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NEW OXOVANADIUM COMPLEXES COORDINATED TO A *fac*-TRIDENTATE ORGANOMETALLIC LIGAND AND X-RAY CRYSTAL STRUCTURE OF [η-CpCo{$P(O)(OC_2H_5)_2$}$_3$VO(acac)]: THEIR ROLE IN OXIDATIVE CATALYSIS

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Summary

Treatment of $VO(acac)_2$ with the facial-tridentate organometallic ligand [η-CpCo{$P(O)(OEt)_2$}$_3$]$^-$ affords a new binuclear compound [η-CpCo{$P(O)(OEt)_2$}$_3$VO(acac)] (I). This compound undergoes protonation with HPF_6 in the presence of 1,10-phenanthroline (phen), or 2,2′-bipyridyl (bipy), to yield binuclear cationic derivatives [η-CpCo{$P(O)(OEt)_2$}$_3$-VO(phen))]$^+PF_6^-$ (II), and [η-CpCo{$P(O)(OEt)_2$}$_3$VO(bipy)]$^+PF_6^-$ (III). The X-ray crystal structure determination and full characterization of I has been performed. The catalytic oxygenation and oxygen transfer to 3,5-di-t-butylcatechol in the presence of I, II$^+$, or III$^+$ complexes is reported.

Well-characterized oxovanadium(IV) and peroxovanadium(V) complexes have proved to be efficient reagents in the epoxidation of olefins and aromatic hydrocarbons [1]. Likewise, they are effective in the non-enzymatic cleavage of aromatic rings, displaying in this case a behaviour analogous to pyrochatecases [2]. As an analogy with molybdenum complexes it has been suggested that vanadium plays an important role as dioxygenase metalloenzyme [3], developing a series of bioinorganic models of oxygen transfer reactions. This type of models indicates that the oxidation site, in this case VO^{2+} and $[VO_2(O)]^+$, is subject to steric and electronic control on the part of the ancillary ligands so that it controls oxygen transfer in a regioselective manner.

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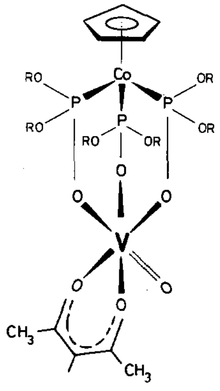
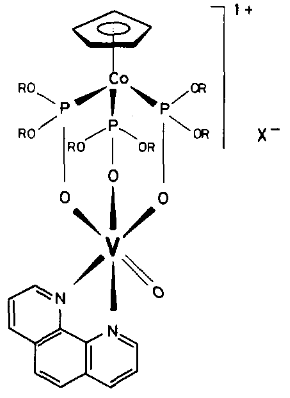
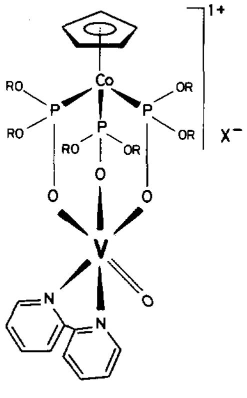
For the present investigation, a tridentate organometallic ligand was selected displaying a rigid and stable facial coordination stereochemistry relative to the vanadyl center. Such *fac*-tridentate organometallic ligand $[\eta\text{-CpCo}\{P(O)(OEt)_2\}_3]^-$ [4], in addition to showing an important steric effect, presents the character of an ancillary ligand with an important σ/π effect. This has given rise to coordination with metals in both high and low oxidation states and has recently been compared with the η-Cp ligand in its coordination properties [5]. The vanadyl complex I was prepared by means of an $(acac)^-$ ligand exchange reaction in the $VO(acac)_2$ complex [6], (0.54 mmol), with an equivalent amount (0.54 mmol) of sodium salt $Na[\eta\text{-CpCo}\{P(O)(OEt)_2\}_3]$ [7] in CH_2Cl_2 (30 ml), under argon, at room temperature, and with magnetic stirring. After further filtration of Na(acac), the filtrate is chromatographed on alumina column (eluant: diethyl ether). The chromatographed product is crystallized from CH_2Cl_2 (yield: 70% green crystals of I). Monocationic binuclear complexes II and III, isolated as hexafluorophosphate salts were prepared from I. Then, HPF_6 (aq. solution) under argon (0.579 mmol) with magnetic stirring at room temperature is added to a methanol solution containing complex I (0.579 mmol), and bidentate ligands: 1,10-phenanthroline (phen),or 2,2′-bipyridine (bipy) (0.579 mmol). The green precipitate is filtered and washed in ether. It is then chromatographed on alumina column (eluant: CH_2Cl_2/diethyl ether). It is then recrystallized from dichloromethane, thus yielding green crystals (yield 70% for II, and 60% for III).



I : ($R = OC_2H_5$)



II : ($R = OC_2H_5$); $X^- = PF_6^-$



III : ($R=OC_2H_5$);$X^-=PF_6$

Microanalyses as well as IR and electronic spectra and magnetic and electrochemical data show unequivocally the structures of the new compounds I, II and III (see also note 8). Magnetic moment, μ (BM), shows values between 1.63 and 1.73, which accounts for a null orbital contribution (or spin only) in vanadium-d^1. Cyclic voltammetry in DMF shows that the three new compounds display a totally-reversible redox single-wave ($E_{pc} = -1.76$ V (SCE); ΔV 40 mV); the monoelectronic redox couple corresponds to Co^{III}/Co^{II} situated inside the *fac*-tridentate ligand. In positive scan, a pseudoreversible couple is observed corresponding to an oxidation of V^{IV} to V^V ($E_{pa} = +0.92$ V (SCE); ΔV 90 mV), similar to the values observed in $VO(acac)_2$ complexes [9]. ESR measurements at 293 K show isotropic g values lower than those for the free electron (g_0

2.0023), in the three compounds reported here. Values for hyperfine coupling constants A_0 and g show a variation owing to the replacement of the oxygenated bidentate ligand $(acac)^-$ by one nitrogenated bidentate ligand. The latter possesses a σ-donor character stronger than that of the oxygenated ligands. This favors the free electron displacement over the nitrogenated ligands; spin-orbital coupling is thus decreased, which results in a value closer to g_0.

The molecular structure of I is shown in Fig. 1, which also contains important bond distances and angles. The vanadium(IV) ion is in an octahedral configuration, VO_6, and it shows only small deviation from the normal octahedral symmetry. The V—O distances are much longer than those found in the $VO(acac)_2$ complex. This may be due to a major σ-donor effect of the *fac*-tridentate ligand in the opposite facial position of the octahedron. Besides, the vanadium—oxygen distances in vanadyl ion (1.587(3) Å) are in the 1.56—1.76 Å range as reported for other vanadyl complexes [13a]. The acetylacetone skeleton is planar as expected for the six-membered ring (deflection from the medium plane: −0.030 and +0.035 Å). The phosphonate group acts as bridging ligands between the

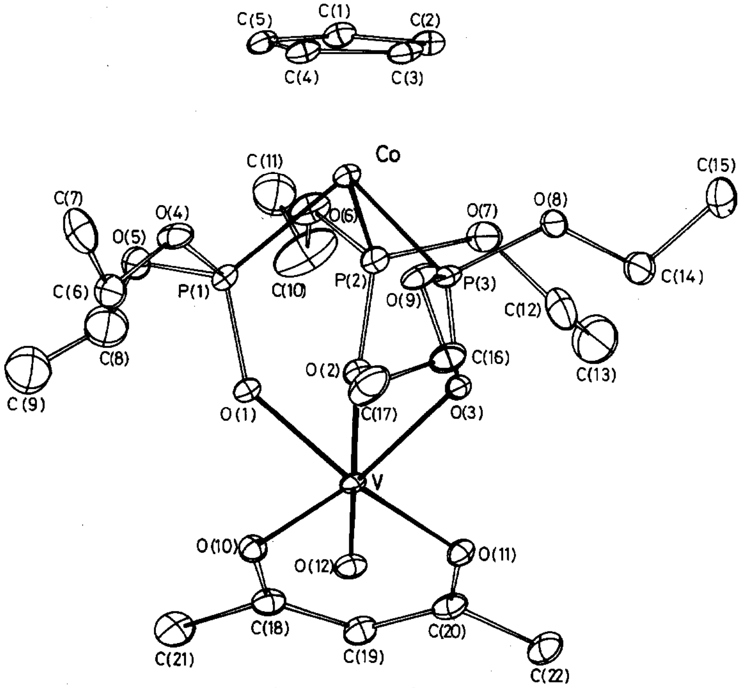
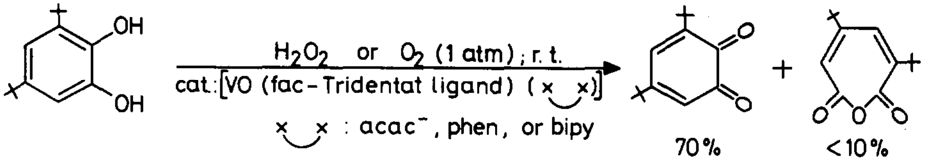


Fig. 1. Molecular structure of $[\eta\text{-}C_5H_5Co\{P(O)(OC_2H_5)_2\}_3VO(acac)]$ (I). The unit cell contains two molecules independent stabilized by Van der Waals forces. Selected distances (Å) and angles (°): Co—P(1) 2.154(1), Co—P(2) 2.159(1), Co—P(3) 2.160(1), P(2)—O(2) 1.488(3), P(2)—O(6) 1.593(3), P(2)—O(7) 1.593(4), O(6)—C(10) 1.434(8), C(10)—C(11) 1.302(11), V—O(1) 2.016(2), V—O(2) 2.212(3), V—O(3) 2.016(3), V—O(10) 2.002(3), V—O(11) 2.004(3), V—O(12) 1.587(3), C(20)—O(11) 1.254(5), C(20)—C(19) 1.393(7), C(19)—C(18) 1.382(7), C(18)—O(10) 1.265(5); P(1)—Co—P(2) 89.70(5), P(1)—Co—P(3) 90.12(4), P(2)—Co—P(3) 90.01(4), Co—P(2)—O(2) 117.8(1), P(2)—O(6)—C(10) 122.0(4), O(6)—C(10)—C(11) 149.4(3), O(11)—V—O(10) 88.6(1), O(11)—C(20)—C(19) 125.1(4), C(20)—C(19)—C(18) 124.9(4), C(19)—C(18)—O(10) 125.4(4), V—O(10)—C(18) 127.6(3), V—O(11)—C(20) 128.2(3).

(Atomic coordinates, tables of angles and distances for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.)

Co^{III} and V^{V} centers. The molecule I presents disorder in the phosphonate ligands and particularly in the ethyl group. This fact precluded *B* factor anisotropic refinement of the terminal carbon atoms of the ethyl group. These deviations has been described as enhanced thermal motions for the same *fac*-tridentate ligand [13b].

Catalytic oxygen transfer reactions and catalytic oxidation of catechol were carried out in the presence of catalytic amounts of any of these three new compounds. Quantitative conversion is obtained through the oxidation of 3,5-di-t-butyl-1,2-dihydroxybenzene (3,5-DTBC) in CH_2Cl_2 in the presence of hydrogen peroxide or dioxygen and catalytic amounts of the binuclear complexes. This process affords 3,5-DTB-1,2-*ortho*-quinone, as the main product and smaller amounts of muconic acid anhydride (see note 11):



Electronic and steric control induced by the facial tridentate organometallic ligand is reflected in the high percentage of *ortho*-quinone obtained, unlike other oxovanadium(IV) catalysts in which the oxygen transfer reaction and cleavage of the catechol ring is more important than the oxidation into *ortho*-quinone [12]. Oxo, peroxo, and dioxo complexes of transition metals with d^0 electronic configuration coordinated to this organometallic ligand are under investigation at present.

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7 The sodium salt, Na(*fac*-tridentate ligand), was prepared by the procedure described in ref. 4.

8 All reactions were conducted using Schlenk standard techniques. Instruments: IR (Perkin—Elmer 567 grating Spectrophotometer); electronic spectra (Unicam SP-1800 Spectrophotometer); ESR (Bruker ER-420 with ER-400X-RL cavity); magnetic susceptibility (Faraday balance and ^1H NMR Spectrometer Varian XL-100 using Evan's method for the determination of magnetic susceptibility). Satisfactory elemental analyses have been obtained for all new compounds at the Service Central d'Analyse (CNRS)-Vernaison (France).

For compound I: IR spectra (cm^{-1}), (KBr-disc): γ_s(V=O) 930(s); δ(P—O) 585(s); γ(C=O)(acac) 1580(m); δ(Cp) 1020(s); γ(C—O—P) 1135; μ 1.60 (BM). Electronic spectra (CH_2Cl_2): λ_1 635 nm (ϵ 8.13 $dm^3\ mol^{-1}\ cm^{-1}$), λ_2 810 nm (ϵ 14.95). ESR spectroscopy: g_{iso} 1.9650 ± 0.00014; A_0 110 ± 1 G; Cyclic Voltammetry (CV) in DMF and TEAP as supporting electrolytes (potentials relative to SCE); E_{pa}+0.94 V, $V^{IV} \rightarrow V^{V}$, pseudo-reversible; $E_{1/2}$ −1.67 V (ΔV 40 mV) corresponding to a reversible redox couple $[Co^{III}] \leftrightarrows [Co^{II}]$, $n = 1$ electron (coulometric determination).

For compound II: IR spectra (cm^{-1}): γ_s(V=O) 940(s); δ(P—O) 585(s); δ(Cp) 1025(s); γ(C—O—P) 1110(m); μ 1.638 (BM). Electronic spectra; λ_1 590 (ϵ 11.92); λ_2 743 (ϵ 31.63). Conductance measures ($MeNO_2$): 1/1 electrolyte. ESR spectroscopy: g_{iso} 1.9690 ± 0.0001, A_0 106 ± 1 G; CV: E_{pa} +0.70 V, monoelectronic, pseudo-reversible; $E_{1/2}$ −1.24 V, monoelectronic, reversible (ΔV 50 mV) corresponding to redox behaviour of the ligand phen; $E_{1/2}$ −1.59 V; reversible (ΔV 50 mV) single-wave corresponding to $[Co^{III}] \leftrightarrows [Co^{II}]$ redox couple, $n = 1$, $E_{1/2}$ −1.79 V (pseudo-reversible) probably corresponding to a second reduction of the ligand phen.

For compound III: IR: γ_s(V=O) 940(s); δ(P=O) 583(s); δ(Cp) 1030(s); γ(C—O—P): 1120(m); μ 1.639 (BM); Electronic spectra: λ_1 595 (ϵ 12.72); λ_2 740 (ϵ 21.36); conductance 1/1 electrolyte. ESR spectroscopy: g_{iso} 1.9710 ± 0.0001, A_0 106 ± 1 G; CV: E_{pa} +0.68 V; $n = 1$; pseudo-reversible; $E_{1/2}$ −1.28, monoelectronic, reversible (ΔV 50 mV) corresponding to redox behaviour of the bipy ligand; $E_{1/2}$ −1.61; reversible (ΔV 50 mV) single Co^{III}/Co^{II} redox couple.

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10 Crystal data: $C_{22}H_{42}O_{12}P_3VCo$, M 701.37, triclinic space group $P1$; lattice constants: a 10.906(2), b 11.694(2), c 13.139(4) Å; α 84.74(2), β 85.30(2), γ 80.04(2)°; U 1639.71 $Å^3$; D_x 1.420 g cm^{-3} for $Z = 2$, $F(000) = 730$, μ 9.746 cm^{-1}. Conventional $R = 0.0548$ using 3660 unique reflections above 3σ, $R_w = 0.078$. (22°, ω—2θ, $2\theta \leqslant 50°$), Four circle Nonius CAD4; λ(Mo-K_α) 0.71073 Å, graphite monochromatized.

11 A typical catalytic oxidation experiment consists of the following: 1.10 g (4.0 mmol) of 3,5-DTBC are dissolved in 30 ml of CH_2Cl_2. Then 40 mg (0.06 mmol) of catalyst I (substrate/cat. ratio 81.6) are dissolved. To this solution are added 10 ml of H_2O_2 (30%), (or under 1 atm of O_2), with continuous magnetic stirring for 6 h. The reaction is controlled by HPLC. The oxidation products, chromatographed and purified by crystallization, are analyzed by means of ^1H NMR, mass spectrometry, and by comparison with authentic samples. The isolation of the neutral active species of V^V, probably $[OV(O_2)$-*fac* tridentate ligand], is under way.

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