SYNTHETIC REVERSIBLE OXYGEN-CARRYING CHELATES

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CONTENTS

I. INTRODUCTION

Synthetic reversible oxygen-carrying chelates, *i.e.*, chelates that can take up and release molecular oxygen reversibly, have been of interest as model compounds in the study of the reversible oxygenation mechanisms involved in the very complex natural oxygen carriers, *e.g.*, the hemoglobins and hemocyanins, and as a means of separating molecular oxygen from the air.

The first example of a synthetic reversible oxygen-carrying chelate was prepared in 1933 by Pfeiffer, Breith, Lubbe and Tsumaki (44), who observed that the red-brown crystals of bis-salicylaldehyde-ethylenediiminecobalt(II) darkened on exposure to air. However, it was not until five years later that Tsumaki (49) proved that the color change was due to reversible sorption of molecular oxygen. Since then a large number of bis-salicylaldehyde-iminecobalt(II) derivatives have been prepared and examined for oxygen-carrying properties by Calvin, Diehl and their associates. Reversible oxygen sorption also has been observed in a number of amino acid and dipeptide complexes of Co(II). Recently, several oxygen-carrying chelates containing coördinating ions other than cobalt have been reported.

This review covers the literature through 1961.

II. BIS-SALICYLALDEHYDE-IMINECOBALT(II) OXYGEN CARRIERS

A. INTRODUCTION

Initially, the study of the bis-salicylaldehyde-iminecobalt(II) oxygen carriers was directed toward an understanding of the very complex natural oxygen carriers (40). During World War II these complexes were investigated as a means of isolating pure oxygen from air (46). For several months during this period the U. S. Navy produced oxygen aboard a destroyer tender for welding and cutting. The cost of producing oxygen by this means did not exceed that of cylinder oxygen, but the process had to be discontinued due to a shortage of cobalt. A survey was made by the Bureau of Mines (46) to determine the economics of production of tonnage quantities of oxygen, for the gasification of coal, utilizing oxygen carriers. The conclusions were that at the time (1959) the process was not economical for such large quantities of oxygen. Recently, however, a new process has been under in-

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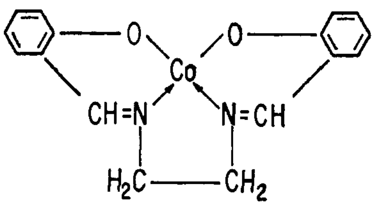
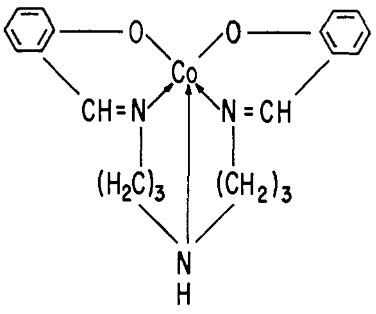
vestigation that would eliminate the necessity for the successive heating and cooling cycles that made the older processes uneconomical (9).

An interesting study was made (5) of the use of the bis-salicylaldehyde-ethylenediiminecobalt(II) oxygen carriers as a means of separating O^{18} and O^{16} isotopes. A slight enrichment of O^{18} in the gas phase was found. This effect was attributed to quantum mechanical rather than steric effects.

Two types of bis-salicylaldehyde-iminecobalt(II) chelates were found to be oxygen-carriers in the solid state as well as in solution in certain solvents (19, 40, 49). Their unsubstituted parent compounds can be represented by I and II, and are designated as type I and type II chelates, respectively.



I



II

Both types of chelates exist in several crystalline modifications, some of which are oxygen carriers and others which are not (10, 40). The type I chelates, in their active forms, carry one molecule of oxygen per two atoms of cobalt. The type I parent compound was studied most extensively, since it was easy to prepare and relatively inexpensive compared to its derivatives and type II chelates.

A number of the chelates were formed using Mn(II), Fe(II), Ni(II) and Cu(II) as the coördinating ions but none of them reversibly sorbed oxygen (10, 11).

B. PREPARATION

A clean crystalline product could be obtained by the direct reaction of salicylaldehyde, ethylenediamine and cobaltous acetate in aqueous ethanol, then recrystallizing (2, 10). However, the activity of the solid was found to depend markedly on the crystal form and physical state (10, 40, 46). Therefore, the complexes for study in the solid state had to be prepared under rigidly controlled conditions.

C. OXYGEN PRESSURE

Measurements of the equilibrium oxygen pressures over solid chelates of type I as a function of temperature and degree of oxygenation indicated that the systems were not simple three-phase types (10, 34). In the region of 75% oxygenation, the unoxygenated phase was completely absent and a solid solution was formed. At 50% oxygenation and 25° the parent type I chelate exhibited an oxygen pressure of about 5 mm. The oxygen pressures over solid type II chelates were in general over 1 atm., but contrary to the type I chelates they reached equilibrium only very slowly.

D. X-RAY STUDIES

X-Ray diffraction studies on the active and inactive forms of type I chelates (10, 40) showed the structures to consist of coplanar molecules arranged in layers. In the active forms, the layers are arranged so as to leave holes in the lattice large enough to accommodate oxygen molecules. The spaces between holes are slightly smaller but are still large enough to allow the oxygen molecules to pass completely through the lattice. In the inactive crystalline forms no such holes are found. The existence of suitably sized holes is not the only criterion for oxygen absorption, however, since some type I chelates do not react readily with oxygen even though the lattice holes are large enough. No crystallographic data have been reported for type II chelates. A detailed description of the crystallography of the type I chelates has been reported (40).

E. KINETICS

In studying the kinetics (3, 10, 40) of the oxygenation of these solid type I chelates, the rate curves at constant oxygen pressure were analyzed well below the optimum oxygenation temperatures since near these temperatures the rate measurements approach the region of equilibrium (in this region absorption and desorption are in competition with each other). The curves showed the oxygenation to be first order with respect to the active type I chelate for the parent compound and the 3-ethoxy derivative but second order for the 3-fluoro derivative. In all cases, the rates were first order in oxygen pressure. The second-order rate behavior for the 3-fluoro derivative requires a two-step process, the first of which is the establishment of an equilibrium involving an activated oxygen molecule and a single chelate molecule in such a way that the oxygen has available to it the entire crystal mass, much as though it were in solution. The second step is considered to involve the formation of complete oxygenated pairs of chelates.

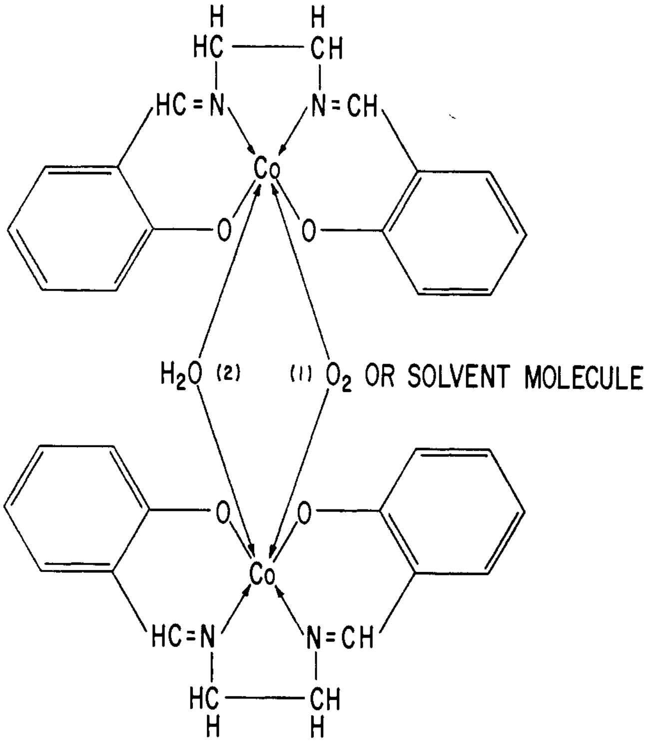
The measured rates of oxygenation depended upon the individual chelates. The fastest rate observed was 80% saturation in 3.5 minutes for the 3-fluoro derivative at 25° and 15.1 cm. oxygen pressure. For the parent compound under the same conditions, the rate was 80% saturation in 30–35 minutes (by extrapolation from measurements made at 76 cm. of oxygen pressure). The oxygenation reaction was exothermic.

F. DETERIORATION AND CYCLIZATION

When the solid parent type I chelate was cycled (oxygenation at room temperature and deoxygenated at 80–100°); it was found to deteriorate to 70% of its original activity after 300 cycles. The solid 3-fluoro type I derivative deteriorated to 60% of its initial activity in 1500 cycles (10, 52). The deoxygenation also could be accomplished by evacuation of the system. In solution (quinoline as solvent), the oxygenation was reversible for only a few cycles (10). Stewart, Estep and Sebastian (46) reported that solutions of the parent type I chelate in either xylene or pyridine could not be oxygenated unless a suspension of the parent compound also was present. Calvin and co-workers (10) used quinoline as the solvent in their solution oxidation studies. From their papers it seems certain that they were aware of the possible formation of heterogeneous systems and took appropriate precautions to detect them. It appears, therefore, that the differences in the results obtained by both groups were due to their choice of solvents.

The most important factor in the deterioration of the chelate is irreversible oxidation (10, 40, 46, 52), but other factors may also contribute. For example, a single crystal of the parent type I chelate was observed under a microscope while subjecting it to several oxygenation cycles (40, 52). The crystal dimensions changed measurably during the cyclizations, causing strains to be set up which gradually led to fragmentation of the crystal. If the crystal surfaces are unable to absorb oxygen, then it would be expected that the fragmentation process would decrease the activity of the chelate. However, this idea might not be compatible with other evidence indicating that fine-grained material is the most efficient (46).

A mechanism has been suggested by some workers for the oxygenation and deterioration of the solid parent type I chelate (18, 46). The coördinating group in position 1 of III is assumed to be a solvent molecule (*e.g.*, pyridine or ethanol) during the preparation of the chelate, which is removed during activation. Thus the sixth coördination position of the chelate is vacated. This site is thought to be responsible for the reversible sorption of oxygen, forming the oxygenated compound proposed in III.



III

Formula III is unique in that it represents the only case where a water molecule shares more than one pair of electrons in a coördination compound. It is an unusual structure from another point of view, *viz.*, it does not have either octahedral or square-planar coördination. Analysis of the oxygenated chelate, however, does indicate the presence of one water molecule per two chelate molecules (22). The proposed mechanism was based on the following: (a) when the chelate was prepared in non-aqueous solvents and then oxygenated, irreversible oxygenation occurred, but when the chelate prepared in non-aqueous solvents was treated with water or when the chelate was prepared in a partly aqueous solvent, it could be reversibly oxygenated; (b) pyridine reacted with the oxygenated chelate, displacing measurable amounts of water and the resulting complex was irreversibly oxidized; (c) magnetic susceptibility measurements indicated the presence of one unpaired electron per cobalt atom for the deoxygenated (paramagnetic) form and that the oxygenated form was diamagnetic (the oxygen having two unpaired electrons probably couples with the single unpaired electrons on two deoxygenated chelate molecules); (d) easily removed molecular oxygen bridges between two cobalt atoms forming a polynuclear coördination compound (ammine-μ-peroxocobalt salts) are known; (e) the sorptive capacity of the chelate decreased in proportion to the loss of water. More quantitative data to support the suggested structure were not obtained because of technical difficulties, *e.g.*, pure samples of the oxygenated species for chemical analysis could not be prepared. It was not possible to use ebullioscopic or cryoscopic molecular weight determinations to confirm the presence of a binuclear compound because the oxygenated chelate was soluble only in solvents that replaced the coördinated water, thus causing a depression instead of an elevation in the boiling point.

It is possible from this evidence to postulate that in non-aqueous solvents the water molecule is rapidly displaced, thus leading to irreversible oxidation at a much faster rate in solution than in the solid state. Upon cycling the solid, the water presumably is lost at a much slower rate; thus irreversible oxidation occurs at a slower rate.

Other researchers (93) indicated, however, that no water was present in the chelates they investigated except in the case of a few derivatives where water of crystallization was readily detected. It is their opinion that deterioration of the solid chelates is due to oxidation of the ethylenediamine and salicylaldehyde rings: Some groups, *e.g.*, the fluoro in the 3-fluorosalicylaldehyde derivative, inhibit the oxidation. In solution, the rapid deterioration of all of the oxygen-carrying chelates is due to irreversible oxidation of Co(II) to Co(III). This, they believe, is caused by the solvent entering the coördination sphere of the cobalt, thus increasing the oxidation potential of the cobalt. In neutral solvents, like benzene, the rate of deterioration is much less than in solvents like pyridine.

G. CONFIGURATION AND ELECTRON DISTRIBUTION

The literature (11) indicates that the type I chelates are square-planar and type II, tetragonal–pyramidal. However, cobalt chelates have a very strong tendency to form octahedral complexes. It is suggested, therefore, that in their solid forms the presumably vacant coordination positions are actually satisfied by neighboring ligands in the crystal lattice and that in solution these positions are occupied by solvent molecules. Therefore, upon oxygenation in the solid state, one of the coördination positions supplied by a neighboring ligand is displaced slightly in favor of the oxygen and the lattice expands slightly. In solution, the oxygen probably displaces a solvent molecule from each chelate molecule.

Magnetic susceptibility measurements (in the solid state), on over a dozen of the type I and type II cobalt derivatives (11) showed that before oxygenation the active type I chelates had one unpaired electron and the active type II had three unpaired electrons. After oxygenation, type I chelates were diamagnetic (no unpaired electrons) and type II chelates contained one unpaired electron. This behavior had been explained in terms of the Pauling concept of donation of electrons by the ligands to the metal atom. It can also be explained in terms of the more recent ligand field theory (43) which has been found to account more accurately for the behavior and properties of complex compounds. A brief and very general description of this theory considers the attractions between the coördinating atoms and the ligands to be primarily electrostatic in nature. In the transition metals, the charge on the metal is balanced by the dipoles of the surrounding ligand (no electron transfer from ligand to metal is considered to occur). Depending on the magnitude of the dipole, the d-level is split into five energy levels. The energy differences between these levels depend on the type of coördination involved. The levels can be filled with electrons in two ways, *viz.*, by pairing as many of the electrons in the lower energy levels as possible, thus forming the most stable state, called the "spin-paired" state, or by filling all the available levels so as to have the largest number of unpaired electrons possible, called the "spin-free" stare. The former state was termed "covalent" by Pauling and the latter "ionic." The energy differences between the levels change when the ligands associated with the metal are not all the same. The number of unpaired electrons present in the unoxygenated solid type I and type II chelates is consistent with square-planar and octahedral splitting for Co(II) (as previously mentioned the octahedral form is preferred). It should also be noted that the diamagnetism observed for the oxygenated type I carrier would also be expected if the cobalt were oxidized to Co(III). However, chemical evidence, presented in the next paragraph, supports an intermediate oxidation state.

The change in the number of unpaired electrons detected after oxygenation of both solid type I and type II chelates would seem to indicate that the role of the absorbed oxygen is more than that of a ligand held by just electrostatic forces. Moreover, the oxygen is not present as a peroxide, since if this were the case it would be expected to give hydrogen peroxide in acids and irreversibly oxidize, which it does not. If it formed a very stable peroxide, then the sorption would not be expected to be reversible. Very likely, the oxygen molecules are in an intermediate state between coordination with the cobalt and actual peroxide formation. Similarly, the oxidation state of the cobalt must be between 2 and 3. Therefore, in effect the oxygen carriers could be considered charge-transfer complexes. Magnetic susceptibility measurements do not indicate how close the unpaired electrons on the oxygen and metal are to each other. They obviously are close enough to reduce the number of unpaired electrons present but not so close as to cause irreversible peroxide formation with resultant oxidation of the cobalt.

It is possible that for oxygenated type I chelates the reduction in the number of unpaired electrons is due to coupling of the unpaired electrons in the Co(II) through an oxygen linkage. Since no crystallographic data were given for type II chelates, it is difficult to say what the explicit structure is, but it is assumed that the crystalline, solid, unoxygenated chelate is octahedrally coördinated with the aid of groups on neighboring molecules. In the oxygenated form an oxygen linkage between layers of molecules may exist.

The behavior of oxygen in these chelates, *i.e.*, causing unexpected changes in their magnetic properties, is somewhat analogous to some of the nitrosyl complexes. Nitrogen oxide, with one unpaired electron, does not in general coördinate as a neutral group (41); *e.g.*, in $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ it would be expected to cause paramagnetism but these compounds have been found to be diamagnetic.

H. CONCLUSIONS

From the preceding discussions, the conditions for reversible sorption of oxygen by chelates may be summarized. The coördinating ion must be capable of existing in more than one oxidation state. However, if the oxidation potential of the ion is too high (the tendency to lose an electron is very great), then irreversible oxidation of the ion to a higher valence state will occur. Accordingly, it is necessary to have ions that have oxidation potentials lying in a certain range so that there is some donation of electrons to the oxygen molecules but not enough to cause irreversible oxidation. The oxidation potentials of the ions can be so adjusted by chelation with the proper ligands.

It should be possible, therefore, to predict which chelates would act as oxygen carriers if the oxidation potentials of the chelates in given solvent systems were known and steric factors were considered. Unfortunately, at this time very few oxidation potential data have been reported for non-aqueous systems or for any but the more common ligands.

III. AMINO ACID AND DIPEPTIDE COBALT(II) CHELATES AS OXYGEN CARRIERS

A. INTRODUCTION

At about the same time that the work on the bis-salicylaldehyde-iminecobalt(II) chelates was published, the results of studies on the reversible oxygen-carrying properties of cobalt(II) dihistidine, some of its derivatives, and on a large number of α- and β-amino acids appeared in the literature (6, 32, 33, 42). Aqueous solutions of the Co(II) salts of histidine, histamine, lysine, arginine, serine, glutamic acid, tryptophan, proline, asparagine and glycine as well as those of 3-methylhistidine, 1-methylhistidine, 3-benzylhistidine, dibenzylhistidine and the peptides anersine, carnosine, L-alanyl-L-histidine and α-L-aspargyl-D-histidine were reported to exhibit reversible oxygen sorption concurrent with some irreversible oxidation. The Co(II) chelate of the dipeptide glycylglycine was also found to sorb oxygen reversibly (28).

The salts were prepared simply by dissolving the histidine, its derivatives, glycylglycine or the amino acids in water at a specified pH and adding a solution of cobalt(II) chloride. Desorption of the oxygen was accomplished by flushing the systems with nitrogen or hydrogen or by changing the pH of the solutions. Most of the data reported were on the cobalt(II) histidine chelates.

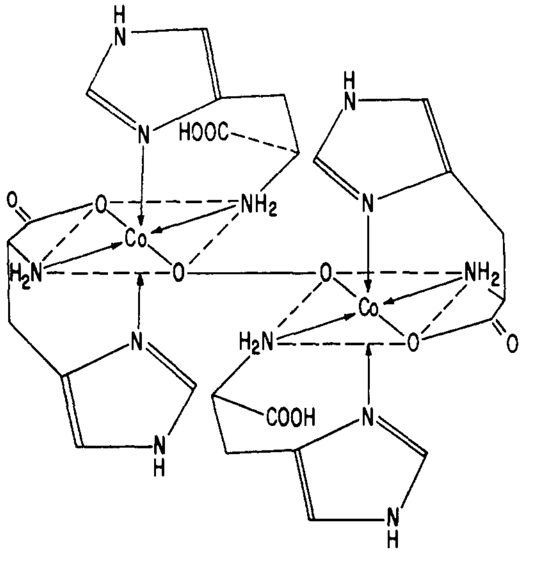
All of the physical measurements on oxygenation of the cobalt amino acid, histidine, histidine derivative and glycylglycine chelates were made in aqueous solutions, although it was possible to isolate some of the oxygenated chelates as solids. In both the cobalt(II) dihistidine and cobalt(II) glycylglycine oxygen complexes there are two atoms of cobalt per molecule of oxygen. Oxygen: chelate ratios for the chelates of the several histidine derivatives and other amino acids were not given.

Refined experimental techniques have indicated that unoxygenated cobalt(II) dihistidine, as a solid or in solution, is in the spin-free, octahedral form (24), whereas earlier workers (32, 33) favored a tetrahedral structure.

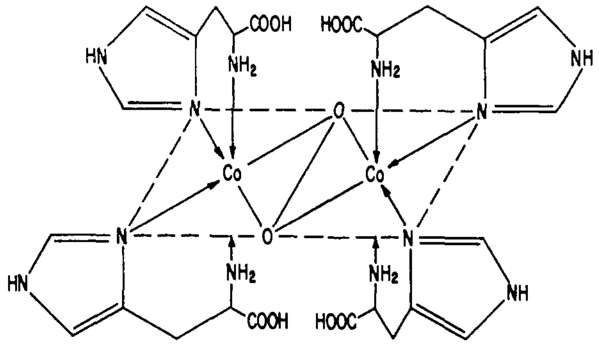
B. MECHANISMS AND STRUCTURES

The aforementioned compounds exhibited reversible oxygen sorption only when chelated with Co(II) (32, 33). Cu(II) and Ni(II) derivatives of histidine were unchanged in the presence of oxygen and the Fe(II) chelate was irreversibly oxidized to the Fe(III) state. In the series Mn(II), Fe(II), Co(II), Ni(II), Cu(II) the oxidation potentials steadily decrease. Chelation with histidine probably increases the oxidation potentials. This would cause Mn(II) and Fe(II) to be oxidized rapidly but the oxidation potentials of Ni(II) and Cu(II) would still be quite low. Since Co(II) is in an intermediate position, an intermediate state of oxidation would exist, sufficient to permit an equilibrium between the oxygenated form and the free chelate and free oxygen, but insufficient to cause oxidation of Co(II) to Co(III).

Two structures IV and V were proposed for the oxygenated cobalt(II) dihistidine chelate in solution (32, 33, 40). Since the oxygenated complex was found to be essentially diamagnetic, the cobalt in structures IV and V would have to be divalent if the oxygen were present in molecular form and trivalent if present in peroxide form. For reasons already discussed in relation to the oxygenated bis-salicylaldehyde-iminecobalt(II) complexes, the oxygen probably is in an intermediate state between coördinated molecular oxygen and peroxide. Thus, the cobalt would have a valence between 2 and 3. In any case, structures IV and V should have over-all positive charges. The magnitude of these charges has not been determined.



IV



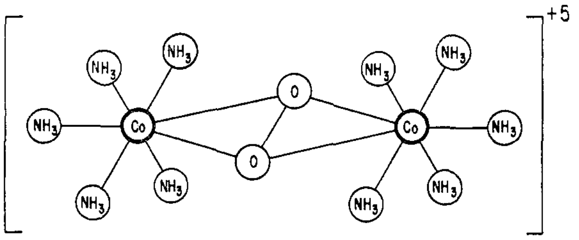
V

While V contains an uncommon combination of four bonds between two cobalt atoms and an oxygen molecule, recent X-ray work has indicated that such bonding probably does occur in the cobalt–ammonia–oxygen complex. This complex will be discussed later.

The kinetics of the oxygenation of the cobalt(II) glycylglycine complex in solution was investigated (47). It was discovered that an intermediate, $[(OH)(GG)_2\text{-}Co\text{–}O_2\text{–}Co(GG)_2(OH)]^-$, was formed by the action of oxygen on $Co(GG)_2(OH)_2^-$. Structures analogous to IV and V were suggested for the oxygenated chelate (47).

Another example of an amine type of reversible oxygen carrier is the complex formed by treating cobalt(II) nitrate solutions with ammonium chloride and ammonium hydroxide (1, 40, 43). The resulting carrier does not actually fall under the classification of oxygen-carrying *chelates*, but will nevertheless be mentioned since it is an amine complex of cobalt, involving a peroxide-like bridge.

Most evidence (4, 50) indicates that the pentavalent complex has structure VI, although unpublished X-ray diffraction data have been referred to in the literature (43) that support a structure in which the O–O bond lies parallel to the Co–Co bond. The pentavalent ion VI is paramagnetic and contains one unpaired electron. This electron is considered to be distributed over the whole structure; thus the valence states of the cobalt ions have equal but not integral values. In solution, the oxygenation is achieved by bubbling oxygen into the solution and is reversed by flushing with nitrogen. Several authors (1, 41, 51) have indicated that the reaction is reversible, but no data were given to indicate whether the sorption was *completely* reversible.



VI

The oxygenation of the Fe(II), Co(II) and Mn(II) chelates of tetraethylenepentamine was studied (36) and, again, reversible oxygenation was observed only with the cobalt chelate.

C. CONCLUSIONS

The cobalt(II) amino acid, histidine, histidine derivative and glycylglycine chelates appear to be very similar in nature to the previously described salicylaldehyde-imine chelates in their reactions toward oxygen. For the latter class of oxygen carriers, irreversible oxidation was the primary cause of deterioration. Recently, a polarographic study of the products of *irreversible* oxidation of the cobalt(II) dihistidine and cobalt(II) glycylglycine chelates showed that the cobalt had been oxidized to Co(III) (7). The same study also found that the ultraviolet spectrum of the reversibly oxygenated cobalt(II) glycylglycine showed an intense charge-transfer band at 29,000 cm.$^{-1}$. This is in keeping with the suggestion already made (section II–H) that in their oxygenated forms the chelates may be considered as charge-transfer complexes.

IV. Iron(II) Dimethylglyoxime Oxygen Carrier

Iron(II) dimethylglyoxime (23) is the first synthetic oxygen-carrying chelate reported that does not have cobalt as the coördinating atom. It dissolves in 50% aqueous dioxane solutions containing added bases such as pyridine, ammonia, histidine or imidazole. In the pH range of 7–11, the reaction with oxygen proceeds according to

$$\mathrm{Fe(DMG)_2\,(base) + O_2 \rightleftarrows Fe(DMG)_2\,(base)\,O_2 + base}$$

The reaction can be reversed readily by bubbling nitrogen through the solution. Both the forward and reverse reactions could be followed by changes in the absorption spectrum. The nature of the added base determined whether the complexes were totally reversible. Up to this time, none of the studies on other oxygen carriers has indicated the existence of a totally reversible system. In every case some irreversible oxidation took place. It is suggested that after a number of sorption cycles it may be found that all of the ferrous complexes show some irreversible oxidation.

Two forms of oxygenated chelates were detected, but it was not clear from the literature whether only certain of the chelates or all of them exhibited two forms. One of the chelates contained two oxygen molecules per cation and the other, one oxygen molecule per cation. The rate of oxygen uptake was slow (no data given) for sorption of the first oxygen and very slow for the second. No X-ray or magnetic data were presented; therefore no conclusions can be drawn regarding the structure of the complexes, other than to postulate that they probably are octahedral and, if they are analogous to the other oxygen carriers, they probably will contain four unpaired electrons (spin-free state) in the unoxygenated form and three or two unpaired electrons after oxygenation depending upon the number of oxygen molecules associated with each chelate molecule. However, the actual situation may be considerably more involved as is indicated in the next section on nickel(II) dimethylglyoximate. There were no indications that an active chelate had been isolated as a solid.

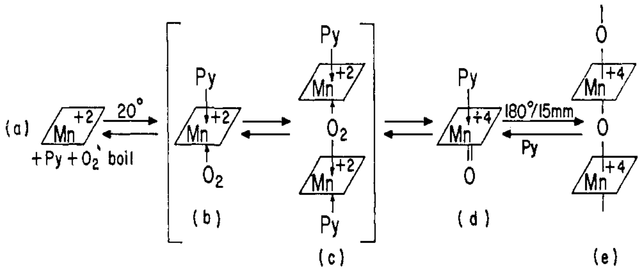
V. NICKEL(II) DIMETHYLGLYOXIME OXYGEN CARRIER

Strong alkaline solutions of nickel(II) dimethylglyoxime reversibly sorb oxygen (45). This is the first nickel oxygen carrier to appear in the literature. The work is in its preliminary stages and few quantitative data are available. A palladium complex also was investigated but it did not show carrier behavior. The desorption of oxygen was accomplished by either increasing the temperature, decreasing the pressure or flushing with argon.

The actual oxygen uptake has not as yet been determined by the authors, but they quote work by Okac and Simek (Czechoslovakia) indicating that the oxygen absorption was a very complicated process involving 16 moles of oxygen per mole of the chelate and that unchelated dimethylglyoxime itself absorbs oxygen in a 1:1 mole ratio. Consequently, if this is true, a completely different process might be occurring with the dimethylglyoximes than with the other oxygen carriers. It appears likely that a considerable degree of irreversible oxidation occurs in this system. Rough magnetic measurements indicated diamagnetism in the oxygenated solutions and slight paramagnetism for deoxygenated solutions, but the measurements were made in glass vessels containing strong alkali (both of which tend to dilute the sample magnetically). No statements were made on the degree of reversibility of the sorption processes or on the existence of a solid form of the active chelate.

VI. MANGANESE(II) PHTHALOCYANINE OXYGEN CARRIER

The proposed mechanism of oxygen sorption by pyridine solutions of manganese(II) phthalocyanine (26) is markedly different from that suggested for the amino acid and bis-salicylaldehyde-iminecobalt(II) chelates. Some evidence is presented that the manganese is *oxidized* reversibly during the process. However, the authors also note that they are not sure whether pyridine N-oxide or oxygen is formed upon "deoxygenation"; thus manganese(II) phthalocyanine may not be a true carrier. The proposed mechanism is shown schematically in Fig. 1.



Mn = Manganese Phthalocyanine, Py = Pyridine

Figure 1.

Spectral data showed the presence of an Mn=O linkage in the isolated product, Fig. 1d, and polarography indicated half-wave potentials corresponding to the reduction of the forms in Fig. 1d to that in Fig. 1a. The form in Fig. 1d also was found to have a magnetic moment corresponding to three unpaired electrons, again consistent with a tetravalent manganese. While the forms in Fig. 1b and 1c were proposed as intermediates, and that in Fig. 1c corresponded to the observed oxygen uptake, there was no evidence for their existence from spectral data. They may, therefore, be present in only small concentrations. A small amount of deterioration of the carrier occurred upon cycling.

If indeed oxygen is reversibly sorbed in this system, it would be the first case where complete oxidation of the coördinating ion was observed.

VII. MISCELLANEOUS OXYGEN CARRIERS

1. New and convincing evidence has been presented that removes the iron-bis-indigo chelate from its classification as an oxygen carrier (37, 38). It was demonstrated that the chelate does absorb oxygen but is irreversibly oxidized in the process. Desorption involved the reducing action of excess iron pentacarbonyl present in the system, on the chelate. Thus, the sorption process could be cycled until all of the excess reducing agent was used up, whereupon the process ceases to be reversible. This process may be analogous to the situation for manganese(II) phthalocyanine in pyridine.

2. Reversible oxygen carriers other than those of the "synthetic chelate" class that have been reported in the recent literature are: (a) the oxychlororhenate ion $(Re_2OCl_{10})^{-4}$ (38), (b) vitamin B_{12a} (35)—the first example of reversible uptake by a Co(III) compound and (c) many aromatic solvents (27, 48), especially amines (spectral studies showed the presence of charge-transfer bands due to the interaction of oxygen as an electron acceptor and the organic solvents as electron donors).

VIII. SUMMARY

The synthetic reversible oxygen-carrying chelates that have been discussed are summarized in Table I.

TABLE I

SYNTHETIC REVERSIBLE OXYGEN-CARRYING CHELATES

Chelate	Molecules O_2 Metal atom	Reference
Cobalt(II) bis-salicylaldehyde-imines		
Type I	1:2	(12–22, 29–31, 39, 40)
Type II	1:1	(12–22, 29–31, 39, 40)
Cobalt(II) glycylglycine	1:2	(47)
Cobalt(II) amino acid chelates		
(1) dihistidine and derivatives	1:2	(6, 32, 33, 40)
(2) other	?	(6, 32, 33, 40)
Iron(II) dimethylglyoxime	1:2 (2:1?)	(23)
Nickel(II) dimethylglyoxime	16:1 ?	(45)
Manganese(II) phthalocyanine?	1:2	(26)

Reversible oxygenation of the Co(II) chelates has been considered to be due to the formation of a partially oxidized metal ion and partially reduced oxygen molecule. The effects of the ligand field on the metal ion undoubtedly permit adjustment to such an oxidation state.

Manganese(II) phthalocyanine in pyridine may be the first oxygen carrier observed in which a definite reversible change in oxidation state occurs. However, experimental evidence is lacking to confirm whether this is the case or whether irreversible oxidation of pyridine to pyridine N-oxide takes place.

Insufficient data are available to be able to classify the nickel(II) and iron(II) dimethylglyoximes into either of the above groups.

NOTES ADDED IN PROOF.—(1) The manganese(II) phthalocyanine chelate has been shown not to be a *reversible* oxygen carrier (*J. Phys. Chem.*, **66**, 2517 (1962)). (2) Recent work by L. Vaska (*Science*, in press) has shown the existence of an iridium oxygen-carrying complex.

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