$Ir_2(CO)_6(PPh_3)_2$ is isolated in high yield. Malatesta, Angoletta, and Caglio[9] observed that $Ir_2(CO)_6(PPh_3)_2$ is converted to $Ir_4(CO)_9(PPh_3)_3$ in refluxing benzene, and we have confirmed that the reaction occurs readily in chlorobenzene at 100 °C. Furthermore, Hanlan and Ozin[21] have recently reported that matrix-isolated $Ir_2(CO)_8$, when warmed above −58 °C, is transformed to a bridged form of $Ir_4(CO)_{12}$. These results suggest that reduction of $Ir(CO)_2$(*p*-toluidine)Cl under the conditions described proceeds first to iridium dimers, which then react further to give the final tetranuclear products.

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Registry No. $Ir_4(CO)_{11}PPh_3$, 53565-22-3; $Ir_4(CO)_{11}PMe_2Ph$, 59532-78-4; $Ir_4(CO)_{11}P(p\text{-tol})_3$, 59532-79-5; $Ir_4(CO)_{11}PEt_3$, 59532-80-8; $Ir_4(CO)_{11}P(OMe)_3$, 59532-81-9; $Ir_4(CO)_{11}P(OPh)_3$, 59532-82-0; $Ir_4(CO)_{10}(PPh_3)_2$, 59532-83-1; $Ir_4(CO)_{10}(PMe_2Ph)_2$, 59532-55-7; $Ir_4(CO)_{10}(P(p\text{-tol})_3)_2$, 59532-58-0; $Ir_4(CO)_{10}(PEt_3)_2$, 29132-21-6; $Ir_4(CO)_{10}(P(OMe)_3)_2$, 59532-54-6; $Ir_4(CO)_{10}(P(OPh)_3)_2$, 59532-57-9; $Ir_4(CO)_{10}$(diphos), 59532-56-8; $Ir(CO)_2$(*p*-toluidine)Cl, 14243-22-2; PPh_3, 603-35-0; PEt_3, 554-70-1; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0.

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Preparation and Properties of a Stable Semiquinone Complex

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In a recent article, we reported the synthesis and characterization of a series of cobalt(III) catecholato complexes.[1] Cyclic voltametric studies of those systems indicated that they tend to undergo two one-electron oxidations, the first of which is quasireversible. Therefore, it appeared to us as if a relatively stable one-electron oxidation product might be found. Such a product would very likely contain a coordinated *o*-semiquinone. Of the several systems we have studied we find a rather stable product formed upon oxidation of (3,5-di-*tert*-butylcatecholato)triethylenetetraminecobalt(III) chloride, [Co(trien)(DBcat)]Cl.[2] The oxidation was found to be a *one*-electron oxidation and, as will be shown below, the compound formed is a stable *o*-semiquinone complex, (3,5-di-*tert*-butyl-*o*-benzosemiquinonato)triethylenetetraminecobalt(III) chloride, $[Co(trien)(DBsq)]Cl_2$. The complex has been isolated as a stable solid and fully characterized.

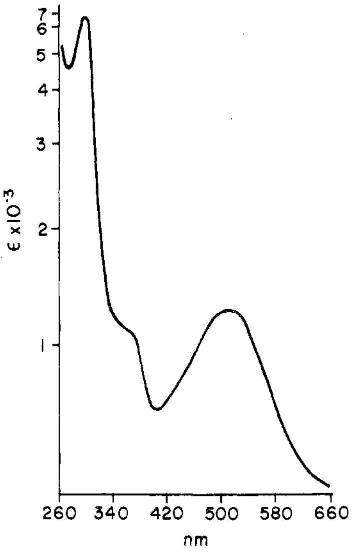

Figure 1. Electronic spectrum of $[Co(trien)(DBsq)]Cl_2$ obtained on an 8.5 × 10^{-4} M solution of the complex in methanol.

Results

The original cyclic voltametric work on [Co(trien)(DBcat)]Cl indicated that a one-electron oxidized species was generated at approximately +0.2 V vs. SCE.[1] Initial attempts to generate this product by chemical oxidation gave a bright red species in solution. The uv–visible spectrum of this species is given in Figure 1. Chemical oxidants which can produce this red complex include Fe^{3+}, Cu^{2+}, Ce^{4+}, and $Pb(OAc)_4$. Spectral titration indicated that when 1 equiv of oxidant had been added, the spectrum shown in Figure 1 was fully formed and additional oxidant caused no appreciable further spectral changes. Thus the intense red species appeared indeed to be the one-electron oxidation product observed in the cyclic voltamograms. Controlled-potential electrolysis at +0.4 V vs. SCE also generated the same species. The observation that the species is a *one*-electron oxidation product was reconfirmed by coulometry.

The fact that this one-electron oxidation product contained a coordinated semiquinone is demonstrated by the ESR spectrum given in Figure 2. The obvious eight-line pattern arises from hyperfine coupling to the cobalt-59 nucleus. This spectrum can be obtained by oxidizing [Co(trien)(DBcat)]Cl with a variety of oxidants, $Pb(OAc)_4$ being the most convenient.

After having generated and characterized this species in solution and observing its stability, we made attempts to isolate it as a pure solid. The complex $[Co(trien)(DBsq)]Cl_2$ has been successfully prepared and isolated by oxidizing [Co(trien)(DBcat)]Cl with hydrogen peroxide in acid solution. The semiquinone complex is isolated as an amorphous red-purple solid. It is soluble in water, methanol, and ethanol and slightly soluble in acetone. Characterization has been accomplished by elemental analysis, conductivity, magnetism, and spectral measurements. The ir spectrum of the complex shows a very

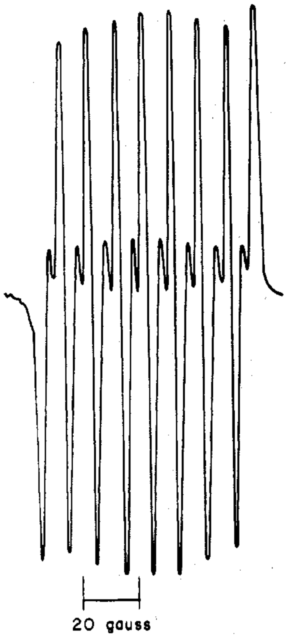

Figure 2. Solution ESR spectrum of [Co(trien)(DBcat)]Cl obtained at 25 °C in methanol solution.

intense band at 1440 cm^{-1} which can be assigned to a C–O stretching vibration of the *o*-semiquinone complex.[1] On the other hand, 3,5-di-*tert*-butyl-*o*-benzoquinone shows a C–O vibration of 1660 cm^{-1}. The uv–visible spectrum of the isolated complex is identical in all respects with the spectrum of the material produced by in situ oxidation of [Co(trien)(DBcat)]Cl, Figure 1. The peak maxima in the visible region occur at 512 nm (ϵ 1270) and 360 nm (ϵ 1145) while the peak maximum in the uv region occurs at 300 nm (ϵ 6680). The ESR spectrum of the isolated complex is also identical in all respects with that given in Figure 2. The molar conductance was found to be 237 Ω^{-1} in water confirming that the complex is indeed a 2:1 electrolyte. The solution magnetic moment was found to be 1.86 μ_B.

Discussion

The ESR spectrum shown in Figure 2. is the most convincing evidence that the complex is correctly formulated as an *o*-benzosemiquinone complex. The eight-line pattern due to ^{59}Co coupling shows a hyperfine coupling constant of 9.76 G. This is a small value compared to the coupling constants found for low-spin cobalt(II) complexes.[3] Additionally, the further splitting due to the proton at C-4 of the *o*-semiquinone ligand shows a coupling constant of approximately 3.5 G which is very close to the hyperfine coupling constant for that proton in free 3,5-di-*tert*-butyl-*o*-benzosemiquinone.[4] Thus the unpaired electron appears to be located largely on the ligand. The position of the C–O stretching vibration (1440 cm^{-1}) is also consistent with this formulation. Therefore, the complex is correctly characterized as containing the 3,5-di-*tert*-butyl-*o*-benzosemiquinone coordinated to cobalt(III) rather than, for example, a quinone coordinated to cobalt(II).

There have been other reports of *o*-semiquinone–metal complexes in the literature. Eaton has reported the ESR spectra of *o*-benzosemiquinone coordinated to a number of metals, primarily non transition metal ions.[5] In that work no complexes were isolated from solution or characterized. Rohrscheid et al. have reported the occurrence of what probably corresponds to coordinated *o*-semiquinone by oxidation of certain bis(catecholato)metal complexes.[6] However, no well-characterized *o*-benzosemiquinone complexes were isolated.

Floriani et al. have reported a series of binary 9,10-phenanthrenequinone complexes of iron, cobalt, and nickel.[7] It appears as if these workers viewed the complexes as quinone complexes of zero-valent metals. However, the C–O stretching vibration in these systems occurs around 1460 cm^{-1}, and based on the work reported here, it seems that Floriani's systems would be more correctly formulated as complexes of the 9,10-phenanthrenequinone and 1,2-naphthoquinone with Fe(salen) which may well be correctly formulated as containing a semiquinone ligand.[8] Balch has reported *o*-semiquinone complexes of tetrahalo-*o*-semiquinones with a number of heavy transition metals.[9] These were prepared and characterized in solution but not isolated.

Of the other cobalt(III) catecholato complexes which we have reported, none gives as stable an *o*-semiquinone complex as the one reported here. This is undoubtedly due to the fact that the bulky *tert*-butyl groups render the *o*-semiquinone ligand kinetically more stable than other *o*-semiquinone ligands. Nevertheless, several of the catecholato complexes show spectra indicating the definite existence of an oxidation product similar to [Co(trien)(DBsq)]Cl$_2$.

Experimental Section

Preparation of Semiquinone Complex. The starting material, [Co(trien)DBcat]Cl, was prepared as described previously.[1] To prepare the semiquinone complex, [Co(trien)(DBcat)]Cl, 1.00 g (2.2 mmol), was dissolved in 100 ml of vigorously deoxygenated 95% ethanol. To this solution was added 0.13 ml (1.1 mmol) of 30% H_2O_2 and 0.18 ml (2.2 mmol) of concentrated HCl. This mixture was allowed to stir under nitrogen for 2 h during which time the solution turned a deep red. After this time the semiquinone complex was obtained quantitatively by evaporation of solvent. The complex was dried under vacuum over P_2O_5.

Physical Measurements. The infrared spectra were obtained as KBr disks on a PE 621 spectrometer. Electronic spectra were measured with a Beckman DB-G. The magnetic moment was determined in aqueous solution by the method of Evans.[10] The ESR spectrum was obtained on a Varian V4502 spectrometer at room temperature in methanol solution.

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Registry No. [Co(trien)(DBsq)]Cl$_2$, 59204-56-7; [Co(trien)(DBcat)]Cl, 57396-04-0.

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Reaction of Superoxide with the Manganese(III) Tetraphenylporphine Cation

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The oxidation of transition metal complexes by dioxygen has been of interest to chemists and biochemists for a long time.[1,2] Nevertheless, the mechanisms of such oxidations are