to the amount of charge consumed in the production of formic acid. The current efficiency of electropolymerized films was nearly 100%.

Both the turnover number and current efficiencies might be larger if other reduction products were also being formed during electrolysis. We have not yet detected products other than formic acid although initial studies by mass spectrometry detected traces of carbon monoxide. Also, the coverage of the platinum gauze is not known to a high degree of accuracy, and high coverages would preclude activity throughout the film.

After 1.1 C of charge was passed through the system, the electrochemistry of the catalyst was still present. However, the amount of electrochemically active material had been reduced to 25% of its initial value. The kinetics of the electrocatalytic carbon dioxide reduction were determined by using the Koutecky-Levich equation (analogous to the oxygen reduction kinetic analysis). The second-order rate constant for the reduction of carbon dioxide by two electrons is 1 (±1) × 10^3 M^{-1} s^{-1}, as determined from the intercept of $1/i_{\text{lim}}$ versus $\omega^{-1/2}$ plots (Figure 7B). Although the rate constant for this reaction is not large, the decrease in the reduction potential due to the polymer film is remarkable.

The polymerized films of $[Co(v\text{-}tpy)_2]^{2+}$ are capable of reducing carbon dioxide to formic acid and thus creating a carbon-hydrogen bond. We propose that carbon dioxide binds to the open coordination site at cobalt and is subsequently reduced. The generation of an open coordination site at cobalt is wholly responsible for this catalytic activity. If this assertion is correct, one would expect that a single quinquepyridine ligand bound to a cobalt center may be even more active. We are currently pursuing the study of the electrochemistry and electrocatalytic activity of $[Co(v\text{-}qpy)]^{2+}$.

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Synthesis and Characterization of (Catecholato)bis(β-diketonato)vanadium(IV) Complexes

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The syntheses of the complexes $[V(cat)(acac)_2]$, $[V(cat)(bzac)_2]$, and $[V(dtbc)(bzac)_2]$ are described, and the complexes' UV-visible, infrared, and mass spectral data are presented. The complexes are nonelectrolytes with a room-temperature magnetic moment of about 1.8 μ_B, consistent with the d^1 vanadium(IV) system. The complexes show reversible one-electron reduction to the vanadium(III) state at -0.22, -0.26, and -0.37 V (NHE), respectively, in acetonitrile and at -0.39, -0.38, and -0.56 V (NHE), respectively, in dichloromethane. Oxidation to the vanadium(V) state does not occur at potentials less positive than 1.0 V, at which the catecholate ligands undergo oxidation. These mixed-ligand vanadium(IV) complexes are more stable to disproportionation than the tris(catecholato) and tris(β-diketonato) complexes, more stable to oxidation than the former complexes, and more stable to reduction than the latter.

Introduction

Only a few non-vanadyl vanadium(IV) fully chelated species are well characterized.[1-6] This is surprising because these types of complexes provide access to a range of vanadium chemistries as they have, in principle, the possibility of oxidation and reduction to equivalent vanadium(V), -(III), and -(II) species, whereas the oxovanadium species are unable to retain their integrity after redox reactions. The only mixed-chelate complexes reported are $[V(bpy)(dtbc)_2]$ and $[V(phen)(dtbc)_2]$.[7,8] This paper reports the synthesis and characterization of mixed catecholate β-diketonate complexes and a comparison of the complexes' properties with those of the tris complexes of these ligands.

Experimental Section

Materials. Catechol and tetrabutylammonium perchlorate were recrystallized twice from ethanol, and 3,5-di-*tert*-butylcatechol was recrystallized from pentane. Sodium methoxide,[9] oxobis(2,4-pentanedionato)vanadium(IV),[10] oxobis(1-phenyl-1,3-butanedionato)vanadium(IV),[11] dichlorobis(2,4-pentanedionato)vanadium(IV),[6] and dichlorobis(1-phenyl-1,3-butanedionato)vanadium(IV)[6] were prepared by literature methods. All solvents were AnalaR grade. Methanol was dried by refluxing over magnesium methoxide, and hexane, toluene, pentane, dichloromethane, and acetonitrile were dried by refluxing over powdered calcium hydride. The distillation of the solvents was carried out under dried high-purity argon just prior to use. Vanadium analyses were carried out by atomic absorption spectroscopy, and the C, H, O analyses were conducted by the University of Queensland's microanalytical service.

For the syntheses of the complexes, all operations were carried out under dry, oxygen-free dinitrogen in a VAC Dri-Lab Model MO40-1 drybox unless otherwise stated.

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(7) Abbreviations: acac, 2,4-pentanedionate; bzac, 1-phenyl-1,3-butanedionate; cat, catecholate; dtbc, 3,5-di-*tert*-butyl-catecholate; bpy, 2,2'-bipyridine; phen, 1,10-phenanthroline; salen, bis(salicylaldiminato)ethylenediamine; dike, β-diketonate.

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Table I. Infrared Spectral Data[a,b]

[V(cat)(acac)$_2$]	[V(cat)(bzac)$_2$]	[V(dtbc)(bzac)$_2$]
1544 vs, 1536 vs, 1531 vs, 1430 m, 1354 s, 1317 w, 1284 m, 1253 w, 1135 m, 1108 vw, 1027 m, 950 vw, 933 w, 879 vw, 803 w, 747 m, 671 m, 614 w, 1027 w, 1011 vw, 998 w, 577 w, 563 vw, 462 s, 416 w, 380 w, 345 vw	1587 s, 1550 vs, 1515 vs, 1488 vs, 1447 s, 1432 s, 1350 vs, 1313 vs, 1303 vs, 1182 w, 1136 s, 1106 s, 1072 w, 1028 m, 1009 m, 999 m, 965 m, 875 w, 850, 805 w, 787 w, 776 m, 738 s, 710 s, 686 s, 620 w, 604 w, 579 w, 561 s, 517 w, 453 m, 436 m	1587 m, 1527 vs, 1487 m, 1449 w, 1361 s, 1326 vw, 1313 vw, 1297 m, 1250 vw, 1223 m, 1200 m, 1180 w, 1158 vw, 1104 m, 1072 vw, 992 w, 964 w, 850 m, 774 m, 713 m, 688 m, 585 vw, 555 m, 482 vw, 440 m, 433 m, 383 w, 363 w, 305 w, 300 w

[a] KBr disks. [b] Abbreviations: s = strong; m = medium; w = weak; v = very.

Table II. UV–Visible Spectral Data for the Mixed-Chelate Vanadium(IV) Complexes

complex	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
[V(cat)(acac)$_2$]	CH_3CN	825 (3540), 508 (3430), 337 (3660), 299 sh (14 000), 275 (17 800)
	CH_2Cl_2	835 (4000), 518 (3680), 337 sh (4000), 274 (18 400)
[V(cat)(bzac)$_2$]	CH_3CN	830 (5400), 518 (5510), 321 sh (23 000), 289 (27 300)
	CH_2Cl_2	835 (5460), 524 (4800), 319 sh (24 600), 291 (26 400)
[V(dtbc)(acac)$_2$][a]	CH_3CN	865 (4100), 578 (4000), 353 sh (4200), 292 sh (15 800), 275 (19 200)
[V(dtbc)(bzac)$_2$]	CH_3CN	865 (6040), 580 (6200), 374 sh (8400), 294 (23 000)
	CH_2Cl_2	870 (6000), 584 (6200), 373 sh (8380), 293 (26 200)

[a] Concentration determined by weighing residue after evaporating a known volume of the aceetonitrile solution.

(Catecholato)bis(2,4-pentanedionato)vanadium(IV). A solution containing catechol (0.32 g, 0.0029 mol) and sodium methoxide (0.32 g, 0.0058 mol) in methanol (10 mL) was added dropwise to a stirred suspension of [VCl_2(acac)$_2$]·0.25CH_2Cl_2 (1.00 g, 0.0029 mol) in methanol (10 mL). Upon addition of the ligand the solution cleared and the yellow-brown color changed to deep green and finally to deep blue-violet, and a white precipitate of sodium chloride formed. The solution was stirred for a further 2 h and then filtered. The filtrate was allowed to evaporate to give a black gum. This was dissolved in warm toluene (15 mL), the solution filtered, and warm hexane (8 mL) added to the filtrate. The filtrate was sealed under nitrogen and was left at −20 °C for 1 week to yield a black precipitate that was filtered off, washed with hexane, and dried in vacuo over P_4O_{10}: yield 0.3 g (29%); mp 180–182 °C. Anal. Calcd for $C_{16}H_{18}O_6V$: C, 53.8; H, 5.1; O, 26.9; V, 14.3. Found: C, 53.9; H, 5.1; O, 26.7; V, 14.2. Principal mass spectral peaks (*m/e* (relative intensity %) [identity]): 357 (18.4) [M]; 348 (5.0) [V(acac)$_3$]; 256 (22.2) [VO(acac)$_2$]; 250 (20.3) [V(acac)$_2$ + 1]; 249 (100.0) [V(acac)$_2$]; 183 (14.0) [VO(acac)$_2$ − C_5H_6O[12]]; 167 (10.0) [V(acac)$_2$ − C_5H_6O[12]]; 166 (35.9) [VO(acac)]; 150 (4.4) [V(acac)]; 110 (42) [catH$_2$]; 100 (24.0) [acacH]; 85 (32.9) [acacH–CH_3]; 67 (8.3) [VO]; 43 (70.4) [CH_3CO].

(Catecholato)bis(1-phenyl-1,3-butanedionato)vanadium(IV). The complex was prepared by the above method using acetonitrile as solvent: yield 62%; mp 173–175 °C. Anal. Calcd for $C_{26}H_{22}O_6V$: C, 64.9; H, 4.6; O, 19.9; V, 10.6. Found: C, 64.1; H, 4.5; O, 19.9; V, 10.5. Principal mass spectral peaks (*m/e* (relative intensity %) [identity]): 534 (49.4) [V(bzac)$_3$]; 482 (5.0) [M + 1]; 481 (16.3) [M]; 390 (11.8) [VO(bzac)$_2$ + 1]; 389 (18.7) [VO(bzac)$_2$]; 374 (22.6) [V(bzac$_2$ + 1]; 373 (100.0) [V(bzac)$_2$]; 244 (11.3); 229 (13.2) [V(bzac)$_2$ + 1 − $C_{10}H_8O$[12]]; 228 (3207) [V(bzac)$_2$ − $C_{10}H_8O$[12]]; 162 (30.0) [bzacH]; 161 (19.4) [bzac]; 150 (12.6); 147 (26.7); 144 (5.9); 129 (39.5); 110 (40.0) [catH$_2$]; 105 (68.1); 85 (13.1); 78 (12.9); 77 (58.5); 69 (47.0); 67 (11.5); 43 (68.9) [CH_3CO].

(3,5-Di-*tert*-butylcatecholato)bis(1-phenyl-1,3-butanedionato)vanadium(IV). A solution of 3,5-di-*tert*-butylcatechol (1.95 g, 0.0088 mol) in acetonitrile (5 mL) was added dropwise to a stirred suspension of [VCl_2(bzac)$_2$] (4 g, 0.0088 mol) in acetonitrile (40 mL). Upon addition of the ligand, the color of the solution changed to green and then deep blue. The solution was boiled under reflux for about 20 h[13] and then left to evaporate at 25 °C to give the desired complex: yield 3.75 g (70%); mp 170–173 °C. Anal. Calcd for $C_{34}H_{38}O_6V$: C, 68.8; H, 6.5; O, 16.2; V, 8.6. Found: C, 68.9; H, 6.5; O, 16.1; V, 8.6. Principal mass spectral peaks (*m/e* (relative intensity %) [identity]): 594 (7.1) [M + 1]; 593 (25.7) [M]; 534 (35.3) [V(bzac)$_3$]; 432 (8.7) [V(bzac)(dtbc)]; 417 (11.1) [V(bzac)(dtbc − CH_3)]; 389 (7.9) [VO(bzac)$_2$]; 374 (30.1) [V(bzac)$_2$ + 1]; 373 (100.0) [V(bzac)$_2$]; 229 (9.8) [V(bzac)$_2$ + 1 − $C_{10}H_8O$[12]]; 228 (30.0) [V(bzac)$_2$ − $C_{10}H_8O$[12]]; 161 (9.9) [bzac]; 129 (17.8); 105 (33.3); 77 (30.5); 57 (26.4); 51 (9.6) [V]; 43 (32.7) [CH_3CO].

Physical Measurements. Infrared spectra were obtained with the compounds dispersed in KBr pellets and in Nujol with CsI windows by using a Mattson Sirius 100 FT–IR spectrophotometer with polystyrene as frequency calibrant. UV–visible spectra were measured with solutions in septum-sealed quartz cuvettes with Hewlett-Packard 8450A and Cary 17 spectrophotometers. Sample preparation was carried out in the Dri-Lab. Conductance measurements were carried out with a TPS Model 3102 bridge and a cell of standard constant that was calibrated with a 0.0200 M KCl solution. Electrochemical experiments were performed with a Metrohm E506 Polarecord–VA scanner E612 apparatus connected to a Houston 2000 X-Y recorder. Platinum-disk and dropping-mercury electrodes (DME) were employed as working electrodes for the cyclic voltammetric and polarographic studies, respectively. A platinum wire was used as an auxiliary electrode, and a calomel electrode in tetraethylammonium perchlorate–saturated dichloromethane or acetonitrile as a reference electrode. The supporting electrolyte was tetraethylammonium perchlorate (0.1 M), and all solutions were 10^{-3}–10^{-4} M in complex. Values of the reduction potentials ($E^{1/2}$) were obtained from the intercepts of plots of log $[(i_d - i)/i]$ versus potential (E), and the number of electrons involved in the reversible electrode process were estimated from the slopes of such plots according to the Heyrovsky–Ilkovic equation:

$$E = E_{1/2} + (RT/nF)\ln[(i_d - i)/i] \tag{1}$$

All potentials throughout this paper are relative to the normal hydrogen electrode (NHE)[14] using ferrocene (+0.400 V vs NHE)[15] as a standard. Magnetic moments were measured by the Gouy method with tris(ethylenediamine)nickel(II) thiosulfate as the susceptibility standard. Conductance, electrochemical, and susceptibility measurements were made at 25 °C. Solution measurements in dichloromethane were made by the NMR method.[16] Melting points were determined (uncorrected) with a Buchi melting point apparatus. Electron impact mass spectral data were obtained with a Kratos MS25RFA spectrometer.

Results and Discussion

Syntheses. One method of synthesis involved the reaction of the catechol with dichlorobis(β-diketonato)vanadium(IV) in refluxing acetonitrile with the evolution of hydrogen chloride. With unsubstituted catecholate, chloride-containing green products were obtained, whereas the desired product was obtained in good yield with 3,5-di-*tert*-butylcatechol and 1-phenyl-1,3-butanedionate (eq 2). With this catechol and 2,4-pentanedionate, the resulting solution contained the desired product according to its spectra and electrochemistry, but the complex's high solubility in organic solvents prevented its isolation as a crystalline solid.

$$[VCl_2(bzac)_2] + dtbcH_2 \xrightarrow{CH_3CN} [V(dtbc)(bzac)_2] + 2HCl \tag{2}$$

As an alternative strategy, deprotonated catechol was reacted with the dichloro compound according to eq 3. This method successfully yielded [V(cat)(acac)$_2$] and [V(cat)(bzac)$_2$].

$$[VCl_2(dike)_2] + cat^{2-} \rightarrow [V(cat)(dike)_2] + 2Cl^- \tag{3}$$

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Table III. Electrochemical Data from Cyclic Voltammetric and Dc-Polarographic Studies of Mixed-Chelate Vanadium(IV) Complexes[a]

complex	solvent	E_{pc}, V	E_{pa}, V	i_{pc}/i_{pa}	ΔE_p,[b] mV	$E^{1/2}$,[c] V
[V(cat)(acac)$_2$]	CH_3CN	−0.26	−0.20	1.0	60	−0.22 (−0.23)
	CH_2Cl_2	−0.52	−0.28	1.0	240	−0.39 (−0.40)
[V(cat)(bzac)$_2$]	CH_3CN	−0.27	−0.21	1.0	60	−0.26 (−0.24)
	CH_2Cl_2	−0.50	−0.26	1.0	240	−0.37 (−0.38)
[V(dtbc)(acac)$_2$]	CH_3CN	−0.42	−0.35	1.0	70	−0.37 (−0.39)
[V(dtbc)(bzac)$_2$]	CH_3CN	−0.40	−0.34	1.0	60	−0.38 (−0.37)
	CH_2Cl_2	−0.71	−0.41	1.0	300	−0.56 (−0.56)

[a] All potentials are vs NHE. [b] $\Delta E_p = E_{pc} - E_{pa}$ at a scan rate of 100 mV s^{-1}. [c] Values of the reduction potentials ($E^{1/2}$) were obtained from the intercepts of plots of log $[(i_d - i)/i]$ vs potential (E); values in parentheses were calculated by using the formula $0.5(E_{pc} + E_{pa})$ from cyclic voltammetry.

Conductance Measurements. The three complexes isolated are nonelectrolytes with no detectable molar conductance in dichloromethane and with the following low values in acetonitrile (Ω^{-1} cm^2 mol^{-1}): [V(cat)(acac)$_2$], 5.6; [V(cat)(bzac)$_2$], 6.0; [V(dtbc)(bzac)$_2$], 4.4.

Magnetic Behavior. The above three complexes' magnetic moments in the solid state and in solution are 1.75, 1.76, and 1.82 μ_B, respectively, in accord with the value expected for d^1, $S = {}^1/_2$ systems.

Mass Spectra. The major EIMS peaks observed for the complexes are given in the Experimental Section. The three complexes exhibit the parent ion, and the most intense peaks are *m/e* 249 and 373 for the 2,4-pentanedionato and 1-phenyl-1,3-butanedionato complexes, respectively, corresponding to V(acac)$_2$ and V(bzac)$_2$. Reactions in the gas phase have produced peaks *m/e* 348 and 534, corresponding to V(acac)$_3$ and V(bzac)$_3$, as well as a number of peaks for vanadyl species.

Infrared Spectra. The peaks in the KBr disk spectra of the three complexes are given in Table I. As the KBr pellets were prepared in air, the spectra of Nujol mulls prepared in the Dri-Lab were also run to check if decomposition had taken place during the preparation of the disks. The two types of spectra had identical features for each of the three complexes, confirming that no decomposition had occurred.

A feature of the infrared spectra of other metal–catecholato complexes is the occurrence of rather intense bands at about 1450–1480 and 1250–1300 cm^{-1}.[17,18] In [V(cat)$_3$]$^{2-}$ strong bands occur at 1450, 1465, and 1260 cm^{-1}.[4] These bands are also observed for free catechols, and they gain intensity upon coordination to a metal ion. The higher frequency bands are assigned to a ring-stretching mode, whereas the lower frequency band is assigned to the C–O stretching frequency. In the mixed-chelate complexes studied here, no strong bands occur in these ranges. Possibly the higher frequency band has been shifted into the region of the β-diketonates' C–O and C–C stretch bands at about 1530 cm^{-1}, and the catechols' C–O stretches appear to have been shifted to about 1350 cm^{-1} for the two catecholato complexes and to about 1360 cm^{-1} for the butyl-substituted catecholato complex, consistent with a weaker C–O bond in association with a stronger V–O band, which in turn causes significant shifts in the vibrations associated with these coordinate bonds.

Most bands observed for [V(dike)$_3$]$^+$ complexes are found in the spectra of the mixed complexes with only small shifts. However, the strong band at 493 cm^{-1} for [V(acac)$_3$][SbCl$_6$], assigned as V–O stretches for other M(acac)$_3$ species,[19] is shifted to 462 cm^{-1}.

UV–Visible Spectra. The electronic absorption spectra of the mixed-chelate complexes are given in Table II. The spectra of tris(β-diketonato)vanadium(IV) and tris(catecholato)vanadium(IV) complexes in acetonitrile and dichloromethane have similar features in the visible region: [V(acac)$_3$]$^+$, 650 (sh), 562, 450 (sh), ~350 nm; [V(bzac)$_3$]$^+$, 596 nm; [V(cat)$_3$]$^{2-}$, 650 (sh), 552, ~450 (sh), 362 nm.[4,6] The peaks above 550 nm have been assigned to ligand (π) → metal (d) charge transfer, and the peak at about 350 nm has been assigned to metal (d) → ligand (π)* charge transfer.[4,6,20] The ligand $\pi \rightarrow \pi^*$ transitions occur at 270 nm for [V(acac)$_3$]$^+$, ~305 and ~290 nm for [V(bzac)$_3$]$^+$, and at ~290 nm for [V(cat)$_3$]$^{2-}$.[4,6] On the basis of the work of Haigh and Thornton,[21] it has been concluded that the dπ orbitals lie in between the π and π^* orbitals of the β-diketonate,[6,20] and from the similarity in the spectra, this would appear also to be true for the catecholate.

The dπ orbitals of the d^1 vanadium(IV) would be separated by a larger energy in lower symmetry mixed-chelate complexes than in the above tris chelate complexes. This is reflected in the greater separation of the ligand (π) → metal (d) charge-transfer bands, giving peaks, for example for [V(cat)(acac)$_2$], at 825 and 508 nm in acetonitrile. This greater splitting of the dπ orbitals must also affect the position of the metal (d) → ligand (π^*) charge-transfer band: it is shifted to wavelengths shorter ([V(cat)(acac)$_2$], 337 nm) than those for the tris complexes ([V(acac)$_3$]$^+$, 351 nm;[6] [V(cat)$_3$]$^{2-}$, ~360 nm[4]).

The ligand $\pi \rightarrow \pi^*$ transitions in the mixed-chelate complexes occur to wavelengths slightly higher than those for the individual chelates' $\pi \rightarrow \pi^*$ transitions in the tris complexes. For example; [V(cat)(acac)$_2$], 299 (sh), 275 nm (CH_3CN); [V(cat)$_3$]$^{2-}$, ~290 nm (CH_3CN);[4] [V(acac)$_3$]$^+$, 270 nm (CH_3CN); [V(cat)(bzac)$_2$], 321 (sh), 289 nm (CH_3CN); [V(bzac)$_3$]$^+$, 303, 288 nm (CH_3CN).

Electrochemistry. The results of the dc cyclic voltammetric and the dc-polarographic studies for the above three complexes in acetonitrile and dichloromethane and for the acetonitrile solution of [V(dtbc)(acac)$_2$] are given in Table III. The dc-polarographic investigations in acetonitrile reveal a one-electron reversible electrochemical process at −0.24 ± 0.02 V (NHE) for the two catecholato complexes and at −0.38 ± 0.01 V (NHE) for the two 3,5-di-*tert*-butylcatecholato complexes. The dc-polarographic studies in dichloromethane show one-electron reversible electrochemical processes at −0.38 ± 0.01 V (NHE) for the two catecholato complexes and at −0.56 V (NHE) for [V(dtbc)(bzac)$_2$].

The cyclic voltammetric examination of the four complexes in acetonitrile reveals a pair of cathodic and anodic peaks in each case. The peak separation (ΔE_p) for each complex is close to that anticipated for a Nernstian one-electron process (59 mV);[22] plots of i_p (peak current) versus SR$^{1/2}$ (SR = scan rate) are linear, and the ratio of the cathodic to anodic peak currents is 1, indicating that the electron transfer is reversible and that mass transfer is limited. In dichloromethane one set of peaks is also obtained for each complex, but the peak separations are 240 mV for the two catecholato complexes and 300 mV for the 3,5-di-*tert*-butylcatecholato complex, indicating irreversible behavior in this solvent.

The one-electron redox process can be unambiguously assigned to the V(IV)–V(III) redox couple on the basis of the following evidence.

(i) Starting with a vanadium(IV) solution, and applying a voltage 200 mV more anodic than the oxidation peak, no current flowed, no color change took place, and the CV of the solution did not change in a subsequent sweep.

(ii) Starting with a vanadium(IV) solution, and applying a voltage 200 mV more cathodic than the reduction peak, the so-

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lution's color changed from dark blue or purple to almost colorless, a current flowed in the direction that would reduce the complex, and the subsequent CV (after the current became almost zero) was changed irreversibly with the introduction of several new peaks.[23]

For $[V(acac)_3]^{+,0}$ and $[V(bzac)_3]^{+,0}$ the potentials are identical,[6] whereas the potential for $[V(dtbc)_3]^{2-,3-}$ is 0.35 V more negative than that for $[V(cat)_3]^{2-,3-}$ due to the electron-releasing alkyl groups.[4] For the mixed-chelate complexes studied here, a change from 2,4-pentanedionate to 1-phenyl-1,3-butanedionate has little effect on the potentials for the vanadium(IV)–vanadium(III) couples, but the alkyl groups' electron-releasing property in the dtbc complex again causes the potential to become more negative by 0.14–0.19 V.

No evidence was obtained for reduction of the mixed-chelate vanadium(III) complexes to vanadium(II). A cyclic voltammetric study of the oxidation of the vanadium(IV) complexes to vanadium(V) is complicated by the oxidation of the catechol ligand in the potential range expected for the metal oxidation. Catechol and 3,5-di-*tert*-butylcatechol in acetonitrile give peaks at 1.26 and 1.14 V (NHE), respectively. $[V(cat)(acac)_2]$ and $[V(dtbc)(bzac)_2]$ give oxidation peaks at 1.1 and 1.0 V, respectively, in acetonitrile with similar behavior in dichloromethane.

The potentials (V vs NHE) for the tris chelate and mixed-chelate complexes are as follows:

$$[V(acac)_3]^{2+} \rightleftharpoons [V(acac)_3]^{+} \rightleftharpoons V(acac)_3] \rightleftharpoons [V(acac)_3]^{-}$$

Me_2SO[6,24]		+0.73	-1.35
Me_2CO[6,25]		+1.13	-1.14
CH_2Cl_2[6]	+0.90	+0.58	

$$[V(cat)_3]^{-} \rightleftharpoons [V(cat)_3]^{2-} \rightleftharpoons [V(cat)_3]^{3-}$$

CH_3CN[4,6]	-0.015	-0.84
H_2O[4,6]		-0.48

$$[V(cat)(acac)_2]^{+} \rightleftharpoons [V(cat)(acac)_2]^{0} \rightleftharpoons [V(cat)(acac)_2]^{-}$$

CH_3CN	>+1.0	-0.22
CH_2Cl_2	>+1.0	-0.39

For the tris(2,4-pentanedionato)vanadium system, the III state is the most stable. The IV state is relatively stable to oxidation but is easily reduced to the III state, which is stable to further reduction. Nevertheless, the IV state is stable to disproportionation. For the catecholato system, the V state is the most stable. The III state is easily oxidized to the IV state, which, although stable to disproportionation, in turn requires a relatively weak oxidizing agent to go to the V state. In contrast to these two tris chelate systems, the mixed-chelate complexes have the IV state as the most stable: $[V(cat)(acac)_2]$ and its related complexes are stable to disproportionation and relatively stable to oxidation and reduction.

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(23) Attempts to isolate the V(III) species by controlled-potential reduction of the V(IV) complexes were unsuccessful. The deep blue or purple color of the V(IV) complexes changed during the electrolysis to give a much lower intensity red-brown and finally green color.

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Synthesis of Polyhedral Phosphaboranes. Crystal Structure of $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$

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The diphosphaborane $1,2\text{-}P_2B_{10}H_{10}$ has been prepared in low yield from $B_{10}H_{14}$ by using PCl_3 as the source of phosphorus. This reaction gives a complex mixture of products, one of which is the *closo*-phosphaborane, $6\text{-}(C_2H_5)_3N\cdot2\text{-}PB_9H_8$, which has been fully characterized, including a single-crystal X-ray structure determination (space group $P2_1/c$, $a = 13.589$ (3) Å, $b = 11.758$ (3) Å, $c = 18.224$ (5) Å, $\beta = 99.57$ (1)°, $Z = 8$). The thermal conversion of $1,2\text{-}P_2B_{10}H_{10}$ to $1,7\text{-}P_2B_{10}H_{10}$ occurred at 560–590 °C in a sealed tube. Aqueous base rapidly removed one phosphorus atom from $1,2\text{-}P_2B_{10}H_{10}$ to form the $7\text{-}PB_{10}H_{12}^-$ ion.

Introduction

There exist a rather extensive number of known borane and carborane derivatives containing group 15 atoms, the synthesis and properties of which are summarized in reviews.[1] Recently, we reported improved methods for the synthesis of $7\text{-}B_{10}H_{12}As^-$ and $1,2\text{-}B_{10}H_{10}As_2$.[2] These results have led us to again study improved methods for the synthesis of phosphaboranes.

Previously, the most readily available derivatives were $7\text{-}B_{10}H_{12}PR$ (R = Me, Et, Pr, Ph) and their metal complexes, $(\eta^5\text{-}C_5H_5)Co(B_{10}H_{10}PR)$.[3] The *nido*-phosphaboranes were prepared by reacting $B_{10}H_{14}$ and $RPCl_2$ in the presence of NaH or triethylamine. Early attempts[4] to obtain $7\text{-}B_{10}H_{12}P^-$ from the reaction of PCl_3, $B_{10}H_{14}$, and a base in diethyl ether gave a mixture containing this anion. Its presence in the mixture was proven by full characterization of the σ-bonded complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2PB_{10}H_{12}$.[5]

We have studied in more detail the synthesis of phosphaboranes from $B_{10}H_{14}$, PCl_3, and a base. Reported here are our initial results on this very complex, but extremely interesting, set of reactions.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.8 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3\cdot O(C_2H_5)_2$ (positive values downfield). Two-dimensional NMR (^{11}B–^{11}B) spectra were obtained on the same instrument. Broad-band ^1H decoupling (3 W) was continuously used. A general description for two-dimensional (^{11}B–^{11}B) NMR technique has been previously discussed.[16] Typically, the 2-D t_1, t_2 matrix was collected as

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