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Electron Transfer from Rieke Cadmium Yielding Cd^{2+} Coordinated and Ion Associated Anion Radical Systems

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The very reactive Rieke cadmium metal was allowed to react under vacuum with benzoquinone in tetrahydrofuran. This resulted in the formation of several different paramagnetic species whose EPR spectra prove them to have doublet multiplicities. The tetrahedral coordination sphere of each of these species consists of three THF molecules and an anion radical that is either asymmetrically coordinated or symmetrically coordinated to the metal dication. This latter species yields a ^{111}Cd hyperfine splitting of 6.86 G. The second anion radical lies outside this coordination sphere, and it can be either asymmetrically ion associated with or dissociated from the tetrahedral metal complex. All species have the general formula $[Cd(C_6H_4O_2^{\bullet-})(THF)_3]^+,C_6H_4O_2^{\bullet-}$ or $\{[Cd(C_6H_4O_2^{\bullet-})(THF)_3]^+ + C_6H_4O_2^{\bullet-}\}$.

Some of the simplest organometallic compounds are produced by electron transfer from a metal to an organic acceptor, resulting in the formation of the ion-paired charge transfer cation−anion radical complex.[1] Arguably more has been learned about ion association via EPR studies of these species than through any other empirical technique.[1] The interaction between a paramagnetic organic anion and an alkali metal can lead to a breaking of the symmetry of the anion radical due to localization of the cation on one end of the anion,[2] line width effects due to the dynamic repositioning of the cation relative to the anion radical,[3] or actual hyperfine splitting from the interaction of the odd electron in the anion with the intimately associated cation.[4]

These EPR studies of anion radical−metal complexes resulting from electron transfer from metals have been limited (for the most part) to anion radicals involving the alkali metals and alkaline earth metals. While aluminum amalgams have been used to reduce *o*-bis(polymethylbenzoyl)benzenes,[5] the only such transfers of s electrons to an organic substrate have involved the alkali or alkaline earth metals. Now, we wish to report the electron transfer from a very active form of the $d^{10}s^2$ transition metal (Cd) yielding a series of novel anion radical−metal complexes with doublet multiplicities. The anion radicals which are generated are found both within the coordination sphere and outside the coordination sphere (ion associated or unassociated) of the central Cd^{2+}, and the structures of the resulting complexes are particularly well revealed by their respective EPR spectra.

Experimental Section

In a typical experiment cadmium iodide (6 mmol) was placed into bulb B of the apparatus shown in Figure 1. Bulb A was charged with 12 mmol of naphthalene, and tube D was filled with 20 mmol of sodium metal and sealed at point 2. Tube C was charged with 15 mmol of benzoquinone ($C_6H_4O_2$) and sealed at point 3. The entire apparatus was then evacuated, with the naphthalene and benzoquinone maintained at −78 °C. The lower stopcock was closed and the $C_6H_4O_2$ was allowed to sublime into tube E, which was also maintained at −78 °C. The sodium metal was distilled into bulb A, and tubes C and D were sealed from the apparatus at points 1 and 5. About 25 mL of tetrahydrofuran (THF) was then distilled from storage over NaK_2 into bulb A, the upper stopcock was shut, and the apparatus was removed from the vacuum line. The naphthalene anion radical solution that resulted from the contact of the THF-solvated naphthalene and the freshly distilled sodium mirror was poured into bulb B containing the group IIB metal iodide. This resulted in the formation of the very active Rieke[6] metal ($CdI_2 + 2C_{10}H_8^{\bullet-},Na^+ \rightarrow Cd^0 + 2C_{10}H_8 + 2I^-,Na^+$). This active metal was allowed to settle to the bottom of the solution, and the liquid was decanted into bulb A. The solid metal was then washed several times with THF (distilled from bulb A) to remove any remaining sodium iodide, naphthalene anion radical, etc. About 20 mL of THF was then distilled into bulb B containing the active metal. After the sealing of bulb A from the rest of the apparatus at point 4, the lower stopcock was opened, and the cadmium slurry was poured over the previously sublimed benzoquinone in tube E. A sample of the resulting anion radical mixture was then poured into the EPR sample tube, which was sealed from the apparatus and submitted to EPR analysis.

EPR measurements[7,8] were carried out as previously described on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit. The computer simulations were generated with a Lorentzian line shape.

Results and Discussion

When a solution of benzoquinone in THF was exposed to freshly prepared Rieke cadmium under high vacuum, the green anion radical of benzoquinone was immediately formed. The composite EPR spectrum of such a solution reveals the presence of several doublet species which contribute much more complexity than that of the normal five-line pattern that is typically obtained for the benzoquinone anion radical. This anion radical ($C_6H_4O_2^{\bullet-}$) when free of ion association yields an EPR spectrum that results from the electron interacting with four equivalent protons ($a_H = 2.4$ G).[9] Careful analysis of the composite EPR pattern shown at the top of Figure 2 reveals that it essentially consists of the spectra from five different anion radicals

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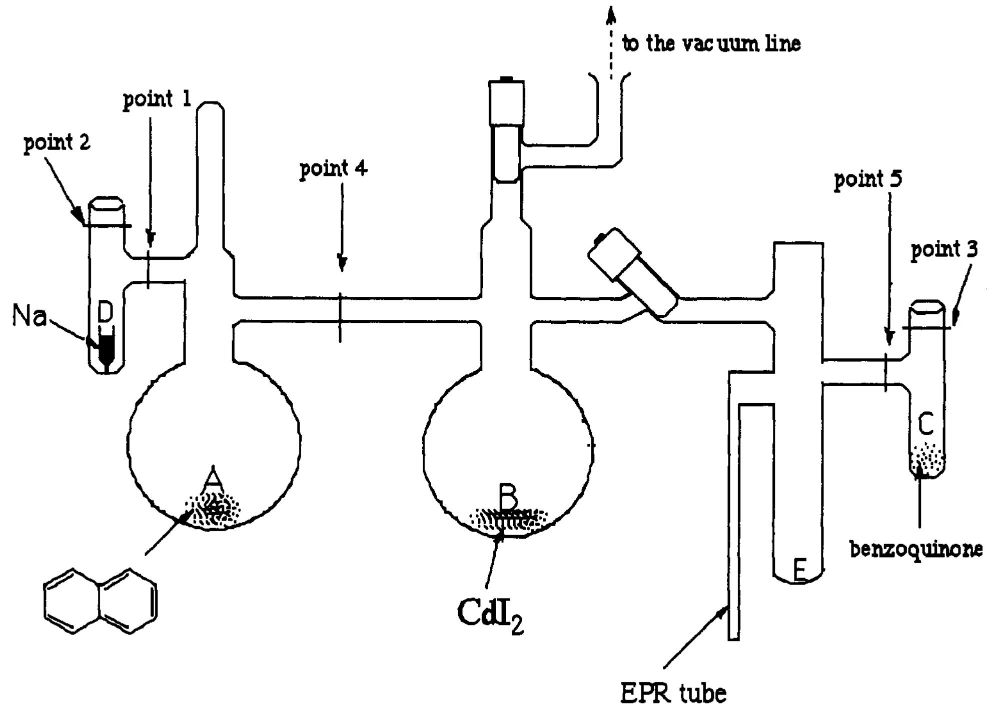
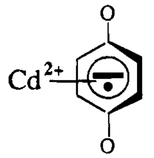


Figure 1. Apparatus used for the generation of the benzoquinone anion radical via electron transfer from cadmium metal.

superimposed upon one another. Simulations of each of these five spectra are shown in Figure 3.

Among contributions to this spectrum is a five-line pattern which reflects an a_H that is 45% smaller in magnitude (Figure 3A) than that of the free anion radical. This clearly means that this benzoquinone anion radical is strongly coordinated in a symmetrical fashion to Cd^{2+}, and the relatively small a_H (1.33 G) means that a significant portion of the spin density resides on the metal dication. Although ^{111}Cd and ^{113}Cd have a spin of $^1/_2$, most of the naturally occurring isotopic abundance of Cd does not have a nuclear spin. Hence, the simple decrease in a_H from that in the free anion radical is the expected result from the symmetrical complexation of the benzoquinone to these nonspin isotopes of Cd^{2+}, and a complex containing the fragment described in structure **I** accounts for this result.

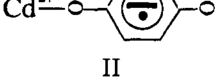


I

The presence of the fragment shown in structure **I** requires that a similar fragment containing the 111 and 113 isotopes of cadmium also be present. These two isotopes have very similar magnetic moments (−0.5943 and −0.6217 nuclear magnetons, respectively) and would give rise to species exhibiting a *pair* of pentets due to the presence of cadmium with spin. Species giving rise to such (superpositioned) spectra are, indeed, present and exhibit an average a_{Cd} of 6.86 G (Figure 3B). The small coupling constant difference between the two isotopic isomers is unresolved and simply contributes to the line width.

The large drop in the a_H from that of the free ketyl indicates that p spin density has shifted away from the quinone ring. Where has it gone? The small a_{Cd} means that the Cd valence s spin density is small; thus p spin density has moved to the Cd p or d orbitals. Are the filled d orbitals (via back-bonding) or are the empty p orbitals participating in the SOMO? This question can be answered, as the spin−orbit coupling constant for an electron in a d orbital is negative while that for an electron in a p orbital is positive. The fact that spectral center for this species is shifted 1.65 G downfield (larger *g* value) from that of the unassociated ketyl suggests that some of this missing spin resides in the Cd d orbitals. This back-bonding yields some d^9 character and a consequently larger observed *g* value. The *g* value of the $4d^9$ Ag^+ ion in liquid solution is 0.131 larger than that for the free electron.[10] The complexity of the many overlapped lines prohibits the detection of any line width variation in single spectral components.

This symmetrical interaction of $C_6H_4O_2^{\bullet -}$ with a counterion is not necessary. Often, simple ion association is asymmetrical, with the counterion localized on one of the oxygen atoms.[11] Such a species is also present, and it accounts for the spectrum shown in Figure 3C. Thus, the composite spectrum in Figure 2 is, in part (41%), due to an anion radical with two different pairs of equivalent protons with a_H's of 1.33 and 3.37 G. In this complex the metal splittings from ^{111}Cd and ^{113}Cd are small and simply contribute to the line width. Thus, only one spectrum resulting from this fragment (structure **II**) is observed.



II

The solvated complexes of Cd^{2+} have a tetrahedral geometry,[12] and in the current case, the remaining three sites are coordinated with the solvent THF. The presence of large amounts of THF allows it to compete favorably with the anion radical for the other three ligand sites. The fact that the EPR spectrum results from doublet as opposed to triplet species means that **probably** only one anion radical is coordinated

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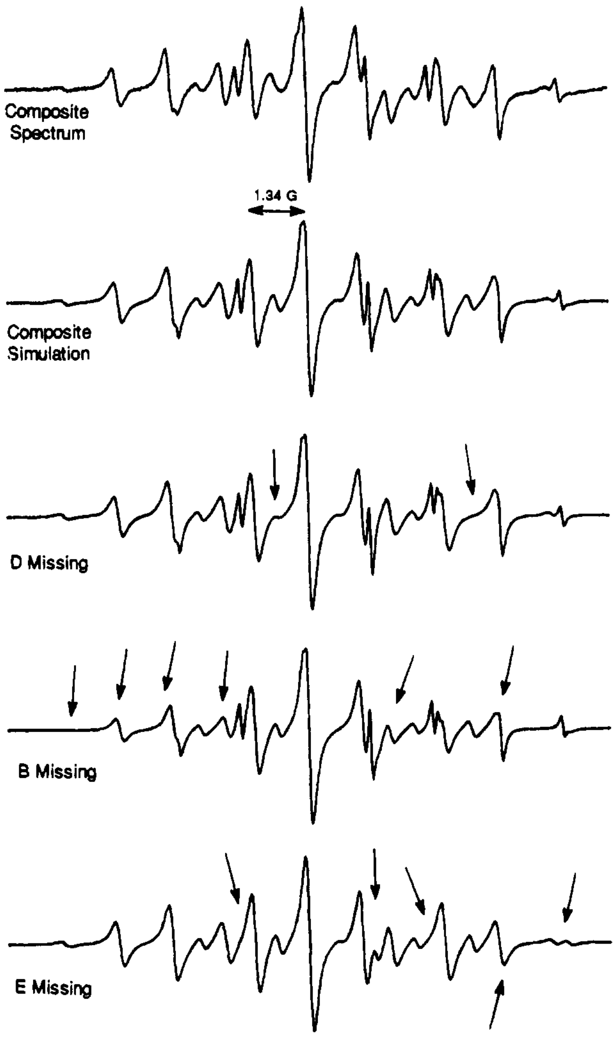

Figure 2. Top: Actual EPR spectrum obtained from the reduction of benzoquinone in THF with cadmium metal recorded at 243 K. This and the other EPR spectra were recorded with a 0.05 G modulation amplitude and a microwave power of 2 mW. Directly below this spectrum is the computer simulation, which includes contributions from all of the species shown in Figure 3. Each of the simulations shown below this composite simulation are missing the contribution from one of the anion radical species. The arrows indicate where the most obvious morphological deviations from the real spectrum occur for these incomplete simulations.

directly to the metal dication and the other is outside this coordination shell. The EPR results **definitely** eliminate the possibility of an $S = 1$ biradical species. The second anion radical could be ion associated to the cation $\{[Cd(C_6H_4O_2^{\bullet -})(THF)_3]^+, C_6H_4O_2^{\bullet -}\}$ or unassociated $\{[Cd(C_6H_4O_2^{\bullet -})(THF)_3]^+ + C_6H_4O_2^{\bullet -}\}$. On the basis of this proposed structure (see Figure 3), the unassociated and asymmetrically externally associated anion radicals should also be present. A simple five-line pattern with an a_H that is close to 2.4 G is to be expected for the unassociated,[9] and it is, in fact, present ($a_H = 2.41$ G, Figure 3D).

The asymmetrically ion associated anion radical is also present. It contributes the spectrum shown in Figure 3E to the composite spectra (Figures 2 and 4). This anion radical would be expected to yield another triplet of triplets, but the degeneracy of the four protons should be split to a lesser degree than in the case where there is direct coordination of the anion radical. This situation is realized, and the species yielding the spectrum in Figure 3E has a_H's of 1.55 and 3.24 G. The dissociated state of the radical yielding the spectrum in Figure 3D is confirmed by the fact that the relative concentrations of the species exhibiting the spectra in Figure 3D,E vary with the total concentration of anion radical; compare Figures 2 and 4. We cannot quantitatively vary the Cd^{2+} and anion radical concentrations, but the time that the quinone solution is exposed to the metal can be varied. The narrow hyperfine components of the spectrum in Figure 3E (Table 1) can perhaps be explained by the absence of two line-broadening mechanisms: (1) spin density modulation to and from an intimate Cd^{2+} ion and (2) the absence of fast intermolecular electron transfer (due to ion association). Ion association is known to greatly attenuate electron transfer rates.[13]

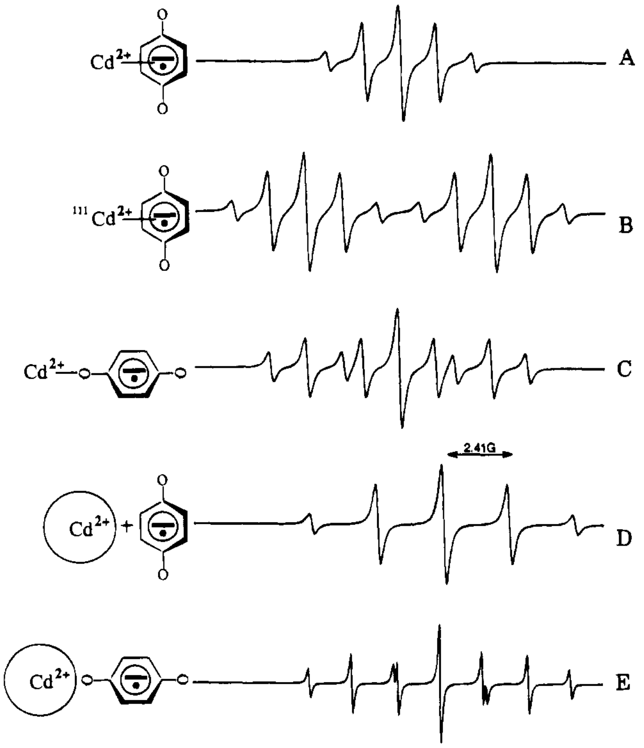

Figure 3. Computer-drawn simulations for each of the anion radical fragments that collectively give rise to the spectrum obtained when benzophenone is reduced in THF with Rieke cadmium. Part B represents both the ^{111}Cd and ^{113}Cd anion radical complexes. ^{111}Cd and ^{113}Cd are the only isotopes of cadmium with a spin, and they account for 25.1% natural abundance. This agrees with the relative amounts of spectra B and A in the composite spectrum (see Figure 4).

Conclusions

All of the species contributing to the composite EPR spectra (Figures 2 and 4) are shown in structures III–VI (Scheme 1) and are keyed to the simulations (Figure 3) of spectra of differently situated benzophenone ketyls. The lower three simulated spectra in Figure 2 express what the morphology of the composite spectrum would be in the absence of selected anion radical species. The parameters for the spectra due to the four compounds are listed in Table 1.

It is proposed that the direct transfer of electrons from metallic cadmium to benzoquinone in THF leads to the four doublet species shown in Figure 3 with their corresponding simulated spectra. In some experiments, the species yielding the spectra in Figure 3D,E (the external anion radicals) account for the same total spin concentration as do the species yielding the spectra in Figure 3A–C (the anion radicals coordinated to the metal center). However, it should be noted here that, in experiments

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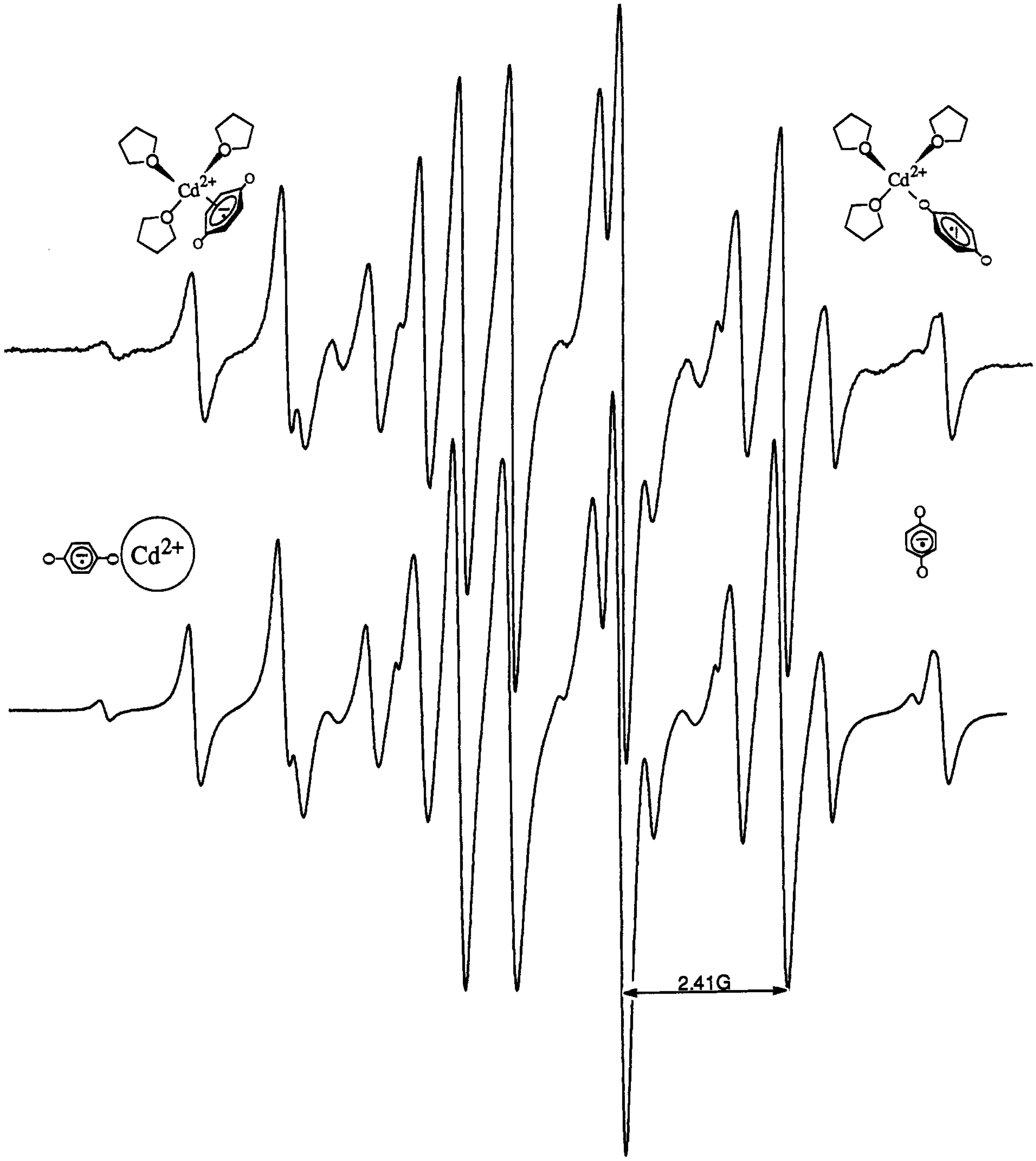
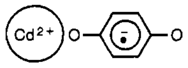
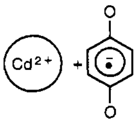
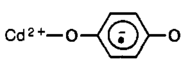
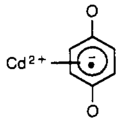


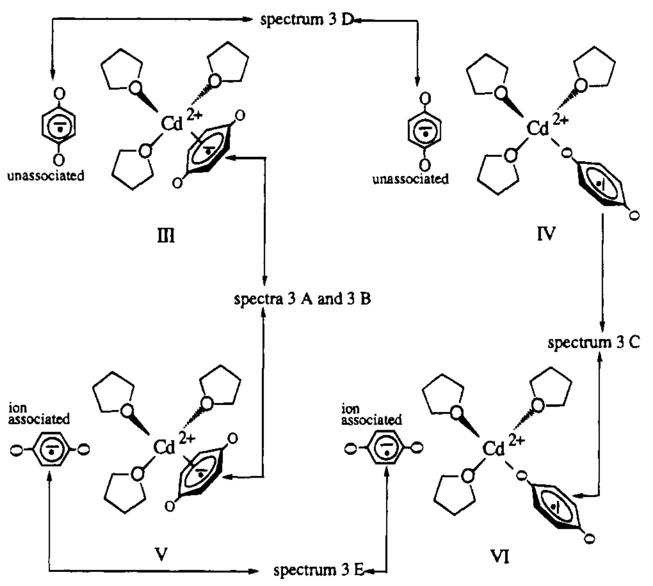
Figure 4. EPR spectrum recorded at 243 K (upper) and computer simulation (lower) of the anion radical of benzoquinone generated via reduction with Cd in THF. The total anion radical concentration is smaller than that in the solution which generated the top spectrum in Figure 2. As a consequence of this, the relative concentrations of the two anion radicals external to the coordination sphere yielding spectra D and E in Figure 3 have changed from 1.0 in Figure 2 to about 0.02 in this figure. Note the reduction in the intensity of the peaks from spectrum E. The composite simulation shown directly below the real spectrum was generated from a mixture of 21% A, 7% B, 28% C, 43% D, and 1% E.

Table 1. Coupling Constants, Peak to Peak Line Widths, Magnetic Field Shifts, and *g* Value Shifts (Δg) Relative to Those for the Unassociated Anion Radical for the Four Differently Coordinated Cadmium Benzoquinone Ketyls[a]

				
a_{Cd}	0	0	0	6.86
a_H	3.24 (2 H) 1.55 (2 H)	2.41 (4 H)	3.37 (2 H) 1.33 (2 H)	1.33 (4 H)
line width	0.09	0.20	0.20	0.20
rel field shift	−0.10	0.00	−1.65	−1.65
Δg	$+5.9 \times 10^{-5}$	0.00	$+9.7 \times 10^{-4}$	$+9.7 \times 10^{-4}$

[a] All parameters are in gauss except Δg, which is unitless. The circle indicates the coordination sphere around the Cd^{2+}.

Scheme 1



yielding higher anion radical concentrations, a single very broad line appears superimposed upon the composite spectrum, and the relative concentrations of the species corresponding to the spectra in Figure 3D,E change (Figures 2 vs 4). A possible explanation is the formation of ion aggregates in which there is very rapid spin–spin exchange of electrons between the externally associated anion radicals. This would decrease the apparent concentration of the species having the spectrum in Figure 3E and give rise to a broad single EPR line representing fast-exchange conditions. The benzoquinone anion radicals are coordinated to Cd^{2+} in a manner that is analogous to the coordination in the ruthenium-bound 2,2′-bipyridine anion radical complexes, which were studied by DeArmond and coworkers.[14]

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