Figure 1. Oxidation of model lignin phenols. Oxidants: (a) 0.3 M $K_3Fe(CN)_6$ in 2 M aqueous KOH; (b) 0.1 M $Ce(HSO_4)_4$ in 1 M aqueous H_2SO_4; (c) PbO_2, solid. Solvents: benzene, toluene, and dichloromethane.

Figure 2. First derivative e.s.r. spectra of radicals 1, 2, and 3.

lines. The propiosyringone radical (3) yields 17 lines, with intensities closely paralleling those predicted from the constants in Table I (e.g., 1:6:2:15:12:21:30:21: 40:21:30:21:12:15:2:6:1); here, the *meta* proton coupling is 1.5 times that of the methoxyl proton. Theoretical spectra, calculated for each of the above, confirmed these assignments.[6] The values for the

Table I. Coupling Constants for Syringol Radicals

Syringol radical	No. of lines	$A^H_{OCH_3}$, gauss	A^H_{meta}, gauss
1	9	1.30	1.30
2	9	1.30	1.45
3	17	1.30	1.95

methoxyl and *meta* proton coupling constants are consistent with previously published values.[7,8]

The visible absorption spectra of all three radical species in solution are almost identical; principal bands appear at 420, 450, 470, and 750 mμ. Over a period of time, the 750 mμ band height decreases while the 470 mμ band height increases. A plot of the log height of the 750 mμ band vs. time is parallel to the plot of the log intensity of the e.s.r. signal vs. time, thus indicating that the radical species is represented by the green 750 mμ band.

A number of conclusions may be drawn from these results: (a) The stability of the phenoxy radical is dependent on the presence of two o-CH_3O substituents, as well as a p-C=O function. Guaiacol derivatives, with a free *ortho* position, apparently dimerize or oxidize rapidly in preference to forming stable phenoxy radicals. (b) The stability of the radical from syringol is remarkable, in light of the fact that the vast majority of previously prepared phenoxyls have been substituted in the 2- and 6-positions by bulky groups, such as *t*-butyl. Mueller, however, did infer[9] that lignin model phenoxyls might be stable when he obtained a poor single line e.s.r. spectrum for a syringylacrylonitrile derivative. (c) Apparently, minor changes in the side chains of 1-3 (R = H, CH_3, C_2H_5) do affect the electron density at the two *meta* positions, giving rise to the different e.s.r. splitting patterns. (d) The slow decay
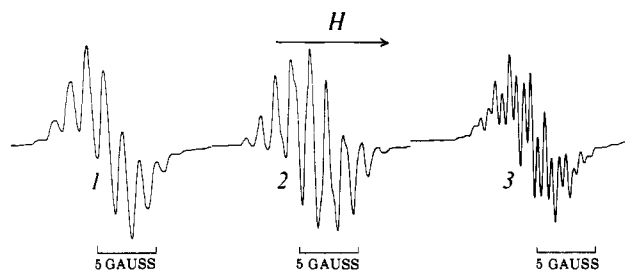
of these radicals to red species (probably o-quinones[10]) is of significance to lignin chemistry. Oxidation of lignins by biological systems or aqueous chemical systems could produce colored decay products, *via* intermediates such as 1, 2, and 3. These radical intermediates are stabilized temporarily by solvents such as benzene, or they may be indefinitely stabilized in the solid lignin matrix, thus contributing to the higher spin concentrations observed in solid, oxidized lignins.[3,4] The α-carbonyl syringyl moiety appears to be an inherent part of native lignin[11] and oxidized lignin[12] structures. Therefore, these well-characterized radicals from syringol constitute excellent models for a study of the course of dehydrogenation reactions of lignins. Such a study is currently in progress.

Acknowledgments. We are deeply grateful to Professor John Willard of the Department of Chemistry, University of Wisconsin, for the use of a Varian 4500 spectrometer (100 kc. field modulation), and to Professor John Harriman of the same department for his many helpful discussions of the e.s.r. spectra. We are also indebted to Mr. J. C. Pew of the Forest Products Laboratory for providing some of the model phenols used in this study.

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Magnetic Peroxyborates. The Pseudo-Superoxides

Sir:

We report that certain peroxyborates are paramagnetic; both static susceptibility and electron spin resonance (e.s.r.) measurements show many unpaired spins. To our knowledge there is no previous suggestion that peroxyborates could be paramagnetic.

Foerster[1] converted, by careful heating, sodium perborate monohydrate[2] to a material which briskly evolved oxygen on being placed in water; hydrogen peroxide is simultaneously formed. Menzel[3] and others[4] prepared similar perborate materials.

(6) We are indebted to Professor John Harriman of the Department of Chemistry, University of Wisconsin, for these computations.
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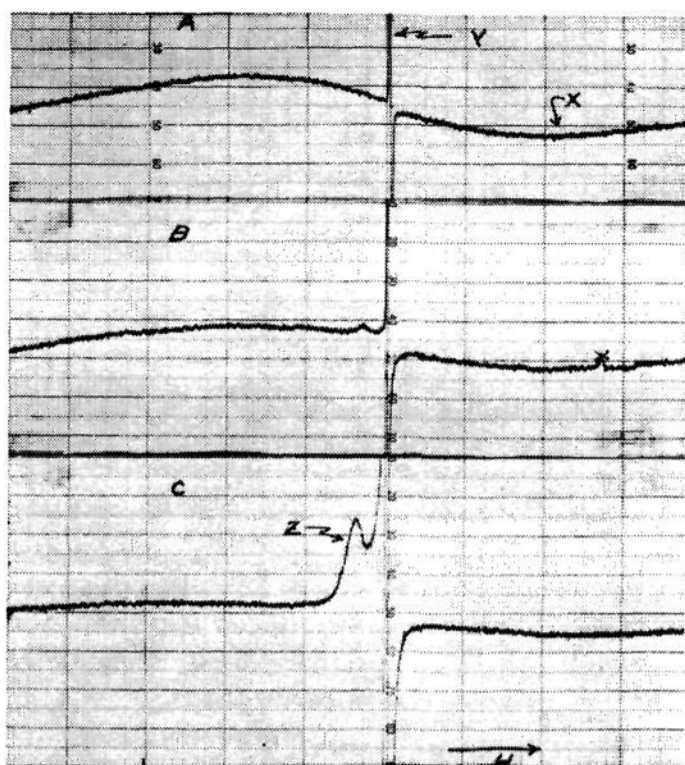
Figure 1. The derivative curve of the e.s.r. absorption in preparation A-3 is shown as a function of magnetic field for three temperatures: A, 300°K.; B, 220°K.; C, 77°K. Instrument parameters were identical for the three temperatures. The left side of the figure is ≃ 0 gauss and the right side 5300 gauss, and the field sweep was approximately linear. In A the broad resonance is denoted by X and the narrow one Y. In B and C the additional absorption is labeled the Z resonance.

Two series of preparations have been studied; all samples are off-white powders which effervesce in water. In Table I, data on some preparations are presented.

Table I. Some Properties of the Modified Sodium Peroxyborates[a]

Prepn. no.	O_2,[b] %	A.O.,[c] %	χ_g ($\times 10^6$)[d]	C.F.W.[e]
A-1	2.2	7.1	1.49	88.3
A-2	4.7	8.1	3.22	89.4
A-3	8.4	6.8	5.10	92.4

[a] References 1, 3, and 4 disclose standard methods for preparing these materials. [b] Calculated from gaseous oxygen released on solution in water. [c] Per cent A.O. (active oxygen) calculated from H_2O_2 (I^- analysis) released on solution of water. [d] Calculated from data at 25° using the equation $\chi_g = \chi_{g(STD)}$ [weight (STD)/Δ weight (STD)][Δ weight (sample)/weight (sample)], where χ_g is the gram susceptibility; not corrected for diamagnetism; standard was $HgCo(SCN)_4$. [e] Chemical formula weight (grams containing 1 g.-atom of boron).

Static susceptibility measurements give for preparation A-3 a concentration of approximately 4×10^{21} spins/cc. assuming spin state $S = \frac{1}{2}$ and $\mu = 2.04$ B.M. The values of χ_g increase monotonically with per cent O_2 for this series; a similar correlation was observed with the other series. There is approximately one unpaired spin for each four boron atoms in preparation A-3.

Separate samples from the same preparation have deviations in the measured quantities per cents oxygen and active oxygen, χ_g, and chemical formula weight (C.F.W.) greater than the experimental error of the appropriate analytical techniques. For example, the

G. Schoenber, British Patent 312,664 (April 10, 1930); H. Kloeper, to DEGUSSA, German Patents 528,873 (June 25, 1931) and 534,282 (Sept. 10, 1931); G. Bretschneider, to DEGUSSA, German Patent 855,737 (Feb. 21, 1957).

C.F.W. values for samples of preparation A-1 varied from 85.2 to 91.8 although our analytical reproducibility was better than ±1%. We conclude that the materials are somewhat heterogeneous, but that all of the preparations are qualitatively similar.

Curie–Weiss plots ($1/\chi_g$ vs. temperature (°K.)) of the data for four different preparations in the temperature range from 77 to 300°K. are approximately linear. The deviation from linearity was, however, greater than the statistical uncertainty of the data; this deviation may result from a complicated magnetic situation.

The e.s.r. absorptions observed with preparation A-3 at three temperatures are shown in Figure 1.[5] The curve in Figure 1a shows two resonances: one, labeled the X resonance, has a width at the inflection points of the derivative curve of $\Delta H \simeq 2500$ gauss, is symmetric, and is centered at $g = 2.0^6$; the other, labeled Y, has a width $\Delta H \simeq 20$ gauss, is asymmetric, and is centered at $g = 2.0095 \pm 0.0009$ (at 300°K.). As temperature was decreased, the following spectral changes were noted: (1) the X resonance decreased in intensity with no change detectable in ΔH; (2) at 222°K. a third resonance, labeled Z, which increased in intensity on decrease in temperature, was observed on the low field side of the Y resonance; (3) the Y resonance also increased in intensity with decrease of temperature and the effective g was 2.004 (at 78°K.); (4) at 4°K. the X resonance was not detected and there was only a small alteration of the shape of the Y and Z resonances as compared to 77°K.

Assuming $S = \frac{1}{2}$, the number of spins in the X resonance at 300°K. of a 0.022-g. sample of preparation A-3 was 7×10^{18}.[7] The concentration was $(6 \pm 3) \times 10^{20}$ spins/cc. (For the Y resonance, we estimate the concentration as 10^{15} to 10^{16} spins/cc.) The spin concentration from e.s.r. measurements is approximately one-tenth of the concentration from susceptibility data. The spin concentration of the X resonance for three preparations exhibited the same trend as per cent O_2 or χ_g.

Infrared spectra give little useful information. The X-ray patterns show diffuse scattering plus lines for some unchanged starting material; therefore the new phase is essentially amorphous. The broad-line n.m.r.[8] in the preparations shows that all boron atoms exist in a tetrahedral environment.

Although the magnetic properties and the chemical behavior show some similarities to the superoxides,[9, 10] the magnetic data (concentrations, e.s.r. spectra) are not consistent with the sole presence of the superoxide ion O_2^- or of O_2 molecules and are not sufficient to determine the electronic structure of the magnetic states. The local configuration in best agreement with our data is

(5) The starting material $NaBO_3 \cdot H_2O$ was not paramagnetic. This fact plus the magnitude of the temperature-dependent paramagnetic susceptibility in the modified preparations exclude the possibility of the magnetism being due to an impurity such as ferric ion, etc.

(6) We define $g = h\nu/\beta H$, where h = Planck's constant, ν = spectrometer frequency, β = Bohr Magneton, and H = field at which the derivative curve changes a sign.

(7) Spin concentration measured by comparison techniques: cf. R. H. Silsbee, Phys. Rev., 103, 1675 (1956).

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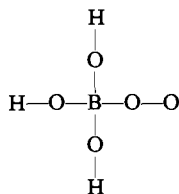
A variety of experiments may shed light on the nature of these "pseudo-superoxides." These experiments will, however, involve a considerable length of time so we feel that the observation on the magnetism should be reported at this time.

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The Structure of Five-Coordinated High-Spin Complexes of Nickel(II) and Cobalt(II) with N-β-Diethylamineethyl-5-chlorosalicylaldimine[1]

Sir:

Ring-substituted salicylaldehydes form with N,N-diethylethylenediamine Schiff bases of the general formula $XC_6H_3(OH)CH=NC_2H_4N(C_2H_5)_2$. These ligands give complexes with nickel(II) of the general formula $[X-SALen-N(C_2H_5)_2]_2Ni$. Paramagnetic octahedral or diamagnetic planar complexes are formed depending on the nature of the X substituent in the benzene ring. When X = 3-Cl, 5-Cl, or 3,4-benzo, paramagnetic compounds (μ_{eff} = 3.3 B.M.) of indeterminate structure are formed. Their reflectance spectra differ from those of the octahedral and planar forms. In solution, the absorption spectra show the existence of octahedral, planar, and unknown species.[2]

$[5-Cl-SALen-N(C_2H_5)_2]_2Ni$ and also $[5-Cl-SALen-N(C_2H_5)_2]_2Co$ are isomorphous with the following crystal data, respectively: a = 12.68, 13.20 Å.; b = 21.77, 21.86 Å.; c = 12.05, 12.15 Å.; β = 122° 48', 126° 25'; Z = 4; d_c = 1.32, 1.31 g./cm.; V_M = 699.4, 705.4 Å.; space group $P2_1/c$.

Three-dimensional data have been collected on the nickel complex by the equi-inclination Weissenberg technique using Cu Kα radiation. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by several cycles of least squares.

(1) Supported by the Italian Consiglio Nazionale delle Ricerche.
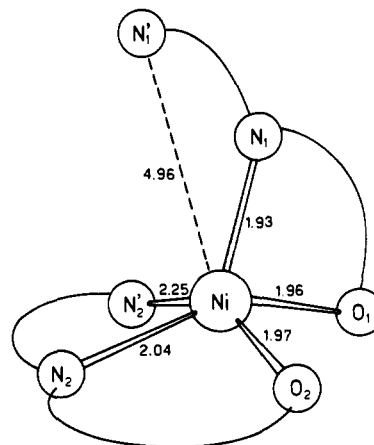(2) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, in press.

Figure 1. Sketch of the molecular structure of $[5-Cl-SALen-N(C_2H_5)_2]_2Ni$. Salicylaldimines residues are schematically represented by full lines.

At the present stage of refinement R is 0.15 over 1033 observed, independent reflections.

The structure consists of discrete molecules in which nickel(II) has a coordination number of five. The coordination polyhedron can be described as a distorted square pyramid (Figure 1). Bond lengths about the nickel atom are shown in the figure. The angles are: O_1-Ni-O_2 = 94°, O_2-Ni-N_2 = 89°, N_2-Ni-N_2' = 80°, $N_2'-Ni-O_1$ = 90°, O_1-Ni-N_1 = 92°, O_2-Ni-N_1 = 100°, N_2-Ni-N_1 = 105°, $N_2'-Ni-N_1$ = 105°. The basal set of four ligands lies in a plane within 0.1 Å. The nickel atom is 0.36 Å. above this plane. The nickel to nonbonded nitrogen atom distance is 4.96 Å. The shortest intermolecular nickel to nonbonded nitrogen distance is 7.81 Å.

This structure represents the first example of a high spin nickel(II) complex so far described with a five-coordinate geometry.

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The Structure of Villalstonine[1]

Sir:

Alkaloid B (m.p. 235–270 dec. (*in vacuo*), $[\alpha]^{25}D$ +79° (*c* 1.0, pyridine)) isolated from *Alstonia muelleriana* Domin by Elderfield and co-workers[2] was characterized by them as an indole alkaloid of approximate composition $C_{40}H_{50}O_4N_4$. A tentative identification[3] of Alkaloid B with villalstonine[4] has been confirmed by a comparison of single crystal X-ray diffraction patterns.[5] We wish to report the result of a crystallographic study which establishes the molecular structure

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