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Cobalt(III) *o*-Semiquinone Complexes

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Received July 28, 1978

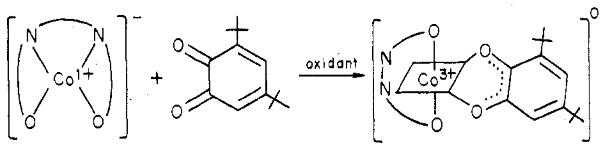
During the course of our work on the preparation of catecholato complexes of cobalt(III)[1] we became interested in the possibility of producing this type of system by oxidative addition of an *o*-quinone to a cobalt(I) species. We have, in fact, obtained a number of cobalt(III) compounds containing a coordinated catecholate dianion by this procedure.[2] However, in the synthesis of a number of cobalt(III) catecholates we obtain, as an additional product, a neutral compound now known to be a cobalt(III) complex of an *o*-semiquinone. It is the purpose of this report to describe the preparation and properties of three cobalt(III) complexes containing one tetradentate ligand and a coordinated 3,5-di-*tert*-butyl-*o*-benzosemiquinone anion. These free radical complexes are rather stable and show the unpaired electron to indeed be localized on the *o*-semiquinone ligand.

The occurrence of *o*-semiquinone complexes is by now well documented. Eaton demonstrated the occurrence of *o*-semiquinone coordination to a number of metal ions in solution.[3] Balch has also demonstrated *o*-semiquinone coordination in solution.[4] Several tris systems containing three *o*-semiquinones are also known.[5] Some of these were originally reported in the literature with a different formulation but have subsequently been characterized as tris(*o*-semiquinone) complexes. These systems are known especially with Fe(III) or Cr(III) in which substantial coupling between ligand and metal electrons occur, leading to unusual and interesting magnetic behavior. This was in part responsible for some delay in recognizing these systems as true examples of *o*-semiquinone coordination. Recent work by Pierpont and Hendrickson has clearly characterized several tris iron(III) and chromium(III) *o*-semiquinone complexes.[6]

Von Zelewsky and Haas have reported in situ observation of a number of *o*-benzosemiquinone and chlorine-substituted *o*-benzosemiquinone complexes similar to those described here.[7] Their systems were prepared by addition of *o*-quinones to a cobalt(II) complex. We have earlier reported a very well-characterized 3,5-di-*tert*-butyl-*o*-semiquinone complex, $[Co(trien)(DBsq)]^{2+}$, which was obtained by oxidation of the corresponding 3,5-di-*tert*-butylcatecholato complex.[8]

Results and Discussion

The reaction scheme shown in eq 1 represents a new method for obtaining cobalt(III) *o*-semiquinone complexes.



(1)

The semiquinone complexes prepared, Co(BAE)(DBsq),[9] Co(F_3BAE)(DBsq),[9] and Co(4,6-$(OCH_3)_2$salen)(DBsq),[9] are all soluble in nonaqueous solvents and form nonconducting solutions. The molecular weight of Co(BAE)(DBsq) has been measured and found to be 500 (theoretical 501.5) providing further evidence for the formulation shown in eq 1. The reaction scheme shown in eq 1 indicates that a one electron oxidation must take place during the course of the reaction to form the product. Since the reaction is carried out in the absence of O_2 the most likely oxidant is the *o*-quinone. Von Zelewsky and Haas have observed similar complexes in situ upon addition of *o*-quinones to a low-spin cobalt(II) complex,[7] thus the product in this reaction may arise from reaction between quinone and cobalt(II). It is also possible in our case that initial reaction between cobalt(I) and the *o*-quinone gives a cobalt(III) catecholato species which then undergoes a one-electron oxidation to the *o*-semiquinone complex.

In order for the *o*-semiquinone ligand to bind to the metal it must occupy cis coordination positions. As a result, the normally near-planar tetradentate ligand is forced to assume a nonplanar orientation. A number of cobalt(III) salen complexes have been reported which contain an additional bidentate ligand.[10] In these cases the configuration depicted in eq 1 has been found (this is the cis-β isomer with respect to the tetradentate ligand). Although definitive structural proof is not available in the complexes described here, the infrared spectra of these complexes have many similarities to the reported infrared spectra of Co(salen)L where L = a bidentate ligand (see Experimental Section).[10] Unfortunately the most interesting aspect of the infrared spectrum, the semiquinone C⩦O stretch which occurs at 1440 cm^{-1} in the $[Co(trien)(DBsq)]^{2+}$ complex ion,[8] is not definitive in these complexes. This is because a rather strong and broad absorption band centered at 1440–1450 cm^{-1} due to the tetradentate ligand overlaps the C⩦O stretch. Nevertheless, the absence of a very strong C=O stretch at 1660 cm^{-1} as well as the lack of a strong C–O stretch around 1250 cm^{-1} indicate the absence of *o*-quinone or catecholate dianion coordination, thus indirectly indicating the presence of the *o*-semiquinone.

The magnetic moment measured for Co(BAE)(DBsq) is 1.79 μ_B, indicating one unpaired electron. Conclusive evidence for the localization of the unpaired electron on the *o*-semiquinone ligand comes from the ESR spectra. Figure 1 shows the ESR spectra of each of the three *o*-semiquinone complexes. Each spectrum shows an eight-line pattern due to coupling with

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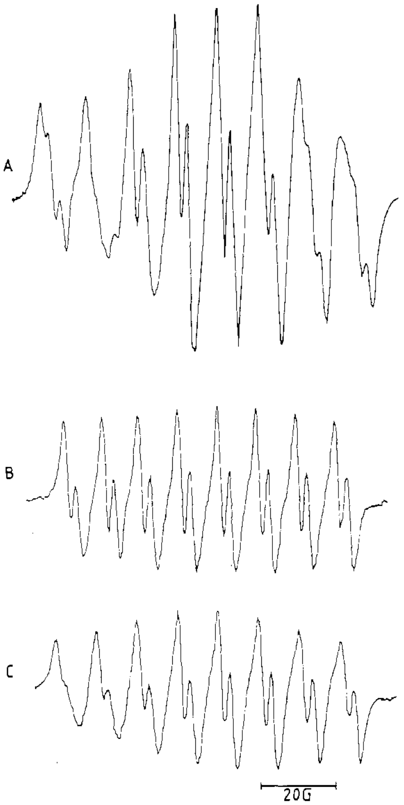

Figure 1. ESR spectra at room temperature in methanol solution for (A) Co(BAE)(DBsq), (B) Co(F_3BAE)(DBsq), and (C) Co(4,6-(OCH_3)$_2$salen)(DBsq).

the ^{59}Co nucleus and an additional splitting to a doublet from the proton at position 4 of the *o*-semiquinone ligand. The hyperfine coupling constants are as follows: Co(BAE)(DBsq), $A_{Co} = 11.7$ G, $A_H \simeq 3.6$ G; Co(F_3BAE)(DBsq), $A_{Co} = 10.2$ G, $A_H \simeq 3.1$ G; Co(4,6-(OCH_3)$_2$salen), $A_{Co} = 10.7$ G, $A_H = 3.1$ G. These cobalt hyperfine coupling constants are in the same range as that which has been previously reported for [Co(trien)(DBsq)]$^{2+}$ and are much smaller than is found for low-spin cobalt(II).[8] In addition, the coupling constants for the proton at position 4 of the *o*-semiquinone ligand are reasonably close to that reported for the free *o*-semiquinone.[11] From these observations it is clear that the unpaired electron is localized predominately on the ligand and that these compounds are correctly formulated as *o*-semiquinone complexes of cobalt(III).

Although the cobalt hyperfine coupling constants are relatively similar for these complexes, the differences are significant and do *not* seem to reflect the relative electron-acceptor power of the cobalt center. For the three ligand systems involved, we expect the relative σ-electron-accepting ability of the cobalt to be Co(F_3BAE) ≥ Co(4,6-(OCH_3)$_2$salen) > Co(BAE). This is based on thermodynamic measurements for adduct formation by five-coordinate complexes containing these ligands which we are currently investigating.[12] If the cobalt hyperfine coupling constants were to reflect the σ-acceptor ability of the cobalt, we would expect A_{Co} to be largest for Co(F_3BAE)(DBsq) and smallest for Co(BAE)(DBsq). Instead, just the opposite trend is observed; A_{Co} varies with the tetradentate ligand as BAE > 4,6-(OCH_3)$_2$salen > F_3BAE. This can be explained by noting that the unpaired electron is primarily in a π orbital of the *o*-semiquinone ligand. If spin is transmitted to the cobalt by cobalt $d\pi \rightarrow$ ligand π back-donation, then the complex with the best electron-donating ligand system, BAE, would have the largest value for A_{Co} as is observed. In this regard, the [Co(trien)(DBsq)]$^{2+}$ ion which we reported earlier is consistent with these ideas.[8] In that complex, which has a formal 2+ charge, the cobalt should be a somewhat more positive center, and we indeed observed a smaller hyperfine coupling constant, 9.8 G, than in any of the neutral complexes reported here. It appears, therefore, that A_{Co} will be larger for complexes in which the counter ligand is a better electron donor.

These complexes add to the growing number of examples of *o*-semiquinone coordination. The means of preparation provides a different method for obtaining a cobalt(III)–*o*-semiquinone system than that which we reported earlier.[8] It is becoming clearer that *o*-semiquinones are rather good ligands which can produce surprisingly stable coordination complexes. In addition, the presence of the free radical ligand also makes these systems of considerable inherent interest.

Experimental Section

The synthesis of Co(BAE)(DBsq) is described completely below; the other complexes were prepared according to the same procedure.

To a solution of 1.15 g (4.08 mmol) of Co(BAE) in 175 mL of deoxygenated THF was added 0.90 g (4.08 mmol) of 3,5-di-*tert*-butylquinone. An intensely green solution was immediately produced which was stirred under nitrogen in the dark for 13 h after which time the THF was removed by rotary evaporation. The residue was dissolved in 30 mL of CH_2Cl_2 and centrifuged to remove suspended material. After carefully decanting the CH_2Cl_2 solution, the solvent was removed under vacuum. The resulting dark blue precipitate was washed with hexane (3 × 5 mL) leaving the desired product (0.25 g). Anal. Calcd for $CoC_{26}H_{38}N_2O_4$: C, 62.3; H, 7.6; N, 5.8. Found: C, 62.2; H, 7.8; N, 4.9. The molecular weight was determined by vapor-pressure osmometry in benzene solution to be 500 ± 20 (calculated 501.5). IR (KBr): 1595 (s), 1580 (s), 1525 (sh), 1512 (s), 1502 (s), 1462 (sh), 1450 (s, b), 1411 (vs), 1368 (sh), 1358 (m), 1325 (m). The magnetic moment at ambient temperature was measured by the Faraday method and found to be 1.79 μ_B. The ESR spectrum was measured on a Varian V4502 spectrometer at room temperature in methanol solution.

Acknowledgment. This work was supported by National Science Foundation Grant CHE7403096A1. D.G.B. is grateful to the Alexander von Humboldt Foundation for the award of a research fellowship for 1978–1979.

Registry No. Co(BAE)(DBsq), 70224-70-3; Co(F_3BAE)(DBsq), 70197-24-9; Co(4,6-(OCH_3)$_2$salen)(DBsq), 70197-25-0; Co(BAE), 35816-74-1.

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