

from averages over 50 pulse intensities, are accurate measurements of the parameters of a scintillating medium. Although the observations of CP 1919 result in similar values for these parameters, it is apparent from Fig. 3 that this source probably has long-term fluctuations in pulse intensity which arise both at the pulsar and in the intervening medium (11). During observations of these pulsars, scintillations due to irregularities in the solar wind caused very weak intensity modulations with time scales of less than a minute. Consequently, the interplanetary medium cannot account for the observed scintillations. If we assume that the scintillations are due to interstellar irregularities that travel at a velocity $V \approx 20$ km/sec, attributable to the relative motion of the pulsar or the medium, or both, with respect to the earth, then our measurement of $\sqrt{2} V \phi_0 / a$ at 318 Mhz (Fig. 1) leads to $a/\phi_0 \approx 4 \times 10^4$ km. If we substitute $\Delta\nu = 1.5$ Mhz at a radio frequency of 318 Mhz and $a/\phi_0 \approx 4 \times 10^4$ km into the equation for $\Delta\nu$, $z \approx 70$ parsecs. A reasonable estimate for the distance d of the pulsar from the earth would be $d \approx 2z \approx 140$ parsecs. This estimate for d is consistent with estimates of pulsar distance based on dispersion measurements (1, 6, 14). These interstellar scintillations would not have been observed if the apparent angular diameter of the pulsars were larger than $a/\phi_0 z \approx 0.3 \times 10^{-5}$ second of arc. The scintillations would cause even a point source to appear to have an angular size

$$\theta_{\text{scat}} = \phi_0 \lambda / 2 \pi a$$

of $\approx 10^{-3}$ second of arc at 318 Mhz. Interstellar scintillation may therefore establish an important limit to the detectable angular size of a radio source.

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15. This paper grew out of collaborations with H. D. Craft and R. V. E. Lovelace. I thank H. D. Craft and J. Comella for useful computer programs. The Arecibo Ionospheric Observatory is operated by Cornell University with the support of the Advanced Research Projects Agency and the NSF under contract with the U.S. Air Force Office of Scientific Research.

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Divalent Phosphate Electrode

Abstract. *Divalent phosphate ion activities can be measured in dilute aqueous solutions in the physiological pH range (7.0 to 7.5) with a liquid ion-exchange membrane electrode system; the organic ion exchanger consists of an amine chloride membrane. Reference solutions may be either aqueous chloride or bicarbonate solutions. An essentially Nernstian slope is obtained.*

We present here data for two liquid ion-exchange membrane systems which serve as electrodes selective for divalent phosphate in an activity range from 10^{-4} to $10^{-2}M$ monohydrogen phosphate in the presence of $10^{-2}M$ chloride. With no chloride present, sensitivities as low as $10^{-5}M$ divalent phosphate are obtained. The systems permit the direct determination of the activities of aqueous solutions of the divalent phosphate ion in certain mineral systems and in biological systems where the monovalent ion concentrations are below 10 meq/liter. Whereas earlier systems (1) have exhibited sensitivity and linearity but not selectivity for phosphate anions,

our systems are both sensitive and selective in the ranges described.

The indicator electrode consisted of an Orion calcium electrode barrel (model 92-20) into which the appropriate organic ion exchanger and aqueous reference phases were inserted. An Orion membrane (model 92-20) was used to support the organic ion exchanger. The reference electrode was a saturated calomel cell.

The potentials of the calibration solutions were measured in the Orion microsample dish at ambient temperatures ($25^\circ \pm 2^\circ C$) with an Orion model 401 meter. The Beckman microassembly was used for pH determinations.

Calibration and reference solutions were prepared from reagent-grade chemicals and distilled water. Solutions of the potassium salts of mono- and dihydrogen phosphates, and of sodium chloride, were mixed to yield the desired anion concentrations at a pH of 7.2. Solutions were then stored anaerobically in capped Luer-Lok syringes. Under these conditions, the pH could be maintained for several days. Activities of the anions were computed from the extended Debye-Hückel equation and the mass action activity coefficients for phosphoric acid (2).

The first system consisted of a primary amine (Rohm & Haas XLA3) which was partially converted to the hydrochloride by the addition of one equivalent of concentrated HCl to 2.1 equivalents of the amine; the mixture was stirred at $50^\circ C$ for 30 minutes. The temperature of the resulting emulsion was then raised gradually, during a period of an hour, to $110^\circ C$. The heat was removed, and the clear, oily product was injected immediately into the electrode chamber. The membrane became transparent. An aqueous NaCl reference solution (0.025M) was used, and the system was conditioned overnight in an external solution of the same composition.

The second system consisted of a quaternary amine chloride (General Mills Aliquat 336). The amine was used as received. The internal refer-

Table 1. Behavior of divalent phosphate electrodes at $25^\circ C$; electrode potential, millivolts; activity, a .

Ion exchanger (chloride salt)	Activity range of HPO_4^{2-} for linear response	Slope (mv/log a)
Primary amine (XLA3, Rohm & Haas)	2×10^{-4} to $1 \times 10^{-2}M$; 2×10^{-3} to $1 \times 10^{-2}M$ in the presence of 10 meq/liter of Cl^-	33
Quaternary amine (Aliquat 336, General Mills)	5×10^{-4} to $1 \times 10^{-2}M$ in the presence of 10 meq/liter of Cl^-	30

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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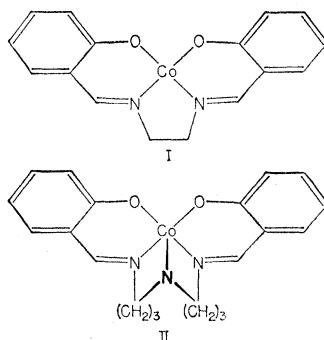
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Structure of an Oxygen-Carrying Cobalt Complex

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).

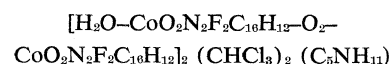


The ethylenediamine compound is able to absorb and desorb oxygen reversibly in the solid state with the metal:O₂ ratio being 2:1. This ratio implies a bridging arrangement of an oxygen molecule between two cobalt atoms; such bridges are well known in μ -peroxo- and μ -superoxidicobalt systems (5). (These 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