color could be restored by mild heating or desiccation, which reduced the water content of the film. The color of the films with benzene complexes was sensitive to the water content of the air. The clay films containing the other exchangeable cations showed no color change on exposure to benzene. The films were scanned in the infrared range from 600 to 4000 cm⁻¹ (Fig. 1). The broad increase in absorption between 1700 and 4000 cm⁻¹ is a striking feature of the Cu(II)-benzene-montmorillonite complex. In addition, the bands at 689, 706, 780 $\pm$ 5, 1192, 1277, 1482, and 1535 cm⁻¹ are in marked contrast to the spectrum of liquid benzene. The spectrum of benzene physically adsorbed on montmorillonite gives mainly a sharp band at 1482 cm⁻¹. Montmorillonite saturated with the other exchangeable cations did not form complexes with benzene. This indicates that benzene was bonded to the Cu(II) cation and not to exposed silica or alumina surfaces of the montmorillonite.

Since the π electrons of benzene are the only ones available for bonding, we made a more detailed study of Fig. 1C to find band changes which might be associated with the π bonding of benzene to copper(II). An increase in the force constant of ν_{11} (CH out-of-plane deformation) is commonly observed with dibenzenechromium(I) and dibenzenechromium(2), in both cases benzene being π -bonded to the metal. The ν_{11} band increased from 675 to 795 cm⁻¹ in dibenzenechromium(I). The infrared spectrum of our Cu(II)-benzene-montmorillonite complex revealed a band at 780 $\pm$ 5 cm⁻¹ partially hidden by a band of the clay. This band is probably associated with the CH out-of-plane deformation (ν_{11}). The

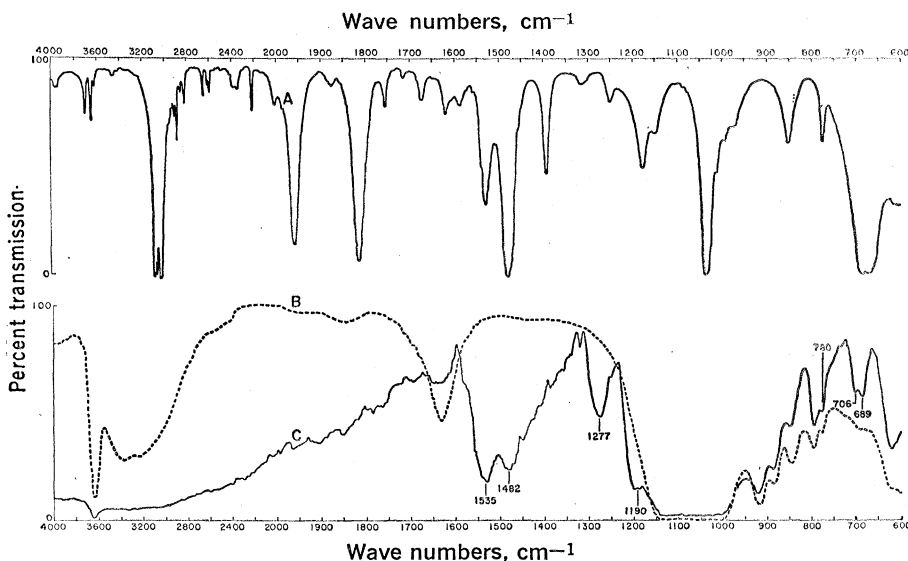


Fig. 1. Infrared spectra of (A) liquid benzene, (B) Cu(II)montmorillonite, and (C) Cu(II)-benzene-montmorillonite complex. Spectra B and C have the same base line.