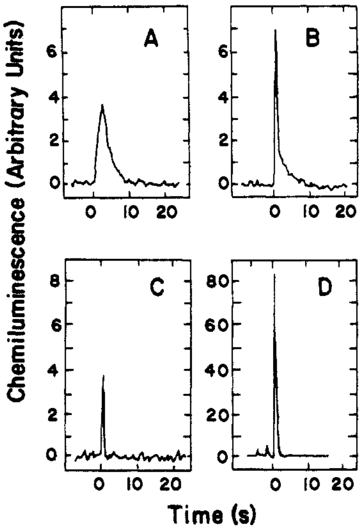

Figure 1. Time course for the 1268-nm emission from the reactions of $O_2^{\bullet -}$ with halocarbons in acetonitrile: (A) 0.4 mM $O_2^{\bullet -}$, 1.3 mM CCl_4; (B) 0.4 mM $O_2^{\bullet -}$, 35 mM α,α,α-trichlorotoluene; (C) 1 mM $O_2^{\bullet -}$, 350 mM 1-bromobutane; (D) 3 mM $O_2^{\bullet -}$, 3.8 mM CBr_4.

Table I. Spectral Analysis of Near-Infrared Emission from the Reactions of $O_2^{\bullet -}$ with Halocarbons in Acetonitrile

Filter (nm)	relative emission[a]			
	O_2^- + CBr_4[b]	O_2^- + CCl_4[c]	O_2^- + $C_6H_5CCl_3$[d]	O_2^- + C_4H_9Br[e]
1070	0.003 ± 0.002	0.03 ± 0.03	−0.04 ± 0.10	0.03 ± 0.02
1170	−0.002 ± 0.001	0.09 ± 0.03	0.10 ± 0.14	0.01 ± 0.03
1268	1.00 ± 0.06	1.00 ± 0.04	1.00 ± 0.03	1.00 ± 0.16
1377	0.61 ± 0.06	0.45 ± 0.03	0.40 ± 0.03	0.39 ± 0.05
1475	0.06 ± 0.01	0.12 ± 0.11	0.21 ± 0.11	0.05 ± 0.03

[a] The emission in each system was normalized so that the value for the 1268-nm filter was 1.0. Emission intensities were corrected for filter transmissions and detector responses. [b] CBr_4 (3.8 mM), 3 mM $O_2^{\bullet -}$. [c] CCl_4 (1.3 mM), 5 mM $O_2^{\bullet -}$. [d] Trichlorotoluene (35 mM), 2 mM $O_2^{\bullet -}$. [e] 1-Bromobutane (700 mM), 1 mM $O_2^{\bullet -}$.

Table II. Chemiluminescence at 1268 nm from the $O_2^{\bullet -}$–CCl_4–^2H_2O System

CCl_4 (mM)	added ^2H_2O (mM)	rel emission[b]
1.3		348 ± 25
1.3	6.8	370 ± 22
	6.8	−1 ± 6
	68	2 ± 11

[a] The initial $O_2^{\bullet -}$ concentration was 1 mM. The acetonitrile solvent contained 4.2 mM water before any additions. [b] Arbitrary units.

et al.[2] for Cl-containing halocarbons. The latter group found that the addition of large amounts of H_2O to suspensions of KO_2 in either CCl_4 or Freon-113 increased the $^1O_2$ production.[2] They attributed the increased $^1O_2$ yield to the H_2O-induced dismutation of $O_2^{\bullet -}$.[2] Alternative explanations exist for their data, however. The addition of large amounts of water to KO_2–halocarbon suspensions will induce the dissolution of KO_2 for enhanced reactivity with the halocarbon and will cause the rapid decomposition of KO_2. The O_2 evolution from the KO_2 particles will increase the reactant mixing rate, which will increase the rate of the surface reaction between KO_2 and the halocarbon. The H_2O-induced decomposition of KO_2 may also heat the reaction mixture and thereby increase the rate of the $O_2^{\bullet -}$/halocarbon reaction.

With 1-bromobutane, $^1O_2$ was produced only when the halocarbon was in large excess. This is consistent with a competition between reaction 3 (producing $^1O_2$ via a Russell mechanism[8]) and reaction 4, which consumes peroxyl radicals. The polyhalogenated halocarbons have been shown to have a more complex reaction mechanism with $O_2^{\bullet -}$ in which there is a sequential removal of halogen atoms. Singlet oxygen is generated in these reactions even when the halocarbons are not in large excess. One explanation for this observation is the production of $^1O_2$ from the reactions of $O_2^{\bullet -}$ with various partially halogenated intermediates.

$$RO_2^{\bullet} + O_2^- \rightarrow RO_2^- + O_2 \qquad (4)$$

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Bimodal Inclusion of Nitroxide Radicals by β-Cyclodextrin in Water As Detected by Electron Spin Resonance

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The most important factor regulating the stability of cyclodextrin inclusion complexes[2] is the charge and the direction of inclusion. With respect to the direction two-way inclusion has been suggested by many investigators.[3-7] This report deals with the detection of bimodal inclusion of a nonsymmetric[8] nitroxide radical into β-cyclodextrin (cycloheptaamylose, β-CD) by electron spin resonance (ESR).

Recently various kinds of artificial molecular receptors which can form inclusion complexes have been reported.[9] Most of them have structures capable of including a substrate by two different ways. It should be noted that enzyme activities could be greatly affected by the presence of bimodal inclusion. In CD's the importance of bimodal inclusion has been discussed from the viewpoint of the driving force for molecular recognition.

Magnetic resonance techniques have been the major tool for the detection of the structure of CD inclusion complexes in solution.[3-5,10,11] However, NMR spectroscopy has failed to separate

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[1] Address is Southwest Ontario ESR/ENDOR Facility.

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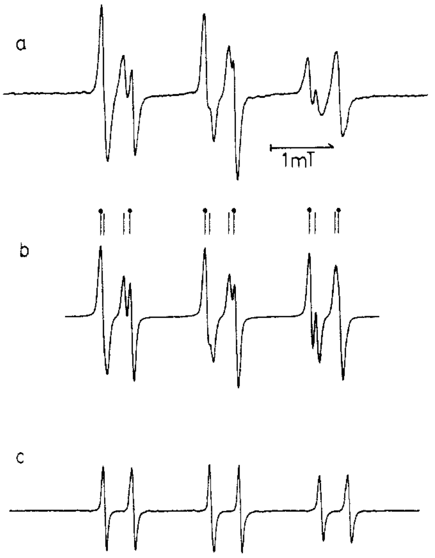


Figure 1. (a) ESR spectrum of **1** in 8 × 10^{-3} M aqueous solution of β-CD. Field modulation amplitude is 0.25 G, and incident microwave power is 13 mw. (b) Computer simulated spectrum for (a). Three components in Table I are superimposed at the area intensity ratio of R0:R1:R2 = 0.04:0.49:0.29. Line widths are 0.06 mT for R0 and 0.07 mT for R1 and R2. Stick spectrum shows the line position for R1 (●) and R2. (c) ESR spectrum of **1** in water at room temperature.

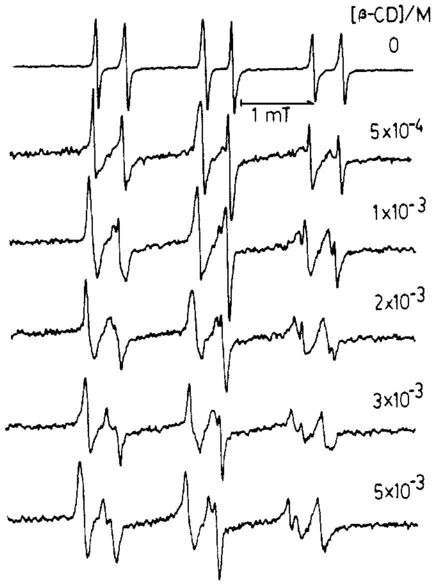


Figure 2. Dependence of ESR spectra of **1** on the concentration of β-CD in water.

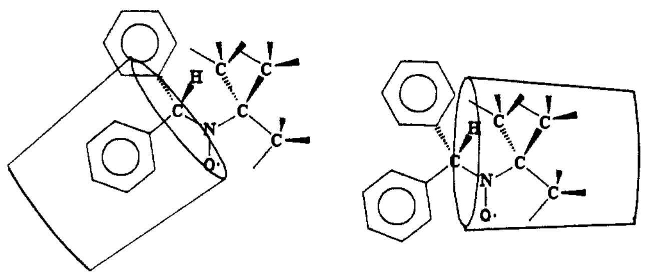


Figure 3. Schematic illustration of two possible ways of inclusion of **1** by β-CD.

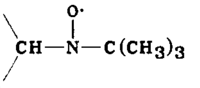
Table I. Hyperfine Splitting Constants of Nitroxide **1** and Association Constants^a

		$A_N/10^{-4}$ T	$A_H/10^{-4}$ T	$K/10^3$ M^{-1}	assignment
R0	in water	15.90	4.22		
R1	in the presence	15.41	4.38	1.8 ± 0.3	*tert*-butyl side
R2	of β-CD	15.65	2.90	1.2 ± 0.3	phenyl side

^{a}Error for hfs is ±0.05 × 10^{-4} T.

free and included species. The reason given so far is that the formation of the complex is reversible and that the rate is above the fast exchange limit of NMR spectroscopy (~10^3 Hz). ESR has a shorter time scale (~10^6 Hz) than NMR and could in principle overcome fast exchange difficulties. In fact ESR spectra of various nitroxide radicals included by CD have been detected, and the structure and dynamic properties have been discussed in detail.[11] However, no examples of bimodal inclusion have been reported.

The ESR spectrum shown in Figure 1a was obtained[12] when diphenylmethyl-*tert*-butyl nitroxide (**1**)[13] was dissolved in water containing 8 × 10^{-3} M β-CD. A comparison of the spectrum



$$Ph_2CH-\overset{O\cdot}{N}-C(CH_3)_3$$

1

of **1** in water (Figure 1b) to that obtained in β-CD solutions (Figure 1a) reveals that two ESR spectroscopically new species are produced upon addition of β-CD. The ESR spectrum in Figure 1a can be reproduced by a computer spectrum simulation by using hyperfine splitting constants (hfs) listed in Table I. When the amount of β-CD is increased from 5 × 10^{-4}–5 × 10^{-3} M the ESR signal of **1** in water decreases in intensity (Figure 2). These facts show that there are two kinds of complexes of radical **1** associated with β-CD.[14,15] Equilibrium constants for the formation of these complexes were estimated[16] by computer spectrum simulation of five spectra and K_1 = (1.8 ± 0.3) × 10^3 M^{-1} for R1 and K_2 = (1.2 ± 0.3) × 10^3 M^{-1} for R2 were obtained.

We interpret these results in terms of a bimodal inclusion of radical **1** by β-CD. Since β-CD has a hydrophobic channel of about 6–7 Å in diameter and about 8 Å in length,[2] it is not likely that β-CD can hold the whole radical in the cavity. On the basis of the size of the substituents in nitroxide **1** there seem to be two

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[12] ESR spectra were obtained by using a Bruker ER 200D SRC spectrometer operated at X band and 100 kHz field modulation. A Pyrex glass tube of i.d. 1 mm was used as a sample tube at room temperature.

[13] Diphenylmethyl-*tert*-butyl nitroxide is produced by adding 0.5 mL of cyclohexane/diethyl ether solution of 2 M phenyllithium to a 1-mL benzene solution of 10^{-2} M *N*-phenyl-*tert*-butylnitrone under nitrogen atmosphere; 1 mL of water was subsequently added, and the organic phase was oxidized by oxygen gas and washed with 1 mL of water. Benzene was purged by nitrogen gas, and the residue obtained was dissolved in 2 mL of water. All chemicals including β-CD were obtained from Aldrich and used as received.

[14] Decomposition of the radical upon inclusion is not a possibility since the ESR spectrum of **1** was recovered from a benzene extract of a β-CD solution of **1**.

[15] The radical was purified by HPLC with a 3:7 water/acetonitrile solution containing 0.02 M potassium phosphate (pH 5.8) as a mobile phase; a C-18 column was used as the stationary phase. The same spectra were obtained without purification. We thank Peter Krygsman for the help with HPLC separations.

[16] Equilibrium constants were estimated by using the equation $K = (f_1/f_2)(C - Rf_1/(f_1 + f_2))^{-1}$, where C and R denote the initial concentrations of CD and the radical, respectively, and f_1 and f_2 are the relative concentrations (area intensity of ESR spectrum) of the included and free species. R is estimated to be 5 × 10^{-5} M from ESR intensity.

ways of inclusion of **1** namely from the *tert*-butyl side or from the phenyl side. In the inclusion from the *tert*-butyl side the radical can go farther into the cavity than in the inclusion from the phenyl side, which is hindered by another phenyl group. Inspection of the hfs of these two compounds shows that one hfs pair changes only its β-H hfs upon inclusion, while the other changes mainly its N hfs. The solvent effect on hfs of **1** has been investigated in great detail, and the N and H hfs' change in the same direction as a function of solvent polarity.[17] The present results do not fit this tendency suggesting that anomalous solvation occurs. The inclusion from the *tert*-butyl side could include the NO group, and thus the N hfs is smaller than that in water due to the hydrophobic environment of interior β-CD. On the other hand inclusion from the phenyl side changes only the bulkiness of the group attached to α-C thus changing only the β-H hfs (Figure 3). Since the polarities of the *tert*-butyl and phenyl group are not very different, the larger equilibrium constant for the formation of the complex assigned to the *tert*-butyl group inside comes solely from the larger area of interaction, because the inclusion from the phenyl side is hindered by the other phenyl group. The possibility of formation of a complex with two or more CD molecules attached to one radical is not supported by the fact that two species appear even at very low concentration of CD (Figure 3). Also the slowing down of the rotational tumbling motion which is revealed by the weaker intensity of the high field line shows that the molecular size for both species is similar.

Acknowledgment. Funding for the EPR spectrometer used in this work was provided by a grant from the Natural Science and Engineering Research Council of Canada. Support for this equipment and continuing research is gratefully acknowledged.

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A Symmetrically Hydrogen-Bonded "Binitrosamine Cation" Produced on Protonation of *N*-Nitrosopyrrolidine

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While reinvestigating the acid–base reactions of the carcinogenic nitrosamines as part of a systematic effort to infer possible cancer prevention strategies from data on their chemical and biological properties,[1] we have unexpectedly isolated a salt in which each acid proton is bound to two nitrosamine molecules rather than one, with the biscoordinate hydrogen apparently being symmetrically and collinearly situated between the two nitroso oxygens. The *N*-nitroso group is thus shown to be one of the limited number of functionalities that are capable of exhibiting this form of very strong hydrogen bonding.[2]

We describe herein the preparation and structure of this interesting compound, which appears to be the first in which the position of nitrosamino group protonation has been confirmed by X-ray crystallography. It was isolated by precipitation from ethereal solutions containing both *N*-nitrosopyrrolidine and hexafluorophosphoric acid during evaporation of solvent. After recrystallization by dissolution in dichloromethane followed by addition of ethyl acetate, the material showed mp 128–132 °C and was analytically pure.[3] The structure of the compound was determined by a single-crystal X-ray diffraction study. The results[4] are illustrated in Figures 1 and 2.

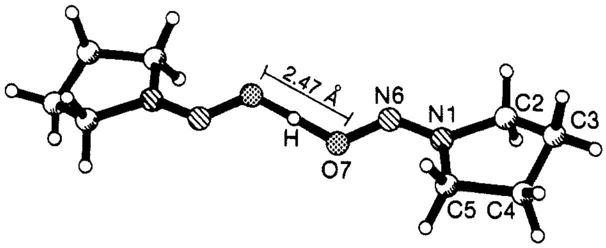

Figure 1. Diagram of the results of the X-ray study. The hydrogen-bonded proton lies on a center of symmetry, with only one of the nitrosamine moieties being crystallographically unique. Bond lengths (Å) and bond angles (deg) are as follows: N1–N6 = 1.270 (6); N1–C2 = 1.454 (7); N1–C5 = 1.475 (7); N6–O7 = 1.276 (6); average C–C = 1.471 (8); O7–N6–N1 = 111.4 (5); N6–N1–C2 = 120.9 (5); N6–N1–C5 = 126.4 (5); C2–N1–C5 = 112.7 (5); average C–C–C = 106.9 (6); average C–C–N 102.9 (7).

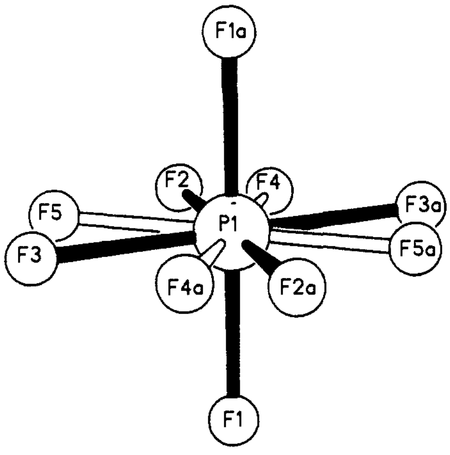

Figure 2. The PF_6^- ion has octahedral symmetry and is disordered such that there are two different positions for the four planar fluorine atoms. The refined ratio for the two positions is approximately 1:1. The phosphorus atom lies on a center of symmetry with only three of the fluorine atoms being crystallographically unique. F1 and F1a are perpendicular to the plane and involved with both sets of disordered fluorine atoms. Bond lengths (Å) and bond angles (deg) are as follows: P1–F1 = 1.558 (4); average for other P–F = 1.508 (13); F1–P1–F1a = 180.0 (0); average for other F–P–F = 90.0 (6).

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[2] Reviewed by Emsley (Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91–124).

[3] Anal. ($C_8H_{17}F_6N_4O_2P$): C, H, N, P.

[4] The compound, $C_8H_{17}N_4O_2^+PF_6^-$, crystallizes in the monoclinic space group, $P2_1/c$, with cell dimensions $a = 6.035$ (2) Å, $b = 10.218$ (2) Å, $c = 12.136$ (3) Å, $\beta = 101.1$ (2)°, $V = 734.4$ (3) Å^3, $Z = 2$ (1/2 formula unit per asymmetric unit), $d_{calcd} = 1.56$ g/cm^3, fw = 346.21, and $\mu = 0.26$ mm^{-1}. The data were collected on a Nicolet R3M diffractometer with X-radiation ($\lambda = 0.71073$ Å) at −65 °C. Because the material had some tendency to decompose, the crystals were kept at <0 °C prior to data collection. The data crystal was then mounted on a glass rod in a hydrocarbon grease in a cold room (~4 °C) and transferred immediately to the cold nitrogen gas stream on the diffractometer. The crystal remained stable long enough to collect a data set of 1207 reflections by using the $\theta/2\theta$ scan technique with $2\theta_{max} = 45°$ at speeds ranging from 10°/min to 30°/min depending upon reflection intensity. The structure was solved by direct methods, and the 119 parameters were refined by full-matrix least-squares techniques to a conventional R-factor of 0.076 [$R_w = 0.068$ and S (goodness of fit parameter) = 1.91] by using the 627 data for which $|F_o| > 3\sigma|F_o|$. All non-hydrogen atoms were refined anisotropically. All hydrogens on carbon atoms were put in at calculated positions and allowed to ride on covalently bonded carbons, C–H distance set at 0.96 Å and coordinate shifts of carbon atoms also applied to H-atoms, with fixed thermal parameters. The thermal parameter for the hydrogen bonded H-atom, which sits on a center of symmetry, fixing its coordinates, was refined isotropically. In addition, F···F distances in the PF_6^- ion were constrained to be close to 2.169 (3) Å.

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