*Inorg. Chem.* **1994**, *33*, 1032–1037

# Molecular Recognition of Phosphite and Phosphate by the Cobalt(II)–OBISDIEN System and Oxidation of Phosphite to Phosphate by Coordinated Molecular Oxygen

**Ramunas J. Motekaitis and Arthur E. Martell***

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

*Received October 7, 1993*®

Potentiometric equilibrium studies were carried out to determine the degree of binding of phosphite and phosphate ions with various protonated forms of OBISDIEN, 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane, with its cobalt 1:1 and 2:1 M:L complexes and with the protonated chelates. The dioxygen affinity of the $\mu$-phosphito–dicobalt(II)–OBISDIEN complex was determined. Kinetic studies at pH 8 and pH 9 were carried out at 60, 70, and 80 °C to measure the rate of degradation of the OBISDIEN–dicobalt–dioxygen–$\mu$-phosphito complex. The phosphate ion produced was identified through $^{31}$P NMR and by an $^{18}$O-tracer experiment.

## Introduction

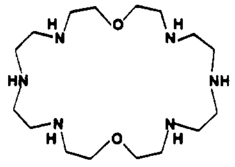
The OBISDIEN molecule, **1**, is a macrocycle containing two diethylenetriamine moieties separated by diethyl ether linkages (see Chart 1). It is potentially binucleating, whereby each metal ion is coordinated by three amino nitrogens, while retaining three coordination sites in close proximity, capable of forming a $\mu$-hydroxo bridge and coordinating a dioxygen molecule, leaving two coordination sites (one site per metal ion) for coordination of a bifunctional bridging substrate.[1–3]

Hosseini et al.[4,5] showed that in the absence of metal ions and at elevated temperatures the hexaprotonated OBISDIEN (the hexapositive ion) is capable of catalyzing the hydrolysis of the biologically important triphosphates such as adenosine triphosphate. The earliest reported redox system consisted of a $\mu$-hydroxo–$\mu$-peroxo–$\mu$-oxalato dicobalt OBISDIEN complex, which yielded carbon dioxide, water, and the dinuclear Co(III) OBISDIEN complex as the products of the intramolecular redox process.[2,3] Later, ketomalonic acid, a four-electron reductant, was shown to enter into a catalytic cycle requiring that Co(II) be regenerated in the redox reaction.[6] Subsequently, other substrates studied in the OBISDIEN–dicobalt–dioxygen system included phosphonoformic acid, malonic acid, ethylenediamine, glycine, catechols, and several others.[7] It had been established that the size-fit relationship is important for the formation of the dioxygen complex containing the bridging substrate and for the subsequent redox reaction to occur. Apparently, the substrate cannot become oxidized unless it first forms the reactive intermediate complex.

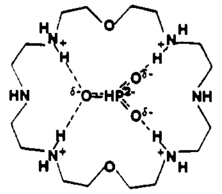
All of the previous studies utilized substrates that contain at least two donors, which act as coordination sites. By contrast, this work will concentrate on the phosphite ion, its equilibrium with the dinuclear cobalt OBISDIEN complex and with dioxygen, and its redox reaction with coordinated dioxygen. The oxidation of phosphite can be written as the insertion of an oxygen atom into the P–H bond to give a P–O–H group and is thus comparable to a hydroxylation reaction:

$$\text{H–P(O)(OH)}_2 + [\text{O}] \rightarrow \text{H–O–P(O)(OH)}_2$$

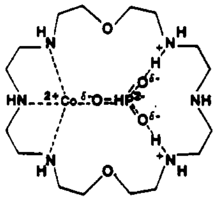
**Chart 1**



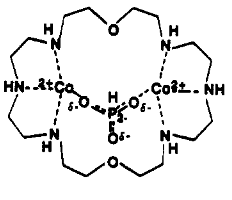
1 OBISDIEN



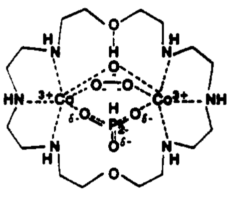
2 Suggested arrangement of H bonds in $H_4BdPs^{2+}$



3 Mononuclear phosphite cobalt(II) diprotonated OBISDIEN complex, $Co(II)PsH_2Bd^{2+}$



4 Dicobalt-$\mu$-phosphito-OBISDIEN complex, $Co(II)_2PsBd^{2+}$



5 Dicobalt $\mu$-hydroxo-$\mu$-peroxo-$\mu$-phosphite OBISDIEN complex $Co_2(OH)O_2PsBd^{3+}$

This redox reaction occurs with the phosphite anion coordinated to the cobalt centers.

While this work focuses entirely on the interactions of OBISDIEN with several guests, other workers have measured macrocyclic ligand interactions with molecules similar to ATP using non-OBISDIEN-like hosts. Recently Andres et al.[8] looked

---

® Abstract published in *Advance ACS Abstracts*, February 1, 1994.

(1) Motekaitis, R. J.; Martell, A. E.; Lecomte, J. P.; Lehn, J. M. *Inorg. Chem.* **1983**, *22*, 609.

(2) Martell, A. E.; Motekaitis, R. J. *J. Chem. Soc., Chem. Commun.* **1988**, 915.

(3) Martell, A. E.; Motekaitis, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8059.

(4) Hosseini, W. M.; Lehn, J. M.; Mertes, M. P. *Helv. Chim. Acta* **1985**, *68*, 818.

(5) Hosseini, W. M.; Lehn, J. M.; Maggiora, L.; Mertes, K. B.; Mertes, M. P. *J. Am. Chem. Soc.* **1987**, *109*, 537.

(6) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 694.

(7) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1992**, *31*, 5534.

(8) Andres, A.; Argao, J.; Bencini, A.; Bianchi, A.; Domenech, A.; Fusi, V.; Garcia-Espana, E.; Paoletti, P.; Ramirez, J. A. *Inorg. Chem.* **1993**, *32*, 3418 and references therein.

0020-1669/94/1333-1032$04.50/0

at the equilibria of ATP and dipolyphosphate with [18]ane$N_6$ and several related compounds.

## Experimental Section

**Potentiometric Titrations.** The potentiometric apparatus was calibrated with standard 0.1000 M HCl at 25.0 °C by dilution to <0.001 M and at an ionic strength of 0.100 M (KCl). The p[H] is defined as $-\log[H^+]$ while $\log K_w = -13.78$,[9] where $K_w = [H^+][OH^-]$ under these conditions.

Into a 100-mL jacketed–thermostated titration cell, equipped with p[H] and reference extension electrodes, fitted with inert gas (Ar) inlet–outlet and a 10-mL precision piston buret, were placed 5.00 mL of 1.000 M KCl (to set the ionic strength at 0.100), a weighed quantity of ligand corresponding to 0.10 mmol, and 45.00 mL of distilled, degassed water. When metal ions were also present, suitable adjustment of the quantity of water was made to make up for the water added with the standard metal ion solution. After a minimum of $^1/_2$-h equilibration, pairs of p[H] *vs* mL of $CO_2$-free 0.0968 M KOH data were recorded at 0.100-mL increments until somewhat more base was added over that necessary to neutralize the titratable protons present.

The Co(II) systems under dioxygen were measured at 0.500-mL increments of standard KOH solution spaced from 6 to 12 h apart in order to reach an acceptable compromise between duration of the experiment and its accuracy.

The potentiometric method for the determination of protonation constants, stability constants, and oxygenation constants has been described in detail.[10]

In this work, in three replicate titrations a total of 213 equilibrium points were measured in the pH range 2.9–11.0 for OBISDIEN. Single titrations for a total of 90 points in the pH range of 2.4–10.7 were measured for both phosphorous and phosphoric acids. Co(II) bindings to phosphite and to phosphate were determined in single titrations in the pH range 2.3–6.8 involving 85 equilibrium points. The OBISDIEN–$Co^{II}_2$/Ar system was rechecked in a single titration range of 3.0–8.5 involving 62 equilibrium pH points. OBISDIEN–phosphate and OBISDIEN–phosphite were each measured in the pH range 2.9–11.0 for a total of 170 equilibrium points. The system OBISDIEN–phosphate–Co was determined in two titrations involving 1 and 2 equiv of Co(II) in the pH range 2.9–11.1 involving 182 data points. The system OBISDIEN–phosphite–Co was determined in two titrations involving 1 and 2 equiv of Co(II) in the pH range 2.5–10.7 involving 179 equilibrium data points. The ternary OBISDIEN–2Co(II)–phosphite–dioxygen system was titrated in the pH range 2.5–9.6 with 53 equilibrium points. The ternary OBISDIEN–2Co(II)–phosphate–dioxygen system was titrated in the pH range 2.9–10.4 with 44 data points. The concentration in the cell was generally $2.0 \times 10^{-3}$ M in each component but was raised to $4.0 \times 10^{-3}$ M in the case of the 2:1 systems and for free phosphite and phosphate systems.

**Chemical Reagents.** OBISDIEN was obtained as a gift from Dr. Ichiro Murase, who synthesized and isolated it as a hexahydrobromide. Titration revealed 100% purity, and protonation constants were found to be virtually identical to those of the hexahydrochloride donated some years ago by J. M. Lehn. All inorganic substances were of reagent grade quality and were used without further purification. The carbonate-free potassium hydroxide solution was obtained from Baker Dilut-it carbonate-free sealed ampules and diluted according to directions. Solid phosphorous acid was from Baker Chemical Co. and was of reagent grade quality. An oxygen-18 ampule was obtained from ICON Isotopes, Mt. Marion, NY, 99.5 atom % $^{18}O_2$.

**Mass Spectra.** Mass spectra were kindly recorded by Professor Douglas Gage of the Biochemistry Department of Michigan State University, East Lansing, MI.

**Electronic Spectra.** UV–vis spectra generally from 900 to 280 nm were recorded with a Perkin-Elmer Model 553 fast-scan spectrophotometer equipped with an adjustable constant temperature cell compartment. Matched 1.000-mm quartz cells were used. The solutions were generally about $1.0 \times 10^{-4}$ M. For kinetics, the spectra were scanned every 5–30 min as required,[11] inversely depending on the temperature of the run: 60, 70, 80 °C. For each degradation run, the excess dissolved oxygen was removed by passing a stream of Ar through the sample. Thus the kinetics represents the internal redox process alone and no free dioxygen was present.

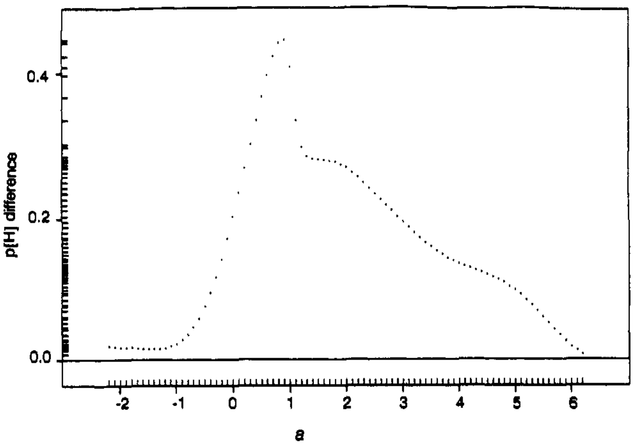


**Figure 1.** Molecular recognition in the OBISDIEN and phosphorus acid 1:1 system. The *a* values are moles of base added per mole of OBISDIEN·6HBr present. The differences are calculated by subtracting the observed p[H] from the values calculated by assuming no interaction.

**Ion-Exchange Phosphate Separation.** A glass chromatography column 1 cm × 20 cm was prepared with Dowex 50W-X8 $H^+$ and rinsed until the eluate was neutral. A dark brown solution of the OBISDIEN–2Co–phosphite–$O_2$ was prepared over a 5-h period at pH 8 using 90.7 mg of OBISDIEN·6HBr, 2.80 mL of 0.0418 M $H_3PO_3$, and 11.0 mL of 0.0213 M $CoCl_2$ diluted to 50.0 mL. Aliquots of 0.0950 M KOH were added as necessary to neutralize the slow release of protons. After thorough equilibration at room temperature (12 h), the solution was purged with argon gas (2 h) and was heated at 60 °C under Ar while the pH was maintained with KOH solution until all brown color disappeared. This decolorization took almost 6 h.

The liquid was evaporated with the help of a partial vacuum and concentrated to 5 mL. This was quantitatively placed on the cation-exchange column and eluted with distilled water. The colorless, strong-acid fraction was collected and diluted to 100.0 mL for further testing (titration, NMR), and in a similar run the [$^{18}$O]phosphate was isolated.

**Computations.** All computations were performed with a MicroAge 486 DX2 50Mz computer equipped with 8-megabyte RAM and a 200-megabyte hard drive running DOS 5.0. Calculations on potentiometric equilibrium data were performed with the program BEST[9] while kinetic data were analyzed with help of an in-house FORTRAN program LSQFIT featuring a function subroutine and an autoscaling high-resolution LaserJet graph. All kinetic data were found to follow the $\log(A - A_\infty)$ *vs* $t$ linear regression, with correlation coefficients in negative excess of $-0.995$ for all the systems studied.

In this work $H_{-1}$ and $OH^-$ are synonymous.

## Results and Discussion

**Recognition of Phosphite.** The algorithm employed in the determination of species resulting from the interaction of various protonated forms of the OBISDIEN molecule with phosphite anions rests on the premise that the deviations in the experimentally measured titration curve from those of the curve calculated from the protonation constants of OBISDIEN and phosphorus acid are a measure of the interactions between these substances. To this end, protonation constants for phosphite and for OBISDIEN were redetermined under the identical experimental conditions for which the recognition equilibria were measured, in order to extract maximum sensitivity from this technique. The successive log protonation constants of phosphite found at 25 °C and $\mu = 0.100$ (KCl) are 6.33(1) and 1.1(1) ($\sigma(pH_{fit}) = 0.002$). The overall log protonation constants of OBISDIEN·6HBr ($\beta$ values) used were 9.62, 18.50, 26.79, 34.41, 38.22, and 41.52. These values were checked by titration and were found to be correct.

Figure 1 is just such a plot of differences between observed pH values and values calculated by assuming no molecular interaction. All the differences are positive, and the magnitude of the

---

(9) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1977; Vol. 3.

(10) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers: New York, 1992.

(11) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

differences is indicative of the magnitude of the interaction. Note that in the beginning region, before any protons are titrated off, the plotted differences are near zero. Then the differences rise all the way to a maximum of 4.47 pH units near $a = 1$ where $[H_5L^{5+}]$ is high and the dinegative ion $HP(O)(O^-)_2$ starts to form. Then as the successive protons are titrated from the macrocycle, the affinity for $HP(O)(O^-)_2$ decreases in steps until $a = 6$ is reached.

There were seven overall stability constants found for the formation of seven distinct species in solution depending on the pH. For convenience, phosphite is treated as an $H_2L$ ligand since the P-bound H is not acidic at all in aqueous solution and its dianion is abbreviated as $Ps^{2-}$ (*p*hosphorou*s*). Bd is the free base OBISDIEN. The overall stability constants found, with standard deviations in parentheses, are as follows:

$$nH^+ + Bd + Ps^{2-} \rightleftharpoons H_nBdPs^{n-2} \qquad \beta = \frac{[H_nBdPs^{n-2}]}{[H^+]^n[Bd][Ps^{2-}]}$$

| $n$ | log β | $n$ | log β | $n$ | log β |
|---|---|---|---|---|---|
| 2 | 20.96 (0.04) | 5 | 44.45 (0.01) | 7 | 52.10 (0.01) |
| 3 | 29.52 (0.02) | 6 | 48.91 (0.01) | 8 | 53.86 (0.02) |
| 4 | 37.71 (0.01) | | | | |

The relation between the shape of the curve shown in Figure 1 and the species formed is exceedingly complex, but in general, the increase in p[H] observed when the two substances are cotitrated is brought about by the stabilization of various protonated forms when the negative phosphite becomes electrostatically bound to the protonated forms of OBISDIEN through a multibridged network of hydrogen bonding.

There are a number of ways these recognition constants may be expressed. Clearest perhaps is the successive set of interactions between dinegative $HPO(O^-)_2$ and protonated forms of OBISDIEN:

$$H_6Bd^{6+} + Ps^{2-} \rightleftharpoons BdH_6Ps^{4+} \qquad \log K_6^R = 7.39$$

$$H_5Bd^{5+} + Ps^{2-} \rightleftharpoons BdH_5Ps^{3+} \qquad \log K_5^R = 6.23$$

$$H_4Bd^{4+} + Ps^{2-} \rightleftharpoons BdH_4Ps^{2+} \qquad \log K_4^R = 3.29$$

$$H_3Bd^{3+} + Ps^{2-} \rightleftharpoons BdH_3Ps^{+} \qquad \log K_3^R = 2.74$$

$$H_2Bd^{2+} + Ps^{2-} \rightleftharpoons BdH_2Ps \qquad \log K_2^R = 2.45$$

The decrease in the magnitude with decrease of proton count indicates the importance of high Coulombic charge leading to strong interaction. Figure 2 shows that even at millimolar concentrations considerable phosphite binding occurs, especially below pH 8. Above this p[H], the phosphite is not effectively bound because monoprotonated and neutral OBISDIEN do not have sufficient attraction for (do not recognize) the dinegative anion. Possible coordinate-bonding and hydrogen-bonding sites in $BdH_4Ps^{2+}$, for example, are indicated by formula **2** (Chart 1). The $Cl^-$ ion also participates in the overall species formed, but the effect is constant and the trends observed are valid within the scope of this work. Water molecules are also probably important in the formation of the ultimate microstructures.

The magnitudes of these phosphite and phosphate recognition constants can be better understood by comparing them to those of other dinegative ligands studied with the protonated forms of OBISDIEN in Table 1. The smaller phosphite ion bonds much more strongly than any of the other guests listed for $n = 6$ and $n = 5$. But note, for example, that an anion such as ketomalonate seems to do better for the lower protonated forms of OBISDIEN, presumably because of size and shape considerations. The protonation constants of the two catecholates listed are too high for effective recognition in that, as the p[H] is raised, the OBISDIEN molecule becomes substantially deprotonated while the potential guest resists deprotonation. The phenylenediamines are not dinegative, so there is no measurable interaction of the neutral and mononegative ions, respectively, with OBISDIEN.

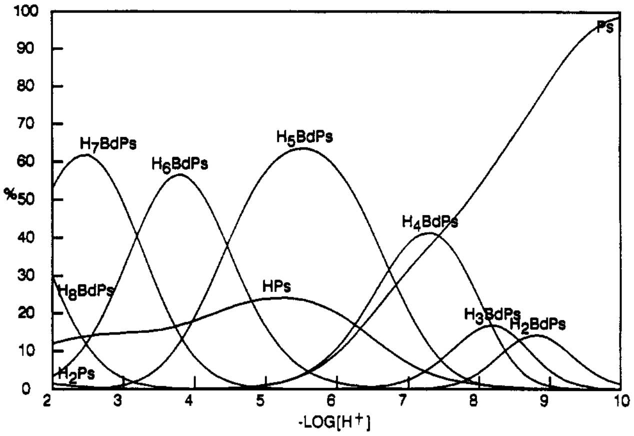


**Figure 2.** Species distribution diagram for a 1:1 molar solution of OBISDIEN and phosphite at 0.002 200 M in each component at 25 °C, $\mu = 0.100$ (KCl). For clarity only phosphite-containing species are shown.

**Recognition of Phosphate.** The recognition by protonated forms of OBISDIEN was determined by potentiometric titration of OBISDIEN in the presence of phosphate. Six overall protonation constants (expressed as β values) were found for OBISDIEN in the presence of an equivalent amount of phosphate:

$$nH^+ + Bd + PO_4^{3-} \rightleftharpoons H_nBdPO_4^{n-3} \qquad \beta = \frac{[H_nBdPO_4]^{n-3}}{[H^+]^n[Bd][PO_4^{3-}]}$$

| $n$ | log β | $n$ | log β | $n$ | log β |
|---|---|---|---|---|---|
| 3 | 31.73 (0.1) | 5 | 48.79 (0.01) | 7 | 60.23 (0.01) |
| 4 | 40.38 (0.05) | 6 | 55.25 (0.02) | 8 | 62.67 (0.02) |

The accuracy of each of these log β's must be better than ±0.01 since the overall $\sigma(p[H]_{fit}) = 0.006$ for this set of p[H] measurements.

Because of the very high first protonation constant of $PO_4^{3-}$, the dianion, $P(O)(OH)(O^-)_2$, and the monoanion, $PO(OH)_2O^-$, are the only important species in the practical working p[H] range, and therefore the abbreviation of the dianion will be formulated as $Pc^{2-}$ (*p*hosphori*c*), in obvious analogy, from a charge viewpoint, with that of phosphite. Practical stepwise constants for interaction of the dinegative biphosphate ion with OBISDIEN can be extracted from the overall constants and other protonation constants. These recognition constants are as follows:

$$H_6Bd^{6+} + Pc^{2-} \rightleftharpoons BdH_6Pc^{4+} \qquad \log K_6^R = 6.97$$

$$H_5Bd^{5+} + Pc^{2-} \rightleftharpoons BdH_5Pc^{3+} \qquad \log K_5^R = 5.29$$

$$H_4Bd^{4+} + Pc^{2-} \rightleftharpoons BdH_4Pc^{2+} \qquad \log K_4^R = 2.64$$

$$H_3Bd^{3+} + Pc^{2-} \rightleftharpoons BdH_3Pc^{+} \qquad \log K_3^R = 1.85$$

$$H_2Bd^{2+} + Pc^{2-} \rightleftharpoons BdH_2Pc \qquad \log K_2^R = 1.49$$

The binding of biphosphate is similar and slightly weaker than that of biphosphite. As seen in Table 1, for phosphate and phosphite there is a similar drop in magnitude of the interactions (recognition constants) in going from $H_5L^{5+}$ to $H_4L^{4+}$ forms of OBISDIEN. It is interesting to express the above set of overall

**Table 1.** log Guest Formation Constants with Protonated Forms of OBISDIEN as Hosts

| | | | log $K_n^R$'s | | | | | |
|---|---|---|---|---|---|---|---|---|
| ion | log $K_1^H$ | log $K_2^H$ | $n = 6$ | $n = 5$ | $n = 4$ | $n = 3$ | $n = 2$ | $n = 1$ |
| phosphite[a] | 6.33 | 1.1 | 7.39 | 6.23 | 3.29 | 2.74 | 2.45 | |
| phosphate[b] | 6.75[b] | 1.72[b] | 6.97[b] | 5.29[b] | 2.64[b] | 1.85[b] | 1.49[b] | |
| malonate | 5.27 | 2.63 | 4.2 | 3.70 | 2.38 | 2.05 | 1.8 | |
| ketomalonate | 3.52 | 1.82 | 5.15 | 4.52 | 3.65 | 4.16 | 3.83 | 3.39 |
| oxalate | 3.38 | 1.0 | 4.68 | 3.59 | 2.06 | | | |
| catecholate | 13.3 | 9.3 | none | | | | | |
| tironate | 12.5 | 7.62 | none | | | | | |
| *o*-phenylenediamine | 4.65 | | | none | | | | |
| *o*-phenylenediamine-4-carboxylate | 5.74 | 3.57 | none | | | | | |

[a] This work. [b] Hydrogen phosphate, $HPO_4^{2-}$, is the guest.

recognition constants in terms of the trinegative phosphate:

$$H_6Bd^{6+} + PO_4^{3-} \rightleftharpoons BdH_6PO_4^{3+} \qquad \log K_6^R = 13.73$$

$$H_5Bd^{5+} + PO_4^{3-} \rightleftharpoons BdH_5PO_4^{2+} \qquad \log K_5^R = 10.57$$

$$H_4Bd^{4+} + PO_4^{3-} \rightleftharpoons BdH_4PO_4^{+} \qquad \log K_4^R = 5.93$$

$$H_3Bd^{3+} + PO_4^{3-} \rightleftharpoons BdH_3PO_4 \qquad \log K_3^R = 4.94$$

It is seen that the most strongly bound phosphate cannot be expressed as $PO_4^{3-}$ because the complex formed contains seven protons and OBISDIEN has only six nitrogens. For this reason it is more logical to express the recognition constants for phosphate in terms of the biphosphate ion, $Pc^{2-}$ (=$HOPO(O^-)_2$). This phosphate work is analogous to the previous report[7] on the investigation of $Cu^{2+}$–OBISDIEN complexes and their recognition of various ions.

**Cobalt–OBISDIEN and Phosphite.** Before accurate values for the recognition of phosphite by the mononuclear $Co^{2+}$–OBISDIEN complex could be determined, the system phosphite–$Co^{2+}$ was studied. From 1:1 and 2:1 titrations it was found that under the conditions of this work (25.0 °C, $\mu = 0.100$ (KCl)) only CoL and CoHL complexes were formed. $\log K_{CoL} = 2.93(1)$ and $\beta_{CoHL} = 6.09(1)$. $\sigma_{fit} = 0.001$.

From 1:1:1 and 2:1:1 M:L:phosphite potentiometric equilibrium measurements under argon a total of five cobalt–OBISDIEN–phosphite complexes were found, and their overall formation constants are as follows:

$$Bd + Ps^{2-} + 2Co^{2+} + H^+ \rightleftharpoons BdCo_2PsH^{3+} \qquad \log \beta = 23.00(5)$$

$$Bd + Ps^{2-} + 2Co^{2+} \rightleftharpoons BdCo_2Ps^{2+} \qquad \log \beta = 15.39(5)$$

$$Bd + Ps^{2-} + Co^{2+} + H^+ \rightleftharpoons BdCoPsH^{+} \qquad \log \beta = 20.33(5)$$

$$Bd + Ps^{2-} + Co^{2+} + 2H^+ \rightleftharpoons BdCoPsH_2^{2+} \qquad \log \beta = 27.47(5)$$

$$Bd + Ps^{2-} + Co^{2+} + 3H^+ \rightleftharpoons BdCoPsH_3^{3+} \qquad \log \beta = 33.55(5)$$

In the absence of phosphite, the only dinuclear species detected is $M_2(OH)L^{3+}$. Because the necessary analogous dinuclear cobalt(II)–OBISDIEN species do not form, the above dicobalt complexes cannot be rewritten into equilibria showing the recognition of the phosphite by a dinuclear complex. However phosphite recognition constants for the mononuclear $Co^{2+}$–OBISDIEN complexes can readily be written:

$$H_2BdCo^{4+} + Ps^{2-} \rightleftharpoons BdH_2CoPs^{2+} \qquad \log K_2^R = 4.03$$

$$HBdCo^{3+} + Ps^{2-} \rightleftharpoons BdHCoPs^{+} \qquad \log K_1^R = 3.16$$

$$H_2BdCo^{4+} + HPs^{-} \rightleftharpoons BdH_3CoPs^{3+} \qquad \log K_3^R = 3.66$$

From these recognition constants, it can be seen that the replacement of two protons by a metal ion ($Co^{2+}$) enhances the recognition constant of phosphite by almost 0.5 log unit. Suggested coordination and hydrogen-bonding sites of the dinuclear and mononuclear phosphite-bridged cobalt–OBISDIEN complexes are indicated by formulas **3** and **4** (Chart 1).

**Cobalt–OBISDIEN and Phosphate.** As with phosphite, from 1:1:1 and 2:1:1 M:L:phosphate potentiometric equilibrium measurements under argon, a total of five cobalt–OBISDIEN–phosphate complexes were found, and the following overall formation constants ($\beta$ values) were determined:

$$Bd + Pc^{3-} + 2Co^{2+} + H^+ \rightleftharpoons BdCo_2PcH^{2+} \qquad \log \beta = 27.74(5)$$

$$Bd + Pc^{3-} + Co^{2+} + 2H^+ \rightleftharpoons BdCoPcH_2^{+} \qquad \log \beta = 31.49(5)$$

$$Bd + Pc^{3-} + Co^{2+} + 3H^+ \rightleftharpoons BdCoPcH_3^{2+} \qquad \log \beta = 38.79(5)$$

$$Bd + Pc^{3-} + Co^{2+} + 4H^+ \rightleftharpoons BdCoPcH_4^{3+} \qquad \log \beta = 44.75(5)$$

$$Bd + Pc^{3-} + Co^{2+} + 5H^+ \rightleftharpoons BdCoPcH_5^{4+} \qquad \log \beta = 51.67(5)$$

Unlike the phosphite case, these five recognized phosphate species involve only one binuclear complex and four mononuclear protonated complexes.

In the absence of phosphate, the stable dicobalt–OBISDIEN species has the formulation $M_2H_{-1}Bd$, with the bridging $OH^-$ ion stabilizing the dinuclear array. In the presence of phosphate, the stable dinuclear species now becomes $M_2PcHBd$. The phosphate ion competes with the hydroxy bridge in the $HPO_4^{2-}$ form to give a dinuclear monohydrogen phosphate bridge. But the completely deprotonated biphosphate–bridged species (i.e. $M_2PcBd$) does not form, because the competition by $M_2H_{-1}Bd$ dominates the solution. Algebraic rearrangement of these equilibrium constants, together with the phosphate free equilibria, the following recognition equilibria involving conversion of free phosphate to the complex in which the phosphate is coordinated and hydrogen-bonded within the macrocycle can be derived:

$$\mathrm{H_2BdCo^{4+} + Pc^{3-} \rightleftharpoons BdH_2CoPc^{+}} \qquad \log K_{20}{}^{R} = 8.08$$

$$\mathrm{HBdCo^{3+} + HPc^{2-} \rightleftharpoons BdH_2CoPc^{+}} \qquad \log K_{11}{}^{R} = 2.58$$

$$\mathrm{H_2BdCo^{4+} + HPc^{2-} \rightleftharpoons BdH_3CoPc^{2+}} \qquad \log K_{21}{}^{R} = 3.69$$

The parallelism in the relative interactions between the phosphate and phosphite coordination chemistry draws the observation that hydrogen phosphate ($Pc^{2-}$) interactions are only slightly weaker than those of the equi-Coulombic hydrogen phosphite ($Ps^{2-}$) ion.

**Cobalt–OBISDIEN and Phosphite under Dioxygen.** To determine whether a $\mu$-phosphito–dicobalt–OBISDIEN–dioxygen complex would form, an appropriate potentiometric equilibrium curve under oxygen, measured in the presence of phosphorous acid, gave an overall stability constant for just such a species. A total of 36 species in addition to this new dioxygen complex had to be taken into account, and the observed curve was decoded into the following overall formation constant:

$$\mathrm{Bd + 2Co^{2+} + Ps^{2-} + O_2 \rightleftharpoons BdCo_2(O_2)(OH)Ps^{+} + H^{+}} \qquad \log \beta = 13.47(4)$$

Since the equilibrium constants for the formation of oxygen complexes of the dinuclear cobalt–OBISDIEN complex are known, the overall equilibrium constant $\beta$ can be recast into a form involving the recognition (combination) of phosphite by the performed dioxygen complex:

$$\mathrm{Co_2Bd(O_2)(OH)^{3+} + Ps^{2-} \rightleftharpoons Co_2Bd(O_2)(OH)Ps^{+}} \qquad \log K^{R} = 8.96$$

The large magnitude of this equilibrium constant shows not only that the performed dioxygen complex is preorganized for acceptance of the substrate but that the cobalt centers have considerable Co(III) character, thus increasing the affinity for the bridging phosphite anion. A possible arrangement of the bridging groups and the coordination sites in the dioxygen complex $Co_2(OH)O_2PsBd^{+}$ is indicated by formula **5** (Chart 1).

**Dicobalt–OBISDIEN–Phosphite–Dioxygen Redox Kinetics.** When warmed to 60 °C or above, the dicobalt–OBISDIEN–phosphite–dioxygen complex undergoes an internal redox reaction whereby bound phosphite undergoes a two-electron oxidation to phosphate and the bound dioxygen is reduced to water. In addition, the two cobalt centers become permanently oxidized to cobalt(III). This redox reaction may be considered as occurring between a dicobalt(III)-bound bridging peroxo group and a dicobalt(III)-bound bridging phosphite. Since the heating is done under argon, it is not possible that the phosphite is oxidized by ambient oxygen. The oxygen transfer from peroxo to phosphite may occur in the manner indicated in Scheme 1.

While no attempts were made to isolate the resulting Co(III) complex after phosphite oxidation, it is certain that both cobalt ions are coordinated with OBISDIEN as inferred from visible spectra over the entire pH scale, from the solubility of the complex at pH > 10, and from the lack of reactivity to further dioxygen treatment. The most likely arrangement is probably one with a di- or triolated pair of Co(III) ions surrounded by an OBISDIEN ligand which coordinates each Co(III) center with three amino nitrogen atoms.

There are no solution conditions where the $BdCo_2(O_2)(OH)Ps^{+}$ species exists alone. Under the experimental conditions, it is observed from Figure 3 that the dioxygen phosphito-bridged species is present from pH to 6.5 to about pH 8.5 with a maximum concentration reaching 57% at pH 7.4. Thus any kinetics measured on this species must take into account the other oxygen complexes present, mainly $Co_2H_{-1}(O_2)Bd$ and $Co_2H_{-2}(O_2)Bd$. The rate of dioxygen complex disappearance was undertaken at three different temperatures and two different pH values in the absence of phosphite and in the presence of 1:1 and 10:1 molar ratios of phosphite to OBISDIEN.

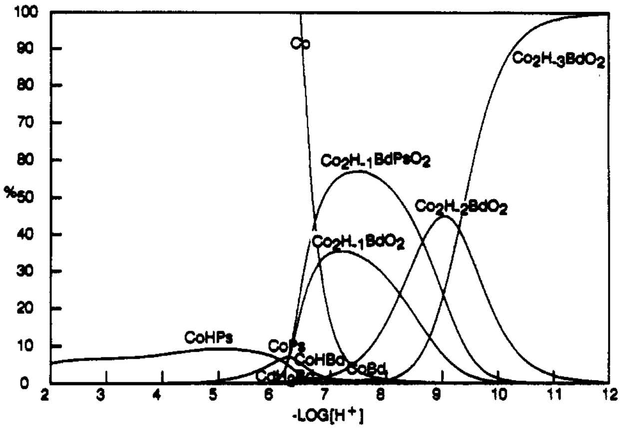
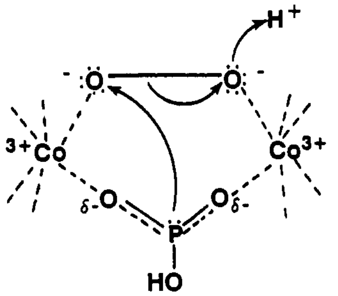


**Figure 3.** Distribution of cobalt-containing species at 1.00 × $10^{-4}$ M OBISDIEN, 2.00 × $10^{-4}$ M $Co^{2+}$, and 1.00 × $10^{-4}$ M phosphite under dioxygen ($P_{O_2}$ = 1 atm).

**Scheme 1.** Proposed Mechanism of Conversion of Phosphite to Phosphate by the $\mu$-Peroxo Group in the Dinuclar Cobalt OBISDIEN Dioxygen Complex



The product, phosphate, was initially identified by $^{31}P$ NMR as a very broad peak centered at +16 ppm from the phosphoric acid external standard. Width at half peak height is approximately 8 ppm, indicating a paramagnetic influence, possibly from incompletely oxidized $Co^{2+}$. Further work aimed at better characterization involved separation of the product on a cation-exchange resin. The $^{31}P$ NMR spectrum of the eluate showed the presence of only one unsplit sharp singlet at 5.60 ppm relative to external phosphoric acid, thus confirming the presence of only phosphate in the eluate of the reaction product. Superimposed in Figure 7 are two arrows pointing to the expected peak positions had the phosphite remained unoxidized. The observed $^{31}P$ NMR is clearly that of phosphate.

Further phosphate substantiation was made by potentiometric titration of a portion of the eluate with standard KOH. After subtraction of the excess strong acid present in the eluate, the protonation constant, 6.79, thus determined is in good agreement for phosphate and is considerably higher than that of phosphite, as listed in Table 1.

Figure 4 shows a typical kinetic run. The sample containing 1 × $10^{-4}$ M BISDIEN, 2 × $10^{-4}$ M $Co^{2+}$, and 1 × $10^{-4}$ M phosphite was treated with atmospheric dioxygen and then with argon at 70 °C and pH 9.0. Each curve was measured at 5-min intervals.

Figure 5 shows the mathematical treatment of the same sample. An excellent pseudo-first-order kinetic plot was obtained with a correlation coefficient $r = -0.9999$ and a slope of 1.7 × $10^{-4}$ $s^{-1}$.

Table 2 is a summary of all the pseudo-first-order rate constants obtained in this work.

From the data in Table 2 one may make the following generalizations. There does not seem to be a strong pH effect under these reaction conditions. In most cases, a drop in pH slows the reaction only somewhat. The addition of phosphite has

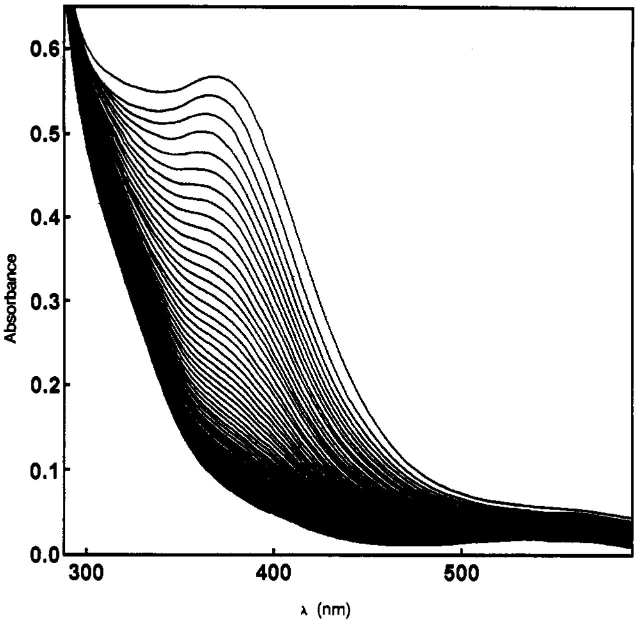


**Figure 4.** A typical spectral kinetic oxidation run. In this case, the sample solution is at 70 °C and p[H] 9.0. The initial concentrations are 0.100 mM in OBISDIEN and phosphite and 0.200 mM in $Co^{2+}$. The solution was prepared and adjusted to pH 9.0 under $O_2$, and the kinetics were run under Ar.

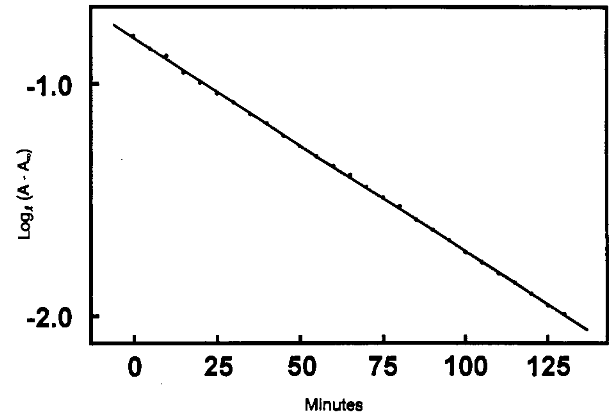


**Figure 5.** Pseudo-first-order rate plot for the disappearance of dioxygen complexes $BdCo_2(O_2)(OH)Ps^+$ and lower concentrations of $BdCo_2(O_2)(OH)_n{}^{4-n}$ (where $n$ = 1–3). $R$ = –0.999; slope = 1.0 × $10^{-2}$ measured at 70 °C and p[H] 9.0.

**Table 2.** Pseudo-First-Order Rate Constants ($s^{-1}$) for the Autodecomposition of OBISDIEN–Dioxygen Complexes in the Absence, Presence, and Excess of Phosphite

| | pH | 60 °C | 70 °C | 80 °C |
|---|---|---|---|---|
| Bd alone | 9.0 | 5.2 × $10^{-5}$ | 1.1 × $10^{-4}$ | 4.0 × $10^{-4}$ |
| | 8.0 | 3.3 × $10^{-5}$ | 1.2 × $10^{-4}$ | 3.7 × $10^{-4}$ |
| | 7.0 | 2.2 × $10^{-5}$ | 5.7 × $10^{-4}$ | 1.4 × $10^{-4}$ |
| Bd/$HPO_3{}^{2-}$, 1:1 | 9.0 | 5.3 × $10^{-5}$ | 1.7 × $10^{-4}$ | 4.7 × $10^{-4}$ |
| | 8.0 | 3.2 × $10^{-5}$ | 1.1 × $10^{-4}$ | 2.3 × $10^{-4}$ |
| Bd/$HPO_3{}^{2-}$, 1:10 | 9.0 | 3.3 × $10^{-5}$ | 1.5 × $10^{-4}$ | 3.2 × $10^{-4}$ |
| | 8.0 | 3.3 × $10^{-5}$ | 1.0 × $10^{-4}$ | 4.0 × $10^{-4}$ |

little effect on the rate of degradation of the dioxygen complexes. Addition of larger amounts of phosphite seems to slow the rate. All these generalizations lead to the conclusion that degradation of $BdCo_2(O_2)(OH)^{3+}$ and $BdCo_2O_2(OH)_2{}^{2+}$ accompanies the redox reaction of the $BdCo_2O_2Ps(OH)^+$ complex in which the oxygen complex is also destroyed and that the data in Table 2 and Figure 4 represent all three reactions occurring simultaneously, although the concentrations of the non-phosphite-containing dioxygen complexes are considerably lower.

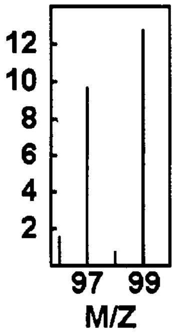


**Figure 6.** Negative FAB mass spectrum of the $H_2PO_4^-$ ion indicating incorporation of $^{18}O$ during oxidation of phosphite to phosphate.

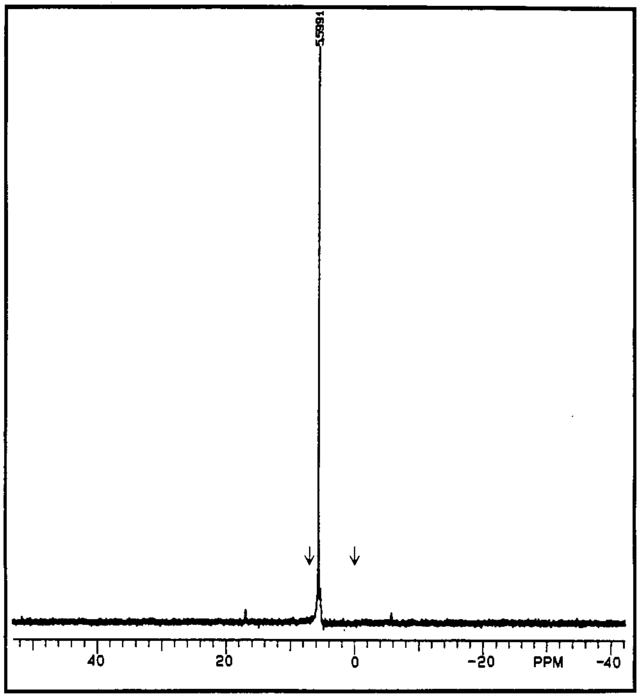


**Figure 7.** $^{31}P$ NMR spectrum of the oxidation product resulting from reaction of phosphite with the dicobalt–dioxygen macrocyclic complex at 60 °C for about 12 h at about pH 8. The highly acidic solution obtained from the $H^+$ form of the cation-exchange resin was adjusted to about p[H] 9.0 with KOH. The pair of arrows indicate the $^{31}P$ NMR spectrum peak positions expected for phosphite under identical conditions of $D_2O$/$H_2O$ solvent and p[H].

**Oxygen-Transfer Mechanism.** In order to further understand the mechanism of oxygen transfer, one phosphite oxidation reaction was carried out by substituting $^{18}O_2$ for natural $^{16}O_2$ in the dicobalt–OBISDIEN–phosphite–dioxygen system. The product isolated through ion-exchange chromatography was subjected to negative FAB analysis, which revealed that in the oxidation of phosphite to phosphate the oxygen was derived from molecular oxygen, which had combined with the dinuclear cobalt–OBISDIEN complex to form the dioxygen adduct. Figure 6 shows a substantial peak for $H_2PO_3{}^{18}O^-$ ($m$ = 99) as well as a smaller peak for $H_2PO_4^-$ ($m$ = 97), indicating that the oxygen atom transfer took place from the coordinated dioxygen to the coordinated phosphite ion. The redox reaction may be visualized as a concerted oxygen-transfer step. Visualization of the molecular model of the dinuclear active site by computer shows the peroxo oxygen positioned laterally against the pH side of the phosphorus atom in phosphite. Scheme 1 indicates how this reaction may occur. The presence of the peak for $H_2P^{16}O_4^-$ is not necessarily indicative of alternative mechanistic pathways but could appear as a result of partial exchange of oxygen with solvent water under the protracted treatment of the complex by ion exchange, concentrated acid, and evaporation with warming.

**Acknowledgment.** This work was supported by the Office of Naval Research.