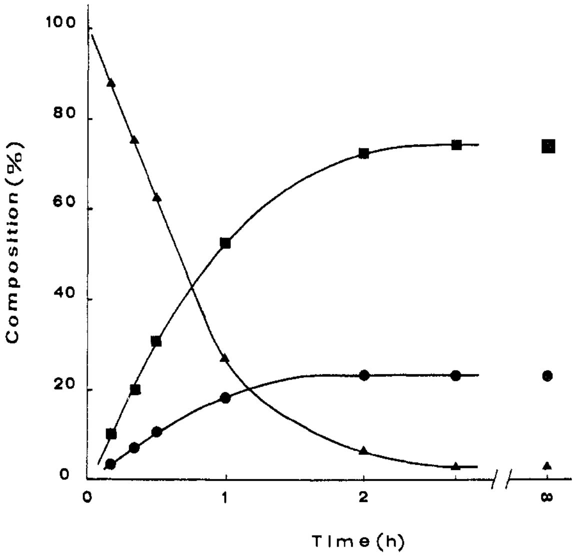

Figure 1. Isomerization of 1-pentene catalyzed by a toluene solution of $Ru_3(CO)_{12}$ in the presence of acetic acid. Variation of composition with time: ▲, 1-pentene; ●, *cis*-2-pentene; ■, *trans*-2-pentene. [Olefin] = 46 m*M*; [complex] = 0.37 m*M*; acetic acid 2.5×10^{-3} v/v solution; temperature = 70.4°C.

almost constant value of the cis/trans ratio, in the range 0.3–0.4, is in agreement with the proposed mechanism. The same mechanism was proved to be operating in the isomerization of 1-pentene with $Fe_3(CO)_{12}$.[2c]

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Registry No. **2**, 56943-14-7; **3**, 56943-13-6; **4**, 21077-76-9; **5**, 34438-91-0; **6**, 56943-12-5; $Ru_3(CO)_{12}$, 15243-33-1; 1-pentene, 109-67-1; CH_3COOD, 758-12-3.

References and Notes

(1) Partially presented at the 167th ACS Meeting, Los Angeles, March 31–April 5, 1974.
(2) (a) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962); (b) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2248 (1973); (c) D. Bingham, B. Hudson, D. E. Webster, and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, 1521 (1974).
(3) O. Gambino, M. Valle, S. Aime, and G. A. Vaglio, *Inorg. Chim. Acta*, **8**, 71 (1974).
(4) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1415 (1974), and references therein.
(5) M. I. Bruce and F. G. A. Stone, *Chem. Commun.*, 684 (1966).
(6) The concentration figure can be slightly different for the solution of **1**, because it could not be obtained as pure sample.
(7) M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 545 (1972).
(8) G. Gervasio, D. Osella, and M. Valle, submitted.
(9) (a) B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 902 (1970); (b) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.*, 447 (1971).
(10) A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **36**, C43 (1972).
(11) A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **43**, C35 (1972).
(12) P. Chini, *Pure Appl. Chem.*, **23**, 489 (1970).
(13) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organomet. Chem.*, **97**, C16 (1975).

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Synthesis and Characterization of Some Cobalt(III) Catechol Complexes

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A number of new cobalt(III) complexes containing one bidentate *o*-dihydroxy aromatic ligand and amine counterligands have been prepared and characterized. The complexes can be prepared by procedures similar to those employed for synthesis of cobalt(III)–amino acid complexes. In addition to normal spectral characterization, a preliminary electrochemical investigation by cyclic voltammetry revealed substantial changes in the properties of the dihydroxyaromatic ligands by virtue of their coordination to the metal.

Introduction

Although the coordination chemistry of catechol and its derivatives has not been studied extensively, these molecules constitute an interesting class of bidentate ligands. The fact that catechol and its substituted derivatives[1] can undergo one- or two-electron oxidations to the *o*-semiquinone or *o*-quinone, respectively, offers the possibility of preparing complexes with unusual oxidation states. A fundamental knowledge of the coordination chemistry of catechol is important for understanding certain biochemical processes. Aromatic dioxygenases normally use some type of catechol derivative as a substrate.[2–7] Since most of the aromatic dioxygenases have a metal ion at the active site (usually iron),[2–11] it is probable that the catechol chelates to the metal during catalysis. Most schematic mechanisms for the action of this class of enzymes include just such a step. Besides developing basic information on the coordination properties of catechol it will be useful to those working in the area of dioxygenase chemistry to know in what ways the chemical properties of the catechol system change upon coordination. Another area of biochemical interest to which catechol coordination chemistry is pertinent is that of certain ferric chelators called siderochromes, in particular, those siderochromes using phenolate ligands. Enterochelin, for example, is a cyclic triester of 2,3-dihydroxy-*N*-benzoyl-L-serine in which the metal binding site is three catechol groups.[12]

There are many reports in the literature of catechol–metal complexes. Most of these are solution studies in which no compounds are isolated. There are also a number of reports in the old literature of catechol complexes with unusual formulations.[13] Röhrscheid et al. have reported preparation and characterization of complexes containing two catecholate or two tetrachlorocatecholate anions.[14] In some cases catechol complexes have been prepared by oxidative addition to low oxidation state metals.[15]

In this paper we report a variety of catechol and substituted catechol complexes of cobalt(III). Our objective was to prepare complexes containing one catechol bound to the metal with counterligands sufficient to complete the coordination sphere. The complexes which have been prepared were characterized and subjected to a preliminary electrochemical study by cyclic voltammetry. This preliminary work indicates that coordination to the metal substantially changes the electrochemical properties of the catechol.

Experimental Section

Materials and Instrumentation. Commercially available catechol, 3,4-dihydroxybenzoic acid, and 3,5-di-*tert*-butylcatechol were used without further purification. *cis*-α-[Co(trien)Cl_2]Cl and *cis*-[Co(en)$_2Cl_2$]Cl were prepared by the methods of Sargeson and Searle[16] and Bailar,[17] respectively.

Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer. The spectra of all complexes were obtained from KBr disks.

Electronic spectra were obtained with either a Cary 14 or a Beckman DB uv visible spectrometer. Spectra of all complexes except those containing 3,5-di-*tert*-butylcatechol were obtained using distilled water as solvent. For the complexes of 3,5-di-*tert*-butylcatechol, 95% ethanol was used as the solvent.

Cyclic voltammograms were obtained with a multipurpose electrochemical scanner described in the literature.[18] Voltammograms were displayed with a Hewlett-Packard 7035B X-Y recorder. All of the cyclic voltammograms were run in quiet solutions utilizing a three-electrode system consisting of a carbon paste working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode.

Preparation of Complexes. In general the procedures employed for preparation of these new complexes were patterned after the synthesis of mixed-ligand–amino acid complexes of cobalt(III).[19] Modifications in the solvents employed for complexes of di-*tert*-butylcatechol were dictated by the insolubility of the ligand and product in water. The complexes of this ligand, however, are soluble in a variety of organic solvents. Because of the instability of catechols to oxygen in basic solution, the syntheses were conducted under a nitrogen atmosphere.

Several of the complexes have been formulated showing water of hydration. In all such cases, vigorous attempts to remove the water were unsuccessful. Many of the complexes showing no water of hydration were initially isolated containing stoichiometric amounts of water but this could be removed by heating under vacuum.

For all the compounds reported, suitable elemental analyses for carbon, hydrogen, and nitrogen were obtained. These are available in tabular form, Table I, in the microfilm edition.

[Co(trien)cat]I. A 1.65-g sample of catechol (0.015 mol) and 4.67 g of *cis*-α-[Co(trien)Cl_2]Cl (0.015 mol) were dissolved in 50 ml of water. To this solution was added, with stirring, 1.2 g of NaOH dissolved in 20 ml of water. The reaction mixture was stirred under nitrogen for 2 hr. After this time, 60 g of NaI was added and the solution was placed in a refrigerator (5°C) overnight. Intensely colored purple crystals formed and were collected by filtration, washed with acetone, and air-dried; yield 4.1 g (63%). Purification was accomplished by recrystallization from 95% ethanol.

[Co(en)$_2$cat]I·H_2O. A 1.65-g sample of catechol (0.015 mol) and 4.27 g of *cis*-[Co(en)$_2Cl_2$]Cl (0.015 mol) were dissolved in 50 ml of water. After addition of 1.2 g of NaOH and 60 g of NaI and cooling as above, intense dark purple crystals were obtained; yield 5.6 g (90%). The complex was purified as above.

[Co(trien)cat]Cl·$^1/_2$$H_2O$. [Co(trien)cat]I was dissolved in a small amount of water and to the solution was added an excess of freshly prepared AgCl. The mixture was stirred for 0.5 hr during which time the cream-colored precipitate AgI formed. The mixture was carefully filtered and the resulting solution was taken to dryness on a rotary evaporator. The recovered solid was dried under vacuum overnight.

[Co(en)$_2$cat]Cl·$^1/_2$$H_2O$. This compound was prepared in the same manner as discussed for [Co(trien)cat]Cl.

[Co(trien)DTBC]I·H_2O. A 0.78-g sample of *cis*-α-[Co(trien)Cl_2]Cl (0.0025 mol) and 0.56 g of 3,5-di-*tert*-butyl catechol (0.0025 mol) were dissolved in 40 ml of 50% ethanol. The solution was deoxygenated by bubbling with nitrogen and 0.3 g of KOH dissolved in 10 ml of 50% ethanol was added dropwise, with stirring. The reaction mixture was stirred under nitrogen for 3 hr, during which time the solution turned very dark green. After this time 15 g of NaI was added. The ethanol was evaporated on a rotary evaporator leaving a pink aqueous solution and a dark tarry residue. This dark residue was dissolved in 50 ml of chloroform. The chloroform solution was then extracted with 20 ml of water containing 15 g of NaI. The chloroform was then evaporated, leaving a dark green solid; yield 1.0 g (70%). The product was purified by dissolving in a small amount of deoxygenated water followed by addition of an equal volume of a 1 *N* NaI solution. This caused precipitation of the pure complex. The final product was washed with ether and dried under vacuum over P_2O_5.

[Co(en)$_2$DTBC]I. A procedure similar to that outlined above was used to prepare this compound. A 0.71-g amount of *cis*-α-[Co(en)$_2Cl_2$]Cl (0.0025 mol) and 0.56 g of ligand (0.0025 mol) were dissolved in 40 ml of 50% ethanol. Addition of KOH, stirring, and addition of NaI were performed as above. The ethanol was removed with a rotary evaporator. This left a clear aqueous solution and dark oily residue. Forty milliliters of benzene was added and the mixture was shaken vigorously until all of the oil had dissolved in the benzene. The dark green benzene layer was separated and the benzene was evaporated, leaving a dark green solid. The product was purified using the procedure outlined for [Co(trien)DTBC]I; yield 1.2 g (91%).

[Co(en)$_2$DTBC]Cl·2H_2O. This complex was prepared by dissolving 0.357 g of *cis*-[Co(en)$_2Cl_2$]Cl (0.00125 mol) and 0.28 g of 3,5-di-*tert*-butylcatechol (0.00125 mol) in 30 ml of degassed 100% EtOH. This mixture was bubbled with nitrogen and a solution of 0.165 g of KOH (0.0025 mol) in 20 ml of 100% EtOH was added dropwise with stirring. KCl precipitated from the reaction mixture and the color changed to a deep green. After 0.5 hr the reaction mixture was filtered to remove the KCl. The resulting solution was taken to dryness on the rotary evaporator, and the soluble residue obtained was dissolved in a small amount of 100% EtOH, filtered, and evaporated to dryness again. The dark green solid recovered was washed with ether and air-dried.

Purification of the product was accomplished by dissolving in a very small amount of deoxygenated water and then reprecipitated by addition of a saturated NaCl solution. The final product was washed with ether and dried under vacuum over P_2O_5.

[Co(trien)DTBC]Cl·H_2O. This complex was prepared using the method described for the synthesis of [Co(en)$_2$DTBC]Cl with cis-α-[Co(trien)Cl_2]Cl as the starting material.

[Co(trien)PCA]I·H_2O. To a mixture of 4.67 g of *cis*-α-[Co(trien)Cl_2]Cl (0.015 mol) and 2.31 g of protocatechuic acid (0.015 mol) in 25 ml of deoxygenated water was added, with stirring, 1.8 g of NaOH (0.045 mol) in 20 ml of water. The reaction mixture was stirred under nitrogen for 3 hr. After this time 1.25 ml of 12 *N* HCl (0.015 mol) was added followed by addition of 15 g of NaI. The solution was cooled at 5°C overnight during which time a finely divided, dark purple solid formed. The product was collected by suction filtration, washed with acetone, and dried under vacuum over silica gel; yield 2.2 g (30%).

[Co(en)$_2$PCA]I·H_2O. This complex was prepared using the method described for the synthesis of [Co(trien)PCA]I with *cis*-[Co(en)$_2Cl_2$]Cl as the starting material.

Results and Discussion

The synthetic procedures used to prepare these catecholato complexes were patterned after a procedure which has been reported for the preparation of amino acid complexes.[19] Because of the instability of catechols to air oxidation in basic solution, all syntheses were conducted under an inert atmosphere. The catecholato complexes, once obtained, are quite stable in air. They decompose slowly in aqueous solution in the presence of oxygen. Substantial decomposition will occur over the period of 1 day. This is probably due to slow aquation followed by oxidation of the liberated catecholate anion.

For the complexes of catechol and protocatechuic acid, crystalline products could be obtained relatively easily only for the iodide salts. However, after the iodide salt was obtained pure, the iodide could be replaced by reaction with the silver salt of another anion, e.g., chloride.

Many of the complexes could be obtained pure only as hydrates. Rigorous heating under vacuum either failed to remove the water or caused partial decomposition. Such behavior is not uncharacteristic of triethylenetetramine or ethylenediamine complexes.

Uv–Visible Spectra. Figure 1 shows the electronic absorption spectra of two typical cobalt(III) catecholate complexes. The spectral data for all the complexes are summarized in Table II. In some of the spectra two bands are observed

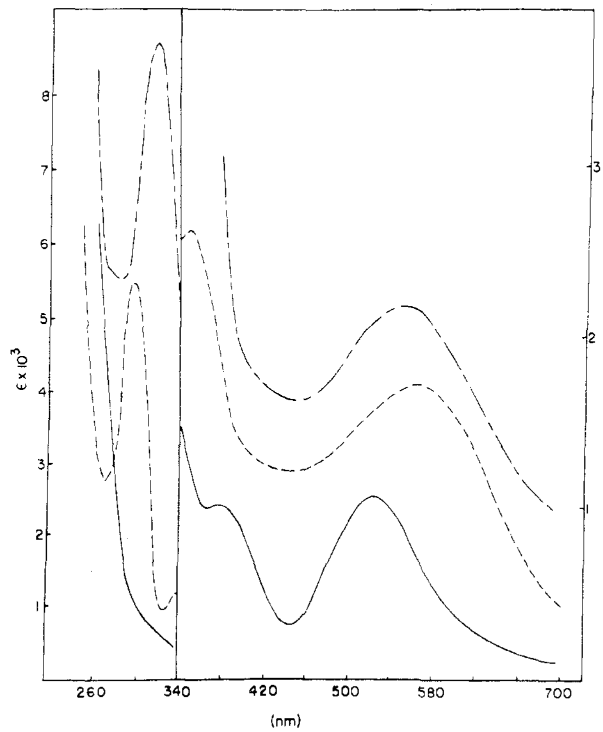

Figure 1. Electronic spectra of *cis*-α[Co(trien)Cl_2]Cl (———), [Co(trien)cat]I (- - - - -), and [Co(trien)PCA]I (– – – -). All spectra were obtained in water.

Table II. Summary of Electronic Spectral Features of the Cobalt–Catechol Complexes

Compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})			
[Co(trien)cat]I	564 (175)		348 (260)	296 (5500)
[Co(trien)cat]-Cl·$^1/_2H_2O$	564 (190)		348 (320)	296 (6500)
[Co(en)$_2$cat]I·H_2O	552 (169)	412 sh	348 (300)	292 (5700)
[Co(en)$_2$cat]Cl·$^1/_2H_2O$	556 (160)	420 sh	348 (258)	296 (6250)
[Co(trien)PCA]I	552 (220)			316 (8600)
[Co(en)$_2$PCA]I·H_2O	544 (188)	412 sh		318 (9590)
[Co(trien)DTB-C]I·H_2O	620 (184)	488 (165)	360 (350)	304 (7130)
[Co(en)$_2$DTBC]-I	616 (162)	496 (149)	360 (333)	304 (6550)
[Co(en)$_2$DTBC]-Cl·$2H_2O$	616 (159)	496 (131)	359 (307)	304 (6580)

in the regions of 350 and 550 nm. These correspond to the $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transitions, respectively, and are found in the same region in these complexes as in other triethylenetetramine or bis(ethylenediamine) complexes.[16] There is, however, a new and characteristic feature in the spectra of these catecholato complexes. This is a new band in the region of 300 nm. The extinction coefficient for this band varies from 5000 to 10000 depending on the particular catechol derivative. We assign this band as a $\pi \rightarrow \pi^*$ transition in the catechol ligand.[27] The catechol dianion itself shows a band at 292 nm with an extinction coefficient of 4500. In general, upon coordination, this band shifts to longer wavelength with an accompanying increase in intensity. This intense band overlaps with the $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transition and, in some complexes, the high-energy d–d band is obscured because of overlap with the $\pi \rightarrow \pi^*$ ligand transition. In all the catecholato complexes the intensities of the d–d transitions are considerably enhanced. Figure 1 shows clearly the increase in intensity of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band in going from [Co(trien)Cl_2]$^+$ to one of the catecholato complexes. This substantial enhancement in extinction coefficients for the d–d transitions accounts for the intense colors of the compounds.

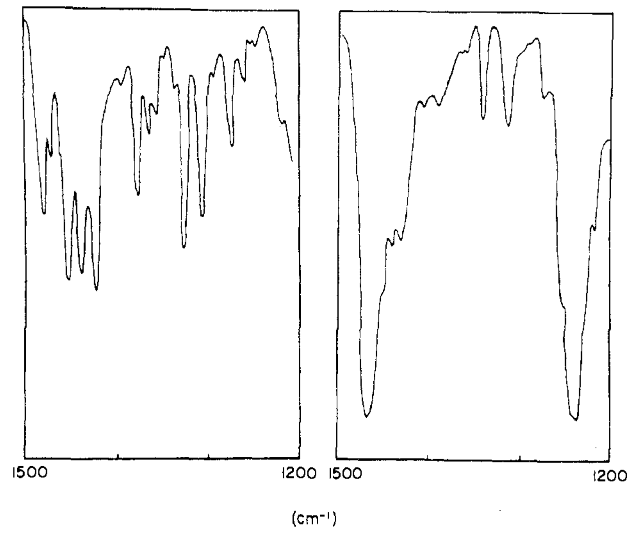

Figure 2. Infrared spectra (1200–1500 cm^{-1}) of *cis*-α[Co(trien)-Cl_2]Cl (left) and [Co(trien)cat]I (right). The prominent bands at 1250 and 1480 cm^{-1} correspond to the catechol C–O stretch and a catechol ring stretching vibration, respectively.

Infrared Spectra. Figure 2 compares a region of the ir spectrum of a typical catecholato complex to the spectrum of the dichloro complex from which it was derived. Inspection of these spectra reveals two intense bands in the catechol complex not present in the precursor. The band at 1480 cm^{-1} corresponds to a skeletal stretching vibration of the aromatic ring. The band which occurs around 1250 cm^{-1} can probably be assigned as a C–O stretch in the catechol ligand.[20] These same bands are present in the catecholato complexes containing either triethylenetetramine or bis(ethylenediamine) as the counterligands. Regardless of which catechol derivative is used, these two prominent and characteristic bands are present with only slight variations in their positions. The occurrence of these two bands in a spectrum is very good qualitative evidence for the presence of coordinated catechol.[21]

The spectra of complexes containing protocatechuic acid show the aromatic ring skeletal vibration and the phenolic C—O stretch at 1495 and 1295 cm^{-1}, respectively. In addition, a prominent C═O stretching vibration appears at 1680 cm^{-1}. The 2500–3500-cm^{-1} region indicates the presence of a free carboxylic acid O—H stretch. From this information it is quite clear that the metal is coordinated through the two hydroxy groups, leaving the carboxylic acid free.

Cyclic Voltammetry. One of the primary reasons for preparing the catecholato complexes reported here was to investigate the redox properties of the coordinated catecholate species. Because of this the complexes prepared have been studied by cyclic voltammetry. Figure 3 shows cyclic voltammograms of three complexes, [Co(trien)cat]Cl, [Co(en)$_2$cat]Cl, and [Co(trien)DTBC]Cl. Cyclic voltammograms could not be obtained for the iodide salts because the iodide ion oxidized in the region of interest. This technique has been discussed by Adams.[22] Very briefly, a triangular-wave potential is applied to the solution and the current which is passed is simultaneously monitored. Commonly the output, which is a plot of applied potential vs. current, is recorded directly on an X-Y recorder. Referring to Figure 3a, as the potential is increased from 0 to 1.0 V, the current is shown by the upper curve. A maximum in the curve indicates an oxidation process. As the maximum potential is reached and returns back to zero, the lower curve shows any cathodic current. A minimum here indicates a reduction process.

The cyclic voltammogram of [Co(trien)cat]Cl is shown in

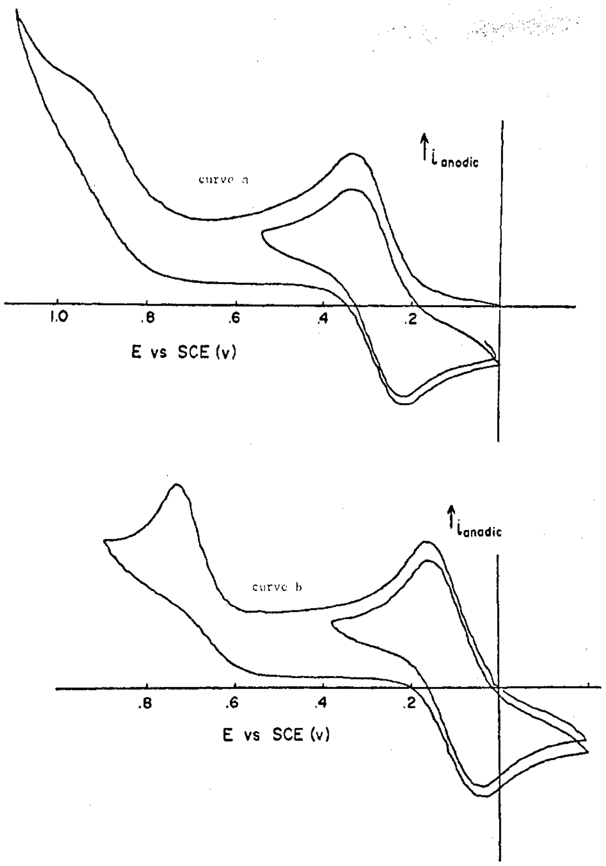

Figure 3. Cyclic voltammograms of [Co(trien)cat]Cl (curve a) and [Co(trien)DTBC]Cl (curve b). The concentration of both compounds was 1.0×10^{-3} *M* in 0.1 *M* $NaClO_4$ solution; scan rate 6 V min^{-1}.

Figure 3a. The outer line is the voltammogram run between 0 and 1.1 V. The inner line is a subsequent sweep run between 0 and about 0.55 V. The outer line indicates an oxidation process occurring at +0.35 V and a second oxidation at about +0.9 V; on the return (cathodic) sweep there is a well-defined peak for a reduction process at +0.27 V. The second sweep (inner line) showing the anodic peak at +0.35 V and the cathodic peak at +0.27 V indicates the presence of a quasi-reversible process. For a strictly reversible one-electron process the separation between the peak should be 58 mV, rather than the value of 80 mV found here. In order to determine whether the reversible process was a one- or two-electron process, the anodic peak current was measured and compared with the corresponding current for a known reversible one-electron system. This indicated clearly that the reversible process in the complex was also a one-electron process. The voltammogram in Figure 3b shows qualitatively similar behavior to that found in [Co(trien)cat]Cl. The initial one-electron oxidation in [Co(trien)DTBC]Cl shows a peak maximum at +0.16 V. This oxidation occurs at lower potential because of the presence of electron-donating *tert*-butyl substituents on the ring.

The electrochemical behavior of the catechol complexes studied here is somewhat different from that found for free catechols. According to Adams, catechol shows a nearly reversible two-electron oxidation.[22] This is the type of behavior found in protic solvents. The potential at which this process takes place is quite dependent on the hydrogen ion concentration. In aprotic solvents, however, the interconversion between the *o*-quinone form and the reduced dianion occurs in two one-electron steps. Peover, for example, reported two one-electron reduction potentials for *o*-benzoquinone in acetonitrile.[23] Ryba et al. have studied the reduction of several alkyl-substituted *o*-quinones in acetonitrile and, in all cases, observed two one-electron reductions.[24] Chambers has recently reviewed the electrochemistry of quinones and included an extensive listing of redox potentials for many quinones.[25]

The complexes studied in this work show two one-electron oxidation processes. The corresponding reduction for the first oxidative step is observed on the reverse sweep of the cyclic voltammograms. In this regard, the coordinated catechols behave somewhat like the free molecule in nonprotic solvents. This is true even though the voltammograms for the complexes were obtained in protic solvents. This is reasonable because of the fact that when the catechol is coordinated to the substitutionally inert cobalt(III), protonation equilibria at the catechhol oxygens do not play a role in the redox processes.

In the complexes, the potentials at which the one-electron oxidations occur have shifted considerably to more positive values (as much as 1 V) compared to the potentials found for the uncoordinated species in nonprotic solvents. This behavior has been observed previously by studying the redox potentials of *o*-quinones in the presence of monovalent cations.[26] In these systems the reduction potentials were shifted to more positive values due to complex formation with the cations.

The first oxidation process in the complexes, which corresponds formally to conversion of the catechol dianion to the semiquinone, appears to be nearly reversible by cyclic voltammetry. Thus the coordinated semiquinone seems to be quite stable and attempts are under way to generate solutions of this intermediate for investigation by ESR and electronic spectroscopy. In general the preliminary electrochemical investigation of these complexes reveals substantial changes in the chemical properties of the catechol by virtue of coordination to the cobalt ion.

Acknowledgment. This work was supported by National Science Foundation Grant GP-42814.

Registry No. [Co(trien)cat]I, 57395-99-0; [Co(en)$_2$cat]I, 57456-86-7; [Co(trien)cat]Cl, 57396-00-6; [Co(en)$_2$cat]Cl, 57457-45-1; [Co(trien)PCA]I, 57396-01-7; [Co(en)$_2$PCA]I, 57396-02-8; [Co(trien)DTBC]I, 57396-03-9; [Co(trien)DTBC]Cl, 57396-04-0; [Co(en)$_2$DTBC]I, 57396-05-1; [Co(en)$_2$DTBC]Cl, 57396-06-2; *cis*-α-[Co(trien)Cl$_2$]Cl, 14883-58-0; *cis*-[Co(en)$_2$Cl$_2$]Cl, 14040-32-5.

Supplementary Material Available: Table I, containing analytical data for all the compounds prepared (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Abbreviations used in this paper are as follows: cat, catechol (1,2-dihydroxybenzene); DTBC, 3,5-di-*tert*-butylcatechol; PCA, protocatechuic acid (3,4-dihydroxybenzoic acid); trien, triethylenetetramine; en, ethylenediamine.
(2) K. Bloch and O. Hayaishi, *Biol. Chem. Aspects Oxygenases, Proc. U.S.-Jpn., Symp.*, (1966).
(3) S. Dagley, *Soil Biochem.*, 287 (1967).
(4) O. Hayaishi, *Biol. Oxid.*, 581–601 (1968).
(5) D. T. Gibson, *Science*, **161**, 1093 (1968).
(6) S. Dagley, *Adv. Microb. Physiol.*, **6**, 1–42 (1971).
(7) D. G. Brown in "Chemistry and Biochemistry of Amino Acids, Peptides, and Proteins", Vol. 3, B. Weinstein, Ed., Marcel Dekker, New York, N.Y., 1974, pp 245–286.
(8) T. Nakazawa, M. Nozaki, and O. Hayaishi, *J. Biol. Chem.*, **244**, 119 (1969).
(9) H. Fujisawa, M. Uyeda, Y. Kojima, M. Nazaki, and O. Hayaishi, *J. Biol. Chem.*, **247**, 4414 (1972).
(10) M. Nozaki, M. Ono, T. Nakazawa, and S. Kotani, *J. Biol. Chem.*, **243**, 2682 (1968).
(11) S. Dagley and M. D. Patel, *Biochem. J.*, **66**, 227 (1957).
(12) I. G. O'Brien, G. B. Cox, and F. Gibson, *Biochim. Biophys. Acta*, **237**, 537–549 (1971).
(13) Examples of these are given in ref 14.
(14) F. Röhrscheid, A. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).
(15) (a) A. Balch, *J. Am. Chem. Soc.*, **95**, 2723 (1973); (b) D. M. Barlex, R. D. W. Kemmitt, and G. W. Little cott, *J. Organomet. Chem.*, **43**, 225 (1972).
(16) A. Sargeson and G. Searle, *Inorg. Chem.*, **6**, 787 (1967).
(17) J. C. Bailar, *Inorg. Synth.*, **2**, 223 (1946).

(18) S. C. Creason and R. F. Nelson, *J. Chem. Educ.*, **48**, 775 (1971).
(19) B. E. Bryant, H. J. Hu, and W. H. Glaze, *Inorg. Chem.*, **5**, 1373 (1966).
(20) Assignment of this band is complicated by the fact that there is also an out-of-plane ring vibration in this region which is present in both the catechol and the quinone. However, the peak at 1250 cm^{-1} occurs with considerable intensity in the complexes. The dianion of catechol shows C–O stretching vibrations and for this reason we have assigned the intense peak in the complexes at 1250 cm^{-1} as a C–O stretch.
(21) In complexes of catechols with other metals, e.g., copper and iron, we also found these prominent bands to be present.
(22) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, p 367.
(23) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).
(24) O Ryba, J. Petranek, and J. Pospisil, *Collect. Czech. Chem. Commun.*, **33**, 26 (1968).
(25) J. Q. Chambers in "The Chemistry of the Quinoid Compounds", S. Patai, Ed., Interscience, New York, N.Y., 1974.
(26) T. Fujinaga, K. Izutsu, and T. Nomure, *J. Electroanal. Chem.*, **29**, 203 (1971).
(27) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 3379 (1968).

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Influence of Anionic Inner-Sphere Substituents on the Kinetics of Ternary Complex Formation of Nickel(II) in Acetonitrile as Solvent. Opposing Effects of Solvent Labilization and Outer-Sphere Destabilization[1]

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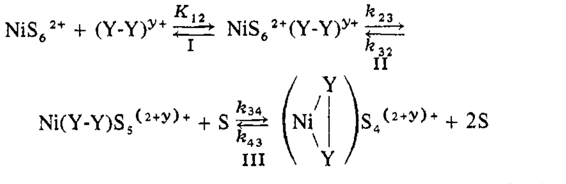
The ratio N of the rate constants of the two reactions (A) $NiXS_n^+$ + Y and (B) NiS_6^{2+} + Y in S = acetonitrile has been determined by stopped-flow measurements for X = chloride, bromide, iodide, thiocyanate, and nitrate, with Y = 2,2',2''-terpyridine and (in the case of X = chloride) with 2,2'-bipyridine and 1,10-phenanthroline as well. The inner-sphere substituents X all produce substantial accelerating effects, the value of N with Y = terpyridine at 25° varying from 10 for nitrate to 800 for chloride. With Y = phenanthroline, the accelerating effect of chloride is much smaller (N = 80). As shown before, the rate of reaction B is notably sensitive to the nature of Y, and, particulary with Y = phenanthroline, it is much higher than predicted by the value of the outer-sphere equilibrium constant calculated from electrostatics. We have attributed this fact to "extra" stabilization of the outer-sphere complex by interaction of the ligand with the polarized acetonitrile molecules of NiS_6^{2+}. This view is now supported by the fact that the rate of reaction A is much less sensitive to the nature of Y than is the case for reaction B, which is consistent with the weaker polarization of S in $NiXS_n^+$ than in NiS_6^{2+}. Consequently, the accelerating influence of anionic inner-sphere substituents is attributed to the net effect of solvent labilization and outer-sphere destabilization.

The reactions of nickel(II) ion with many (not all) ligands in aqueous as well as nonaqueous solutions are consistent with a dissociative interchange (I_d) mechanism in which solvent exchange constitutes the rate-determining step. The details of the reaction scheme may be illustrated as in eq 1 for the



$$NiS_6^{2+} + (Y\text{-}Y)^{y+} \underset{I}{\overset{K_{12}}{\rightleftharpoons}} NiS_6^{2+}(Y\text{-}Y)^{y+} \underset{\underset{II}{k_{32}}}{\overset{k_{23}}{\rightleftharpoons}} Ni(Y\text{-}Y)S_5^{(2+y)+} + S \underset{\underset{III}{k_{43}}}{\overset{k_{34}}{\rightleftharpoons}} \left(Ni\begin{matrix}Y\\|\\Y\end{matrix}\right)S_4^{(2+y)+} + 2S \qquad (1)$$

case of a bidentate ligand $(Y\text{-}Y)^{y+}$ in a solvent S. Process I (outer-sphere complexation) is diffusion controlled and therefore rapid, and process III (ring closure) usually, but not always, is also rapid. Hence, process II (solvent exchange) represents the rate-determining step. Usually the concentration of the outer-sphere complex is small as compared to that of free ligand, in which case the observed rate constant for ligand substitution, k_l, is given by the relation[2] $k_l = K_{12}k_{23}$. Evidence in support of this reaction scheme has been summarized for water,[2] dimethyl sulfoxide,[3-7] acetonitrile,[4,8,9] and several other solvents.[4] Such evidence comes mainly from a comparison of rate constants and activation parameters for ligand substitution with the corresponding quantities for solvent exchange. For example, k_{23} should be related to the rate constant for solvent exchange, k_s, through a statistical factor f representing the probability that the ligand will occupy a particular coordination site vacated by a solvent molecule, so that $k_{23} = fk_s$. It is convenient to consider a dimensionless ratio R given by

$$R = k_l/K_{12}fk_s \qquad (2)$$

which should have a value near unity if the I_d mechanism applies. For the statistical factor f a value of $^3/_4$ has been proposed.[10] The equilibrium constant for the outer-sphere complex, K_{12}, usuallly cannot be evaluated experimentally and must be estimated through the theoretical relationship from electrostatics[11,12]

$$K_{12} = \frac{4\pi N a_1^3}{3 \times 10^3} e^{-U a_2/kT} \qquad (3a)$$

where

$$U(a_2) = \frac{z_1 z_2 e^2}{\epsilon a_2} - \frac{z_1 z_2 e^2 \kappa}{\epsilon(1 + \kappa a_2)} \qquad (3b)$$

Here, a_1 represents the center-to-center distance of closest approach of the solvated metal ion and the *reaction site* on the ligand, a_2 is the corresponding distance between the two *charge sites* for the case of a charged ligand, and κ is the Debye–Hückel function of the ionic strength, I, given by

$$\kappa^2 = 8 \times 10^{-3} \pi N^2 e^2 (\epsilon RT)^{-1} I^{1/2} \qquad (3c)$$

where ϵ is the dielectric constant of the medium. Other symbols have their customary meaning. Uncertainties in the application of eq 3 have been discussed.[12] Of particular significance to the results presented in this and the next paper is the fact that the equation cannot apply if specific interactions occur between the inner and outer coordination spheres.

It has been found that in *aqueous solution* reactions of nickel(II) with a number of incoming ligands Y^{y+} are influenced to varying degrees by ligands X^{x+} already present in the inner coordination sphere of nickel. (For simplicity, dentate numbers of Y and X are omitted henceforth.) We