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## Complexing of Metal Ions with Semiquinones. An Electron Spin Resonance Study

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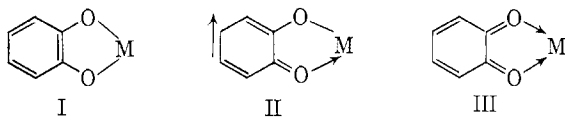
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Complexing of the *o*-semiquinone radical with diamagnetic ions of the group II and group III metals Mg, Ca, Sr, Ba, Zn, Cd, Al, Y, and La has been studied by e.s.r. Changes in the proton hyperfine coupling constants and the appearance of additional splitting due to interaction with the nuclear moment of the metal have been observed. Correlations between the e.s.r. results and the heats of hydration of the metal ions have been found. Calculations based on a simple model in which the effects of the complexing are expressed in terms of variation of the Coulomb integral of the semiquinone oxygen atoms give results in qualitative agreement with experiment. The effects of complex formation on the oxidation-reduction potentials of the semiquinones are discussed.

### Introduction

Many physical techniques have been used to study the complexing of metal ions in solution, but the applications of electron spin resonance to this field have been rather sparse. In favorable circumstances, though, e.s.r. can provide detailed and specific information regarding metal-ligand bonding. We have, accordingly, examined the e.s.r. spectra of several *o*-semiquinones in the presence of metal ions and have found evidence for chelate formation.

Chelate complexes of catechol are well known and more recently a number of chelate complexes with *o*-quinones have been prepared.<sup>1</sup> The possibility of forming radical chelates with the intermediate *o*-semiquinones is attractive for a number of reasons. Thus, it is possible to stabilize certain valencies of transition metal ions by complex formation, e.g.,  $\text{Co}^{3+}$ , and it seemed interesting to determine whether unusual valence states of ligands, *i.e.*, free radicals, could be similarly stabilized. A precedent for such a possibility is perhaps provided by the recently reported neutral complexes of 2,2'-dipyridyl which in many cases are stable compounds.<sup>2,3</sup> A compound such as  $\text{Be}(\text{dipy})_2$  can be regarded as either the combination of Be(II) with two dipyrindyl radical anions or of Be(0) with two dipyrindyl molecules. The *o*-semiquinones provide similar possibilities. Thus, the valence bond structures I-III can



be written for *o*-quinone chelates in various stages of oxidation. The chelate bonding in II is formally analogous to that of a metal acetylacetonate and a number of resonance structures, some placing spin on the ligand and some on the metal, can be written.

Secondly, the study of spin density distributions by n.m.r. in the chelates of paramagnetic metals has been a

subject of some interest recently.<sup>4</sup> In these compounds the electron spin is located predominantly in the metal orbitals but may be partly delocalized to the ligand. In a radical chelate such as II we are concerned with the converse process of delocalizing spin from the ligand to the metal. In general, the two types of experiments are complementary both in the techniques employed and in the type of information that can be obtained. Thus, n.m.r. experiments on the aminotroponimineates<sup>4</sup> have allowed a wide variation in ligand structure but are relatively restricted in the metals that can be employed. The e.s.r. experiments must be confined to rather simple ligands but allow a study of metal-ligand bonding with a wider array of metals.

### Experimental

Spectra were obtained with a Varian 100 kc./sec. e.s.r. spectrometer in conjunction with a 12-in. electromagnet. Commercial samples of catechol and of various metal salts (chlorides or nitrates) were used without further purification. Oxidation was generally effected by bubbling air or oxygen through the alkaline solutions. pH values were measured with a Beckman pH meter. Catechol solutions of approximately 0.1 *M* concentration were used, with the metal ions being present at approximately 0.5 *M* concentration.

### Results

Complex formation may be expected to affect the e.s.r. spectra in three ways, namely: (1) Modification of the spin density distribution within the ligand and hence changes in the proton hyperfine coupling constants. (2) Coupling between the electron spin and the nuclear spin of the metal (if this not equal to zero) and hence the appearance of additional hyperfine structure. (3) Interaction between the unpaired electrons of the ligand and those of the metal if the latter is paramagnetic. The present results involve only the first two of these effects.

The *o*-semiquinone radical is particularly well suited to a study of this kind in that it gives an easily resolved and analyzed nine-line e.s.r. spectrum.<sup>5</sup> In the pres-

(4) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(5) (a) G. Vincow and G. K. Fraenkel, *ibid.*, **34**, 1333 (1961); (b) M. Adams, M. S. Blois, and R. H. Sands, *ibid.*, **28**, 774 (1958); (c) R. Hoskins, *ibid.*, **23**, 1975 (1955).

(1) P. J. Crowley and H. M. Haendler, *Inorg. Chem.*, **1**, 904 (1962).

(2) S. Herzog and R. Taube, *Z. Chem.*, **2**, 208 (1962).

(3) G. E. Coates and S. I. E. Green, *J. Chem. Soc.*, 3340 (1962).

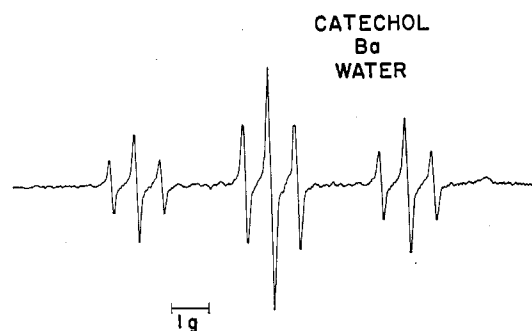


Fig. 1.—E.s.r. spectrum of *o*-semiquinone in the presence of excess  $\text{Ba}^{2+}$  ion.

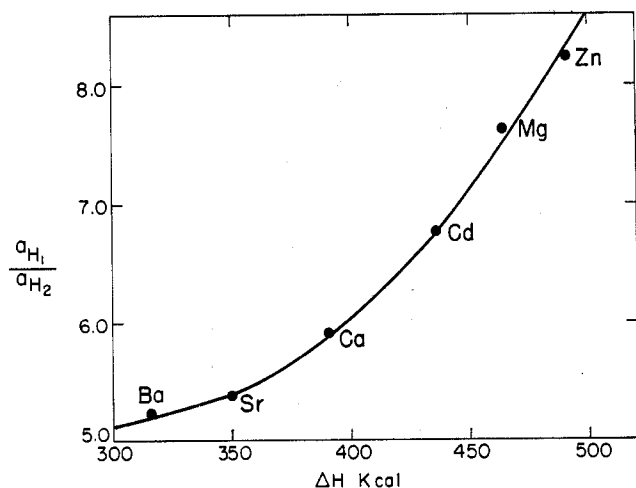


Fig. 2.—Heats of hydration of metal ions vs. the ratio of hyperfine coupling constants.

ence of excess of the metal ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$ , nine-line spectra are also observed but the coupling constants depend markedly on the metal ion and are also different from that of the presumably uncomplexed radical produced with  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{N}(\text{CH}_3)_4^+$  as the cation. An example of such a spectrum is shown in Fig. 1. The hyperfine coupling constants, spin densities, and the ratio of the two coupling constants for this series of spectra in aqueous solution are

TABLE I  
DATA ON *o*-SEMIQUINONE COMPLEXES IN WATER

Metal	$a_H$ , gauss	$\rho^c$	Ratio	Heat of hydration, kcal. <sup>a</sup>
(Na)	3.65 <sup>b</sup>	0.162 <sup>b</sup>	3.84 <sup>b</sup>	
	0.95	0.042		
Mg	3.97	0.176	7.61	464
	0.52	0.023		
Ca	3.85	0.171	5.91	382
	0.65	0.029		
Sr	3.68	0.164	5.38	350
	0.69	0.030		
Ba	3.75	0.167	5.23	316
	0.72	0.032		
Zn	3.95	0.176	8.25	491
	0.48	0.021		
Cd	3.71	0.165	6.77	436
	0.55	0.024		

<sup>a</sup> Values from ref. 6. <sup>b</sup> Values from ref. 5 in alkaline ethanol. In water the ratio of the coupling constants is 4.85. <sup>c</sup> Spin density  $\rho$  calculated from  $a_H = Q\rho$ , assuming  $Q = 22.5$  gauss.

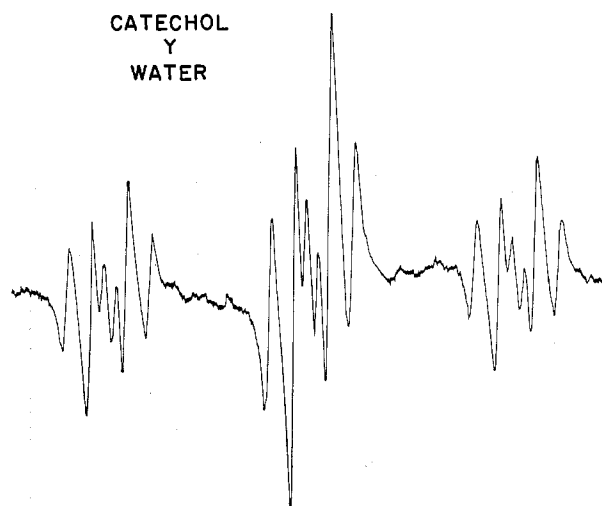


Fig. 3.—E.s.r. spectrum of *o*-semiquinone in the presence of excess  $\text{Y}^{3+}$  ion.

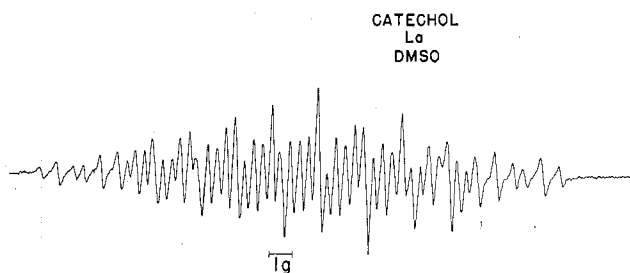


Fig. 4.—E.s.r. spectrum of *o*-semiquinone in the presence of excess  $\text{La}^{3+}$  ion.

given in Table I. It may be noted that the ratio of the coupling constants is particularly sensitive to the metal ion and that this quantity can be easily and accurately obtained from the spectra. These ratios correlate smoothly with the heats of hydration<sup>6</sup> of the metal ions as is shown in Fig. 2.

In the presence of  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  ions the spectra shown in Fig. 3 and 4 are obtained. These show additional splittings due to the metal ion.  $\text{Y}^{89}$  has a spin of  $1/2$  leading to an 18-line spectrum from which a coupling constant  $a_Y = 0.65$  gauss is obtained. With  $\text{La}^{139}$  ( $I = 7/2$ ) 52 of the theoretical 72 lines can be resolved and  $a_{\text{La}} = 2.07$  gauss.

Some qualitative observations regarding the stability of the free radicals have also been made. With variation of the cation this increases in the series ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{N}(\text{CH}_3)_4^+$  <  $\text{Ba}^{2+}$  <  $\text{Sr}^{2+}$  <  $\text{Ca}^{2+}$  <  $\text{Mg}^{2+}$  <  $\text{Zn}^{2+}$ ). Thus, the uncomplexed radical decomposes rapidly in the presence of air, but when  $\text{Zn}^{2+}$  is present the e.s.r. spectrum is unchanged over a period of several hours. There is also a pronounced increase in the difficulty of oxidation in the same series. Thus, alkaline catechol will oxidize by shaking with air but in the presence of  $\text{Zn}^{2+}$  (at the same pH) prolonged bubbling of oxygen is necessary. With  $\text{Al}^{3+}$  no oxidation occurs under these conditions, but on warming with sodium peroxide a poorly resolved spectrum was obtained. This has a prominent spacing of 1.96 gauss which is assigned to

(6) R. J. P. Williams, *J. Phys. Chem.*, **58**, 121 (1954).

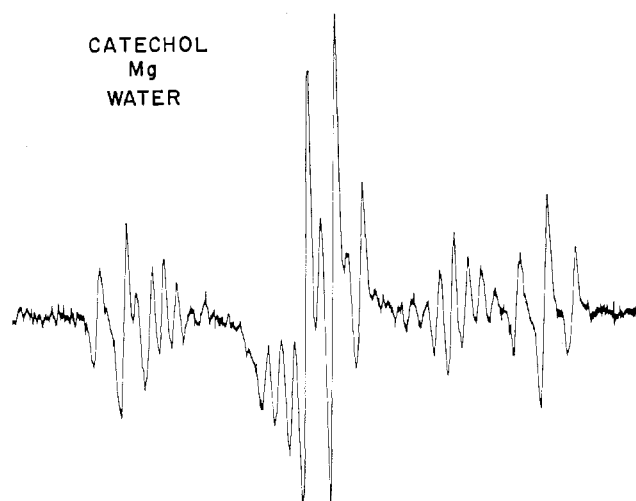


Fig. 5.—E.s.r. spectrum of *o*-semiquinone in the presence of excess  $Mg^{2+}$  ion.

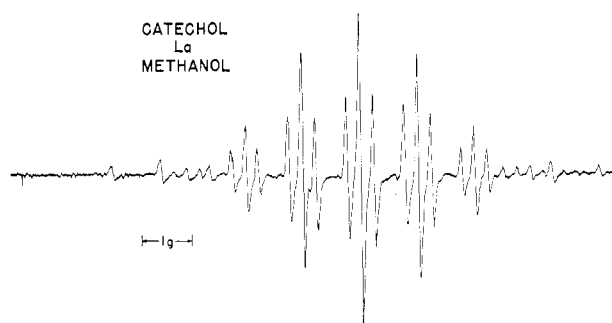
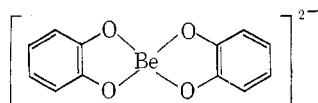
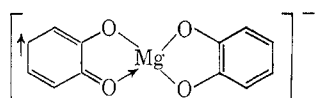


Fig. 6.—E.s.r. spectrum of *o*-semiquinone plus  $La^{3+}$  in methanol.

coupling with the  $Al^{27}$  ( $I = 5/2$ ). With  $Be^{2+}$  no oxidation was effected under any conditions. This presumably reflects the great stability of the complex ion



Boron gives a similar very stable complex ion. In the case of  $Mg$  in a number of experiments a second more complex spectrum was observed in addition to the nine-line spectrum (Fig. 5). Because of overlap of the lines it was not possible to analyze this spectrum, but the larger number of lines indicates that there are couplings from more than the four protons of a single semiquinone molecule. It may possibly arise from a species such as



Essentially similar results have been obtained with dimethyl sulfoxide and methanol as solvents, although the differences between the metals are less pronounced. Thus, in methanol the ratios of the coupling constants with the cations  $Na^+$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$  were 4.05, 4.51, 4.59, and 4.89, respectively. In methanol a further complication was observed in that an additional spectrum consisting of seven triplets appeared with many metal ions (Fig. 6). The coupling constants of

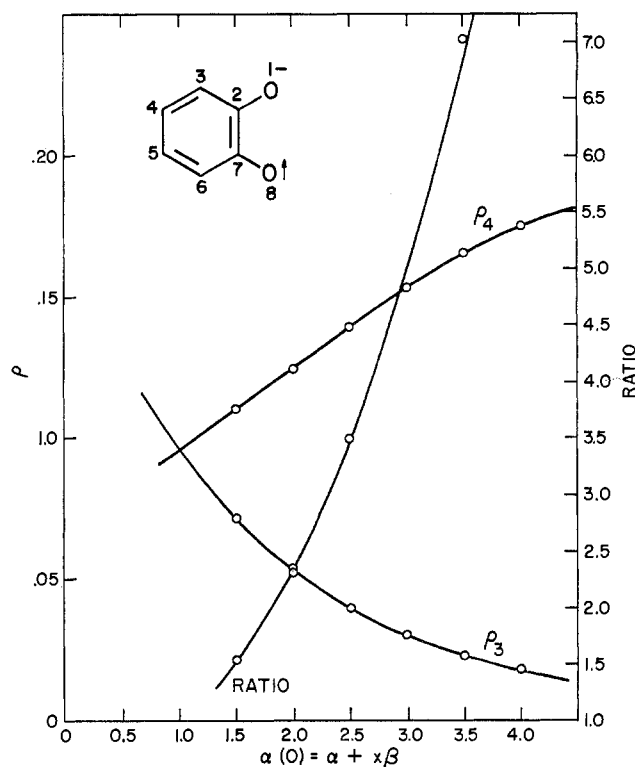
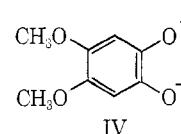


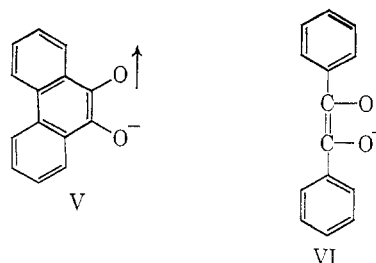
Fig. 7.—Hückel molecular orbital calculation of the spin densities of the *o*-semiquinone ion.

this spectrum are independent of the metal ion, and the most probable explanation is that the semiquinone radical has reacted with the solvent to give



The coupling constants are  $a_{CH_3} = 1.20$  and  $a_H = 0.26$  gauss. This reaction is apparently catalyzed by metal ions. Possibly neutralization of the negative charge on the oxygen by complexing with positive metal ions facilitates the attack of  $OCH_3^-$  on the aromatic ring. A spectrum attributable to the complexed methoxy radical (IV) was obtained with  $Ca^{2+}$ . It is apparent that similar reactions can occur in ethanol, although the spectra are less well resolved. Very similar reactions of *p*-semiquinones with alcohols have been reported by Reitz, *et al.*<sup>7</sup>

The interaction of metal ions with the two radicals V and VI has also been examined. Qualitatively, the

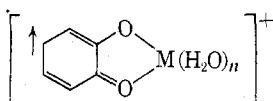


(7) D. C. Reitz, J. R. Hollahan, F. Dravnick, and J. E. Wertz, *J. Chem. Phys.*, **34**, 1457 (1961).

results are quite similar to those obtained with *o*-semiquinone. However, since the initial spectra are relatively complex and incompletely resolved, no detailed analysis has been attempted.

### Discussion

The marked dependence of the proton hyperfine coupling constants of *o*-semiquinone on the nature of the added metal ion together with the smooth correlation with the heats of hydration shown in Fig. 2 are taken as evidence for metal-semiquinone complex formation. The spectra of the divalent metal complexes indicate that: (1) Either only one semiquinone molecule is involved in the complex or, if more than one is involved, there is slow electron exchange between the different ligands. (2) There are two pairs of equivalent protons in the complex so that both oxygens are equivalently involved in the metal bonding. A chelate species such as



is perhaps most likely for the divalent metals. Some support for the occurrence of chelates is provided by the observation that metal ions have no pronounced effect on the e.s.r. spectrum of *p*-semiquinone.

A rather simple model can be used as a basis for calculations on these complexes. If the bonding is essentially ionic, the effect of the metal is to neutralize partly the negative charge on the oxygen and hence to increase its electronegativity. In the Hückel approximation this is equivalent to varying the Coulomb integral of the oxygen. Strong bonding involves considerable neutralization of the negative charge and hence a large increase in the Coulomb integral. Weak bonding involves a proportionately smaller increase. Gendell, Freed, and Fraenkel<sup>8</sup> have used a similar model to discuss the solvation of semiquinone ions. The results of such a calculation are shown graphically in Fig. 7. A resonance integral  $\beta_{CO} = 1.4\beta$  was used throughout. As  $\alpha(o)$  increases,  $\rho_3$  diminishes and  $\rho_4$  increases so that the ratio (which is also the ratio of the hyperfine coupling constants since  $a_H = Q\rho_C$ ) increases rapidly. The experimental ratio can therefore be used to obtain an "effective" Coulomb integral for each of the complexes.

(8) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

This calculation serves to rationalize the observed correlation between the ratio of the coupling constants and the heats of hydration of the metal ions since both complexing and hydration involve the formation of M-O bonds the strength of which can be expressed in terms of changes in the effective oxygen Coulomb integral. Calculations at this level of approximation should, however, be regarded as having qualitative rather than quantitative significance since no account has been taken of spin polarization effects. Such effects will tend, for a given value of  $\alpha(o)$ , to increase the large spin density,  $\rho_4$ , and decrease the small spin density,  $\rho_3$  (possibly even making it negative<sup>9</sup>), so that changes in the ratio are exaggerated.

The observation of hyperfine splitting from the metal indicates some degree of covalent bonding between the metal and the ligand. The smaller value found for the Y coupling constant than for the La coupling constant is consistent with the much smaller nuclear moment of Y.

Finally, it is interesting to inquire how the complexing affects the stability of the semiquinone relative to the oxidized and reduced forms. The Hückel calculation indicates that both the ionization potentials hydroquinone  $\rightarrow$  semiquinone and semiquinone  $\rightarrow$  quinone are increased as the strength of the metal bonding increases. At this level of approximation the two are of course equal. This increase is in agreement with the qualitative observations on the stabilities of the radicals. Increasing strength of chelation protects the radical from further oxidation but also increases the difficulty in obtaining it in the first place. Thus, in the series B, Be, Al, Zn, Mg, Sr, Ba, the radical chelates of *o*-semiquinone of the first members cannot be readily obtained by oxidation while those of the last members are relatively unstable to further oxidation. In this system Mg and Zn complexes provide the most favorable cases for obtaining the radical. The ability of metal ions to control the oxidation potentials of organic molecules by complexing may be significant in biological electron-transfer systems. The widespread occurrence of Mg and Zn ions in biological processes, *e.g.*, oxidative phosphorylation, is particularly noteworthy in this connection.<sup>10</sup>

(9) G. Vincow, *ibid.*, **38**, 917 (1963).

(10) In a table of enzymes activated by metals given by Martell and Calvin, 25 out of 32 of the examples involving diamagnetic metals require Mg or Zn: A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 404.