Bridging the Gap between Polyoxometalates and Classic Coordination Compounds: A Novel Type of Hexavanadate Complex

Markus Piepenbrink, Michael U. Triller,
Neville H. J. Gorman, and Bernt Krebs*

Dedicated to Professor Roald Hoffman on the occasion of his 65th birthday

Polyoxometalates have gained great interest because of their remarkable chemical properties and their enormous potential shown in fields of catalytic, technical, and medical applications.[1] During the last decade, the research in this rapidly growing area has focused on the design of new compounds, among them many in interdisciplinary fields between solid-state chemistry, material science, and organic synthesis.[2,3] To find new pathways for the synthesis of catalysts and to understand the mechanistic background of catalysis, one of the most challenging tasks is the development of novel selective and highly efficient catalytic systems containing polyoxoanions.[4] Therefore, our group has focused on the design of novel polyoxometalate catalysts for directed oxygen-transfer processes.[5]

In comparison to the extensive work on polyoxomolybdates and polyoxotungstates, considerably less research has been conducted in the field of polyoxovanadates. Among the structural types known in this area, the $\{V_6O_{19}\}^{n-}$ core is extremely rare.[6] A small number of compounds containing this structural motif (with tris(alkoxo) ligands as the only substituents) have been reported.[7] In addition, some polyoxometalate-supported organometallic complexes have been synthesized and characterized where heterometal fragments $(Cp^*M^{2+})_n$ ($Cp^* = C_5Me_5$, M^{2+} = Rh, Ir) cap the hexavanadate core.[8] These few species represent the only structurally characterized vanadium clusters incorporating the Lindqvist structure type ($\{V_6O_{19}\}^{n-}$).

Herein we present the first example of a $\{V_6O_{19}\}^{n-}$ core that is substituted by two vanadyl moieties ligated by exchangeable ligands. With this new approach of combining polyoxometalate chemistry and classic coordination chemistry we hope to enhance the catalytic potential of polyoxovanadates. The coordination sphere of the two scaffolding vanadyl moieties resembles the structural motif in the active site of vanadium-containing haloperoxidases.[9] These vanadium centers are ligated by the new ligand bis(1-methylimidazol-2-yl)-4-methoxyphen-1-ylmethanol (bmimpm) and are attached to the hexavanadate core by oxygen atom bridges. The two vanadyl complexes cap the polyoxovanadate and are tilted towards the polyoxometalate unit (Figure 1). This tilt is facilitated by a hydrogen bond originating from the ligand OH-group towards one edge of a VO_6 octahedron.

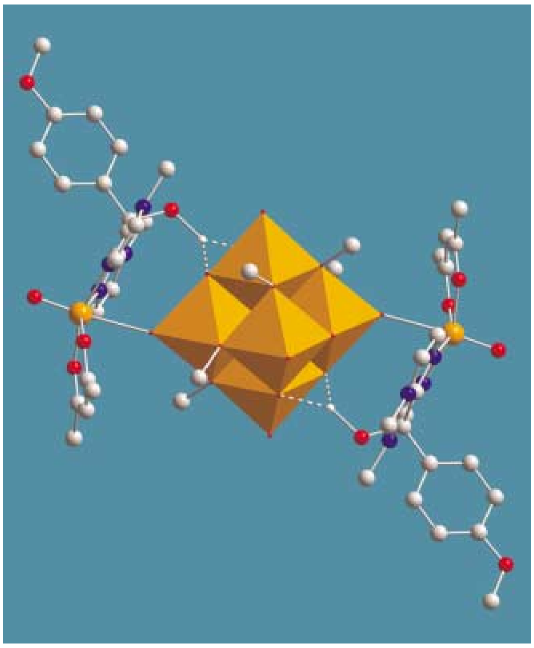

Figure 1. The polyoxovanadate core $\{V_6O_{13}(OMe)_6\}^{2-}$ linked to two vanadyl moieties containing organic ligands (polyhedral view).

$[\{VO(bmimpm)(acac)\}_2\{V_6O_{13}(OCH_3)_6\}]$ (**1**; acac = acetylacetonate) was synthesized in methanolic solution by adding $[VO(acac)_2]$ to bmimpm. After one day, orange prismatic crystals were obtained and characterized by X-ray diffraction.[10] The hexavanadate located in the center of the molecular structure consists of six VO_6 octahedra which build up an octahedron of the Lindqvist type (Figure 2). The oxygen framework contains four oxygen atoms bound to vanadium centers by double bonds (O8, O10), six μ_2-oxo bridges (O6, O7, O9), one central oxygen atom (O5), and six μ_2-alkoxo bridging methanol oxygen atoms (O11, O12, O13). The incorporation of methanol into polyoxovanadates has been described previously.[7a]

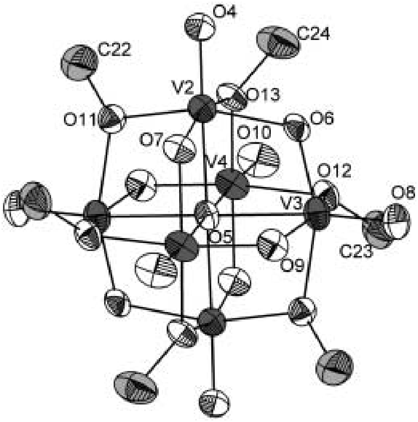

Figure 2. Central molecular part of the structure of **1** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å]: V2-O4 1.624(3), V2-O5 2.224(1), V2-O6 1.897(3), V2-O7 1.752(4), V2-O13 2.034(3).

The hexavanadate core can formally be regarded as a $\{V_6O_{13}(OMe)_6\}^{2-}$ ion. As part of this subunit, one terminal oxygen atom O4 forms a bridge to the outer-shell vanadium atom. Remarkably, the observed distance between V2 and O4 is 1.624(3) Å, which is expected for vanadyl bonds (V=O), whereas the V1−O4 bond is unusually long (2.381(3) Å), a

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[*] Prof. Dr. B. Krebs, M. Piepenbrink, M. U. Triller, N. H. J. Gorman
Westfälische Wilhelms-Universität Münster
Institut für Anorganische und Analytische Chemie
Wilhelm-Klemm-Strasse 8, 48149 Münster (Germany)
Fax: (+49) 251-833-8366
E-mail: krebs@uni-muenster.de

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result of being *trans* to the oxo group O1 (Figure 3). The atom V1 has a distorted-octahedral coordination environment. The two nitrogen atoms of the bidentate ligand bmimpm together with the two oxygen atoms of the acetylacetonate ligand form the equatorial plane; the atom V1 is located 0.376 Å above this N_2O_2 plane.

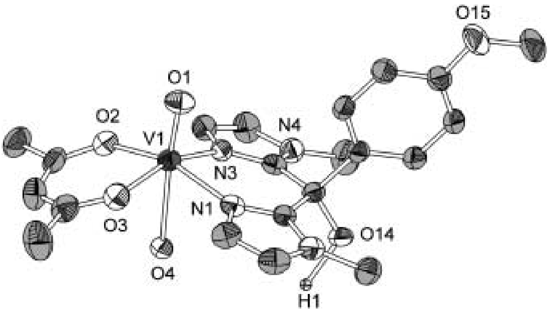

Figure 3. Coordination sphere of V1 and the organic ligand system (thermal ellipsoids set at 50% probability).

Compound **1** exhibits interesting structure-determining hydrogen-bonding interactions. The hydrogen atom H1 of the ligand bmimpm forms a hydrogen bond with O7 (1.717 Å) and O9 (1.893 Å) of the hexavanadate cluster thus tilting the ligand bmimpm towards the hexavanadate cluster (see Figure 1). This effect results in a V1-O4-V2 angle of 154.6°, which deviates considerably from 180°.

According to our experience in polyoxometalate molecular science the calculation of oxidation states by using bond-valence parameters for solids is a particularly suitable method to determine whether or not the distribution of the oxidation states is disordered. Application of the parameters presented by Brese and O'Keeffe resulted in $V_{V1} = 3.994$ (by using bond-valence parameters of O for N) and 4.209 (by using bond-valence parameter for N without considering the vanadium oxidation state).[11] The oxidation states of the three vanadium atoms forming the polyoxovanadate core were calculated to be $V_{V2} = 5.092$, $V_{V3} = 5.070$, and $V_{V4} = 5.078$. Therefore we propose the vanadium atoms V2, V3, and V4 to exist in the +V oxidation state, leading to a net charge of −2 for the polyoxometalate cluster, which is counterbalanced by the two formally positively charged vanadyl moieties (V^{IV}). This configuration is in accord with cyclic voltammetry measurements.

A number of experiments are prompted by the results presented herein. Variation of the scaffolding vanadyl moieties offers a way to fine tune potential catalytic properties of the polyoxovanadate unit. We have already started to synthesize new ligand systems with similar coordination sites. Furthermore, ligand-exchange experiments appear to be successful. Since the hydrogen bond facilitates the tilt of the ligand towards the polyoxometalate core, control over the protonation state might allow for discrimination between different substrates in catalysis by using the hydrogen bond as a molecular switch. By linking transition-metal complexes containing asymmetric organic ligands to the described hexavanadate species, it should be possible to generate a series of new compounds containing steric information for better directed oxygen-transfer processes. These compounds would also serve as models to clarify catalytic mechanisms in polyoxometalate chemistry.

Experimental Section

bmimpm: In a three-neck flask equipped with a dropping funnel, a gas inlet, and a gas outlet, 1-methylimidazole (75.4 mmol, 6 mL) was dissolved in dry diethyl ether (200 mL) under a protective argon atmosphere and cooled to −78 °C. *n*-Butyllithium (75.4 mmol, 47 mL, 1.6 M in hexane) was added dropwise. The reaction mixture was allowed to warm to 0 °C to complete deprotonation. After cooling to −78 °C, 4-methoxyethylbenzoate (prepared by acid-catalyzed esterification of 4-methoxybenzoic acid with ethanol) was slowly added dropwise. The reaction mixture was allowed to warm to 0 °C over a period of 12 h and then quenched with water (50 mL). The phases were separated and the aqueous phase extracted with diethyl ether (2 × 30 mL) and $CHCl_3$ (3 × 30 mL). The combined colorless organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure to leave a colorless oil from which the crude product precipitates as a white solid upon storage of the oil at −20 °C. Recrystallization from acetone and $CHCl_3$ yields colorless crystals (yield: 4.5 g, 40%). Elemental analysis (%) calculated for $C_{16}H_{18}N_4O_2$: C 64.41, H 6.08, N 18.78; found: C 64.13, H 6.20, N 18.65; ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 3.38$ (s, 6H; CH_3), 3.77 (s, 3H; OCH_3), 6.82 (d, $^3J(H,H) = 9$ Hz, 2H; CH_{Im}), 6.84 (d, $^3J(H,H) = 1$ Hz, 2H; CH_{Ph}), 6.93 (d, $^3J(H,H) = 1$ Hz, 2H; CH_{Ph}), 6.98 ppm (d, ^3J (H,H) = 9 Hz, 2H; CH_{Im}); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta =$ 34.5 (CH_3), 55.1 (OCH_3), 76.4 (COH), 113.5 (CH_{Ph}), 123.2 (CH_{Ph}), 125.7 (CH_{Im}), 128.5 (CH_{Im}), 134.0 (C_{Ph}), 148.4 (C_{Im}), 192.9 ppm (COMe); IR (KBr pellet; 4000–400 cm^{-1}): $\tilde{\nu} = 2954$ (m), 1609 (m), 1587 (w), 1511 (s), 1481 (m), 1405 (w), 1251 (s), 1055 (m), 1035 (m), 756 (s), 683 (w), 594 (w); MS (70eV): *m*/*z* (%): 299 (20) $[M^+ + H]$, 298 (100) $[M^+]$, 191 (32) $[C_9H_{11}N_4O^+]$.

1: bmimpm (0.2 mmol, 59 mg) and triethylamine (3 drops) were dissolved in methanol (5 mL) and $[VO(acac)_2]$ (0.8 mmol, 212 mg) was added. The reaction mixture was stirred for 12 h. From the resulting orange solution, orange rhombical crystals suitable for X-ray diffraction grew upon leaving the solution to stand for one day (yield: 36.7 mg, 24%). IR (KBr pellet; 4000–400 cm^{-1}): $\tilde{\nu} = 3408$ (m, br), 3118 (w), 3079 (w), 2920 (m), 2811 (w), 1606 (m), 1586 (s), 1524 (s), 1507 (s), 1443 (m), 1374 (s), 1282 (m), 1252 (m), 1185 (w), 1158 (m), 1146 (m), 1070 (m), 1032 (s, br), 987 (m), 956 (vs), 920 (vs), 839 (m), 784 (m), 756 (s), 733 (m), 660 (m), 594 (m), 542 (w), 499 (w), 463 (w), 443 (m); cyclic voltammetry (saturated in methanol (< 1 mM), supporting electrolyte tetrabutylammonium hexafluorophosphate 100 mM): Measurement taken at a Perkin-Elmer 263A Potentiostat with a glassy-carbon working electrode, Ag/AgCl reference electrode, and Pt counter electrode. An irreversible oxidation peak at 130 mV was found corresponding to the V^{IV}/V^V redox couple.

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[10] Crystal-structure analysis for **1**: Single-crystal X-ray diffraction data were collected on a Bruker Nonius Smart diffractometer with a CCD detector ($\lambda(\mathrm{Cu}_{K\alpha}) = 1.54184$ Å) at 200(2) K, crystal dimensions $0.16 \times 0.12 \times 0.06\ \mathrm{mm}^3$. Structure solution was achieved by applying direct statistical methods of phase determination using the SHELXS program, and full-matrix least-squares refinements were performed using the SHELXL-97 software: Monoclinic, space group $P2_1/c$, $a = 15.132(3)$, $b = 15.934(3)$, $c = 13.290(3)$ Å, $\beta = 98.78(3)°$, $V = 3166.8(11)$ Å^3, $\rho_{\mathrm{calcd}} = 1.708\ \mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 51.9°$, total collected reflections 18280, unique reflections 5858, $R_{\mathrm{int}} = 0.0786$, $\mu = 1.218\ \mathrm{mm}^{-1}$, $R_1 = 0.0597$ and $wR_2 = 0.1539$ for $I > 2\sigma(I)$, $R_1 = 0.0878$ and $wR_2 = 0.1627$ for all reflections, 425 total parameters, GooF = 0.967 on $|F^2|$, max./min. residual electron density $1.131/-0.555$ e Å^{-3}. CCDC-176210 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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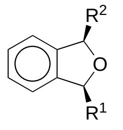
Benzylic *endo*-Alkylation of Phthalan–Cr(CO)$_3$ Complexes via Temporary Silylation: An Entry to *trans*-1,3-Disubstituted Dihydroisobenzofurans[**]

Saskia Zemolka, Johann Lex, and Hans-Günther Schmalz[*]

Substituted 1,3-dihydroisobenzofurans (phthalans) represent an interesting class of compounds owing to their promising pharmacological potential,[1] but they have received only little attention from synthetic chemists in the past.[2] In particular, almost no general methods are available for the stereoselective synthesis of *cis*- or *trans*-1,3-disubstituted derivatives of type **1** and **2**, respectively.[3] With regard to the usefulness of such compounds as intermediates for the synthesis of bioactive oxonanes[4] and the established biological activity of compounds of type **3**,[5] the search for efficient stereoselective entries to 1,3-disubstituted phthalans remains a challenging task.



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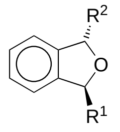

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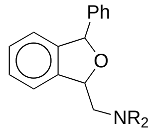

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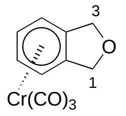

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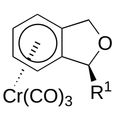

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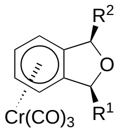

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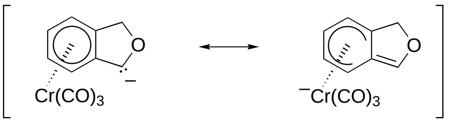
In 1989, Davies and co-workers reported the preparation of a few *cis*-configured compounds of type **1** (R^1, R^2 = Me, D) starting from the [phthalan–Cr(CO)$_3$] complex **4**.[6] In two successive benzylic deprotonation/alkylation steps, **4** can be transformed (via *rac*-**5**) into bis-*exo*-alkylated complexes of type **6**, from which the free ligands **1** are easily obtained by oxidative decomplexation.[6] The method exploits both the ability of the Cr(CO)$_3$ fragment to stabilize a negative charge in the benzylic position[7] and the strong steric effect of the metal fragment (shielding of the *endo* face).[7b, 8] The stabilization of the anionic intermediate **7a** derived from **4** by benzylic deprotonation can be understood in terms of the resonance structure **7b** in which the charge is delocalized to the Cr(CO)$_3$ unit (Scheme 1).[9]



7a **7b**

Scheme 1. Resonance structures of the benzylic anion derived from **4**.

In the course of our research on the application of chiral arene–Cr(CO)$_3$ complexes in the stereoselective synthesis of bioactive compounds,[10] we were interested in using the silylated complex **8** as a building block for the synthesis of new 1,3-disubstituted phthalans. Compound **8** was selected since it is easily prepared, even in the optically active form,[11] from the parent complex **4**. Herein we disclose the results of a study which has led to the discovery of some unexpected, remarkably selective transformations and to the development of an efficient and completely stereoselective route to 1-*endo*-alkylated complexes and to *trans*-1,3-disubstituted phthalans.

When complex *rac*-**8** was treated with *t*BuLi at low temperatures (−100 to −78 °C) followed by quenching of the resulting anion with different electrophiles, we were surprised to find that the 1,1-disubstituted products (*rac*-**11**) were formed with complete regio- and diastereoselectivity (Table 1). Evidently, the deprotonation of *rac*-**8** does not, as

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[*] Prof. Dr. H.-G. Schmalz, S. Zemolka, Dr. J. Lex[+]
Institut für Organische Chemie, Universität zu Köln
Greinstrasse 4, 50939 (Germany)
Fax: (+49)221-470-3064
E-mail: schmalz@uni-koeln.de

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[+] X-ray crystallographic analysis.

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