a smaller chemical shift anisotropy than terminal carbonyls[16] and thus can aid in the assignment of peaks. The overlap of spinning sidebands at 4.2-kHz spinning rate is such that sidebands due to the bridging carbonyls occur at higher field than those due to terminal carbonyls within a cluster of bands. In the sideband progressions at low field (to the left) in the spectrum at 4.2 kHz, the peaks assigned to bridging carbonyls diminish faster than those for the terminal carbonyls as expected. A more detailed analysis of the sideband unfortunately is not possible due to the broadness of the peaks.

An estimate of the average value for the carbon T_1's in solid $Co_4(CO)_{12}$ by the inversion recovery method gives a value of approximately 500 ms. This is much shorter than typically observed for metal carbonyls[17,18] and is consistent with scalar relaxation of the second kind, through coupling with rapidly relaxing ^{59}Co nuclei, as the dominant relaxation mechanism in the solid state.[4]

The prediction of the expected MAS ^{13}C NMR spectrum for solid $Co_4(CO)_{12}$ for both dynamic and static structures is straightforward:

Case I. The observation of a single line in the MAS ^{13}C NMR spectrum may only be observed when the 12 carbonyls in solid $Co_4(CO)_{12}$ are equivalent on the NMR time scale due to a dynamic process. Such a process can be envisioned by an interconversion of the C_{3v} structure in the solid state and a higher energy T structure. A structure of T symmetry has recently been predicted by Lauher for $M_4(CO)_{12}$ molecules.[19] Since both of these structures are based on an icosahedral arrangement of carbonyl ligands, they may be interconverted by a rotation of the Co_4 core within the icosahedral array of carbonyl ligands. The magnitude of the rotation necessary to interconvert the structures is reported to be 12°.[19]

Case II. A more limited dynamic process may involve the rapid interconversion of the two orientations of the Co_4 core that are present in the crystalline solid. If rotation about the crystallographic 2-fold axis is rapid on the NMR time scale, then a six-line NMR spectrum is expected: four terminal carbonyl signals, one bridging carbonyl signal, and one signal that represents the time average of a bridging and terminal carbonyl. This type of reorientation has been proposed to occur in crystalline $Fe_3(CO)_{12}$.[20,21]

Case III. A static structure would be expected to yield an NMR spectrum containing 12 carbonyl resonances: 9 in the terminal carbonyl region and 3 in the bridging region. Fewer than 12 signals could be obtained through accidental degeneracies. Although 12 distinct terminal carbonyl resonances have been recently observed in solid $Os_3(CO)_{12}$,[22] such resolution cannot be anticipated for cobalt carbonyls due to the influence of the quadrupolar ^{59}Co nuclei.

The experimental spectra for solid $Co_4(CO)_{12}$ at room temperature and 68 MHz cannot conclusively distinguish between cases II and III. For case II to hold, the peak at 244.9 ppm must be due to a true bridging carbonyl and the peak at 236.1 ppm must represent the time average of a bridging and a terminal carbonyl. Although the latter is shifted upfield from the isotropic chemical shift of the bridging carbonyls for $Co_4(CO)_{12}$ (243.1 ppm[4]), this may be due to solid-state effects. For example, the range of chemical shifts for the axial carbonyls in solid osmium carbonyls is 8 ppm.[22]

For case III to hold, there must be degeneracies for both terminal and bridging carbonyl resonances. Without the observation of more than four signals assignable to terminal carbonyls, a definitive argument for a static structure at room temperature cannot be made. (It should be noted that the presence of additional lines due to residual coupling with cobalt, although minimized at high field, is still a possibility; vide supra.)

In conclusion, the use of high-field MAS ^{13}C NMR has allowed the observation of signal(s) due to bridging carbonyls as required by either a dynamic (case II) or static (case III) $Co_4(CO)_{12}$ structure. The failure to observe bridging carbonyl resonances at low field is most likely due to residual coupling to the quadrupolar cobalt nucleus and/or rapid and selective scalar relaxation of the carbonyl ligands by the cobalt.

Experimental Section

The MAS ^{13}C NMR spectra were recorded at 68 MHz on a Varian 270-MHz spectrometer. The rotors were made of Delrin; no decoupling was used since the samples contain no protons. Tetracobalt dodecacarbonyl was prepared from $Co_2(CO)_8$ by refluxing in *n*-octane for 2 h. The sample was enriched in ^{13}CO by stirring under ^{13}CO in hexane at room temperature and recrystallized prior to use.

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Failure To Observe Peroxide in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 by Reaction with Permanganate

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The high-temperature superconductors $YBa_2Cu_3O_7$[1] and $La_{1.8}Sr_{0.2}CuO_4$ behave as oxidizing agents toward I^-, Br^-, Fe^{2+} when dissolved in acidic solution.[2-4] In the absence of a good reducing agent, O_2 (whose atoms are derived from the solid, not the solvent[5]) is evolved.[1,6] Iodometric titrations used to measure the oxygen content of $YBa_2Cu_3O_{7-x}$, can be interpreted in terms of the formula $YBa_2Cu^{II}{}_{2+2x}Cu^{III}{}_{1-2x}O_{7-x}$ ($0 \le x \le 0.5$) (assuming that no O_2 is evolved in the procedure).[1,2] The average copper oxidation state inferred from such titrations is in good agreement[1] with that deduced from the mass lost in the reaction of yttrium barium copper oxide with H_2 at elevated temperature, in which the products are Y_2O_3, BaO, Cu, and H_2O.

It is possible that all copper in $YBa_2Cu_3O_{7-x}$ is Cu^{2+} and that some oxygen is present as peroxide. This gives the formula $YBa_2Cu^{II}{}_3(O^{2-})_{6+x}(O_2{}^{2-})_{0.5-x}$ ($0 \le x \le 0.5$), which is indistinguishable from $YBa_2Cu^{II}{}_{2+2x}Cu^{III}{}_{1-2x}O_{7-x}$ by iodometric titration or by reaction with H_2. On the basis of copper 2p X-ray photoelectron and X-ray absorption spectra, some studies concluded

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(1) The formulas $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 are used for convenience in this paper. The oxygen content is actually variable, but close to that of the ideal formula.

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that Cu^{3+} is present in $YBa_2Cu_3O_7$, $La_{1.85}Ba_{0.15}CuO_4$, and $Y_{0.4}Ba_{0.6}CuO_{4-x}$,[7] while other studies failed to find Cu^{3+} in $YBa_2Cu_3O_7$[8] and $La_{1.85}Sr_{0.15}CuO_4$.[9] The oxygen 1s photoelectron spectrum of $YBa_2Cu_3O_7$ has been interpreted as indicating the presence of peroxide,[10,11] but the spectrum of $La_{1.85}Sr_{0.15}CuO_4$ freshly cleaved under a vacuum of 5×10^{-11} Torr was interpreted in terms of oxide only.[9] Another photoelectron study of $YBa_2Cu_3O_7$ was inconclusive about the states of both copper and oxygen but did note that reactivity of the surface with the atmosphere made it difficult to deduce which features were inherent in the bulk material.[12] Studies of Co and Fe substitution for Cu[13] and of La substitution for Ba[14] in $YBa_2Cu_3O_7$ have been claimed to provide evidence for peroxide ion formation in the unsubstituted phase.[15] Failure to observe Ni^{3+} in the photoelectron spectrum of La_2NiO_{4+x} is the basis for a claim that there is peroxide in this compound,[16] while superoxide (O_2^-) is purported to be present in La_2CuO_{4+x} on the basis of iodometric and gravimetric analysis.[17] One study of the electron paramagnetic resonance spectrum of $YBa_2Cu_3O_7$ was interpreted as indicating that there is a hole localized on copper (Cu^{3+}) at 4 K but that the hole is transferred to oxygen at and above 90 K.[18] Other electron paramagnetic resonance experiments draw conclusions about the oxidation state of copper but make no inferences about oxygen.[19,20] An elegant theoretical study proposes that the holes in $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ are localized on oxygen atoms but does not suggest O–O (superoxide or peroxide) bond formation.[21]

In the present work, we sought simple chemical evidence for the presence of peroxide in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, La_2NiO_4, and $BaCuO_2$. Peroxide is a well-known oxidizing agent that can oxidize Br^-, I^-, or Fe^{2+}. However, in the presence of a strong oxidant, peroxide can behave as a reducing agent:[22]

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O \quad (1)$$

Our strategy was simply to dissolve the suspected compounds in acidic solutions containing permanganate and look for production of Mn^{2+}.

Experimental Section

General Information. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-109 instrument at 9.5 GHz using a quartz flat cell at room temperature with 0.5-mT modulation amplitude and 71-mW microwave power. Raman spectra of powders in glass capillary tubes were obtained with a Spex 1-m double monochromator instrument using backscattered radiation. The Ar^+ laser beam (300 mW) was passed through a filter to isolate the 514.5-nm line (reducing the power to 100 mW) and focused to a 0.1-mm spot at the sample. Spectra were the average of eight scans in the range 400–1200 cm^{-1} with 3-cm^{-1} resolution (1.5 cm^{-1} per point, 1-s integration time per point). $KMnO_4$ solution (0.0214 M, standardized by titrating sodium oxalate[23]) was prepared by dissolving 0.42 g of reagent grade material in 125 mL of distilled water, heating just below boiling for 1 h, cooling, and filtering through a medium-porosity glass frit into a brown screwcap bottle stored in the dark. The first 10 mL of filtrate was used to rinse the bottle and was discarded. From the amplitude of the EPR signal of Mn^{2+}, it is estimated that 0.4% of the manganese in the $KMnO_4$ solution is Mn^{2+}. Barium peroxide (Baker Analyzed Reagent from Allied Chemical Co.) was found to contain 83.3% (by mass) BaO_2 by dissolving in 1 M $HClO_4$ and titrating with $KMnO_4$.[24] KO_2 was obtained from Alfa. Hydrated $CuSO_4$ and $NiSO_4$ were commercial reagents.

Table I. Reaction of Oxides with Permanganate[a]

sample	μmol of sample	μmol of $KMnO_4$	mol of Mn^{2+} found/mol of sample	appearance
$YBa_2Cu_3O_{6.85}$	9.3	0.107[b]	4×10^{-4}	very pale pink soln
$La_{1.8}Sr_{0.2}CuO_{4.0055}$	20.0	1.07	3×10^{-4}	$KMnO_4$ purple color
$La_{1.8}Sr_{0.2}CuO_{4.0055}$[c]	18.7	1.07	1×10^{-4}	$KMnO_4$ purple color
$La_2CuO_{4.0040}$	19.7	1.07	$<3 \times 10^{-5}$[d]	wine red liq; dark solid
$La_2NiO_{4.135}$	20.7	1.07	2×10^{-3}	colorless liq; brown solid[e]
$La_2NiO_{4.135}$	21.0	5.35	$<3 \times 10^{-5}$[d]	colorless liq; brown solid
$La_2NiO_{4.135}$[c]	19.7	1.07	1×10^{-4}	colorless liq; dark solid
$BaCuO_{2.048}$	32.5	0.107	0.11	colorless liq

[a] Solid Sample was added to a solution containing 400 μL of 0.5 M $HClO_4$ plus 50 μL of $KMnO_4$. After mixing, the Mn^{2+} produced was measured by EPR. The control used to establish the expected Mn^{2+} EPR signal amplitude for complete reaction was a stoichiometric mixture containing 0.107 μmol of $KMnO_4$, 0.267 μmol of BaO_2, and the same concentration of $HClO_4$ used in all reactions in this table. [b] Similar results were observed when 0.043 or 0.021 μmol of $KMnO_4$ was used. [c] The 400-μL $HClO_4$ solution contained 21 mg of dissolved $B(OH)_3$. [d] Estimated limit of detection of Mn^{2+}. [e] Identified as NiO by X-ray diffraction.

Table II. Interference with Peroxide/Permanganate Reaction[a]

sample	μmol of sample	μmol of $KMnO_4$	% Mn^{2+} found[b]	appearance
$YBa_2Cu_3O_{6.85}$	9.0	0.107	56, 58	pale yellow soln
$YBa_2Cu_3O_{6.90}$	9.5	0.107	74	pale yellow soln
$La_{1.8}Sr_{0.2}CuO_{4.0055}$	17.0	0.107	36	light pink soln
$La_2CuO_{4.0040}$	16.0	0.107	84	pale yellow soln
$La_2NiO_{4.135}$	16.5	0.107	8	dark pink soln
$CuSO_4$	31	0.107	95	pale blue soln + $BaSO_4$
$NiSO_4$	29	0.107	101	pale green soln + $BaSO_4$

[a] Sample was added to 0.267 μmol of BaO_2 in 400 μL of 0.5 M $HClO_4$. After dissolution of the sample, 50 μL of 2.14 mM $KMnO_4$ was added and the Mn^{2+} produced was measured by EPR. [b] Reproducibility of signal amplitude due to cell positioning is approximately ±5%.

Sample Preparation and Iodometric Analysis. All syntheses were carried out in alumina combustion boats using tube furnaces open to the air. Quantities of reagent grade reactants were calculated according to the desired metal stoichiometry in the product. Reactants and intermediate products were mixed by grinding at least 15 min with an agate mortar and pestle. All samples were placed into hot furnaces and air-quenched, except as noted. Products were pure phases according to X-ray

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powder diffraction, except $BaCuO_2$, which contained a trace of $BaCO_3$.

$YBa_2Cu_3O_7$ was prepared from Y_2O_3, $BaCO_3$, and CuO. Heating cycle sequence for sample 1 (6 g): 910 °C, 14 h; 930 °C, 3 h; 945 °C, 12 h; cooled in 7 h to 125 °C. Sequence for sample 2 (20 g): 875 °C, 24 h; cooled in 9 h to 25 °C; 945 °C, 12 h; cooled in 9 h to 25 °C.

La_2O_3, $SrCO_3$, CuO, and NiO were used to synthesize $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4. (The last was prepared in a nickel combustion boat.) For all three compounds, the first two heating cycles were the same. Cycle 1: heated in 2 h to 900 °C, held 6 h; heated in 1 h to 1100 °C, held 12 h; cooled in 5 h to 455 °C. Cycle 2: heated in 2 h to 1100 °C, held 8 h; cooled in 3 h to 800 °C, held 8 h; cooled in 5 h to 450 °C, held 8 h; cooled in 6 h to 25 °C. The cuprates were phase-pure according to X-ray powder diffraction. The La_2NiO_4 required a third heating cycle: heated in 0.5 h from 814 to 1100 °C, held 24 h; cooled in 9 h to 25 °C.

$BaCuO_2$ was prepared from $BaCO_3$ and CuO in two heating cycles. Cycle 1: heated in 2 h to 850 °C, held 48 h; cooled in 9 h to 25 °C. Cycle 2: heated over 2 h to 875 °C, held 12 h; cooled in 9 h to 25 °C.

The oxidizing capacity of each material was measured by the iodometric procedure of Appelman et al.[3] The formulas $YBa_2Cu_3O_{6.90}$ (sample 1), $YBa_2Cu_3O_{6.85}$ (sample 2), $La_{1.8}Sr_{0.2}CuO_{4.0055}$, $La_2CuO_{4.0040}$, $La_2NiO_{4.135}$, and $BaCuO_{2.048}$ were calculated by assuming that the ratio of metal atoms in the product was the same as in the reaction mixtures.

Reaction of BaO_2 with $KMnO_4$. When BaO_2 in acid solution is titrated with $KMnO_4$, the permanganate is decolorized after each addition until the equivalence point is reached (eq 1). The amplitude of the Mn^{2+} EPR signal of the reaction solution increases in proportion to the volume of $KMnO_4$ added prior to the equivalence point. Beyond the equivalence point the solution is metastable. After a few minutes in the presence of excess $KMnO_4$, a brown precipitate forms. The Mn^{2+} EPR signal decreases until it is essentially gone when an additional 4 equiv of $KMnO_4$ has been added (total mol of $KMnO_4$/mol of BaO_2 = 2). This is consistent with the precipitation of brown barium manganate.[25]

$$Mn^{2+} + 4MnO_4^- + 4H_2O = 5MnO_4^{2-} + 8H^+ \qquad (2)$$

$$Ba^{2+} + MnO_4^{2-} = BaMnO_4(s) \quad K_{sp} = 10^{-9.6} \qquad (3)$$

Because of this reaction, excess permanganate added to a suspected peroxide in the presence of barium will destroy the Mn^{2+} produced in the reaction between the peroxide and the $KMnO_4$. This required us to use small quantities of $KMnO_4$ for experiments with Ba-containing samples in Table I and a stoichiometric ratio of $KMnO_4$ and BaO_2 for experiments in Table II.

Procedure for the Reaction of Suspected Peroxides with $KMnO_4$. Standard 2.14 mM $KMnO_4$ was prepared by a fresh dilution of 21.4 mM $KMnO_4$ with distilled water. Fresh standard peroxide solution was prepared by dissolving a known mass of BaO_2 in 0.5 M $HClO_4$. In a typical experiment in Table I, 50 μL of 2.14 mM $KMnO_4$ was added to 400 μL of 0.5 M $HClO_4$ in an acid-rinsed test tube. Then 6 mg of $YBa_2Cu_3O_7$ was added and dissolved with swirling and effervescence. The amplitude of the Mn^{2+} EPR signal was then measured. A control was prepared by replacing the $YBa_2Cu_3O_7$ with $CuSO_4$ and adding a 25% excess of BaO_2 solution to react with all of the $KMnO_4$. A blank containing $CuSO_4$ but no BaO_2 gave a Mn^{2+} signal 1.5% as tall as the control signal.

Interference with the $KMnO_4$/Peroxide Reaction. In a typical experiment in Table II, 6 mg of $YBa_2Cu_3O_7$ was added to 400 μL of 0.5 M $HClO_4$ solution containing 0.267 μmol of freshly dissolved BaO_2. After dissolution, 50 μL of 2.14 mM $KMnO_4$ solution was added and the Mn^{2+} produced was measured by EPR.

Attempted Reaction of Superoxide with $KMnO_4$. It is possible that the oxidized species in the compounds under study is superoxide (O_2^-). To see if this could be detected with permanganate by a reaction analogous to eq 1, 1.0 mg of solid KO_2 was added to 10 mL of 0.0107 M $KMnO_4$ in 0.5 M H_2SO_4. Only a background level of Mn^{2+} was observed in the EPR spectrum, indicating no reduction of permanganate by superoxide. KO_2 decomposes very rapidly when added to water, so superoxide may not exist long enough in solution to react with permanganate.

Results

Reaction of Suspected Peroxides with $KMnO_4$. Figure 1 shows the EPR spectrum of a solution containing Cu^{2+} and Mn^{2+} at concentrations representative of those encountered in our experiments. The amplitude of the high-field Mn^{2+} peak near 360 mT was used to measure the Mn^{2+} produced in each reaction. When $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, or La_2NiO_4 was dissolved in acid solution containing $KMnO_4$, very little Mn^{2+} was produced (Table I), indicating that very little peroxide was available. The quantity of $KMnO_4$ in the experiments with $YBa_2Cu_3O_7$ was kept low because excess permanganate reacts with Mn^{2+} in the presence of Ba^{2+} to precipitate $BaMnO_4$ (eq 2 and 3). A low concentration of $KMnO_4$ allows us to place a small upper limit on the amount of peroxide that could be in the sample. For example, in the first line of Table I, 9.3 μmol of $YBa_2Cu_3O_7$ does not completely convert 0.107 μmol of $KMnO_4$ to Mn^{2+}. Therefore, there must be less than 2.5 × 0.107 = 0.268 μmol of peroxide present in the $YBa_2Cu_3O_7$ (on the basis of the stoichiometry of eq 1). This corresponds to <0.029 mol of peroxide/mol of $YBa_2Cu_3O_7$.

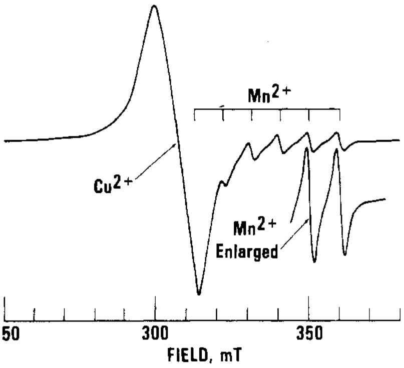

Figure 1. EPR spectrum of 0.5 M $HClO_4$ solution containing 33.6 mM $CuSO_4$ and 0.235 mM Mn^{2+} from the reaction of BaO_2 with $KMnO_4$.

When Na_2O_2 is dissolved in acid, some oxygen is lost unless boric acid is present to trap all of the peroxides as a "perborate".[24] Titration of the perborate with $KMnO_4$ then gives the total peroxide in the original sample. To see if peroxide in our compounds could be trapped with boric acid, two experiments in Table I (with $La_{1.8}Sr_{0.2}CuO_4$ and La_2NiO_4) included boric acid. No significant amount of peroxide was observed.

$BaCuO_2$ is the only compound in Table I that did consume all of the $KMnO_4$. In an iodometric titration, 1 mol of $BaCuO_2$ consumed 0.095 mol of electrons. In a titration of $BaCuO_2$ by $KMnO_4$, 1 mol of $BaCuO_2$ donated 0.029 mol of electrons. This suggests that both Cu^{3+} and peroxide are present in the sample. The peroxide could simply be a trace of BaO_2 (too little to be observed by X-ray diffraction) formed as a byproduct of the preparation.

Interference with the Peroxide/Permanganate Reaction. $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, or La_2NiO_4 was dissolved in acid solution containing standard peroxide. When $KMnO_4$ was added to each solution, less Mn^{2+} than expected was observed (Table II). Neither $CuSO_4$ nor $NiSO_4$ had this effect. Control experiments showed that every permutation of order of addition of $YBa_2Cu_3O_7$, BaO_2, and $KMnO_4$ gave the full expected amount of Mn^{2+} unless $YBa_2Cu_3O_7$ was added after BaO_2 and before $KMnO_4$. It appears that $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 partially react with H_2O_2 and destroy it as they dissolve.

Discussion

The failure to detect peroxide in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 implies either that (1) there is no discrete peroxide liberated into solution as the compounds dissolve or (2) peroxide present in the solids is destroyed at the surface of the dissolving solid before reaction with permanganate can occur. The compounds $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 all appeared to react with peroxide in solution, whereas $CuSO_4$ and $NiSO_4$ did not (Table II). Iodometric titrations described in the Experimental Section show that each of the reactive compounds contains some oxidized species, whereas $CuSO_4$ and $NiSO_4$ do not. If the oxidized species in the solids is peroxide, it is difficult to explain why the dissolving solids should destroy peroxide already present in the solution. If the oxidized species is Cu^{3+} or Ni^{3+}, it may directly oxidize peroxide to O_2, as does MnO_4^-.

If there were discrete peroxide species in $YBa_2Cu_3O_7$, one would expect to observe the O–O stretching mode in the Raman spec-

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trum. This occurs in the range 760–950 cm^{-1} in simple ionic peroxides[26] and in the range 800–940 cm^{-1} in a variety of transition metal–peroxo complexes.[27] The superoxide O–O stretch is observed at 1140–1150 cm^{-1} in KO_2 and RbO_2.[28] There is now a multitude of contradictory Raman spectra of $YBa_2Cu_3O_7$ in the literature,[29] but none exhibit bands in the peroxide stretching region. One single paper[30] reports a weak, broad band in the superoxide region near 1100 cm^{-1}, but the spectrum in this report is not representative of the spectra in other reports.[29] It is difficult to obtain reliable Raman spectra of highly absorbing black solids with visible light, and the variable literature results may reflect different surface impurities on individual samples. We attempted to record the Raman spectrum of $La_2NiO_{4.135}$, whose oxidized species has been assigned as peroxide.[16] Only a very weak peak at 996 cm^{-1} was observed at the same position as a weak background signal present in the glass capillary cell. There are no conclusive Raman data supporting the assignment of peroxide species in the solid state.

In conclusion, our experiments offer no support for the idea that peroxide is present in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, or La_2NiO_4. The destruction of peroxide in solution when these compounds dissolve might be indicative of Cu^{3+} or Ni^{3+}.

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Registry No. $YBa_2Cu_3O_{6.85}$, 110584-09-3; $La_{1.8}Sr_{0.2}CuO_4$, 107499-44-5; La_2CuO_4, 12053-92-8; $La_2NiO_{4.14}$, 119325-54-1; $BaCuO_{2.05}$, 119325-55-2; Y_2O_3, 1314-36-9; $BaCO_3$, 513-77-9; CuO, 1317-38-0; La_2O_3, 1312-81-8; $SrCO_3$, 1633-05-2; NiO, 1313-99-1; BaO_2, 1304-29-6; $KMnO_4$, 7722-64-7; KO_2, 12030-88-5; $YBa_2Cu_3O_{6.90}$, 108470-72-0; $CuSO_4$, 7758-98-7; $NiSO_4$, 7786-81-4.

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Hydroxide-Induced Reduction of Elemental Sulfur (S_8) to the Trisulfur Anion Radical ($S_3^{\bullet-}$)

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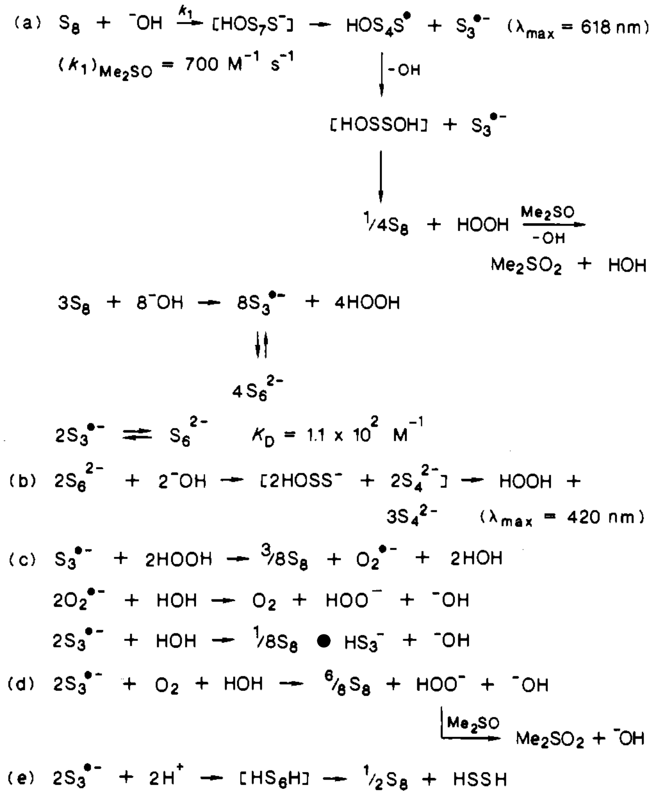
In aprotic solvents hydroxide ion reacts with elemental sulfur (S_8) to give the trisulfur anion radical $S_3^{\bullet-}$ as the major product. The reaction stoichiometry (eight ^-OH per three S_8 to give eight $S_3^{\bullet-}$) is consistent with the results for the electrochemical reduction of S_8 in dimethyl sulfoxide[1,2] and in acetonitrile.[3]

Scheme I



$$3S_8 + 8e^- \xrightarrow{-0.6\ \mathrm{V\ vs\ SCE}} 8S_3^{\bullet-} \quad (1)$$

$$2S_3^{\bullet-} \rightleftarrows S_6^{2-} \qquad K_D = 1.1 \times 10^2\ (25\ ^\circ\mathrm{C}) \quad (2)$$

Dissolution of alkali polysulfides in hexamethylphosphoramide also yields substantial amounts of $S_3^{\bullet-}$.[4]

Although the hydroxide ion induced formation of $S_3^{\bullet-}$ from S_8 is unique in our experience, several previous observations were brought to our attention by a helpful reviewer. A blue color was noted when elemental sulfur was heated with alkaline water[5,6] and when S_8 was dissolved in KOH–acetone solutions.[7] This blue species, which has been identified as $S_3^{\bullet-}$,[1,8] also resulted when partially hydroxylated MgO was combined with S_8.[9] Polysulfides (S_n^{2-}) in aprotic solvents undergo dissociation and disproportionation reactions to yield $S_3^{\bullet-}$,[10] and it is formed from the reaction of HS^- with S_8.[11]

A recent study[12] has demonstrated that hydroxide ion (^-OH) in acetonitrile reduces anthraquinone to its anion radical ($AQ + e^- \rightleftarrows AQ^{\bullet-}$; $E^{\circ\prime}_{MeCN} = -0.82$ V vs SCE).

$$AQ + {}^-OH \rightarrow AQ + \tfrac{1}{2}HOOH \quad (3)$$

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