Inorg. Chem. **1990**, *29*, 1589-1592 **1589**

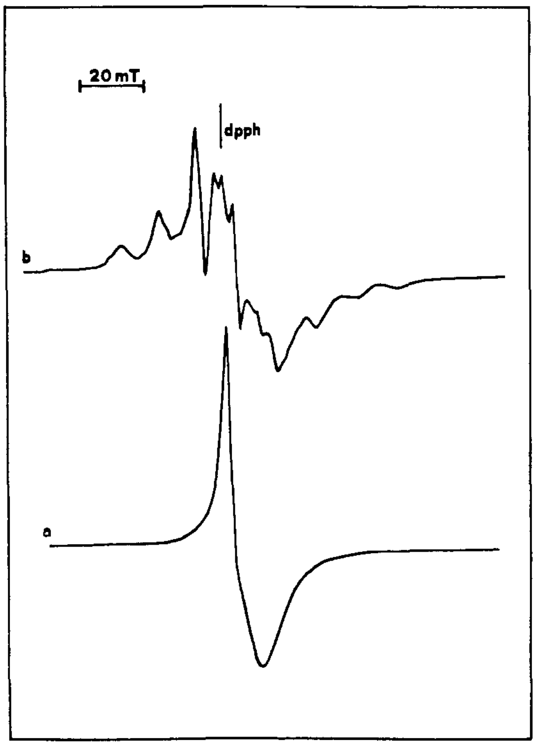

Figure 4. ESR spectra of $Tl_2[V(cat)_3]$: powder ESR spectrum recorded at room temperature (a); glassy spectrum of a 2.4×10^{-2} M solution in DMSO (b).

points to the conclusion that the 3:1 species is a V(IV) complex, consistent with the previous interpretation of Cooper, Koh, and Raymond. This study establishes that in aqueous solution, where hydrogen bonding of triethylammonium ions to the phenolate oxygens is unimportant, the species retains the same geometry as in the solid state. Whatever the solvent (water, CH_3CN, or DMSO) or the counterion (Na^+, Tl^+, or Et_3NH^+), the tris(catecholato) species gives the same ESR spectra, which supports a d_{z^2} ground state. In all the known cases of d_{z^2} ground state for V(IV), the coordination geometry is distorted toward a trigonal-prismatic geometry.[29] The catecholate ligand is notable in stabilizing distorted-trigonal-prismatic geometries in the trischelated complexes, the extreme example being a recently detected perfectly trigonal-prismatic ferric complex with a macrocyclic catechol ligand.[30] This property is the result of constraints imposed by the short ligand bite (ratio of the O–O ring distance to the M–O distance).[3] The metal geometry is severely trigonally distorted in $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$,[26] the twist angle between the triangular faces of the coordination polyhedron being ≈39°. This angle is expected to be 60° for an ideal octahedron and 0° for a trigonal prism. Crystal field diagrams, calculated by the method of Companion and Komarynsky,[31] show that for the 39° twist angle the d_{z^2} orbital is lowest by $0.67Dq$. Hence, the change of the ground state from d_{xy} in mono- and bis(catecholato)oxovanadium(IV) complexes to largely d_{z^2} in tris(catecholato)vanadate(IV), as substantiated by the ESR data, is fully consistent with the solid-state structure.

In conclusion, the trigonal-prismatic distortion imposed by the tris chelation has a dramatic effect on the ordering of the vanadium electronic levels, producing a change of the ground state from d_{xy} (typical of $V^{IV}O$ square-pyramidal complexes) to d_{z^2}. Furthermore, it may be noted that $[V(cat)_3]^{2-}$ is the first catecholate complex for which the trigonal-prismatic distortion has been directly observed in solution.

Acknowledgment. We thank Tim Karpishin for his assistance.

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Helical Heptacoordinate Complexes of Cobalt Derived from 2,2':6',2'':6'',2''':6''',2''''-Quinquepyridine Derivatives

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Received November 7, 1989

We have shown[1] recently that electropolymerized layers of $[Co(v\text{-}terpy)_2]^{2+}$ exhibit properties and chemical reactivity patterns different from those of $[Co(terpy)_2]^{2+}$ in solution and that these differences were attributed to constraints imposed by incorporation of the metal complex in a polymeric system as well as by the tridentate nature of this ligand. An especially interesting property of the electropolymerized films of $[Co(v\text{-}terpy)_2]^{2+}$ was the electrocatalytic reduction of carbon dioxide to formic acid and of oxygen to water and hydrogen peroxide. This reactivity was attributed to the generation of vacant catalytic sites on the cobalt in its reduced state. Analogous cobalt complexes of quinquepyridine are of particular interest as they have the possibility of generating an empty coordination site with relative ease and may provide evidence for the mode of action of the polymerized $[Co(v\text{-}terpy)_2]^{2+}$.

2,2':6',2'':6'',2''':6''',2''''-Quinquepyridine was first reported[2] in 1938, and synthetic routes to it and its derivatives have usually involved high-temperature Ullmann condensations with brominated pyridines, bipyridines, and terpyridines. These were "poor-yield" reactions that gave mixtures of oligopyridines which were difficult to separate. An alternative approach has been the condensation[3] of 1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium chloride with 2,6-dicinnamoylpyridine or 2,6-bis[(1-dimethylamino)-3-oxopropenyl]pyridine, the former reagent leading to phenyl-substituted derivatives. In this present study,[4] α-oxoketene dithioacetal methodology[5] was used in the synthesis (Scheme I) of the vinyl-substituted quinquepyridine (quinpy) ligands. We anticipated that these quinquepyridine–cobalt complexes would also exhibit electrocatalytic activity, and our results are described below.

Experimental Section

A. Synthesis. 4',4'''-Bis(methylthio)-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine (**3a**) was prepared in 55% yield[6] from the α-oxoketene dithioacetal **1a** and the bis(potassium enolate) of 2,6-diacetylpyridine (4 equiv of $KOBu^t$, THF, room temperature). The intermediate bis(1,5-enedione) was not isolated; its deep red potassium salt was treated directly with ammonium acetate and hot acetic acid, leading to **3a**, which crystallized as colorless needles from DMF; mp 271–272 °C. The corresponding 4',4'''-bis(*n*-propylthio) derivative **3b** was obtained from **1b** in an analogous fashion in higher yield (64%), also crystallizing from DMF as tan needles, mp 155–158 °C. Conversion of **3a** into **4** occurred after heating with CH_3MgBr and $(Ph_3P)_2NiCl_2$ (benzene, 60 °C, 4 days), giving **4** in 65% yield as colorless microneedles from EtOAc; mp 230–232 °C. Under analogous conditions, **3b** was converted into **4** in only 12% yield. The addition of lithium tetramethylpiperidide (3 equiv) in THF to a cooled (−20 °C) solution of **4** in THF, followed after 20 min by a "one-shot" addition of bromomethyl methyl ether (3.3 equiv), stirring the resultant reaction mixture at −20 °C for 4 hours, warming to room temperature over 12 h, and reaction work up by quenching with water, removal of the THF, and extraction with CH_2Cl_2 (drying), resulted in a colorless product. This was chromatographed on neutral alumina[7] (hexane:EtOAc = 10:1) with the monoalkylated product[8] **5a** eluting first [colorless microneedles (17%) from cyclohexane; mp 141–144 °C], followed by the bis(alkylated) product **5b** [colorless microneedles (48%) from cyclohexane; mp 177–179 °C]. Introduction of the vinyl group(s) occurred readily on treatment of **5a** and **5b** with $KOBu^t$ (3 and 5 equiv, respectively, THF, room temperature), giving **5c** (72%, colorless microprisms from cyclohexane; mp 214–216 °C) and **5d** (68%, colorlesss microneedles from cyclohexane; mp 237–239 °C).

^1H NMR data[9] for **3b** showed that in solution the preferred conformation was one in which the pyridine nitrogen atoms were trans to one

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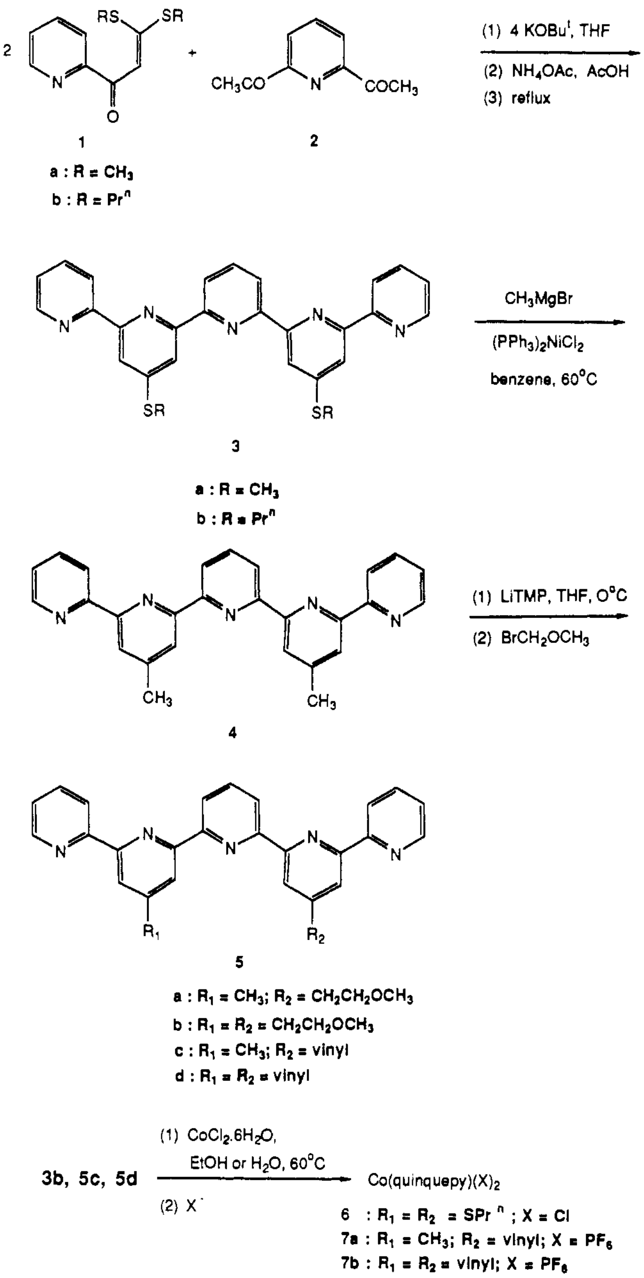
Scheme I



another. This same conformation was observed in all these quinquepyridinyl derivatives and is consistent with that reported in the 2,2′:6′,2″-terpyridinyl series.[5]

The synthesis of the cobalt complex was achieved by the addition of cobaltous chloride hexahydrate (1 equiv; absolute ethanol), to a suspension of **3b** in absolute ethanol. The reaction mixture was warmed at 70 °C for 2 h, giving a homogeneous mixture, which was cooled to room temperature, and the ethanol was removed (reduced pressure). Recrystallization of the green residue from ethanol–ether afforded greem prisms, mp >320 °C (83%). Analytical data established an empirical formula of $C_{31}H_{29}N_5Cl_2S_2Co$, and the complex had a magnetic susceptibility $\mu_{eff}(300\ K) = 4.78\ \mu_B$, indicative[10] of a paramagnetic Co^{2+} complex, **6**.

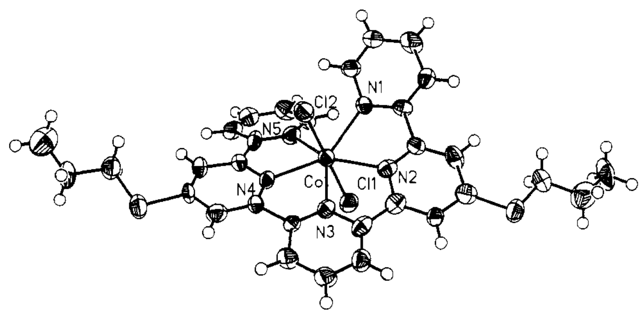


Figure 1. Ortep representation of dichloro[4′,4‴-bis(*n*-propylthio)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine]cobalt(II) (**6**).

Table I. Bond Lengths (Å) and Bond Angles (deg) for Dichloro[2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine]cobalt(II) (**6**)

Bond Lengths			
Co-N(1)	2.275	Co-N(5)	2.292
Co-N(2)	2.224	Co-Cl(1)	2.549
Co-N(3)	2.202	Co-Cl(2)	2.537
Co-N(4)	2.170		
Bond Angles			
Cl(1)-Co-Cl(2)	177.4	N(4)-Co-N5)	71.1
N(1)-Co-N(2)	70.4	N(1)-Co-N(3)	139.1
N(2)-Co-N(3)	71.4	N(1)-Co-N4)	145.4
N(3)-Co-N(4)	70.7	N(2)-Co-N(5)	144.0

B. Reagents. Acetonitrile and dimethylformamide (DMF) (Burdick & Jackson distilled in glass) were dried over 4-Å molecular sieves. Tetra-*n*-butylammonium perchlorate (TBAP; G. F. Smith) was recrystallized three times from ethyl acetate and dried under vacuum at 90 °C for 72 h. Water was purified by passage through a Milli-Q purification train. THF was dried over Na/benzophenone and distilled immediately before use. All other reagents were of at least reagent grade quality and were used without further purification.

C. Electrochemical Experiments. Electrochemical techniques and procedures were as described previously for the analogous $[Co(v\text{-}terpy)_2]^{2+}$ complexes.[1c]

Results and Discussion

Structure of Dichloro[4′,4‴-bis(*n*-propylthio)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine]cobalt(II) (6). Single-crystal X-ray analysis of **6** showed it to be a neutral 1:1 complex with unique 7-coordination geometry, and the structure[11] is shown in Figure 1 with selected bond lengths and bond angles listed in Table I. The five pyridine rings are arranged in a relatively flat helix about the central cobalt atom with two axial chlorides distanced 2.549 and 2.537 Å from the cobalt. The Co–N bond distances range from a low of 2.170 Å [Co–(N$_4$)] to a high of 2.292 Å [Co–N(5)]. The longest bond [C(15)–C(16)] separating two pyridine rings is 1.521 Å (rings 3 and 4) while the shortest bond [C(10)–C(11)] is 1.435 Å (rings 2 and 3) (supplementary material). It is of special interest to compare these crystallographic parameters with those of $Co^{2+}(tetrapy)(NO_3)_2{\cdot}2H_2O$ in which cobalt is coordinated to the tetrapyridine ligand in a nearly planar N_4 geometry with two axial oxygen ligands.[12] Here the Co–N(1) bond length of 2.139 Å is close to that of Co–N(4) at 2.115 Å;

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(1) (a) Potts, K. T.; Usifer, D.; Guadalupe, A. R.; Abruña, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 361. (b) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogstad, A.-L.; Abruña, H. D. *J. Am. Chem. Soc.* **1988**, *110*, 3462. (c) Hurrell, H. C.; Mogstad, A.-L.; Usifer, D. A.; Potts, K. T.; Abruña, H. D. *Inorg. Chem.* **1989**, *28*, 1080.

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(3) Krohnke, F. *Synthesis* **1976**, 1.

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(6) All yields reported are purified yields.

(7) Fisher brand, neutral alumina 80–200 mesh was used.

(8) ^1H NMR data (200 MHz) were consistent with the assigned structures.

(9) ^1H NMR (200 MHz, $CDCl_3$): δ 8.71 (dt, 2, $J_{5,6} = 4.7$ Hz, $J_{4,6} = 1.8$ Hz, H_6), 7.35 (m, 2, $J_{4,5} = 7.4$ Hz, $J_{5,6} = 4.7$ Hz, $J_{3,5} = 1.2$ Hz, H_5), 7.87 (td, 2, $J_{3,4} = J_{4,5} = 7.8$ Hz, $J_{4,6} = 1.9$ Hz, H_4), 8.64 (bd, 2, $J_{3,4} = 8.0$ Hz, H_3), 8.53 (d, 2, $J_{3',5'} = 1.8$ Hz, $H_{5'}$, $H_{3'''}$), 8.36 (d, 2, $J_{3',5'} = 1.8$ Hz, $H_{3'}$, $H_{5'''}$), 8.66 (bd, 2, $J_{3'',4''} = J_{4'',5''} = 7.8$ Hz, $H_{3''}$, $H_{5''}$), 8.01 (t, 1, $J_{3'',4''} = J_{4'',5''} = 7.8$ Hz, $H_{4''}$), 3.21 (t, 4, $SCH_2CH_2CH_3$), 1.89 (sextet, 4, $SCH_2CH_2CH_3$), 1.17 (t, 6, $SCH_2CH_2CH_3$).

(10) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(11) The unit cell contained some unresolved diffraction patterns from trace amounts of solvent. The single crystal of **6** was mounted directly from the crystallization liquor and covered immediately with epoxy, the X-ray determination being carried out at low temperature (−20 °C) to avoid phase transitions.

(12) von Henke, W.; Kremer, S.; Reinen, D. *Z. Anorg. Allg. Chem.* **1982**, *491*, 124.

the Co–N(2) (2.075 Å) and Co–N(3) bonds (2.084 Å) differ by only 0.009 Å. The C–C bonds joining the pyridine rings range from 1.474 Å (rings 2 and 3) to 1.492 Å (rings 1 and 2) while the axial Co–O(1) and the Co–O(2) bond lengths are 2.124 and 2.146 Å, respectively. Thus Co^{2+} and quinpy, not able to accommodate the five pyridine rings in a planar arrangement, can do so by adopting a helical coordination. The flexibility in the quinpy ligand is reflected in the elongated bond lengths between Co and N_{py} and between the pyridine rings.

Exchange of the chlorides in **6** with sodium perchlorate resulted in a complex whose FT-IR spectrum showed the two perchlorate groups to be covalently bound to the cobalt. This represents the first recorded example of a 7-coordinate, divalent cobalt complex with a quinquedentate ligand arranged in a helix about the central cobalt atom. The two axial chloride ligands complete the 7-coordination sphere. The bonding geometry and electron count for **6** is of special interest. From the crystal structure, it is clear that the geometry of this complex is most appropriately described as pentagonal bipyramidal. Although the electron count for such a system would be 21, it is generally recognized that the 18-electon rule often does not apply to high-spin coordination compounds.

Hoffmann and co-workers have pointed out[13] that the ligand field d-orbital splitting diagram for such a geometry would have a low-lying e_1'' level consisting of the d_{xz} and d_{yz} orbitals, followed by two antibonding combinations, e_2' (composed of d_{xy} and $d_{x^2-y^2}$ orbitals) and a_1' (d_{z^2}). This pattern is analogous to that of a trigonal bypyramid (5-coordinate) except that the d_{xy} and $d_{x^2-y^2}$ orbitals are shifted significantly to higher energy because of additional interactions. This orbital splitting diagram is fully consistent with our observation that **6** is a high-spin Co(II) (i.e., d^7) complex so that the d_{xz} and d_{yz} orbitals are doubly occupied with the remaining ones being singly occupied to yield three unpaired electrons.

When the ligand **3b** (2 equiv) was treated with cobaltous chloride (1 equiv) a 2:1 ligand–metal complex was isolated as its hexafluorophosphate or perchlorate salt along with the 1:1 ligand–cobalt complex **6**. The gold colored bis complex most likely had an octahedral coordination geometry and was a mixture of several possible coordination patterns. When attempts were made to isolate the corresponding chloride directly, the products that resulted were the 1:1 ligand–cobalt complex **6** and 1 equiv of the uncomplexed ligand **3b**.

Structure **6** is also particularly interesting in view of two recently reported metal complexes of quinquepyridine: with Ag(I) the complex is mononuclear with a near-planar arrangement of the ligand about the metal,[14a] and with Cu(II) a binuclear complex[14b] is formed. In the latter the two ligands are coordinated to the metal in a double-helical arrangement involving three pyridine rings bound to one copper metal center in a distorted octahedron while the remaining two pyridine rings of each ligand occupy four coordination sites of the distorted trigonal-bipyramidal environment of the second copper ion. Other double-helix complexes of Cu(I) and poly(bipyridinyl) strands have also been reported recently.[15]

Coordination of the monovinylquinquepyridine **5c** with cobaltous chloride hexahydrate was carried out in water by warming the heterogeneous mixture (equimolar amounts) of the ligand and the metal salt at 60 °C until homogeneity occurred. Addition of an excess of aqueous ammonium hexafluorophosphate gave a pale green precipitate, which was purified by dissolving in acetone and reprecipitating with water. Analytical and mass spectral (FAB) data showed this to be a 1:1 complex. FT-IR indicated that an axial coordination site on the cobalt was occupied by a water ligand, the counterions being hexafluorophosphate. Similarities in the physical characteristics of **6** and this $[(Co^{2+}(v\text{-}quinpy))(PF_6^-)_2{\cdot}H_2O]$ complex suggested a similar pyridine ligand coordination geometry with its formula being represented by **7a**. Coordination of the divinylquinquepyridine **5d** with $CoCl_2{\cdot}6H_2O$ was carried out in the same way, and analytical, mass spectral (FAB), and FT-IR data were all consistent with structure **7b**.

Table II. Electrochemical Data for Quinquepyridine (quinpy) Complexes[a]

complex	$E^{\circ\prime}_{M^{III/II}}$, V	$E^{\circ\prime}_{M^{II/I}}$, V	$E^{\circ\prime}_{\text{ligand based}}$, V
[Co(quinpy)]	+0.92	−0.90	−1.20, −1.39, −1.73
$[Co(quinpy)_2]$	+0.70	−0.77	−1.25, −1.59
[Co(v-quinpy)]	+0.74 (+0.97)[b]	−0.88 (−0.58)[b]	−1.28, −1.48
$[Co(v_2\text{-}quinpy)]$[c]	+0.71	−0.86	−1.26, −1.53

[a] In acetonitrile/0.1 M tetra-*n*-butylammonium perchlorate. All potentials vs SSCE. [b] Present only in electropolymerized film. [c] Two vinyl groups present in the ligand.

Electrochemistry. The voltammetric responses of these complexes are similar to those of the analogous vinylterpyridine complexes,[1b] and a compilation of formal potentials is presented in Table II along with values for related complexes. On a reductive cyclic voltammetric sweep from 0.0 to −1.90 V (vs SSCE), the monovinylquinquepyridine metal coordination complex monomer **7a** in acetonitrile/0.1 M tetra-*n*-butylammonium perchlorate (TBAP) exhibited three reductions with formal potentials of −0.88, −1.28, and −1.48 V. On the reverse sweep (oxidative), an additional wave was observed at a peak potential of −0.56 V, and on subsequent negative sweeps, a cathodic counterpart to this wave was observed at −0.61 V. This redox process with a formal potential of −0.58 V was not observed for the complex in DMF solution, pointing toward a much stronger interaction between the complex and acetonitrile than with DMF, again analogous to the vinylterpyridine complexes. Voltammetric scans extended to positive potentials exhibited two small waves with formal potentials of +0.74 and +0.97 V.

The waves with formal potentials +0.74 and −0.88 V correspond to the Co(III/II) and Co(II/I) couples, respectively, and occur consistently at these potentials for the Co(quinpy) complexes with either one or two vinyl groups. The waves at formal potentials of +0.97 and −0.58 V, which only occur in complexes with a vinyl substituent, correspond to the Co(III/II) and Co(II/I) couples, respectively, of the mixed-ligand complex of acetonitrile and quinquepyridine. It should be mentioned that these waves appear only after electropolymerization of the monomeric metal complex into a constrained polymer network. We attribute the remaining two waves to ligand-localized reductions. Both the mono- and divinylquinquepyridine metal coordination complexes **7a** and **7b** are polymerizable, and the presence of two vinyl groups facilitates polymerization. Rapid polymerization is initiated only if the potential is cycled more negative than −1.40 V or beyond the first ligand-localized reduction. Figure 2A shows a representative series of consecutive cyclic voltammograms in acetonitrile/0.1 M TBAP at a glassy-carbon electrode depicting electropolymerization of the divinylquinquepyridine cobalt complex. The increase in the peak currents with each successive scan is a clear indication of polymerization occurring on the electrode surface.

The fact that coordination to the cobalt metal center by acetonitrile occurred at electropolymerized films infers that an empty coordination site is available for binding by solvent (acetonitrile) or other small molecules, a step that is generally considered necessary in the activation of small molecules, and we have investigated the electrocatalytic reduction of oxygen. Figure 2B,C shows rotated disk voltammograms (at 500 rpm) in oxygen-saturated pH 8.7 aqueous phosphate buffer for a bare and a surface-modified ($\Gamma = 5 \times 10^{-9}$ mol/cm^2) glassy-carbon electrode, respectively. Whereas it appears that the first reduction (to peroxide) is slightly inhibited at the modified electrode, there is a significant catalytic effect for the four-electron reduction of oxygen to water. Using the rotating ring–disk electrode technique, it was found that the ratio of the two-electron (yielding peroxide as product) to the four-electron reduction (giving water as product) was dependent upon the polymer coverage on the electrode surface in a manner analogous to the $[Co(v\text{-}terpy)_2]^{2+}$ case.[1b] We find that, at coverages of less than 5×10^{-9} mol/cm^2, the two electron reduction is the predominant process whereas, at higher coverages,

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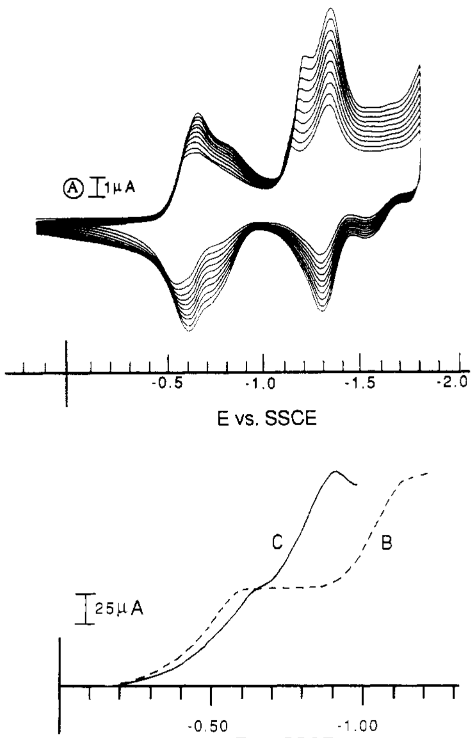

Figure 2. (A) Consecutive cyclic voltammograms at 100 mV/s for a glassy-carbon electrode in contact with an acetonitrile/0.1 M TBAP solution of the cobalt divinylquinquepyridine complex. (B, C) Rotated disk voltammograms (at 500 rpm) at 10 mV/s in oxygen-saturated pH 8.7 aqueous phosphate buffer for bare (B) and surface-modified (C) ($\Gamma = 5 \times 10^{-9}$ mol/cm^2) glassy-carbon electrodes.

the four-electron reduction dominates. A similar coverage dependence has been reported by Murray et al.[16] for the reduction of oxygen at electrodes modified with a cobalt porphyrin.

The close proximity of two cobalt centers for simultaneous electron transfer may be essential, or dimers may be formed so as to achieve a four-electron transfer. The close proximity of the metal centers may arise as a result of changes in the packing density of the electropolymerized material as a function of surface coverage. We have previously shown that this occurs for the $[Co(v\text{-}terpy)_2]^{2+}$ complex, and we assume that a similar process is operative here.

From plots of $1/i_{lim}$ vs $\omega^{-1/2}$ and the Koutecky-Levich equation, we determined that for electrodes modified with polymeric films of the cobalt complexes (at coverages ranging from 5×10^{-9} to 10×10^{-9} mol/cm^2) the second-order rate constant for the four-electron reduction of oxygen to water in pH 8.7 aqueous buffer was $2\ (\pm 1) \times 10^6$ M^{-1} s^{-1}.

We have also investigated the reduction of carbon dioxide, but the catalytic effects are not as strong as for the $[Co(v\text{-}terpy)_2]^{2+}$ case. We ascribe this to changes in the electronic environment around the cobalt center by the presence of the axial chloride ligands. Thus, there appears to be a delicate interplay between electronic and structural factors in the catalysis.

Conclusions. We have demonstrated that the use of quinquedentate pyridine-based ligands enforces a heptacoordinate helical coordination around Co(II). Such an unusual coordination (to our knowledge, the first reported for a cobalt complex) is a direct result of the steric constraints imposed by the ligand. In addition, the incorporation of vinyl groups allows for the smooth electropolymerization of the monomer complexes to yield adherent and electrochemically active polymer films that exhibit catalytic activity in the four-electron reduction of oxygen to water. We believe that this activity is largely due to the ease of generation of an empty coordination site at the metal where binding and activation of the substrate can readily occur. We believe that this may be a general reactivity pattern, and we are currently characterizing other catalytic processes as well as elaborating on the synthesis of related ligands.

Acknowledgment. K.A.G. thanks the U.S. Department of Education GPOP for the award of a fellowship and American Cyanamid for financial support. H.C.H. acknowledges support by a fellowship from the Aerospace Corp. H.D.A. is a recipient of a Presidential Young Investigator Award (1984-1989) and a Sloan Fellowship (1987-1991). Financial support by the National Science Foundation and the Materials Science Center at Cornell University is gratefully acknowledged. We thank Dr. R. Kullnig and Dr. F. Tham for the single-crystal X-ray determination.

Supplementary Material Available: Tables of crystal data, positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (6 pages). Ordering information is given on any current masthead page.

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A Convenient Synthesis of Solvated and Unsolvated Anhydrous Metal Chlorides via Dehydration of Metal Chloride Hydrates with Trimethylchlorosilane

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Received November 8, 1988

Although there are several methods for preparing anhydrous metal halides,[1] thermal and chemical methods of removing water from hydrated metal halides are the most frequently employed. The pyrolysis of metal halide hydrates has been studied extensively and can lead to anhydrous salts although temperature control is important for many hydrates because water is released stepwise and mixtures of hydrates can be obtained.[2] Dehydrating agents such as 2,2-dimethoxypropane and thionyl chloride are efficient and have been widely used although each has some disadvantages.

2,2-Dimethoxypropane, for example, reacts with metal hydrates producing acetone and methanol, which often complex to the metal halide[3] (eq 1). Both groups are barriers to further reactions with active metals and many organometallic reagents. Thionyl chloride reacts with water, evolving hydrogen chloride and sulfur dioxide as gases, thereby reducing the opportunity for contamination of the product halide[4] (eq 2). However, thionyl chloride is a severe lachrymator that must be freshly distilled before use. Moreover, it must be used in excess to achieve reasonable rates and removing the last traces of thionyl chloride is sometimes difficult.

$$MX_n \cdot xH_2O + xCH_3C(OCH_3)_2CH_3 \rightarrow MX_n + x(CH_3)_2CO + 2xCH_3OH \qquad (1)$$

$$[Cr(H_2O)_6]Cl_3 + 6SOCl_2 \rightarrow CrCl_3 + 12HCl + 6SO_2 \qquad (2)$$

We report here our finding that trimethylchlorosilane is a quick and efficient dehydrating agent for metal chloride hydrates that is free of the drawbacks mentioned above (eq 3).

$$MX_n \cdot xH_2O + 2x(CH_3)_3SiCl \rightarrow MX_n + [(CH_3)_3Si]_2O + 2xHCl \qquad (3)$$

Experimental Section

All reactions were carried out in a hood. Commercially available metal chloride hydrates and trimethylchlorosilane were used without further purification. Tetrahydrofuran (THF) was freshly distilled from

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