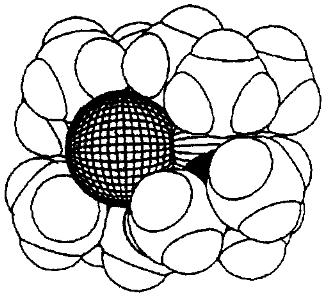

Figure 2. Space-filling drawing of $[KN(SiMe_3)_2]_2$, indicating the exposure of the potassium ion (crosshatched sphere). The adjacent nitrogen atom is banded, and the silicon is solid black.

(N–Si–C(7)) and 110.0 (2)° (N–Si–C(10)), which are the smallest such angles on their respective trimethylsilyl groups. The closest K–H_3(C) contacts are 2.96 and 3.16 Å; as these are roughly equal to the sum of the van der Waals radius for hydrogen and the covalent radius of K (3.1 Å), and as the hydrogens are not oriented toward the metal for optimum interaction, it would appear that any direct K···H···C involvement is slight.

Of additional interest are the Si–N distances, which average 1.682 (4) Å, and the Si–N–Si′ angle of 129.18 (18)°. These parameters are similar to those found in the polymeric sodium structure (Si–N = 1.690 (5) Å; Si–N–Si′ = 125.6 (1)°),[9] but are appreciably longer and narrower, respectively, than the 1.64 (1) Å Si–N distance and 136.2 (1.2)° Si–N–Si′ angle observed in $K[N(SiMe_3)_2]\cdot 2C_4H_8O_2$.[8] These structural trends (short Si–N distances coupled with wide Si–N–Si angles and vice versa) follow a well-established pattern in bis(trimethylsilyl)amide complexes.[2]

The correlation between the Si–N distance and the Si–N–Si′ angle in silylamides has been the subject of considerable discussion.[3c,9,24] Partial multiple bonding between Si and N, in which the lone-pair electrons on nitrogen are delocalized onto silicon, has been invoked as an explanation for the Si–N distance/Si–N–Si′ angle relationships, but steric interactions may also play a critical role in determining the geometries.[2c,9,12] The latter effects are difficult to quantify, since both the relative steric bulk and the orientation of various alkyl and aryl groups must be taken into account. One way this problem might be assessed in silylamides with the same substituents is by measuring the separation of the silicon centers; the Si···Si′ distance should be relatively constant if the bond length and angles are linearly related to each other. This separation is calculated in Table IV for a variety of transition-metal, main-group, and f-element bis(trimethylsilyl)amide complexes and is found to have the nearly constant value of 3.02 (3) Å. The persistence of this number over a wide range of metals suggests that it probably is of steric origin, i.e., that ~3.0 Å represents the limit imposed by interligand repulsions on the close approach of two $SiMe_3$ groups. Hence, bis(trimethylsilyl)amide complexes containing short Si–N bonds must necessarily possess relatively large Si–N–Si′ angles to avoid violating the minimum $SiMe_3$···$SiMe_3$′ separation. It should be stressed that the 3.0 Å Si···Si′ distance applies only to (trimethylsilyl)amides; different substituents on the nitrogen will affect this value. Both $HN(SiPh_3)_2$ and the $[Ph_3SiNSiPH_3]^-$ ion, for example, have Si···Si′ separations of 3.19 Å.[23b]

Alkane Solubility of $[KN(SiMe_3)_2]_2$. The solubility of [bis(trimethylsilyl)amido]potassium in hexane, already somewhat unusual if the compound is regarded as a "salt" (i.e., $\{K^+[N(SiMe_3)_2]^-\}_2$), becomes even more remarkable in light of the present structure. Although hydrocarbon solubility of potassium "salts" of transition-metal species has previously been described (e.g., in $[KOsH_3(PMe_2Ph)_3]_2$[25] and $K\{H_3Rh_3(\mu\text{-}Cl)[\mu\text{-}OP(O\text{-}i\text{-}C_3H_7)_2]_2[P(O\text{-}i\text{-}C_3H_7)_3]_3\}$[26]), these compounds owe their solubility to the virtual encapsulation of the K^+ by the surrounding ligands, so that a hydrocarbon shell is displayed toward the solvent. As indicated in a space-filling drawing of $[KN(SiMe_3)_2]_2$ (Figure 2), however, the potassium atoms are exposed to external molecules and are not appreciably shielded by the trimethylsilyl group of the amide. The only adequate explanation of the alkane solubility would seem to be an unusually strong ion-pairing interaction between the K^+ and $N(SiMe_3)_2^-$, so that the term "salt" is not a meaningful description of the nature of the compound. Such pairing would also account for the low electrical conductivity of molten $K[N(SiMe_3)_2]$.[16]

Conclusion

The determination of the solid-state dimeric configuration of $[KN(SiMe_3)_2]_2$ establishes a third structural type for unsolvated bis(trimethylsilyl)amides of the alkali metals. Even though a polymeric geometry is observed in $\{Na[N(SiMe_3)_2]\}_n$, the fact that the bis(trimethylsilyl)amide group supports a two-coordinate environment for the much larger potassium ion suggests that the interplay of the factors controlling the structures of these complexes (e.g., crystal-packing effects, entropic forces, etc.) are more subtle than previously expected.[9] Their influence on the structures of other heavy-pretransition-metal bis(trimethylsilyl)amides and related complexes remains to be determined.

Acknowledgment is made to an Exxon Education Foundation Grant of Research Corp. for support of this research.

Supplementary Material Available: Tables of crystal and data collection parameters, hydrogen atom fractional coordinates, bond distances and angles involving hydrogen atoms, and anisotropic thermal parameters (4 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Formation and Structure of the Tris(catecholato)vanadate(IV) Complex in Aqueous Solution

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Received October 12, 1989

The coordination chemistry of simple catechols continues to be the object of extensive interest because of this ligand's involvement at the active sites of biological chelators, e.g. siderophores.[2-11] Catechols have a pronounced affinity for ions in high oxidation states or with high charge-to-radius ratios. Low molecular weight pigments known as tunichromes serve as complexing agents in the accumulation and storage of vanadium in some marine organisms. The catechol derivative, tunichrome b_1, has been isolated from the blood of *Ascidia nigra* and is suggested to be such a vanadium complexing agent.[12-14]

Over the years much effort has been devoted to characterizing vanadium–catechol complexes. Beginning with the pioneering work of Rosenheim,[15] the nature of the blue species formed by the interaction of V(IV) or V(V) with catechol has been studied extensively.[21-27] For some time it was unclear if, in addition to the mono- and bis(catecholato)oxovanadium(IV) complexes, the tris(catecholato)vanadate(IV) species also was formed in the catechol–$V^{IV}O$ system. Indeed, in spite of the isolation of the thallium(I) salt of the $[V(cat)_3]^{2-}$ complex,[21] which exhibited properties suggestive of a tris octahedral structure at the V(IV) atom, several potentiometric studies failed to provide evidence for the existence of such a species in solution.[18-20,22] The rather contradictory literature in this field was reconciled by Cooper,

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Table I. ESR Parameters of the Complexes[a]

complex	g_0	A_0	g_z	A_z	$g_{x,y}$	$A_{x,y}$
[VO(cat)]	1.968	96	1.943	170	1.976	63
$[VO(cat)_2]^{2-}$	1.975	82	1.947	154	1.981	50
$[V(cat)_3]^{2-}$	1.955	76	1.991	14	1.937	107

[a] ESR measurements at ambient temperature and at 100 K; *A* values in 10^{-4} cm^{-1}.

Koh, and Raymond,[26] who reported the first structural characterization of a tris(catecholato)vanadate(IV) species: $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$. This complex retains its structure in CH_3CN solution, as substantiated by ESR and electrochemical measurements at room temperature. However, an EPR spectrum was not observed for aqueous solutions of this complex, although the reversible redox behavior was consistent with the complex remaining intact. Since the triethylammonium cations apparently form a neutral tight ion pair with the $[V(cat)_3]^{2-}$ complex in CH_3CN[26] (through hydrogen bonding to the octahedral oxygens), ion dissociation in aqueous solution could lead to significant differences in the behavior of the aqueous complex. We have now reexamined the problem in an attempt to reach a more definitive conclusion about the formation and nature of the tris(catecholato)vanadate(IV) species in aqueous solution. It is found that this species yields characteristic ESR spectra, which may allow the structure to be reliably interpreted.

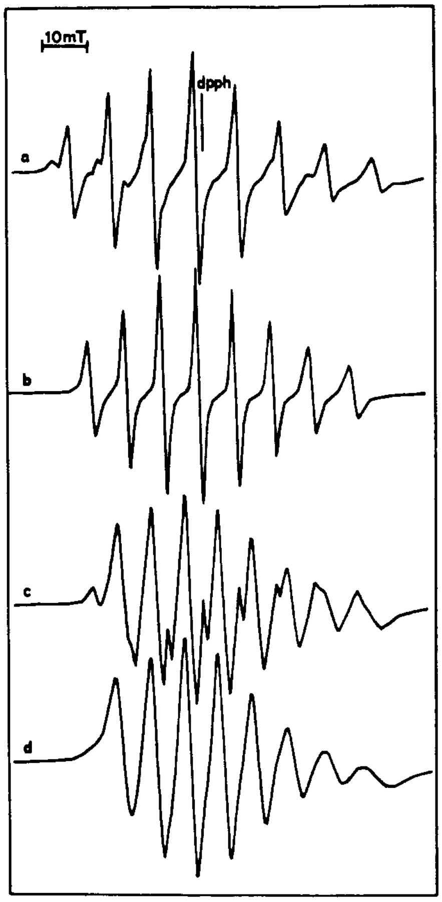

Figure 1. Room-temperature ESR spectra of aqueous solutions of VO^{2+} and catechol as a function of total metal concentration, ligand-to-metal molar ratio (L:M) and pH: 4 × 10^{-3} M VO^{2+}, L:M = 1, pH 4.0 (a); 4 × 10^{-3} M VO^{2+}, L:M = 2, pH 7.5 (b); 4 × 10^{-3} M VO^{2+}, L:M = 100, pH 7.0 (c); 2.4 × 10^{-2} M VO^{2+}, L:M = 100, pH 7.2 (d).

Experimental Section

Chemicals. Catechol (Aldrich) was purified by sublimation. CH_3CN and Et_3N were distilled under nitrogen over P_2O_5 and CaH_2, respectively, prior to use. All other chemicals, $VOSO_4\cdot 3H_2O$, $VO(acac)_2$, and CH_3COOTl (Aldrich), were reagent grade and were used as received. All the syntheses and the manipulations of solutions were made under a nitrogen atmosphere in order to prevent the air oxidation of catechol or vanadium(IV).

Syntheses. $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$ and $Tl_2[V(cat)_3]$ were prepared according to procedures reported previously.[21,26] Anal. Calcd (found) for $C_{32}H_{47}N_3O_6V$: C, 61.92 (61.37); H, 7.63 (7.40); N, 6.77 (6.45). Calcd (found) for $C_{18}H_{12}O_6Tl_2V$: C, 27.58 (27.38); H, 1.54 (1.52).

Physical Measurements. X-Band ESR spectra were recorded on Varian E9 and Bruker 220 instruments at room temperature or 110 K using quartz flat cells or cylindrical tubes sealed under nitrogen. Measurements were also made in cells sealed under vacuum after the solvent was repeatedly degassed by freeze–pump–thaw cycles. Spectra for the $V^{IV}O$–catecholate system in aqueous solution were recorded, as a function of pH, on solutions containing VO^{2+} and catechol at ligand-to-metal molar ratios ranging from 1:1 to 200:1. NaOH was used as the base. For low-temperature measurements, DMSO was added to solutions in order to ensure good glass formation. Microanalyses (C, H, and N) were made with a Perkin-Elmer 240 analyzer.

Results

The $V^{IV}O$–Catecholate System in Aqueous Solution. Examination of the pH dependence of ESR spectra, recorded at either room temperature or 110 K, allowed identification of the species taking part in the complex equilibria on the basis of their ESR (*g* and *A*; see Table I) parameters. The mono- and bis(catecholato)oxovanadium(IV) complexes, which were found as the predominant species in dilute solutions (e.g. VO^{2+} = 4 × 10^{-3} M) at the 1:1 and 2:1 ligand-to-metal molar ratios (Figure 1), exhibited the same parameters as those reported previously.[26] A

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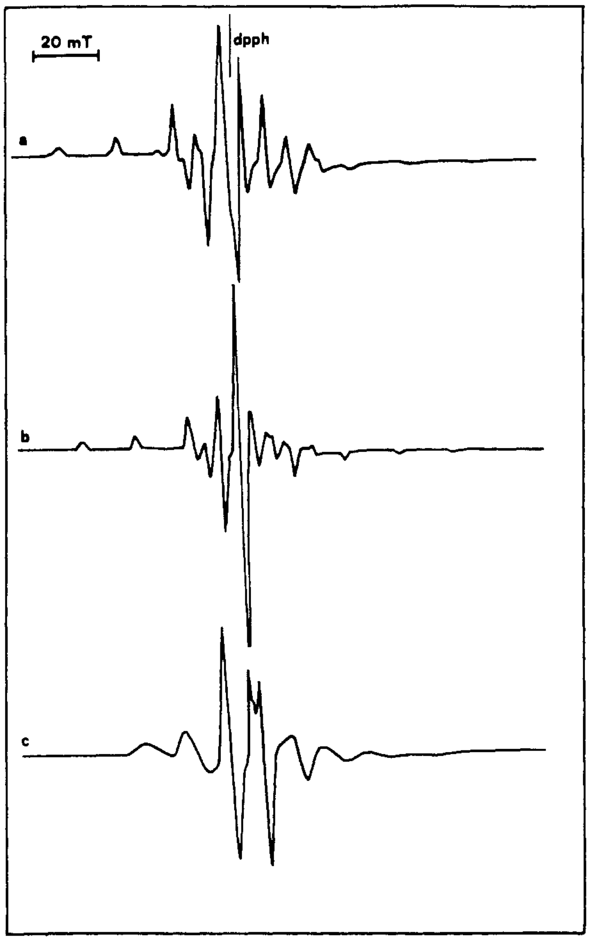

Figure 2. ESR spectra recorded at 100 K on frozen aqueous solutions of VO^{2+} and catechol as a function of total metal concentration, ligand-to-metal molar ratio (L:M), and pH: 4×10^{-3} M VO^{2+}, L:M = 2, pH 4.5 (a) and pH 7.5 (b); 2.4×10^{-2} M VO^{2+}, L:M = 100, pH 7.2 (c).

third complex was detected as a minor species, over the pH range 4–9, at ligand-to-metal molar ratios as high as 5, and it became predominant when the ratio was raised to 100:1. The relative amount of the species increased with the total concentration; at 2.4×10^{-2} M VO^{2+} concentration and 100:1 ligand-to-metal ratio, the third species represented almost 100% of total vanadium in the pH range 5–7. The value of the isotropic hyperfine constant (^{51}V) for this species is 76×10^{-4} cm^{-1}, almost the same as that measured previously on solutions of the triethylammonium salt of the $[V(cat)_3]^{2-}$ complex in CH_3CN.[26]

The spectra recorded on frozen solutions were more informative. In fact, those of the mono- and bis(catecholato)oxovanadium(IV) species (Figure 2) were typical for square-pyramidal $V^{IV}O$ complexes having the unpaired electron largely in a d_{xy} orbital (for the ligands along x and y), inasmuch as they exhibited $A_z > A_x$, A_y and $g_z < g_x$, g_y as well as parameters lying in the expected range for catecholate coordination.[28] The features of the glass spectrum of the tris complex differed (Figure 2) in showing a striking resemblance to those described by Jezierski and Raynor for V(IV) hexacoordinated complexes with a d_{z^2} ground state.[29] As is clearly illustrated in that paper, the distinguishing features of this type of spectrum are $g_z \approx 2$, g_x, $g_y < 2$, and $A_z \ll A_x$, A_y. Typically, for $VCl_2(trop)_2$ (trop = tropolonato), the reported parameters are $g_x = 1.938$, $g_y = 1.944$, $g_z = 1.996$, $A_x = 110 \times 10^{-4}$ cm^{-1}, $A_y = 102 \times 10^{-4}$ cm^{-1}, and A_z (calcd) = 1×10^{-4} cm^{-1}. Analogously, in our spectrum the A_z splitting was too low to be resolved. Moreover, the x, y anisotropy was small, at least as judged by measurements at the X-band frequency. Therefore, by neglecting the small x, y anisotropy, one may estimate the g_z and A_z values by using the isotropic data. Such an analysis yielded the parameters g_x, $g_y = 1.937$, $g_z = 1.991$, A_x, $A_y = 107 \times 10^{-4}$ cm^{-1}, and $A_z = 14 \times 10^{-4}$ cm^{-1}, confirming the change from a d_{xy} to a d_{z^2} ground state (in a new symmetry and with new axes) as a result of the coordination of the third catecholate molecule to vanadium and the consequent displacement of the oxo ligand.

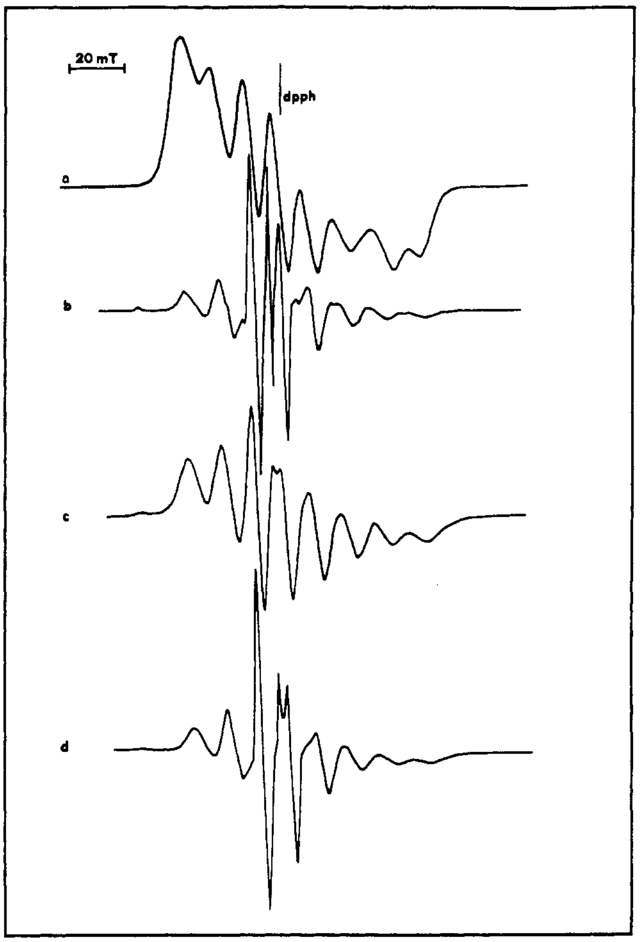

Figure 3. ESR spectra of $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$: powder ESR spectrum recorded at room temperature (a); glassy spectra of 2.4×10^{-2} M solutions in water (b), in 4.8×10^{-2} M aqueous catechol (c), and in CH_3CN (d).

Tris(catecholato)vanadate(IV) Complexes in the Solid State. The reported powder ESR spectrum of the solid complex $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$ was rather broad, as expected for a nonmagnetically dilute compound (Figure 3). Nevertheless, the splittings detectable even at room temperature suggested a close similarity between these patterns and those of the frozen solutions of the tris complex formed in the aqueous $V^{IV}O$–catechol system. In contrast, ^{51}V hyperfine splittings were absent in the ESR spectrum of $Tl_2[V(cat)_3]$, which was of the exchange-narrowed type (Figure 4).

When dissolved, both $[Et_3NH]_2[V(cat)_3]\cdot CH_3CN$ (in water or CH_3CN) and $Tl_2[V(cat)_3]$ (in DMSO) yielded, at either room temperature or 110 K, the distinctive patterns described above for the trischelated species formed in the $V^{IV}O$–catechol system. However, unless an excess of ligand was added to the solution, signals of the bis(catecholato)oxovanadate(IV) species (Figure 3b) or even those of the solvated VO^{2+} ion (Figure 4b) were detected, due to partial dissociation of the tris complex.

Discussion and Conclusion

The results presented here confirm that complexes with 1:1, 2:1, and 3:1 ligand-to-metal ratios are formed in the $V^{IV}O$–catechol system in aqueous solution. The first two species involve the coordination of one or two bidentate catecholates, respectively, to vanadium, which achieves the square-pyramidal geometry typical of the $V^{IV}O$ complexes. All the spectroscopic evidence

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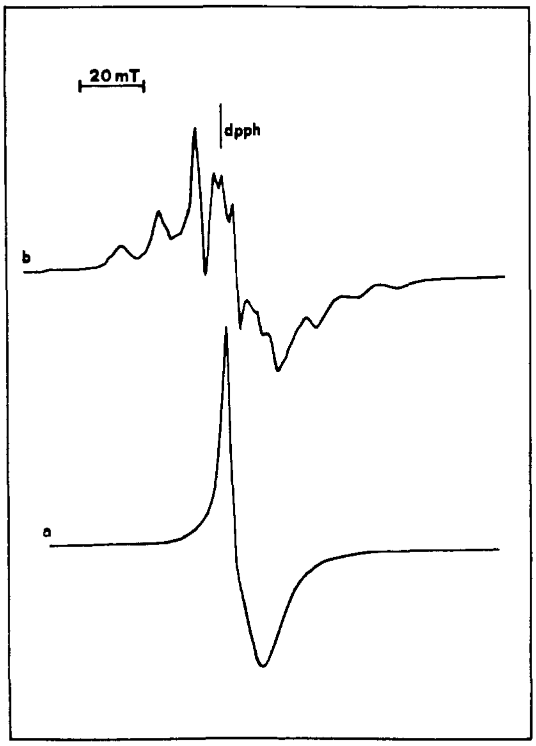

Figure 4. ESR spectra of $Tl_2[V(cat)_3]$: powder ESR spectrum recorded at room temperature (a); glassy spectrum of a 2.4×10^{-2} M solution in DMSO (b).

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 0.67*Dq*. 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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0020-1669/90/1329-1589$02.50/0 © 1990 American Chemical Society