markable that the initial complexes formed, IIa–c, do not contain a Mo–Mo bond. This type of complex, in which Se is replaced by O, has previously been observed from the reactions of α-diazo ketones with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$,[12] thereby illustrating the similarity of complexing behavior of the ring-closed selenadiazoles and ring-opened α-diazo ketones. The second complex formed in the sequence, IIIa–c, represents a transition metal complexed α-seleno keto ketene, similar to those isolated from the reactions of 1,2,3-selenadiazoles with iron carbonyls. The hydrazonato complex IV is a dead end in the transformation since it decomposes without formation of isolable products.

Overall we have been able to secure a new route to the formation of metal-stabilized alkynes and, more interesting, ring-strained cycloalkynes which act as bridging ligands as opposed to the "normal" terminal examples. The detailed mechanism of the process and the chemistry of the complexed cycloakynes are currently under investigation.

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Supplementary Material Available: Crystallographic experimental data, tables of crystal data, data collection, least-squares parameters, atomic coordinates, complete bond lengths and bond angles, and anisotropic thermal parameters (10 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Bromine Perbromate: Synthesis and Bromine K-Edge EXAFS Studies

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Although first reported in the 1930s,[2] bromine oxides remain the least well characterized series of main-group oxides, reflecting both their thermal instability and intractability. We recently reported[3] a detailed spectroscopic study of brown dibromine monoxide, Br_2O, which demonstrated that both the solid and vapor consist of C_{2v} molecules. Bromine K-edge EXAFS (extended X-ray absorption fine structure) data was refined to give $d(\text{Br–O}) = 1.85$ Å and $d(\text{Br}\cdots\text{Br}) = 3.07$ Å, and hence by triangulation a Br–O–Br angle at 112°. Here we report preliminary spectroscopic and EXAFS data on solid bromine dioxide.

Schwarz and Schmeisser obtained yellow BrO_2 by passing a mixture of bromine and oxygen through a discharge tube cooled in liquid air,[4] and Schmeisser and Joerger[5] subsequently prepared what appeared to be the same compound by ozonization of bromine in Freon-11 at low temperature. The material usually given the name "bromine dioxide" is stable at low temperatures, but decomposes above ca. −50 °C to Br_2O and O_2. It is EPR silent, and since the BrO_2 monomer is an odd electron molecule, it has been assumed to be the dimeric species $O_2Br\text{–}BrO_2$. A preliminary Raman study[6] supported this formulation.

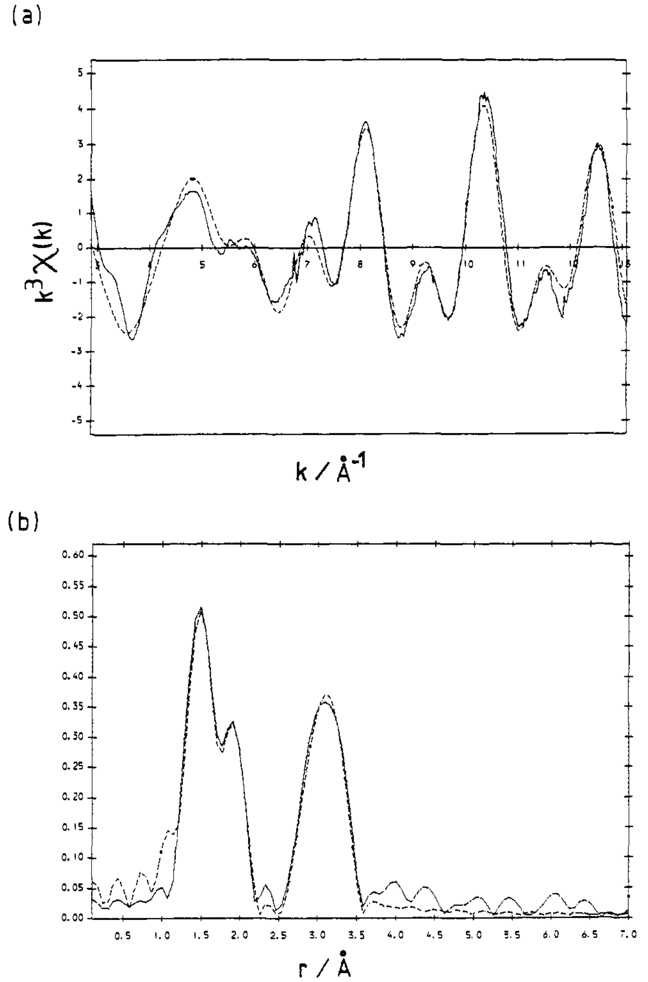

Figure 1. Background-subtracted k^3-weighted EXAFS data (a) and corresponding Fourier transform (b) obtained from an unsmoothed X-ray absorption spectrum of $BrOBrO_3$. Solid line, experiment; broken line, theory.

Our "bromine dioxide" was made by the discharge route, as described previously,[3,7] and its composition was confirmed by measuring the ratio $Br_2{:}O_2$ formed upon complete decomposition. The yellow solid is violently hydrolyzed by 2 mol dm^{-3} aqueous NaOH. Immediate examination of the solution thus produced using a combination of ^{81}Br and ^{17}O NMR spectroscopy[8] identified Br^-, BrO^-, some BrO_3^-, and most surprisingly, BrO_4^-. After 2 days, only Br^- and BrO_3^- remain, as reported previously.[9,10] The presence of BrO_4^- was confirmed by a Raman spectrum obtained from the freshly hydrolyzed solution. Perbromate, BrO_4^-, has never been observed as a product of the disproportionation of lower oxidation states of bromine, and its presence among the hydrolysis

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(7) A 1:3 Br_2/O_2 mixture at ca. 1 mm of pressure was subjected to high-voltage discharge (1600 V, 30 mA), and the product condensed at low temperature. For Raman studies a glass cell fitted with an optically flat outer window and a central glass cold-finger cooled to −126 °C (methylcyclohexane slush) was used since liquid nitrogen cooling also condenses excess ozone, which is unpredictably explosive. Cautious warming in high vacuum removed any co-condensed bromine.

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Table I. Refined EXAFS Parameters for $BrOBrO_3$[a]

shell	occupation	distance/Å	Debye–Waller factor, $2\sigma^2$
Br═O	1.5	1.605 (3)	0.0108 (3)
Br—O	1	1.862 (2)	0.0029 (3)
Br···Br	1	3.053 (2)	0.0088 (2)
E_0 = 12.6 (3) eV, FI[b] = 0.40, R^b = 24.7			

[a] Standard deviations in parentheses; errors arising from data collection and analysis are estimated to be ±1.0–1.5% in well-defined shells (Corker, J. M.; Evans, J.; Leach, H.; Levason, W. *J. Chem. Soc., Chem. Commun.* **1989**, 181–183. [b] As defined in ref 3.

products suggests that Br(VII) is present in the BrO_2 and that a possible formulation is bromine perbromate (bromine(I) bromate(VII)), $BrOBrO_3$.

Raman spectroscopy[11] of the freshly deposited yellow solid at 77 K showed prominent bands at 35 (vs, br), 46 (vs), 453 (s), 582 (s), 594 (m), 842 (s), and 856 (m) cm^{-1}; of particular note are the vibrations between 500 and 600 cm^{-1}, assignable to the Br–O–Br bridge. Our Raman spectrum thus differs significantly from that of "BrO_2" obtained by ozonization of bromine in solution,[6,12] which shows no evidence for such a bridge (our spectra also showed weaker, variable features corresponding to those reported[6]). We believe that the two materials have different structures.

Bromine K-edge EXAFS data were obtained in the transmission mode[13] from samples deposited on a thin aluminum window.[14] Data reduction and curve fitting were performed as previously described,[3] and the unsmoothed, background-subtracted EXAFS spectrum and corresponding Fourier transform are shown in Figure 1 together with the best fit simulated curves. The refined parameters are shown in Table I. Three distinct shells are observed corresponding to terminal Br–O, bridging Br–O, and nonbonded Br···Br distances at 1.61 (2), 1.86 (2), and 3.05 (3) Å, respectively, concomitant with the proposed structure. No evidence of residual Br_2, $d(Br-Br)$ = 2.28 Å, was found. The terminal Br–O distance compares with that in perbromate (1.61 Å (av)[8]) indicative of Br^{VII}–O bonds, while the bridging Br–O bond length and the nonbonded Br···Br distance correspond closely to the distances in Br_2O,[3] in keeping with the bridged species proposed. A Br–O–Br angle of 110 ± 3° may be calculated by triangulation.

We have thus shown that the yellow "BrO_2" obtained by high-voltage discharge of Br_2/O_2 mixtures is structurally bromine perbromate, an analogue of the known $ClOClO_3$[15] and $BrOClO_3$.[16] An investigation of the reaction chemistry of this new oxide will be reported in due course. Further studies to establish the structure of the yellow product obtained from Br_2 and O_3 in solution[6] are also planned.

Acknowledgment. We thank the SRFC for support and the director of the Daresbury Laboratory for the provision of facilities.

Registry No. $BrOBrO_3$, 141438-65-5; Br^-, 24959-67-9; BrO^-, 14380-62-2; BrO_3^-, 15541-45-4; BrO_4^-, 16474-32-1.

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(11) Raman spectra were obtained on a Coderg T 800 with a krypton ion laser operating at 647.1 nm.

(12) In ref 6, major features were reported at 205 (vs) ν(Br–Br), 861 (m), 878 (s), 882 (sh), 910 (s), and 919 (s) cm^{-1} ν(Br–O), in addition to weaker bends and deformations. The absence of any features in the Br–O–Br bridging region should be noted.

(13) Bromine K-edge EXAFS data were measured on beam line 9.2 at the Daresbury Synchrotron Radiation Source, operating at 2 GeV and with an average beam current of 150 mA. A double crystal Si(220) monochromator was utilized, and the spectra were calibrated to the Au L_{II} edge (13.731 keV) of a 10-μm gold foil.

(14) The sample was prepared as described in ref 7, but utilizing a glass cell fitted with 75-μm Kapton outer windows and a central cold-finger fitted with a copper block attached to a glass dewar with a graded seal. The aluminum window was then bolted to the bottom of the copper block and cooled by liquid nitrogen in the dewar. The imperfect thermal contact led to a base temperature of ca. −160 °C at the window.

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Efficient Catalysis of a Redox Reaction by an Artificial Enzyme

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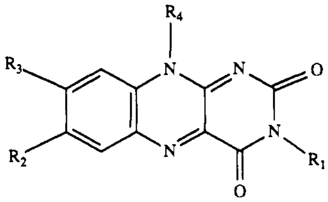
Models of flavoenzymes[1] have been used with limited success to illustrate the importance of the binding process in enzymatic catalysis.[2,3] The highest acceleration factor for an artificial flavoenzyme over riboflavin reported[2] so far is 29. We now report an acceleration factor of 6.5 × 10^2 for the oxidation of *p-tert*-butylbenzyl alcohol by a system that we recently synthesized.[4] We further demonstrate that binding of the substrate to the artificial enzyme plays an important role in these rate accelerations.

The oxidation reaction of several substituted benzyl alcohols to their corresponding aldehydes, catalyzed by 2-[(7α-*O*-10-methyl-7-isoalloxazino)methyl]-β-cyclodextrin (**1**) and by riboflavin (**2**) under photochemical conditions at low pH,[5] was investigated.[6] The reactions catalyzed by **1** were found to be considerably faster[6b] than those catalyzed by either **2** or 7,10-dimethylflavin[7] (**3**). For example, the **1**-catalyzed oxidation of *p-tert*-butylbenzyl alcohol is complete within 2.5 h, whereas the same reaction catalyzed by **2** or **3** is very slow.[6b] It is observed that **2** decomposes under photochemical conditions and can exhibit up to only 7 turnovers, whereas the artificial enzyme is more stable[8] and can exhibit more than 100 turnovers under these conditions. The initial oxidation rates of various substituted benzyl alcohols, by the artificial enzyme and riboflavin, are given in Table I. The structural similarity of the flavin moiety in **1** and **3** suggests that the change in the oxidation potentials caused by the substituents on flavin is not responsible for the rate acceleration exhibited by **1** over **3** or **2**. The oxidation rate of *p-tert*-butylbenzyl alcohol



1 $R_1=R_3=H$, $R_4=CH_3$, R_2= 2-(*O*-methylene)-β-cyclodextrin
2 $R_1=H$, $R_2=R_3=CH_3$, R_4=ribityl
3 $R_1=R_3=H$, $R_2=R_4=CH_3$
4 $R_1=R_4=CH_3$, R_2,R_3=1',4',7',10',13',16'-hexaoxacyclooctadec-2'-ene (18-crown-6)
5 $R_1=H$, $R_2=CH_3$, R_4=ribityl, R_3=6-(*S*-methylene)-α-Cyclodextrin

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(6) (a) A reaction mixture consisting of aqueous solutions of substituted benzyl alcohols (5.0 × 10^{-4} M), flavin (5.0 × 10^{-5} M), and $HClO_4$ (0.037 M, pH 1.7 remains constant throughout the reaction) was irradiated at 360 nm < λ < 440 nm, and the reaction was monitored for appearance of the corresponding aldehydes by HPLC. (b) See supplementary material for details.

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