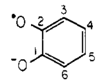
o-Benzosemiquinone and Its Metal Chelates. Electron Spin Resonance Investigation of Radicals from the Photolysis of Catechol in the Presence of Complexing Metal Ions

Christopher C. Felix and Roger C. Sealy*

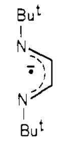
Contribution from the National Biomedical ESR Center, Department of Radiology, Medical College of Wisconsin, Milwaukee, Wisconsin 53226. *Received June 1, 1981*

Abstract: A photolytic method for preparing *o*-benzosemiquinone and its complexes with diamagnetic metal ions in aqueous solution is described. Semiquinone free radicals from the photoionization of catechol are readily trapped by di- or tripositive metal ions to form chelate complexes. In this way, complexes of *o*-benzosemiquinone with group 2A, 2B, 3A, and 3B metal ions have been prepared and their magnetic parameters determined by ESR spectroscopy. *g* values and hyperfine couplings (to protons and, where possible, to ^{13}C and to metal isotopes) were measured for each complex. From an analysis of proton and ^{13}C hyperfine data the spin densities at all eight atoms have been obtained for *o*-benzosemiquinone and its complexes with Mg^{2+}, Sr^{2+}, and Ba^{2+}. For *o*-benzosemiquinone it is confirmed that spin densities at all the atoms are positive, and it is shown that the spin distribution in the semiquinone moiety is closely related to that in *p*-benzosemiquinone. A decrease in spin density at the carbonyl oxygen atoms was found to occur upon complexation. Proton hyperfine couplings measured for metal complexes correlate with the polarizing power (charge/ionic radius) of the metal ion, consistent with a Coulombic interaction between the radical and the metal ion. Metal ions from groups 2B, 3A, and 3B all gave complexes with ESR spectra showing hyperfine splitting to nuclear isotopes present in natural abundance. Estimates of the s-orbital spin population at the metal ion indicate that it is small (ca. 0.14–0.50% in the complexes studied) and that it, too, generally varies with the polarizing power of the metal ion. The low spin density at the metal ion confirms that these complexes are largely ionic. Complexes with group 2A metal ions did not show hyperfine splitting from metal isotopes, indicating that the lifetime of the metal ion in these complexes is less than ca. 10^{-6} s.

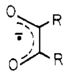
Several chelate complexes of simple free radicals with diamagnetic metal ions are known. Some early examples were reported by Eaton,[1] who studied complexes of *o*-benzosemiquinone (**1**) with a number of metal ions. Some of these complexes were later reinvestigated by Kuwata and Shimizu.[2] In other studies von Zelewsky and co-workers investigated some complexes of the radical **2**,[3] while Dobbs et al.[4] have characterized several complexes of semidiones **3** and Müller et al.[5] have generated flavin semiquinone complexes with Zn^{2+} and Cd^{2+} (**4**). These studies mostly employed non-transition-metal ions. There is also a growing body of literature specifically concerned with complexes of free radicals with transition-metal ions,[6] many of which involve substituted *o*-semiquinones.[6,7]



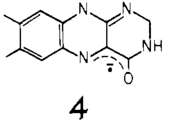
1



2

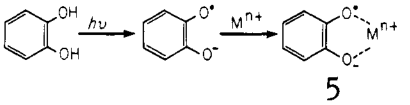


3



4

Complexes of **1** and related semiquinones are of particular interest since there is evidence[8] that such complexes are readily formed by melanin biological pigments in the presence of metal ions. However, reported methods for the preparation of complexes of **1** in aqueous solution are limited in number. In the first studies,[1,2] the semiquinone complexes were generated by air oxidation of alkaline solutions of catechol in the presence of metal ions. However, some complexes were very difficult to produce by this method, and some data could therefore be obtained only for nonaqueous solvents. (Some studies of complexation of *o*-semiquinones by organometallics in nonaqueous solvents also have been undertaken.[9,10]) We later reported[8] that the zinc complex of **1** could be obtained at pH ca. 5 by the addition of zinc ions to solutions of catechol partially oxidized with ferricyanide. More recently, we observed[11] ESR spectra attributable to metal complexes of semiquinones during UV photolysis of the catecholamine Dopa in the presence of some divalent metal ions. This suggested that UV photolysis of catechol/metal ion solutions would be a useful procedure for the preparation of complexes of **1**. We now report that complexes (**5**) with a large number of diamagnetic metal ions, M^{n+}, can indeed readily be generated by continuous UV photolysis of aqueous solutions of catechol in the presence of the metal ion at around neutral pH (reaction 1). Since the metal ions stabilize the radical species, the complexes can easily be produced in high steady-state concentration.



5 (1)

Information on complexes of this kind is useful from both chemical and biochemical standpoints. First, it allows one to

---

(1) D. R. Eaton, *Inorg. Chem.*, 3, 1268–1271 (1964).

(2) K. Kuwata and Y. Shimizu, *Bull. Chem. Soc. Jpn.*, **42**, 864–870 (1969).

(3) P. Clopath and A. von Zelewsky, *J. Chem. Soc., Chem. Commun.*, 47–48 (1971); *Helv. Chim. Acta*, **55**, 52–67 (1972).

(4) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 2053–2056 (1972).

(5) F. Müller, A. Ehrenberg, and L. E. G. Ericksson in "Magnetic Resonance in Biological Systems", A. Ehrenberg, A. Malmstrom, and T. Vanngard, Eds., Pergamon Press, Oxford, 1967, pp 281–288.

(6) For a compilation, see A. von Zelewsky and C. Daul in "Landolt-Börnstein New Series, Group II, Vol. 9, Part A", H. Fischer and K.-H. Hellwege, Eds., Springer-Verlag, Berlin, 1977, pp 290–341.

(7) For recent work on transition-metal complexes of *o*-semiquinones, see: M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald, and C. G. Pierpont, *J. Am. Chem. Soc.*, **103**, 3961–3963 (1981); M. W. Lynch, R. M. Buchanan, C. G. Pierpont, and D. N. Hendrickson, *Inorg. Chem.*, **20**, 1038–1046 (1981), and references therein.

(8) C. C. Felix, J. S. Hyde, T. Sarna, and R. C. Sealy, *J. Am. Chem. Soc.*, **100**, 3922–3926 (1978).

(9) H. B. Stegmann, K. B. Ulmschneider, and K. Scheffler, *J. Organomet. Chem.*, **101**, 145–170 (1975).

(10) G. A. Razuvaev, G. A. Abakumov, E. S. Klinov, E. N. Gladyshev, and P. Ya. Bayushkin, *Bull. Acad. Sci., USSR, Div. Chem. Sci. (Engl. Transl.)*, **26**, 1034–1037 (1977).

(11) C. C. Felix and R. C. Sealy, *J. Am. Chem. Soc.*, **103**, 2831–2836 (1981).

0002-7863/82/1504-1555$01.25/0

systematically study the redistribution of electron density within the free-radical ligand as a function of the complexing metal ion. Thus, for *o*-benzosemiquinone it was found that for a number of dipositive metal ions the ratio of the measured proton hyperfine splittings in the complex correlates quite well with the heat of hydration[1] and the Pauling electronegativity[2] of the metal ion. In this paper we show that a more general correlation exists between each of the proton hyperfine splittings and the polarizing power (charge/ionic radius) of the metal ion. Also, from measurements of ^{13}C hyperfine splittings, we are able to provide additional information on the spin density distribution in *o*-benzosemiquinone and its metal complexes. The spin density distribution in uncomplexed *o*-benzosemiquinone has been the subject of considerable debate[12] since theoretical calculations do not easily reproduce the measured proton hyperfine coupling constants. Our data allow us to estimate spin densities at all eight atoms and to compare these with theory. For the metal complexes our data confirm that the complexes are largely ionic, with only small amounts of spin density on the metal ion, and we also show that association with the group 2A metal ions is weaker than with other metal ions studied.

Secondly, measurements of hyperfine splittings to metal ions possessing a nuclear moment can be important for the elucidation of the structure of free-radical units in biological polymers. For example, the free radicals in melanins show a single broad ESR line with no resolved hyperfine structure and are consequently difficult to identify with certainty. We have pointed out[8] that measurement of hyperfine splittings to diamagnetic metal ions may allow one to distinguish between different kinds of radical subunits in these and related polymer systems. Reference data for complexes of model free radicals such as **1** are necessary for this. Accordingly, we have measured hyperfine splittings from a series of metal isotopes that possess nuclear moments.

Experimental Section

Catechol was obtained from Aldrich Chemical Co. and was used without further purification. This material possibly contains small amounts of *p*-hydroquinone as an impurity, since we were sometimes able to detect its oxidation product, *p*-benzosemiquinone, especially at high pH. Metal ions used were present as their chloride or sulfate salts, which were obtained from either Fisher or Alfa Chemical Co. Solutions of catechol were made up in nitrogen-saturated deionized water prior to addition of metal ions. The pH was then adjusted in the range 5–11 by the addition of small amounts of 10 M sodium hydroxide solution.

Radicals were generated by photolysis of these solutions as they were passed (flow rate 1–2 mL/min) through a flat cell contained in the ESR cavity. The irradiation source was an Eimac 300UV 300-W xenon arc, whose output was filtered through 5 cm of deionized water to remove infrared radiation before being focused onto the flat cell through the irradiation slots in the cavity. The temperature of the sample during irradiation was 28 ± 2 °C.

Electron spin resonance spectra were recorded on a Varian E-109 spectrometer using 100-kHz field modulation, with a microwave power of 0.5–1.0 mW. Hyperfine splittings and *g* values were obtained from measurements of magnetic field and microwave frequency made with a Radiopan gaussmeter and DANA 300 frequency counter. Unless otherwise stated, hyperfine splittings were measured to ±0.03 G, *g* values to ±0.0001.

Results

Spin Density Distribution in *o*-Benzosemiquinone. Whereas photolysis of catechol in several nonaqueous solvents gives the spectrum of neutral *o*-benzosemiquinone,[13] photolysis in aqueous solutions at pHs between 5 and 11 gave strong signals of the anionic radical (**1**) as shown in Figure 1a. The anion radical is expected, since *o*-benzosemiquinone should, like other *o*-semiquinones,[14] have a pK_a of ca 3–4. Steady-state signal intensities increased with pH, probably because of the combined effects of an increased yield of photoionization and a decreased termination rate for the free radical. Small amounts of *p*-benzosemiquinone (a^H = 2.37 G) also were detected at the higher pHs.

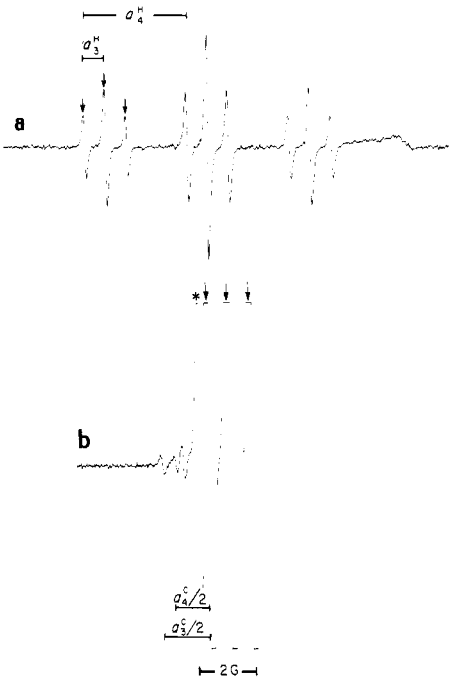


Figure 1. (a) ESR spectrum of *o*-benzosemiquinone (**1**) from continuous UV photolysis of deoxygenated aqueous solutions of catechol, pH 7. A small irradiation signal in the ESR cell is present at high field. (b) The region of the downfield triplet (lines arrowed in (a)) under conditions of increased gain, showing ^{13}C satellites. For an increase in signal-to-noise ratio, this partial spectrum was obtained at pH 11. Under these conditions a small amount of *p*-benzosemiquinone is also present, contributing the line marked with an asterisk.

Proton hyperfine splittings measured for radical **1** are 3.67 and 0.75 G, in good agreement with those reported by Neta and Fessenden[15] for this radical generated by radiolysis of aqueous solutions of catechol. Comparison of data for *o*-benzosemiquinone with specifically substituted compounds has indicated[16] that the larger of the two splittings is associated with the protons at C-4 and C-5, the smaller with protons at C-3 and C-6 (the numbering of the carbon atoms is indicated in structure **1**). Since proton hyperfine splittings (a^H) are related to the spin densities (ρ) at the respective carbon atoms through the McConnell relationship[17]

$$a^{H}{}_{i} = Q_{CH}\rho_i \qquad (2)$$

where Q_{CH} is generally of the order of −27 G, $|\rho_4| \gg |\rho_3|$. However, this ordering is not easily reproduced by theory. Debate has continued over this and also over the signs of the two proton hyperfine splittings. MO calculations using the Hückel[1,2] and McLachlan[2,18,19] methods, the INDO approximation,[12,20-22] and an unrestricted open-shell SCF approach[2] have been carried out, but the results are generally in poor agreement with the experimental data.

At the simplest level, Hückel calculations in which the Coulomb integral was varied to give the correct ordering ($|\rho_4| > |\rho_3|$) and the best fit to the experimental data suggest[1,2] that ρ_4 and ρ_3 are both positive. The results of the calculations can be used to explain, in a qualitative manner, the effects of complexation with metal ions (see below). In contrast to the Hückel calculations,

---

(12) For example, J. Spanget-Larsen, *Int. J. Quantum Chem.*, **18**, 365–367 (1980), and references therein.

(13) K. Loth, F. Graf, and H. H. Gunthard, *Chem. Phys. Lett.*, **45**, 191–196 (1977).

(14) P. S. Rao and E. Hayon, *J. Phys. Chem.*, **77**, 2274–2276 (1973).

(15) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **78**, 523–529 (1974).

(16) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1488–1494 (1965).

(17) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(18) G. Vincow, *J. Chem. Phys.*, **38**, 917–919 (1963).

(19) J. Pilar, *J. Phys. Chem.*, **74**, 4029–4037 (1970).

(20) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201–4209 (1968).

(21) J. A. Pedersen and J. Spanget-Larsen, *Chem. Phys. Lett.*, **35**, 41–44 (1975).

(22) J. Spanget-Larsen, *Theor. Chim. Acta*, **47**, 315–328 (1978).

McLachlan calculations have generally been taken to indicate that ρ_3 is *negative*[2,18] (an exception to this is the work by Pilar[19]).

The INDO method, although it has been successfully used to calculate hyperfine coupling constants for many types of radicals, yields poor results for semiquinone radical anions.[12,20-22] In particular, for *o*-benzosemiquinone it predicts that $|\rho_3| > |\rho_4|$. It has been proposed[12,21,22] that this discrepancy arises from neglect of interaction of the radical with solvent. Inclusion of a solvent interaction into the calculation by means of an effective solvent field gives the correct ordering, with the ratio of the spin densities depending on the choice of the solvent field.[22,23] Finally, the unrestricted open-shell calculation of Kuwata and Shimizu[2] reproduces the experimental proton hyperfine couplings while predicting that ρ_4 and ρ_3 are both positive.

To obtain additional experimental data on the spin distribution in *o*-benzosemiquinone in order to help resolve these questions, we measured ^{13}C hyperfine coupling constants in the radical. Besides the usual proton hyperfine lines, under conditions of higher gain satellite peaks from ^{13}C nuclei present in natural abundance were easily detected (see Figure 1b). From this spectrum hyperfine splittings of 3.35 and 2.40 G were measured. The intensity of these satellites was 1% of the major lines, corresponding to two contributing carbon atoms in each case. The other expected ^{13}C coupling was not observed, and we conclude that it is too small to measure in this experiment, i.e., less than ca. 1.0 G, since wide-field scans established that no coupling >3.35 G was present.

According to Karplus–Fraenkel theory,[25] ^{13}C couplings (a^C) are related to π-electron spin densities through the relation

$$a^C{}_i = \left(S^C + \sum_{j=1}^{3} Q^C{}_{CX_j}\right)\rho_i + \sum_{j=1}^{3} Q^C{}_{X_jC}\rho_j \qquad (3)$$

where the atoms X_j are bonded to carbon atom i. For a C_x-(C_yC_zH) fragment, taking $S^C = -12.7$ G, $Q^C{}_{CH} = +19.5$ G, $Q^C{}_{CC'} = +14.4$ G, and $Q^C{}_{C'C} = -13.9$ G,[25]

$$a^C{}_x = 35.6\rho_x - 13.9(\rho_y + \rho_z)$$

For *o*-benzosemiquinone we have $\rho_3 = \rho_6$ and $\rho_4 = \rho_5$, so that

$$a^C{}_4 = 21.7\rho_4 - 13.9\rho_3 \qquad (4)$$

and

$$a^C{}_3 = 35.6\rho_3 - 13.9\rho_4 - 13.9\rho_1 \qquad (5)$$

We know from the measured hyperfine couplings that $|\rho_4| \gg |\rho_3|$. Then, if we assume that ρ_4 is positive as all the calculations suggest, one would predict that $a^C{}_4$ should be large and *positive* and that $a^C{}_3$ should probably be large and *negative*. We can use eq 4 in conjunction with the McConnell relationship to obtain a value for Q_{CH} appropriate for this system. If we next assume that ρ_3 also is positive (we shall later show that a negative ρ_3 is incompatible with the present data), then both $a^H{}_3$ and $a^H{}_4$ are negative and $Q_{CH} = -69.2/a^C{}_4$. The smaller of the two measured ^{13}C couplings, if positive, then gives a value for Q_{CH} of −28.8 G, in keeping with expectation, whereas the larger coupling gives a value of −20.7 G. The latter value of Q_{CH} seems too high (i.e., too positive), it having been concluded[26] from data for the related *p*-benzosemiquinone species that a value for Q_{CH} of less than ca. −26 G is required for internal consistency. On this basis, we assign a ^{13}C coupling of +2.40 G to the carbon atoms at positions 4 and 5, and with $Q_{CH} = -28.8$ G, we calculate ρ_3 and ρ_4 as 0.026 and 0.127, respectively.

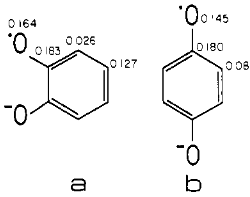


Figure 2. (a) Spin density distribution in *o*-benzosemiquinone in aqueous solution (this work). (b) Spin density distribution in *p*-benzosemiquinone in ethanol–water (from Das and Fraenkel[26]).

Table I. Hyperfine Couplings to Protons and g Values of Metal Complexes of *o*-Benzosemiquinone in Aqueous Solution

metal ion	r, Å[a]	z/r[b]	$a^H{}_3 = a^H{}_6$, G	$a^H{}_4 = a^H{}_5$, G	g
none			0.75	3.67	2.0045_5
Mg^{2+}	0.72	2.78	0.51	3.92_5	2.0042
Al^{3+}	0.535	5.61	ca. 0.20[c,d]	4.26	2.0041
Ca^{2+}	1.00	2.00	0.64	3.80	2.0043
Sc^{3+}	0.72	4.17	0.30	4.20	2.0038
Zn^{2+}	0.74	2.68	0.48	3.92	2.0039
Ga^{3+}	0.62	4.84	ca. 0.30[d]	4.05	2.0040
Sr^{2+}	1.18	1.69	0.68	3.75	2.0042
Y^{3+}	0.90	3.33	0.43	4.01	2.0038
Cd^{2+}	0.95	2.11	0.50	3.81	2.0039
In^{3+}	0.80	3.75	ca. 0.35[d]	3.99	2.0035
Ba^{2+}	1.35	1.48	0.71	3.71	2.0040
La^{3+}	1.03	2.91	0.50	3.95	2.0033

[a] Effective ionic radius for 6-coordination.[28] [b] Charge/ionic radius for the metal ion. [c] Hyperfine splitting incompletely resolved. [d] ±0.05 G.

Assuming that the other major coupling is that to carbon atoms at positions 3 and 6 and that it is *negative*, we are in a position to calculate ρ_1 through the use of eq 5. In this way we obtain $\rho_1 = 0.183$, and since for conservation of spin density $\sum\rho_i = 1$, ρ_0 is calculated to be 0.164, giving the spin density distribution shown in Figure 2a. This distribution is almost exactly reproduced by the open-shell SCF calculation of Kuwata and Shimizu,[2] which gives $\rho_1 = 0.123$, $\rho_3 = 0.030$, $\rho_4 = 0.163$, and $\rho_0 = 0.183$. Comparing these values with those for *p*-benzosemiquinone in ethanol–water (Figure 2b), we see that the spin densities on oxygen and on the adjacent C atoms are quite similar in the two systems, while the mean of the spin densities on the other four C atoms in *o*-benzosemiquinone approximates the spin density on each of the four equivalent C atoms in *p*-benzosemiquinone.

However, if we assume that ρ_3 is negative as has been suggested,[18] than a very different spin density distribution results. In this case, to obtain a reasonable value for Q_{CH} (−26.9 G), one must set $a^C{}_4 = +3.35$ G. For $a^C{}_3 = -2.40$ G, this gives $\rho_3 = -0.028$, $\rho_4 = 0.136$, $\rho_1 = -0.035$, and $\rho_0 = 0.427$, while for the less likely case of $a^C{}_3 = +2.40$ G, $\rho_3 = -0.028$, $\rho_4 = 0.136$, $\rho_1 = -0.380$, and $\rho_0 = 0.772$ are obtained. One can rule out both these possibilities on the basis of the small (<1 G) ^{13}C coupling to the carbon atom at position 1. For a $C_x(C_yC_zO)$ fragment the ^{13}C coupling is

$$a^C{}_x = (16.1 + Q_{CO})\rho_x - 13.9(\rho_y + \rho_z) + Q_{OC}\rho_O \qquad (6)$$

and since $\rho_1 = \rho_2$ in this case

$$a^C{}_1 = (2.2 + Q_{CO})\rho_1 - 13.9\rho_6 + Q_{OC}\rho_O \qquad (7)$$

Das and Fraenkel[26] have calculated values of Q_{CO} and Q_{OC} in semiquinone systems for various values of Q_{CH}, and for $Q_{CH} = -27$ G, obtained $Q_{CO} = 17.7$ G and $Q_{OC} = -27.1$ G. For $Q_{CH} = -28.8$ G, one can estimate from their data values for Q_{CO} and Q_{OC} of ca. 15 and −20 G, respectively, and with values for ρ_1, ρ_6, and ρ_0 from Figure 2, $a^C{}_1$ is estimated to be −0.48 G, i.e., consistent with the experimental findings. The other possibility, using $Q_{CH} = -26.9$ G, $Q_{CO} = 17.7$ G, and $Q_{OC} = -27.1$ G, gives values for $a^C{}_1$ of −11.9 G for $a^C{}_3 = -2.40$ G and of −28.1 G for $a^C{}_3 = 2.40$ G. Such values of $a^C{}_1$ would have given easily detectable ^{13}C

---

(23) Shinagawa et al.[24] have performed an INDO calculation with a geometry-fitting procedure which reproduces the experimental values of the proton hyperfine splittings. However, the best fit with $|\rho_4| > |\rho_3|$ was obtained only with an extremely distorted radical structure as Spanget-Larsen has pointed out.[12]

(24) Y. Shinagawa, Y. Shinagawa, N. Uyesaka, and K. Fukuda, *Int. J. Quantum Chem.*, **18**, 357–366 (1980).

(25) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312–1323 (1961).

(26) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350–1360 (1965).

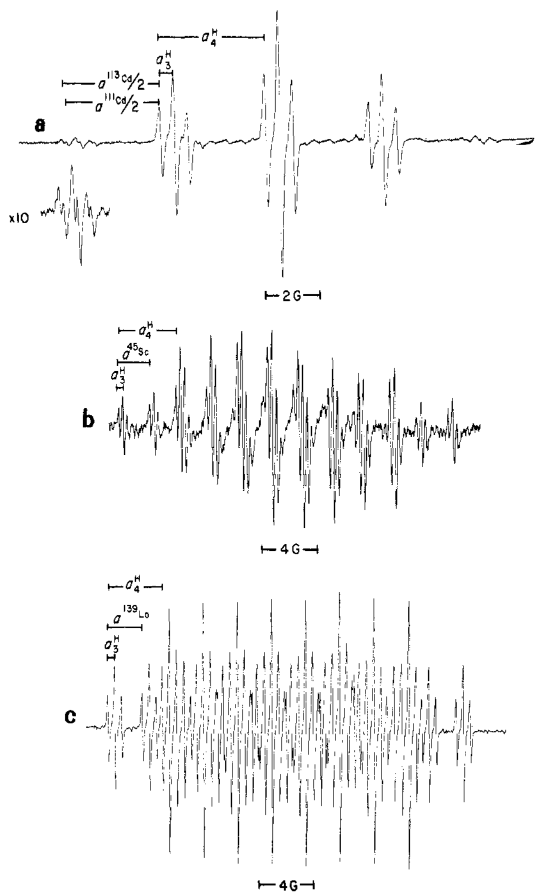


Figure 3. ESR spectra of complexes of *o*-benzosemiquinone with metal ions, pH ca. 6. (a) Spectrum of **5** ($M^{n+} = Cd^{2+}$). Major lines are from the complex with ^{114}Cd ($I = 0$) while satellite lines are from complexes with ^{111}Cd and ^{113}Cd (both have $I = {}^1/_2$). The inset shows a set of satellite lines with the spectrometer gain increased by a factor of 10. (b) Spectrum of **5** ($M^{n+} = Sc^{3+}$) in which the triplet of triplets associated with the uncomplexed radical is further split by interaction with ^{45}Sc ($I = {}^7/_2$). (c) Spectrum of **5** ($M^{n+} = La^{3+}$) showing interaction with ^{139}La ($I = {}^7/_2$).

satellites. We therefore feel that a negative value for ρ_3 can be discounted.[27]

Spin Densities in Metal Complexes of *o*-Benzosemiquinone. The inclusion of diamagnetic metal ions (10^{-3}–10^{-1} M) in the catechol solution resulted in the appearance of a new radical spectrum, characterized by altered proton couplings and a lower g value, attributable to the corresponding metal complex (**5**). In spectra are shown in Figure 3. The ESR spectrum of the complex was generally much more intense than that of the uncomplexed radical. The tripositive metal ions and Zn^{2+} and Cd^{2+} gave higher concentrations of complexed radicals than did the group 2A metal ions, consistent with the weaker complexing abilities of the latter ions. Magnetic parameters for all the species detected are given in Table I, which also includes the effective ionic radius (r) taken from the data of Shannon and Prewitt[28] and calculated values of charge/ionic radius (z/r) for each ion. The empirical radii of Shannon and Prewitt are generally felt to represent the best estimates of ionic sizes currently available. Most probable (Ladd) radii[29] also are widely used, but these are not available for all the metal ions employed in this study. The radii given in Table I are for a coordination number of 6.[30] Where comparisons can be made, there is generally quite good agreement between the data reported here and those reported earlier.[1,2]

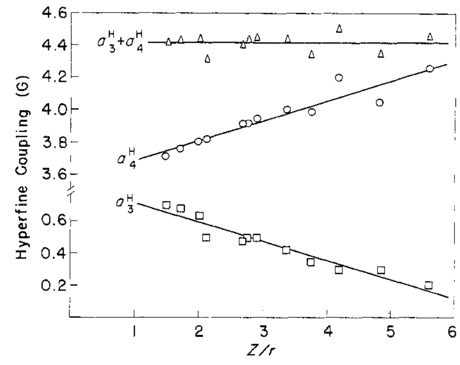


Figure 4. Correlation of proton hyperfine splittings in metal complexes of *o*-benzosemiquinone with the polarizing power of the metal ion (data taken from Table I): (□) a^H_3; (○) a^H_4; (Δ) $a^H_3 + a^H_4$.

Table II. ^{13}C Data and Calculated Spin Densities for *o*-Benzosemiquinone and Metal Chelates

metal ion	a^C_3, G[a]	a^C_4, G[b]	ρ_1	ρ_3	ρ_4	ρ_0
none	3.35	2.40	0.183	0.026	0.127	0.164
Ba^{2+}	3.50	2.47	0.185	0.024	0.129	0.160
Sr^{2+}	3.65	2.55	0.192	0.024	0.132	0.152
Mg^{2+}	3.95	2.90	0.193	0.017	0.136	0.154

[a] Taken to be negative (see text). [b] Taken to be positive (see text).

Several general points can be made: (i) upon complexation $a^H_{4,5}$ increase while $a^H_{3,6}$ decrease; (ii) the sum of the proton hyperfine couplings changes very little and is thus almost independent of the complexing metal ion; (iii) the changes in hyperfine couplings that occur depend on the ionic radius of the metal ion; (iv) for metal ions having the same ionic radius, the tripositive ions are more effective than the bipositive ions in modifying the hyperfine couplings. Moreover, points iii and iv can be combined in a more general statement—changes in hyperfine couplings depend on the ratio of the charge to the ionic radius for the metal ion. Thus Zn^{2+} and La^{3+}, which have very similar values of z/r, have almost identical proton hyperfine couplings. Figure 4, in which a^H_3, a^H_4, and their sum ($a^H_3 + a^H_4$) are plotted against z/r for all the metal complexes studied, shows a linear correlation of both a^H_3 and a^H_4 and z/r, while the sum is practically invariant. (Qualitatively similar, but slightly less linear, plots are obtained if one uses Pauling radii[31] rather than Shannon and Prewitt radii.) From Figure 4, a^H_3 and a^H_4 may be expressed as follows:

$$a^H_3 = 0.84 - 0.120z/r$$

$$a^H_4 = 3.55 + 0.127z/r$$

With few exceptions, for a metal ion with given z/r, these expressions allow the estimation of hyperfine couplings to within ±0.05 G of the experimental values.

Another correlation that can be made, although a less general one, is between the hyperfine couplings and the heat of hydration of the metal ion. This correlation is less general since it is not possible to obtain a smooth correlation that includes both dipositive and tripositive metal ions. However, for dipositive ions Eaton obtained[1] a smooth curve by plotting the ratio of the proton hyperfine couplings (a^H_4/a^H_3) against the heat of hydration for these ions. In fact, from the data in Table I and hydration energy data,[32] it can easily be shown that a^H_3 and a^H_4 each show a linear

---

(27) If a^C_4 = +3.35 G, another potential alternative is for a^C_1 to be ±2.49 G and a^C_6 too small to be measured in this experiment. However, this possibility can be ruled out since small values of a^C_3 require large negative values of ρ_1 and large positive values of ρ_0, which are incompatible with values for a^C_1 as small as 2.40 G.

(28) R. D. Shannon, *Acta Crystallogr. Sec. A*, **A32**, 751–767 (1976); R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B.*, **B25**, 925–946 (1969).

(29) M. F. C. Ladd, *Theor. Chim. Acta*, **12**, 333–336 (1968).

(30) Corrections for coordination numbers other than 6 should be relatively small. For example, a change in coordination number from 6 to 8 is estimated to increase the effective ionic radius of La^{3+} from 1.03 to 1.16 Å.[28]

(31) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., Interscience, New York, 1980, p 14.

Table III. Hyperfine Couplings to Metal Ions in Metal Complexes of *o*-Benzosemiquinone

metal ion, M^{n+}	z/r^a	a^M, G	A^M, G^b	$\rho^{M,c}$ %
$^{27}Al^{3+}$	5.61	2.37	468	0.50
$^{45}Sc^{3+}$	4.11	2.25	718	0.31
$^{89}Y^{3+}$	3.33	0.67	286	0.23
$^{67}Zn^{2+}$	2.68	1.40	622	0.22
$^{69}Ga^{3+}$	4.84	5.05	2260	0.22
$^{71}Ga^{3+}$	4.84	6.42	2880	0.22
$^{115}In^{3+}$	3.75	7.10	3556	0.21
$^{139}La^{3+}$	2.91	2.50	1383	0.18
$^{111}Cd^{2+}$	2.11	6.79	5137^d	0.14
$^{113}Cd^{2+}$	2.11	7.11	5137^d	0.14

[a] Values from Table I. [b] Hyperfine splitting in the ion $M^{(n-1)+}$, taken from the tabulation in ref 37. [c] *s*-orbital spin population, assuming that $A^M \approx Q_M$ (see text). [d] Separate splittings for the two isotopes not measured.

dependence on the heat of hydration of dipositive ions. That the data show a dependence on both $1/r$ and the heat of hydration is not unexpected since for ions of the same charge, heats of hydration are generally inversely related to ionic radius.[33]

Since the effect of complexation is evidently to increase ρ_4 and decrease ρ_3, one would predict that in the complexes $a^C{}_4$ would be more positive and $a^C{}_3$ more negative; i.e., these hyperfine splittings should both increase relative to the uncomplexed ion. Consistent with this, we find that the two measurable ^{13}C couplings both increase in magnitude in those complexes (Ba^{2+}, Sr^{2+}, and Mg^{2+}) where they could be measured easily (Table II). In addition, using eq 2–5 with the further assumption (see below) that the amount of spin density on the metal ion is extremely small and can be neglected, one can obtain spin densities at all eight carbon and oxygen atoms in the same way as for the uncomplexed radical. The spin densities calculated in this way for the various atoms in the complexes are given in Table II. The effect of complexation is then seen to involve changes in spin density at all eight positions. Spin density on oxygen is reduced while that on the carbonyl carbon increases; $\rho_1 + \rho_0$ remains approximately constant.

Hyperfine Couplings to Metal Ions. Hyperfine couplings, a^M, were observed from all the major magnetic isotopes of the group 2B, 3A, and 3B metal ions studied (Table III). This confirms that complexation is occurring, with some transfer of spin density from the ligand onto the metal ion. Since the equivalence of the two sets of protons is not lost, the metal ion is evidently not localized on one of the oxygens, as has been observed in some related organometallic complexes at reduced temperature.[34]

As with complexes of the alkali metals the hyperfine couplings may be expressed in the form[35] $a^M = Q_M\rho^M$, where ρ^M is the s-orbital spin population and Q_M is the hyperfine splitting of an electron in the outermost populated s orbital of the ion. Approximate values of Q_M can be obtained by calculation from wave functions or from experimental data for the appropriate ion immobilized in a matrix. However, experimental values of hyperfine splittings in metal ions, A^M, can be expected to depend on the covalency of the environment in the matrix and also on the symmetry of the site, which may allow the admixture of non-s orbitals into the orbital of the unpaired electron and thereby decrease s-orbital spin population, so that in general $A^M < Q_M$. Theoretical estimates of Q_M are limited,[36] so we have compared our data with experimental values of A^M taken from the compilation by Morton and Preston.[37] If one assumes that $A^M \approx Q_M$, then one can estimate ρ^M. Despite the approximations inherent in this approach, it is clear that values of ρ^M are very small, ranging from ca. 0.14% (Cd^{2+}) to 0.50% (Al^{3+}). With the exception of Ga^{3+} and In^{3+}, these values also correlate reasonably well with the polarizing power of the metal ion, as might be expected.

Estimation of hyperfine interactions from nuclear moments (or vice versa) is usually only of limited accuracy because of complications in theoretical analysis and lack of precision in electronic wave functions. For a given gyromagnetic ratio, we find that the experimental hyperfine couplings in the complexes studied generally increase with increasing atomic number (data not shown).

We were unable to detect hyperfine splittings from group 2A metal ions, which in fact assisted in the resolution of the ^{13}C hyperfine splittings in their complexes. The reason for this appears to be that there is weak association[38] between the radical and the metal ion, so that the residence time of the metal ion in the complex, τ_M, is quite short. Since the hyperfine splitting expected for the metal ion in, for example, the Mg^{2+} complex, is of the order of 0.4 G (cf. data for semidiones[4]),[39] i.e., ~1 MHz, τ_M must be less than ca. 10^{-6} s. Where metal ion couplings are observed, τ_M is evidently much longer; i.e., there is strong association[38] between the metal ion and the radical.

As with other metal complexes,[2,4,8,40] the *g* value decreases upon complexation, consistent with spin density in a vacant metal orbital.[41] The effect is largest for the heaviest atoms studied (La^{3+} and In^{3+}).

Discussion

The data reported here appear to settle the question of the magnitudes and signs of the spin densities in *o*-benzosemiquinone. The data are fully consistent with $|\rho_4| > |\rho_3|$, with both ρ_4 and ρ_3 positive. One may note that of the theoretical calculations carried out so far, the magnitudes of the spin densities obtained in this work are quantitatively reproduced only by the unrestricted open-shell calculation of Kuwata and Shimizu.[2]

The variation of the proton splittings in the semiquinone anion upon complexation is caused by a metal-ion-induced redistribution of the π-electron spin density. Upon complex formation one expects the oxygen atoms in the semiquinone to be more electronegative than in the uncomplexed species, an effect similar to that of solvation.[41] By analogy with the solvation model of Gendell et al.,[42] it was proposed[1] that one can account for the changes in proton hyperfine splittings with metal ions on a similar basis, i.e., by allowing the effective electronegativities of the oxygen atoms to vary. This factor can be introduced into spin density calculations by varying the Coulomb integral. As indicated earlier, Hückel molecular orbital calculations using this approach qualitatively reproduced this experimental pattern,[43] giving increases in ρ_4 and related decreases in ρ_3 so that $\rho_4 + \rho_3$ remains essentially constant as is found experimentally. The correlation of the hyperfine splittings with z/r is consistent with the view that the main effect of the complexing metal ion is Coulombic in origin.

Similarities between solvation and complexation are also apparent from the ^{13}C data, which shows that complexation, like solvation, has the effect of reducing spin density on oxygen while increasing spin density at the carbonyl carbon.[42] For example, for *p*-benzosemiquinone in ethanol–water and DME, it was found that the total spin density on these two atoms is essentially the same in the two solvents,[25] and one may infer from the data of Pedersen and Spanget-Larsen[21,22] that this is also the case for

---

(32) A listing of heats of hydration is given by D. R. Rosseinsky, *Chem. Rev.*, **65**, 467–490 (1965).

(33) J. E. Huheey, "Inorganic Chemistry", 2nd ed., Harper and Row, New York, 1978, p 93.

(34) N. A. Malysheva, A. I. Prokof'ev, S. P. Solodovnikov, N. N. Bubnov, and M. I. Kabachnik, *Bull. Acad. Sci., USSR, Div. Chem. Sci. (Engl. Transl.)*, **28**, 933–938 (1979).

(35) H. Nishiguschi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *J. Chem. Phys.*, **40**, 241–242 (1964); *Mol. Phys.*, **9**, 153–161 (1965).

(36) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967, p 21.

(37) J. R. Morton and K. F. Preston in "Landolt-Börnstein New Series, Group II, Vol. 9, Part A", H. Fischer and K.-H. Hellwege, Eds., Springer-Verlag, Berlin, 1977, pp 5–289.

(38) F. Gerson, "High Resolution E.S.R. Spectroscopy", Wiley, New York, 1970, p 137.

(39) See also the Discussion.

(40) J. W. M. DeBoer, K.-S. Chen, Y.-C. Chang Chung, and J.-K.-S. Wan, *J. Am. Chem. Soc.*, **101**, 5425–5427 (1979).

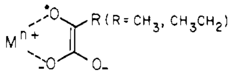
(41) Reference 36, pp 11–12.

(42) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832–2841 (1962).

(43) See Figure 7 of ref 1.

o-benzosemiquinone in DMF–water mixtures, since $\rho_4 + \rho_3$ (and therefore $\rho_1 + \rho_0$) is practically constant in their systems.

The hyperfine couplings to metal ions measured in this study may be compared with those measured[4] for semidiones from α-keto acids (**6**). For the ions Zn^{2+}, Al^{3+}, and La^{3+}, the hyperfine splittings in **5** are in each case about 50% greater than in the semidione (**6**), indicating slightly greater s-orbital spin population in the semiquinone. Couplings to group 2A metal ions Be^{2+} and Mg^{2+} in **6** are reported to be 0.3 G. However, we were unable to observe these couplings, which we would expect to be 0.4–0.5 G in the group 2A metal ion complexes of the *o*-semiquinone. This suggests that there is stronger association of the metal ion with the keto acid semidiones than with *o*-semiquinone, so that the residence time of the metal ion in the semidione complex is long enough for the coupling to the metal ion to be observed.



6

The similarity between the couplings that we find at around neutral pH with those obtained in alkaline solution[1] suggest that the spectra are not very sensitive to hydrolysis of the metal ion, which must occur at high pH; i.e., whether the additional ligands to the metal ion are H_2O or OH^- does not appear to greatly influence the spin distribution.

Finally, it is notable that the hyperfine splitting to ^{111}Cd in the cadmium complex of *o*-benzosemiquinone (7 G) is larger than that estimated for cadmium complexes of free radicals in natural melanin from bovine eyes (ca. 3.2 G).[8] The reason for this may be that the melanin free radicals, although evidently possessing an *o*-semiquinone structure (complexation would not otherwise occur), are largely derived from units of 5,6-dihydroxyindole,[44] in which case they might be expected to possess rather less spin density in the *o*-semiquinone moiety.

Acknowledgment. This work was supported by National Institutes of Health Grants AM-26950, GM-29035, and 5-P41-RR01008.

Registry No. 1 (anionic radical), 20526-43-6; Mg, 7439-95-4; Al, 7429-90-5; Ca, 7440-70-2; Sc, 7440-20-2; Zn, 7440-66-6; Ga, 7440-55-3; Sr, 7440-24-6; Y, 7440-65-5; Cd, 7440-43-9; In, 7440-74-6; Ba, 7440-39-3; La, 7439-91-0; *o*-benzosemiquinone, 583-63-1; catechol, 120-80-9.

---

(44) R. A. Nicolaus, "Melanins", Hermann, Paris, 1964, p 90.

(45) **Note Added in Proof**: We note that our assignments of ^{13}C hyperfine couplings in *o*-benzosemiquinone differ from the tentative assignments made for this radical in another solvent system (M. Brustolon, L. Pasimeni, and C. Corvaja, *J. Chem. Soc., Faraday Trans. 2*, 193–200 (1975)).

Stereoselective Cyanation of Vinyl Halides Catalyzed by Tetracyanocobaltate(I)

Takuzo Funabiki,* Hiroaki Hosomi, Satohiro Yoshida, and Kimio Tarama

Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received July 3, 1980*

Abstract: Tetracyanocobaltate(I), $[Co(CN)_4]^{3-}$, which is formed in an aqueous alkaline solution under a hydrogen atmosphere, catalyzes the cyanation of vinyl halides to form 2-alkenenitriles. The reaction is stereoselective, forming nitriles with retention of configuration, except for (*Z*)-2-bromobut-2-ene, which forms a mixture of nearly equimolar isomeric nitriles. Reactivity is dependent on the CN:Co ratio and is highest when the ratio is slightly lower than 5:1. Presence of excess cyanide ion inhibits the reaction, but a dropwise addition of the KCN solution to maintain CN:Co $\lesssim$ 5:1 is effective for the cyanation of a large excess of vinyl halides. σ-Vinyl complexes, $[\sigma\text{-vinyl-}Co(CN)_5]^{3-}$, were detected as intermediates by ^1H and ^{13}C NMR spectroscopy, indicating that the reaction proceeds stepwise. In the first step, the σ complex is formed by the oxidative addition of a vinyl halide to $[Co(CN)_4]^{3-}$ via a radical nonchain process; in this step stereoselectivity is determined. In the second step, which is rate determining, a 2-alkenenitrile is formed by the reductive coupling of the vinyl and cyano ligands, regenerating $[Co(CN)_4]^{3-}$. Clear NMR evidence has been obtained for the formation of $[\pi\text{-olefin-}Co(CN)_4]^{3-}$, where the olefin is (*E*)- or (*Z*)-cinnamonitrile. A high degree of electron transfer from $[Co(CN)_4]^{3-}$ to olefin was indicated by the large upfield shifts of the olefinic carbon atom resonances by coordination.

Since α,β-unsaturated nitriles serve as versatile intermediates in organic synthesis, efforts have been made to develop new methods of synthesis of the nitriles. Stereoselective cyanation of vinyl halides is one of the useful reactions developed in the last decade.[1] Some metal cyanides such as $NaCu(CN)_2$,[2] CuCN,[3] and $K_4Ni(CN)_6$[4] are known to be effective for stoichiometric synthesis of cinnamonitriles from β-bromostyrenes at elevated temperatures. Recently, Yamamura and Murahashi[5] reported that $Pd(PPh_3)_4$–KCN–crown ether catalyzed the cyanation of not only bromostyrenes but also alkenyl halides such as $C_4H_9CH{=}CHBr$ in benzene. However, no mechanistic study has been performed with these catalysts.

Pentacyanocobaltate(II), $[Co(CN)_5]^{3-}$, has been of interest for its high reactivity with various organic and inorganic substrates, but it has not been used as a catalyst for the synthesis of nitriles despite the complex having cyano ligands. Nitriles were formed by the decomposition of alkyl-, aryl-, and vinylpentacyanocobaltate(III) with acid and base,[6] but the reaction is far from being synthetically useful. We show here that cyanocobaltate is

---

(1) (a) hydrocyanation of diolefins, e.g.: Albanese, P.; Benzoni, L.; Carnissio, G.; Crivelli, A. Italian Patent 869 900, 1970 (Chem. Abstr. **1973**, *78*, 135 701k). (b) Oxycyanation of olefins, e.g.: Nakajima, H. Japanese Patent 74 33 930, 1974 (*Chem. Abstr.* **1975**, *82*, 155 416g). (c) Peichucki, C. *Synthesis* **1974**, 869–870. (d) Loupy, A.; Sogadji, K.; Seyden-Penne, J. *Ibid.* **1977**, 126–127. (e) Tanaka, K.; Ono, N.; Kubo, Y.; Kaji, A. *Ibid.* **1979**, 890–891. (f) DiBiase, S. A.; Gokel, G. W. *Ibid.* **1977**, 629. (g) D'Incan, E.; Seyden-Penne, J. *Ibid.* **1975**, 516–517. (h) Westmijze, H.; Vermeer, P. *Ibid.* **1977**, 784–785. (i) Traas, P. C.; Takken, H. J.; Boelenes, K. *Tetrahedron Lett.* **1977**, 2027–2030. (j) Ono, N.; Tamura, T.; Hayami, J.; Kaji, A. *Ibid.* **1978**, 763–764. (k) Moriconi, E, J.; Jalandoni, C. C. *J. Org. Chem.* **1970**, *35*, 3796–3800. (l) Wilt, J. W.; Ho, A. J. *Ibid.* **1971**, *36*, 2026–2027. (m) Descamps, B.; Lefebre, G.; Seyden-Penne, J. *Tetrahedron* **1972**, *25*, 4209–4222. (n) Uemura, S.; Miyoshi, H.; Wakasugi, M.; Okano, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 553–554. (o) Uemura, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* **1980**, *194*, 277–283.

(2) House, H. O.; Fischer, W. F. *J. Org. Chem.* **1969**, *34*, 3626–3627.

(3) Lapouyad, R.; Deney, M.; Lapenue, M.; Bouas-Laurent, H. *Bull. Soc. Chim. Fr.* **1973**, 720–721.

(4) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233–1234.

(5) Yamamura, K.; Murahashi, S. *Tetrahedron Lett.* **1977**, 4429–4430.

(6) (a) Kwiatek, J.; Seyler, J. K. *J. Organomet. Chem.* **1965**, *3*, 433–437. (b) Kwiatek, J. *Catal. Rev.* **1967**, *1*, 38–72. (c) Johnson, M. D.; Tobe, M. L.; Lai Y. W. *J. Chem. Soc. A* **1967**, 491–497; **1968**, 923–928; 929–933.

0002-7863/82/1504-1560$01.25/0