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A new structure type in polyoxoanion chemistry: Synthesis and structure of the $V_5O_{14}^{3-}$ anion

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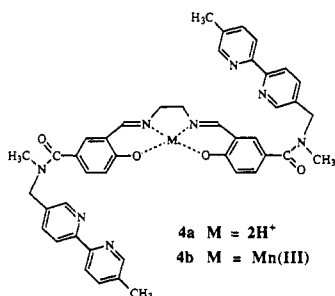
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be inconsistent with the findings reported below, particularly the dependence of selectivity on the particular substrate and the particular catalyst used.

The bis-nicotinate **2a** had essentially half the reactivity of prenyl benzoate (**3**) with catalyst **1c** in the absence of added Cu^{2+} ($S = 0.5$), but with 4 equiv Cu^{2+} per catalyst there was a 20/1 preference for epoxidizing the doubly binding substrate **2a** ($S = 20$), a 40-fold increase in S . With the singly binding substrate **2b** the addition of Cu^{2+} enhanced S by only 2-fold, to $S = 1$. In our earlier studies with ion pairing we had also seen that binding both ends of a substrate, to stretch it across a reactive center, is much more effective than is simple binding of one end.⁷

Molecular models show that a substrate related to **2a** but with isonicotinate groups cannot productively bridge across catalyst **1c** as in Scheme 1. As expected, we find that its reactivity in competition with **3** is not increased on the addition of Cu^{2+} . Also consistent with double binding of substrate **2a** to catalyst **1c** via Cu^{2+} bridging (Scheme 1) is our finding that in the absence of Cu^{2+} up to 9% of the epoxide of **2a** is trans, but in the presence of Cu^{2+} the product is >99% cis. The stereospecific formation of cis-epoxide is expected if the two ends are immobilized.

The salen catalyst precursor **4a**¹⁵ was prepared from the cor-



responding salicylaldehyde derivative and converted to the Mn^{III} derivative as the PF_6^- salt **4b**.¹⁶ Since **4b** was not soluble in acetonitrile in the absence of Cu^{2+} , the bis-copper complex of **4b** was compared with the Mn^{III} complex of salen itself (**4b** without the bipyridyl appendages) under conditions similar to those above. The double binding substrate **2a** had S of 0.029 with salen- Mn^{III} (the intrinsically lower reactivity of **2a** relative to **3** is accentuated with this more discriminating catalyst), but with the **4b** bis-copper complex this relative reactivity increased by 43-fold to $S = 1.24$. The nonbinding substrate **2c** increased its selectivity ($S = 0.036$ with salen- Mn^{III}) by less than 2-fold to $S = 0.06$. Interestingly, in the salen series even the singly binding substrate **2b** showed a 30-fold increase in S (to 1.0) on changing salen- Mn^{III} to the bis-copper complex of **4b**.

The contrast with the porphyrin case, where double binding was much more effective than single coordination, may reflect the high flexibility of catalyst **4b** compared with the rigid **1c**. Consistent with this, even the bis-isonicotinate ester related to **2a** gave an increased selectivity of 30-fold with the $\text{Cu}^{2+}/\mathbf{4b}$ complex, so this flexible catalyst can adapt to the different geometry of the isonicotinate. The substrates must be chiefly singly bound to the salen catalyst, judging from the small presumably just statistical advantage of **2a** over **2b**. As expected from this we find that with catalyst **4b** all the substrates, under all conditions, show the nonstereospecific formation of epoxide containing ca. 7% of the trans isomer.

Molecular models indicate that double binding of substrate **2a** to catalyst **1c** should indeed hold the double bond over the oxygen of a $\text{Fe}=\text{O}$ intermediate. Thus the observed selective epoxidation is expected (but the formation of a metalloxetane intermediate, as in some mechanistic proposals,¹⁷ looks almost impossible).

Furthermore, with only 1% of the tetra- Cu^{2+} complex of **1c** we see eight turnovers in the epoxidation of **2a**, so we are dealing with true turnover catalysis. It remains to be seen whether the use of metal ions in these two ways—one to perform epoxidation and the others to bind substrates—proves to be a useful general procedure, as is the Sharpless oxidation¹⁸ in which substrates bind to the catalytic metal. In any case, with the addition of selective multipoint substrate binding the catalyst **1c** increasingly resembles the P-450 enzymes which inspire this entire field.

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A New Structure Type in Polyoxoanion Chemistry: Synthesis and Structure of the $\text{V}_5\text{O}_{14}^{3-}$ Anion

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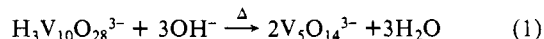
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The $\text{Mo}_2\text{O}_7^{2-}$ and $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$ anions are soluble in aprotic, polar solvents as tetra-*n*-butylammonium salts and have proved to be suitable starting materials for the synthesis of numerous covalent polyoxomolybdate derivatives.⁴ Since analogous unprotonated polyvanadate salts might serve as the starting point for the synthesis of polyoxovanadate derivatives, we have begun to explore the chemistry of tetra-*n*-butylammonium isopolyvanadates. We report here the first structurally characterized⁵ species of this type,⁶ $\text{V}_5\text{O}_{14}[(n\text{-C}_4\text{H}_9)_4\text{N}]_3$.

When 4.5 mL of 0.41 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ in CH_3CN (1.8 mmol)⁷ is added with stirring to a solution of 0.97 g (0.58 mmol) of $\text{H}_3\text{V}_{10}\text{O}_{28}[(n\text{-C}_4\text{H}_9)_4\text{N}]_3$ in 25 mL of CH_3CN at ambient temperature, the resulting solution contains at least four different polyvanadates according to ^{51}V NMR spectroscopy. This dark orange solution can be converted to a virtually colorless solution containing a single polyvanadate species (see eq 1) by filtering



off a small amount of insoluble material and then reducing the

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(6) Several polyvanadic acid salts have been prepared that are soluble in organic solvents. (a) $\text{HV}_4\text{O}_{12}^{3-}$: Fuchs, J.; Mahjour, S.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 374. (b) $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$: Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991 and references cited therein. (c) $\text{H}_3\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$: ref 5 and Corigliano, F.; DiPasquale, S. *Inorg. Chim. Acta* **1975**, *12*, 99.

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(16) Anal. Found (Calcd for $\text{C}_{44}\text{H}_{40}\text{N}_8\text{O}_4\text{MnPF}_6 \cdot 3\text{H}_2\text{O}$): C, 53.28 (52.91); H, 4.40 (4.04); N, 11.04 (11.22); F, 11.21 (11.41); Mn, 5.34 (5.50). MS, FAB 800 ($M + 1$).

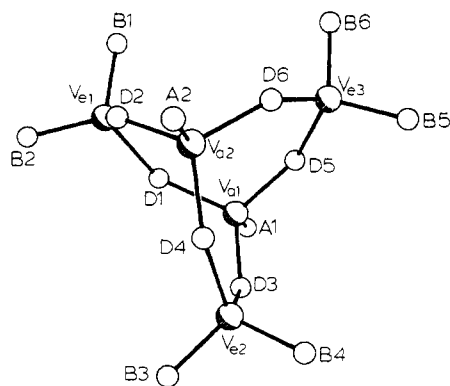


Figure 1. Perspective plot of the $V_5O_{14}^{3-}$ anion as observed in crystalline $[V_5O_{14}][(\eta-C_4H_9)_4N]_3$. Vanadium atoms are represented by shaded spheres and oxygen atoms by open spheres. Oxygen atoms are labeled with a capital letter (A, B, or D) and a number.

solution volume to 15–20 mL by boiling off solvent over a 15–20-min period. Crystalline $V_5O_{14}[(\eta-C_4H_9)_4N]_3$ (1.1 g) is obtained in 80% yield by adding 30–40 mL of diethyl ether to the reaction solution at ambient temperature with stirring and crystallizing the resulting white precipitate by dissolving it into 15 mL of acetone followed by 2–3 mL of ethyl acetate and cooling to -7°C for 12 h. The compound is slightly moisture-sensitive and should not be exposed to atmospheric moisture for extended time periods.

X-ray structural analysis¹⁰ of crystalline $(V_5O_{14})[(\eta-C_4H_9)_4N]_3$, obtained as described above, revealed the presence of discrete $(\eta-C_4H_9)_4N^+$ cations¹¹ and $V_5O_{14}^{3-}$ anions which each contain five tetrahedral vanadium(V) centers in a nearly trigonal-bipyramidal arrangement (Figure 1). The two "axial" vanadiums (V_{a1} and V_{a2}) each have a single terminally bonded (O_A) oxygen, while the three "equatorial" vanadiums (V_{e1} , V_{e2} , and V_{e3}) each have two (O_B). Although the $V_5O_{14}^{3-}$ anion possesses no rigorous crystallographic symmetry in the solid state, it approximates rather closely its maximum possible symmetry of D_{3h} . The three "equatorial" V_e atoms and their six terminal O_B oxygens are coplanar to within 0.07 Å; each of the three ($O_A V_a$)₂ $V_e(O_B)_2$ groupings are coplanar to within 0.21 Å, and their least-squares mean planes make dihedral angles of 115.2–125.9° with each other and dihedral angles of 89.8–90.0° with the "equatorial" [$V_e(O_B)_2$]₃ mean plane. D_{3h} -averaged bond lengths and angles of interest include the following: V_a-O_A , 1.580 (7, 3, 3, 2) Å;¹² V_e-O_B , 1.601 (8, 14, 28, 6) Å; V_a-O_D , 1.723 (7, 11, 25, 6) Å; V_e-O_D , 1.818 (7, 11, 26, 6) Å; and $V_a-O_D-V_e$, 143.3 (4, 62, 105, 6)°. The 30

O–V–O angles range from 107.6 (4)° to 112.7 (3)°. This anion provides the first example of a transition-metal polyoxoanion cage structure based on corner-sharing of tetrahedral coordination polyhedra, a type of cage structure frequently observed for main group polyoxoanions.

The $V_5O_{14}^{3-}$ salt reported here has good solubility in polar organic solvents such as acetonitrile, acetone, 1,2-dichloroethane, and dichloromethane. Preliminary experiments indicate that $(V_5O_{14})[(\eta-C_4H_9)_4N]_3$, like $(Mo_2O_7)[(\eta-C_4H_9)_4N]_2$ and $(\alpha-Mo_8O_{26})[(\eta-C_4H_9)_4N]_4$, is reactive toward a wide variety of inorganic, organometallic, and organic reagents. We are currently investigating the products of these reactions.

Acknowledgment. We acknowledge the National Science Foundation for support of this work. Chris Frank provided invaluable technical assistance.

Supplementary Material Available: Crystal structure analysis report, Table I (atomic coordinates for non-hydrogen atoms), Table II (anisotropic thermal parameters for non-hydrogen atoms), Table III (atomic coordinates for methylene hydrogen atoms in the cations), Table IV (bond lengths and angles for the anion), Table V (bond length and angles for the cations), Figure 2a–c (perspective ORTEP plots of nitrogen, carbon, and methylene hydrogen atoms in the three cations), and Figure 3 (perspective ORTEP plot of the anion) (23 pages); table of observed and calculated structure factors for $(V_5O_{14})[(\eta-C_4H_9)_4N]_3$ (14 pages). Ordering information is given on any current masthead page.

Ground Electronic States of the ScCO and NbCO Molecules

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An earlier paper considered the variation in bonding among the first-row transition-metal monocarbonyl molecules,^{1,2} and here this is extended by electron spin resonance (ESR) studies of ScCO, NbCO, and attempts to observe FeCO. The ground state of ScCO is found to be $^4\Sigma$ with a low-lying $^4\Pi$ excited state, confirming the recent theoretical calculations of Jeung and Koutecký³ and Barnes and Bauschlicher.⁴ NbCO has a $^6\Sigma$ ground state, as did VCO,⁵ but no experimental confirmation of the predicted $^3\Sigma$ or $^5\Sigma$ ground state of FeCO has been obtained.⁶

Figures 1 and 2 show the X-band ESR spectra of ScCO in solid argon at 4 K exhibiting eight hyperfine (hf) lines (^{45}Sc , $I = 7/2$) and NbCO with 10 hf lines (^{93}Nb , $I = 9/2$), respectively. The introduction of up to 0.2% ^{13}CO in the argon led to no observable splitting in the ScCO lines indicating that the hfs is within the line width, i.e., <1.5 G. Only the weaker series of lines in Figure 2 were split by ^{13}CO (~ 6.6 G), as shown in the inset, and are therefore identified with NbCO. Prior to ^{13}CO addition the stronger series of lines in Figure 2 exhibit hf structure and are

(9) IR (Nujol, 450–1000 cm^{-1}) 474 (w), 530 (w), 737 (m), 814 (vs), 886 (s), 941 (s), 967 (s); ^{51}V NMR (0.02 M, 25 $^\circ\text{C}$, acetone) δ –539 (3V), –613 (2V) relative to external VOCl_3 . Anal. Calcd for $C_{48}H_{108}N_3V_5O_{14}$: C, 47.80; H, 9.03; N, 3.48; V, 21.12. Found: C, 47.69; H, 8.93; N, 3.50; V, 20.96.

(10) Single crystals of $[V_5O_{14}][(\eta-C_4H_9)_4N]_3$ are at $20 \pm 1^\circ\text{C}$, orthorhombic, space group $Pbca-D_{2h}^{15}$ (no. 61) with $a = 32.708$ (5) Å, $b = 16.956$ (3) Å, $c = 24.344$ (5) Å, and $Z = 8$ [$d_{\text{calc}} = 1.187$ g cm^{-3} ; $\mu_r(\text{Mo K}\alpha) = 0.76$ mm^{-1}]. A total of 9299 independent data having $2\theta(\text{Mo K}\alpha) < 45.8^\circ$ were collected on a Nicolet P1 autodiffractometer using graphite-monochromated Mo K α radiation and full 0.90° wide ω scans. The structure was solved using (SHELXTL) "direct methods" techniques, and the resulting structural parameters have been refined by using counter-weighted cascade block-diagonal least-squares techniques to R_1 (unweighted, based on F) = 0.059 and R_2 (weighted, based on F) = 0.067 for 3182 independent reflections having $2\theta(\text{Mo K}\alpha) < 45.8^\circ$ and $I > 3\sigma(I)$. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all included hydrogen atoms. All methylene hydrogens of the cations (except for those on C_{43} of cation 1) were included in the structural model at fixed idealized positions (assuming sp^3 -hybridization and a C–H bond length of 0.96 Å), but hydrogens of terminal methyl groups were not included. The terminal methyl carbon C_{43} of cation 1 is statistically disordered between two sites in the lattice.

(11) See paragraph at end of paper regarding Supplementary Material.

(12) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the averaged value.

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