Synthesis, Characterization, and Catalysis of β_3-[(Co^{II}O$_4$)W$_{11}$O$_{31}$(O$_2$)$_4$],$^{10-}$ the First Keggin-Based True Heteropoly Dioxygen (Peroxo) Anion. Spectroscopic (ESR, IR) Evidence for the Formation of Superoxo Polytungstates

Juan Server-Carrió,[†] Julia Bas-Serra,[†] María Elena González-Núñez,[†] Amadeo García-Gastaldi,[†] Geoffrey B. Jameson,[‡] Louis C. W. Baker,[‡] and Rafael Acerete*,[†]

Contribution from the Departament de Química Inorgánica, Facultat de Farmacia, Universitat de València, Avda. Vicente Andrés Estelles, s/n, 46100-Burjassot, Valencia, Spain, and Department of Chemistry, Georgetown University, Washington, D.C. 20057

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Abstract: Reactions of hydrogen peroxide with several lacunary polyoxometalates of the 1:11 series, XW$_{11}$O$_{39}$$^{m-}$ (X = Co^{3+}, Ga^{3+}, Fe^{3+}, Si^{4+}, and P^{5+}), are reported. Synthetic pathways to new polyoxotungstates incorporating dioxygen moieties (peroxo and/or superoxo) are developed. The key step involves treating lacunary precursors with H$_2$O$_2$ in strongly buffered aqueous solutions. Upon reaction of H$_2$O$_2$ with α-[Co^{3+}W$_{11}$O$_{39}$],$^{9-}$ (a) the central tetrahedral Co^{3+} is reduced to Co^{2+} and (b) each of the four unshared oxygens surrounding the vacancy are replaced by a peroxide group, yielding salts of the tetraperoxide anion β_3-[(Co^{2+}O$_4$)W$_{11}$O$_{31}$(O$_2$)$_4$]$^{10-}$ (**1**). These results are unequivocally established by a combination of elemental analysis, spectroscopy (UV−Vis−near-IR and IR), magnetic moment determination, and complete X-ray crystal structure analysis of (NH$_4$)$_9$K-[(Co^{2+}O$_4$)W$_{11}$O$_{31}$(O$_2$)$_4$]·5H$_2$O. The dioxygen O−O bonds are 1.41 and 1.44 Å, typical of peroxo complexes. Salts of **1** are excellent stereoselective catalysts for the oxidation/epoxidation by H$_2$O$_2$. Reaction of 2-cyclohexenol with H$_2$O$_2$ catalyzed by **1** yields *cis*- and *trans*-2,3-epoxycyclohexen-1-ol (59.3% and 3.6%, respectively) and 2-cyclohexen-1-one (28.3%). According to ESR and IR spectroscopic results, the reaction of H$_2$O$_2$ with other lacunary XW$_{11}$O$_{39}$$^{m-}$ anions (X = P^{5+}, Si^{4+}, Ga^{3+}, and Fe^{3+}) proceeds by a different mechanism which involves the loss of heteroatom and formation of an isopolytungstate containing superoxo moieties (g_1 = 2.039, g_2 = 2.014, g_3 = 2.009; ν_{0-0} = 1040 and 1060 cm^{-1}).

Introduction

Polyoxometalates of Mo(VI) and W(VI) constitute a well-known, large, and rapidly expanding category of compounds.[1−5] The long-standing and increasing interest in their chemistry stems not only from fundamental considerations,[1a,6] but also from the consolidated use found by many of them in important industrial applications[7] based on their (acid and oxidation) catalytic activity, specialized redox behavior, and electron exchange characteristics.[2,3,8−12] Additionally, these compounds may, soon, become important in medicine[2b,13,14] and material science,[3,4,15] among other novel applications.

About 10 years ago, our group initiated a small research project undertaking the synthesis of a new polyoxotungstate, namely, [Co^{2+}W$_{11}$O$_{39}$],$^{10-}$ which would have the highest

[†] Universitat de València. E-mail: Rafael.Acerete@uv.es.

[‡] Georgetown University.

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negative charge known for a member of the lacunary 1:11 series. The obvious approach was based on the reduction of $[Co^{3+}W_{11}O_{39}]^{9-}$, recently reported by us.[16] After several unsuccessful attempts using typical reducing agents, we decided to try with hydrogen peroxide. Treatment of $[Co^{3+}W_{11}O_{39}]^{9-}$ with hydrogen peroxide did in fact reduce the Co(III) center to yield a $Co^{2+}W_{11}$ species. Unsuspectedly, the complete X-ray crystal structure analysis of this new complex (vide infra) revealed the presence of four peroxide groups, as bidentate (η^2-peroxo) ligands, one on each of the four W atoms around the vacancy of the parent $[Co^{3+}W_{11}O_{39}]^{9-}$. To our knowledge, this constitutes the first reported case of a peroxoheteropolymetalate related to the Keggin structure. Apparently, this type of reaction does not take place with *saturated* XW_{12} Keggin compounds, while other lacunaries do react with H_2O_2, yielding new dioxygen derivatives. Thus, our results open a novel and simple rational method for the synthesis of new polyoxometalates in which peripheral oxo ligands are replaced by dioxygen moieties. This method involves the controlled addition of hydrogen peroxide to appropriate (buffered) solutions of lacunary polyoxometalates. The new derivatives obtained may have potential applications as catalytic and/or stoichiometric epoxidants and specialized selective oxidants. Dioxygen complexes of group 6 transition elements have been recently reviewed.[17]

The main thrusts of the results reported herein are (1) synthesis and complete characterization, in the solid state and in solution, of β_3-$[(CoO_4)W_{11}O_{31}(O_2)_4]^{10-}$, **1**, the first *true* heteropolymetalate of W or Mo containing dioxygen (peroxo) moieties in a Keggin-related structure, (2) the finding that the new peroxo derivative **1** is an excellent catalyst for epoxidation and oxidation reactions with H_2O_2, as demonstrated on 2-cyclohexenol, (3) the demonstration that strong buffering and the use of lacunary polyoxometalate precursors are critical factors for the formation of the novel dioxygen complexes reported herein, and (4) the finding that addition of H_2O_2 to buffered aqueous solutions of a series of other lacunary $XW_{11}O_{39}{}^{m-}$ complexes (X = Si^{4+}, P^{5+}, Ga^{3+}, Fe^{3+}) yields in all four cases studied the same white crystalline material (independently of the heteroatom), which, on the basis of its ESR and IR spectra, should be formulated as a superoxo complex.

Results and Discussion

Solid-State Structure. The atomic−molecular structure of the heteropoly anion **1** and the numbering scheme for the
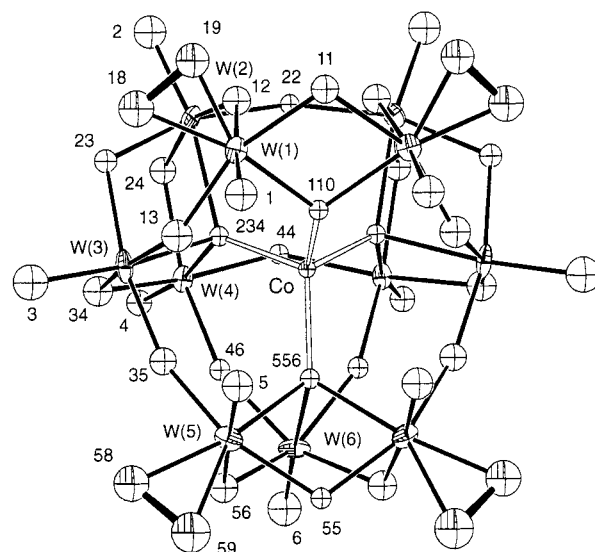

Figure 1. ORTEP view of the X-ray crystallographically determined structure and numbering scheme of the β_3-$[Co^{2+}W_{11}O_{35}(O_2)_4]^{10-}$ anion. Thermal ellipsoids at 30% probability level. Oxygen atoms are labeled only with their numbers, for clarity.
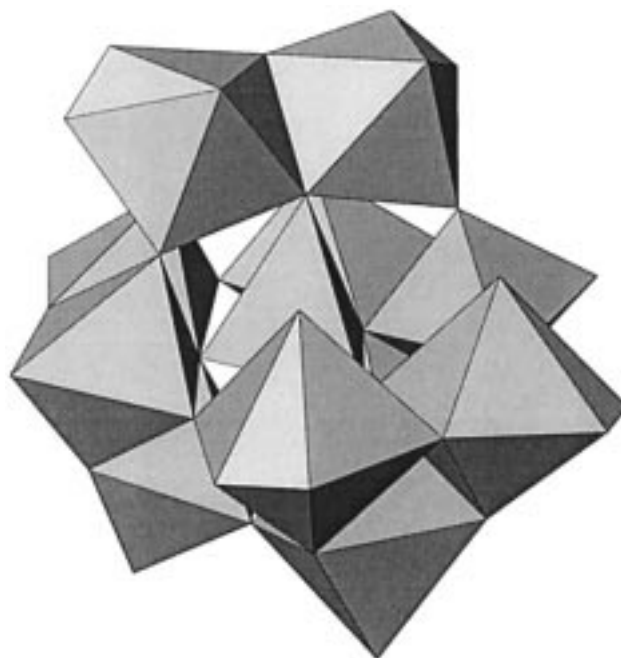

Figure 2. Polyhedral representation of the β_3-$[Co^{2+}W_{11}O_{35}(O_2)_4]^{10-}$ anion.

crystallographically unique atoms are illustrated in Figure 1 by an ORTEP diagram. Figure 2 shows an alternative polyhedral representation of **1**. Selected bond distances and angles are listed in Table 1. The anion structure shows the gross metal−oxygen framework of the general lacunary XW_{11} series of compounds, formally derived from the Keggin structure by removal of one W atom and its terminal oxygen. One of the most significant structural features of **1** is the fact that each of the four W atoms that surround the vacancy has one bidentate dioxygen (η^2-peroxo) ligand cis to the terminal W=O bond. That is, **1** contains four *cis*-W(O)(O$_2$) groups instead of *cis*-W(O)$_2$ groups around the vacancy in an otherwise XW_{11} structure. Each peroxide replaces what was a terminal W=O oxygen atom in a Keggin dodecatungstate. Thus, binding of dioxygen results in the characteristic heptacoordination for the peroxidized W atoms, which exhibit the pentagonal-bipyramidal geometry of other

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Formation of Superoxo Polytungstates

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Table 1. Selected Bond Distances (Å) and Angles (deg) in β_3-$[Co^{2+}W_{11}O_{35}(O_2)_4]^{10-}$ (**1**)

Bond Distances			
W(1)−O(1)	1.71(1)	O(18)−O(19)	1.41(2)
W(1)−O(11)	1.96(1)	O(58)−O(59)	1.44(2)
W(1)−O(12)	2.21(1)	Co−O(110)	1.95(2)
W(1)−O(13)	2.06(1)	Co−O(234)	1.95(1)
W(1)−O(18)	1.96(1)	Co−O(556)	1.96(2)
W(1)−O(19)	1.89(1)		
W(1)−O(110)	2.03(1)		

Bond Angles			
O(11)−W(1)-O(1)	97.3(7)	O(19)−W(1)-O(13)	123.1(6)
O(11)−W(1)-O(13)	152.1(6)	O(19)−W(1)-O(18)	42.9(6)
O(12)−W(1)-O(11)	174.9(5)	O(110)−W(1)-O(1)	95.2(7)
O(12)−W(1)-O(11)	82.6(7)	O(110)−W(1)-O(11)	73.6(6)
O(12)−W(1)-O(13)	84.8(5)	O(110)−W(1)-O(12)	79.8(6)
O(13)−W(1)-O(1)	93.1(6)	O(110)−W(1)-O(13)	79.7(5)
O(18)−W(1)-O(1)	98.5(6)	O(110)−W(1)-O(18)	156.1(6)
O(18)−W(1)-O(11)	123.4(6)	O(110)−W(1)-O(19)	153.5(6)
O(18)−W(1)-O(12)	85.8(6)	O(110)−Co-O(556)	117.3(7)
O(18)−W(1)-O(13)	80.2(6)	O(234)−Co-O(110)	109.3(5)
O(19)−W(1)-O(1)	96.8(6)	O(234)−Co-O(234)	95.8(7)
O(19)−W(1)-O(11)	81.4(6)	O(234)−Co-O(556)	111.5(4)
O(19)−W(1)-O(12)	88.3(6)		

oxomonoperoxo complexes of Mo and W,[17] as illustrated in Figures 1 and 2. The O−O distances observed for the dioxygen fragments are 1.41 and 1.44 Å, which do not differ significantly from the usual value around 1.45 Å seen in other peroxo complexes.[17,18] Also the W−O distances (1.89−1.96 Å) and O−W−O angles (42.9° and 43.4°) involving the peroxidic O atoms (see Table 1) are similar to those found in other peroxotungstates and molybdates previously reported (1.81−2.00 Å and 44.2−44.7°, respectively).[12b,19]

Figures 1 and 2 also reveal an additional structural feature of **1** that merits brief mention. The anion contains three $W_3O_{13/15}$ groups of edge-shared polyhedra with the same relative orientation as in the α-Keggin structure, while the remaining edge-shared group, $W_2O_8(O_2)_2$, which contains the vacancy and two of the peroxides, has a 60°-rotated orientation relative to the α-Keggin structure. Thus, the structure of **1** corresponds to the β_3 configuration.[20] As far as we know, this constitutes the first reported case of a β_3 structure. The observed α → β isomerization probably takes place to relieve the overcrowding of the four peroxo moieties.
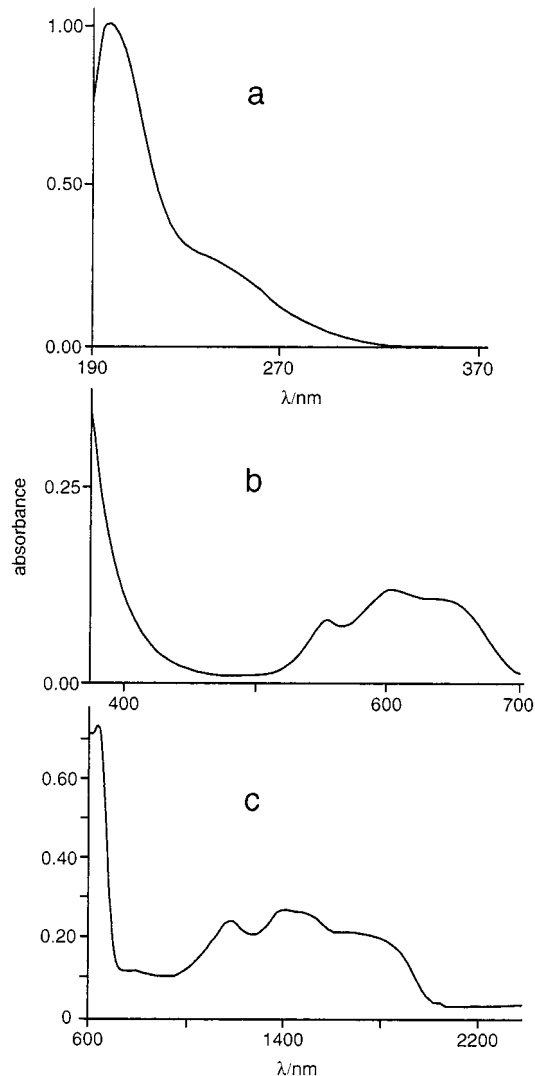
Spectroscopic Characterization. Figure 3 shows the optical spectra of the ammonium salt of **1** in the UV, visible, and near-IR ranges. The spectral parameters, shown in Table 2, are in good agreement with those reported for other tetrahedral Co(II) complexes,[21−23] also included in Table 2. These spectra

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Figure 3. Optical spectra of β_3-$K_{10}[CoW_{11}O_{35}(O_2)_4]$: (a) UV spectrum of a 10^{-5} M solution; (b) visible spectrum of a 10^{-3} M solution; (c) near-IR spectrum of a 2.5×10^{-5} M solution.

Table 2. Spectral Parameters for Tetrahedral Co(II) Species

compound	D_q (cm^{-1})	B' (cm^{-1})	β (B'/B)	$\|\lambda\|$ (cm^{-1})	μ_B	ref
$[Co(N_3)_4]^{2-}$	392	658	0.68	146 ± 20	4.47	27d
$[Co(NCO)_4]^{2-}$	415	720	0.745	115 ± 20	4.32	27d
$Hg[Co(NCS)_4]$	488	691	0.715	135	4.32	27e
$[Co(TMG)_4]^{2-}$	445	816	0.844		4.77	27f
$Co[(C_6H_5)_3PO]_2(NCS)_2$	403	725	0.75	148	4.46	27e
$[(CH_3)_4N]_2[Co(NCS)_4]$	455	691	0.715	149	4.40	27e
Co:ZnO	390	700	0.72			27g
Co:MgAl$_2$O$_4$	400	735	0.76			27g
$[CoO_4W_{12}O_{36}]^{6-}$	484	672	0.69	125	4.27	22
	460	650	0.67	160	4.41	23
$[CoO_4W_{11}(O_2)_4O_{31}]^{10-}$	410	733	0.76	93	4.22	this work

taken together unambiguously confirm the presence of Co(II) as the tetrahedral heteroatom. In other words, the analysis of the optical (UV, visible, and near-IR) spectra of **1** definitely proves that it contains a tetrahedrally coordinated Co(II) center

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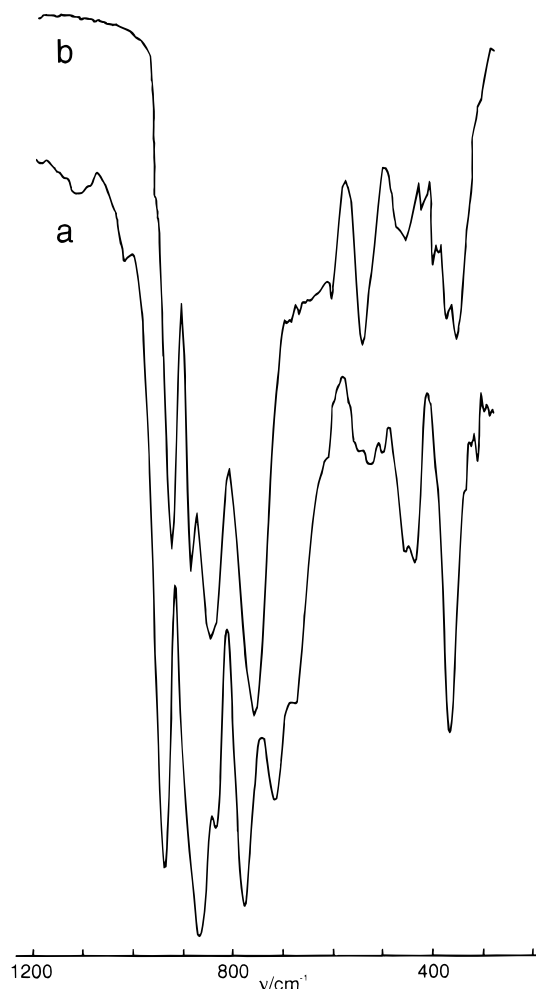
Figure 4. IR spectrum of (a) β_3-$K_{10}[CoW_{11}O_{35}(O_2)_4]$ and (b) K_9-$[Co^{3+}W_{11}O_{39}]\cdot 12H_2O$.

as the (primary) heteroatom. The positions, intensities, structures, and widths of the observed absorption bands clearly confirm this interpretation, excluding other possibilities. The intense absorptions observed in the UV region (51 020 cm^{-1} with a shoulder at 40 000 cm^{-1}) are common to most polyoxometalates of W and Mo, and have been assigned to charge-transfer bands within the ligand M_xO_y (M = Mo or W) frame. Recent single-crystal analyses of polarized optical and ESR spectra[23] have shown that the multiplet bands observed in the visible and near-infrared regions, at ca. 700 and 16 700 cm^{-1}, respectively, should be assigned to the ν_2 and ν_3 transitions within the ^4F term of a tetrahedral Co(II) in a D_2 *local* symmetry. Spectral analysis gives $D_q = 410$ cm^{-1} for **1**, in good agreement with the values found for other tetrahedral Co(II) oxide lattices (see Table 2).

Figure 4 shows the most characteristic part (the 1100−200 cm^{-1} region) of the IR spectrum of **1** together with that of its parent CoW_{11}, included for comparison. The spectrum of **1** shows bands at 928, 885, 848, and 760 cm^{-1}, corresponding to the W−O, W−O−W, and O−O (peroxo) modes of vibration.[12k,23c,24] Although it is not possible now to make a definitive assignment, the band at 885 cm^{-1} probably corresponds to the *side-on* (bidentate) η^2-peroxidic stretch, ν_{as}(O−O), while the

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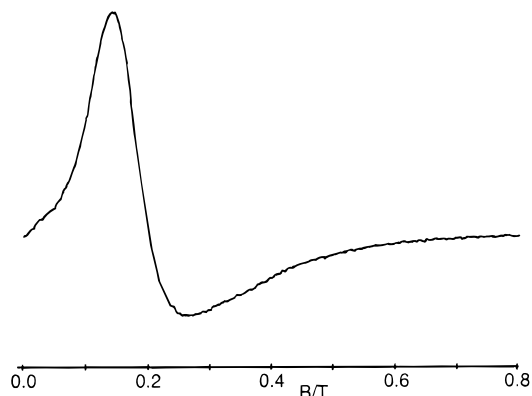

Figure 5. X-band ESR spectrum (9.43 GHz, 105 K) of a polycrystaline sample of **1**.

IR band at 550 cm^{-1} may be confidently assigned to the ν_s(W(O$_2$)) vibration.[25]

The ESR spectrum of a polycrystalline sample of the ammonium salt of **1** at 105 K is shown in Figure 5. It displays a broad asymmetric band ($\Delta H_{ppd} = 2000$ G) centered at $g' = 3.5$. Band-shape analysis suggests an ESR spectrum with $g_{||}' < g_{\perp}'$, and this, in turn, indicates a flattened tetrahedral coordination for the Co(II) center.[23b] This distortion is clearly revealed by our crystal structure results, which show significant deviations of O−Co−O angles (117.3° and 95°; see Table 1) with respect to their ideal values.

Magnetic Moment Determination. The magnetic moment of **1** was determined by the Evans Method,[26] using reference and sample solutions containing 33.1 mg/mL H$_4$[SiW$_{12}$O$_{40}$] and β_3-K_{10}[CoW$_{11}$O$_{35}$(O$_2$)$_4$], respectively, in pH 5 acetic buffer. $\Delta\nu$ for *tert*-butyl alcohol was 91.6 Hz. This corresponds to a molar magnetic susceptibility of $\chi_M = 0.007\ 24$ cps, which, after correction for diamagnetism, gave an effective magnetic moment of $\mu_{eff} = 4.18 \pm 0.05\ \mu_B$. This value is very similar to the one reported by Simmons[22] for the parent [Co^{2+}W$_{12}$O$_{40}$]$^{6-}$ (4.27 μ_B), and within the range expected for tetrahedral Co(II) in oxide lattices (3.94−4.28 μ_B).[27] A combination of reduction in symmetry, covalency, and second-order spin−orbit coupling effects is probably responsible for this value being significantly higher than the spin-only value (3.87 μ_B), with an orbital contribution of ca. 0.3 μ_B. This is in good agreement with the results reported for other tetrahedral Co(II) complexes for which the orbital contribution ranges between 0.2 and 0.9 μ_B.[27a,28]

The effective magnetic moment is given by $\mu_{eff} = \mu_{so}(1 - a\lambda'/10D_q)$. The magnitude of the apparent spin−orbit coupling constant, λ', can be calculated from the equation above after substitution of the experimental μ_{eff} (4.18 μ_B), the spin-only magnetic moment for Co(II), $\mu_{so} = 3.87\ \mu_B$, the experimental $10D_q = 4100$ cm^{-1}, and $a = 4$, to yield $\lambda' = -82.10$ cm^{-1}.

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This value represents a reduction to 46% of its free-ion value (-178 cm^{-1}), which in turn implies an important delocalization of d-electrons (covalency), in agreement with previously reported conclusions.[6f] Nevertheless, this should be taken as only a rough estimate of the degree of mixing (covalency), since (a) there are other contributions and (b) uncertainty in estimating λ' from the experimental measurements is large. The effective magnetic moment found for **1** (4.18 μ_B) falls ca. midway between the values observed in different tetrahedral Co(II) oxide lattices (3.94$-$4.28 μ_B),[22,27] in good correlation with the relative magnitude of $10D_q$ (4100 cm^{-1}), which also falls ca. midway between the values observed for the same series of oxide lattices (4300$-$3700 cm^{-1}).

Comments Concerning the Synthesis Procedure. The reactions of hydrogen peroxide with polyoxometalates of W and Mo, as well as with simple MO_4^{2-} (M = Mo and W), have been extensively studied during the last 10 years.[12b,f,j,29] The study of such binary (and ternary) systems has been stimulated by the interest in synthetic routes to new peroxopolymetalates, potentially useful as specialized and selective oxidants and/or catalysts for the oxidation of organic substrates with hydrogen peroxide. The procedure generally followed in the systems studied to date involved direct addition of relatively large excess of 30% hydrogen peroxide (ca. 7:1 or greater H_2O_2:M molar ratios) to aqueous solutions of MO_4^{2-}, H_2MO_4, or saturated polyoxometalate precursors. During our initial tests we observed that addition of hydrogen peroxide to the aqueous solution of the lacunary precursor, CoW_{11}, leads to a rapid and large drop in the pH. Such release of protons can be expected to limit the species yielded by the reaction to those stable at low pH values, while other possible intermediate species of interest would pass undetected as a result of proton-induced decompositions. This observation suggested to us the advisability of using strongly buffered aqueous solutions of the precursor and a lower proportion of H_2O_2 added dropwise, to prevent acid decomposition. Strong buffering appears to be a critical condition for the synthesis of the title and other similar heteropoly peroxo metalates.

Our serendipitous synthesis of **1** reveals an additional (and potentially important) critical condition: the use of a lacunary (CoM_{11}) heteropolymetalate as the precursor. Most saturated Keggin 12$-$tungsto species apparently do not react directly with hydrogen peroxide to form peroxy derivatives. This lack of reactivity of saturated Keggin complexes toward hydrogen peroxide has been previously reported.[12f,j] It has been reported,[12j] for instance, that while $H_3[PM_{12}O_{40}]$ (M = Mo, W) forms peroxo (probably polynuclear) species with H_2O_2, $H_4[SiW_{12}O_{40}]$ is unreactive. Thus far, the different reactivity pattern toward H_2O_2 between $H_3PM_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ has remained unexplained. We herein propose a reasonable explanation, according to which reactivity toward H_2O_2 to form peroxo derivatives requires the intervention of a lacunary (*open*) polyoxometalate precursor. It is well-known that dodecatungsto (and molybdo) phosphates have lower hydrolytic stability than most other Keggin complexes, which show greater robustness in water. In other words, conversion from PW_{12} to PW_{11} occurs at significantly lower pH than for most other Keggin anions (pH ca. 1.5 compared to pH 4.5).[30] Thus, even moderately acidic water solutions of PM_{12} contain significant equilibrium con-
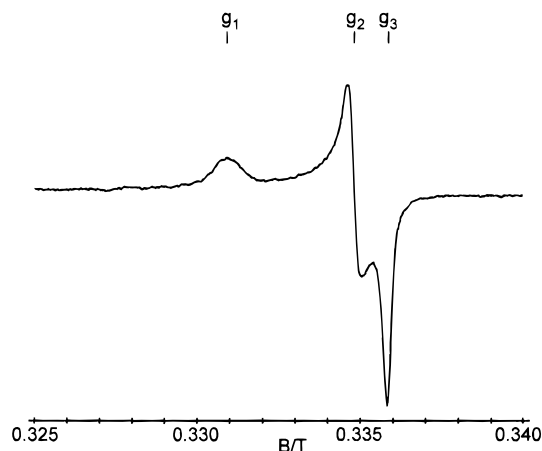

Figure 6. X-band ESR spectrum (9.44 GHz, 270 K) of the crystalline material obtained from the reaction of $XW_{11}O_{39}{}^{n-}$ (X = P^{5+}, Si^{4+}, Ga^{3+}, and Fe^{3+}) with H_2O_2.

centration of the lacunary PM_{11}, which explains the lacunary-like reactivity of PM_{12} solutions toward a variety of reagents. For instance, addition of $VOSO_4$ to water solutions of $H_3PW_{12}O_{40}$ leads to the slow formation of the same $PW_{11}VO_{40}$ biheteropoly complex formed instantaneously in the well-known reaction between $VOSO_4$ and lacunary $XW_{11}O_{39}{}^{x-}$ anions.[31] Other common (saturated) Keggin anions do not undergo such addition reactions unless previously decomposed to the lacunary. The increased reactivity of lacunary vs saturated complexes toward H_2O_2 is probably related to the increased lability (longer M$-$O bonds) of terminal oxygens in the *cis*-dioxo octahedra around the vacancy (type II in the Pope nomenclature) as compared to the monooxo octahedra (type I).[4]

Consequently, our results seem to indicate that strong buffering (to prevent acid attack) and use of lacunary precursors are critical conditions for the formation of novel peroxy polynuclear complexes of the type reported herein. We have applied our new general procedure to other lacunary undeca-tungstates, $XW_{11}O_{39}$ (X = Si^{4+}, P^{5+}, Ga^{3+}, and Fe^{3+}), as described in the Experimental Section. In sharp constrast with the tetraperoxo complex obtained from $Co^{3+}W_{11}$, the reaction of H_2O_2 with the above-mentioned four undecatungstates yields a structurally different dioxygen polynuclear complex not previously reported. Unfortunately, all attempts thus far on our part to grow X-ray diffraction quality single crystals of this new complex have failed. Nevertheless, our results indicate that the complex obtained is the same in all four cases studied, independently of the heteroatom, and that, unexpectedly, the complex contains dioxygen ligands of the superoxo type. These conclusions are based on the following experimental evidence: (1) The crystalline white solid obtained is ESR active. Its ESR spectrum at 270 K, shown in Figure 6, consists of a rhombic band with $g_1 = 2.039$, $g_2 = 2.014$, and $g_3 = 2.009$, typical of the superoxide radical.[18b,32,33] (2) The IR spectrum, shown in Figure 7, contains medium-intensity bands at 1040 and 1060

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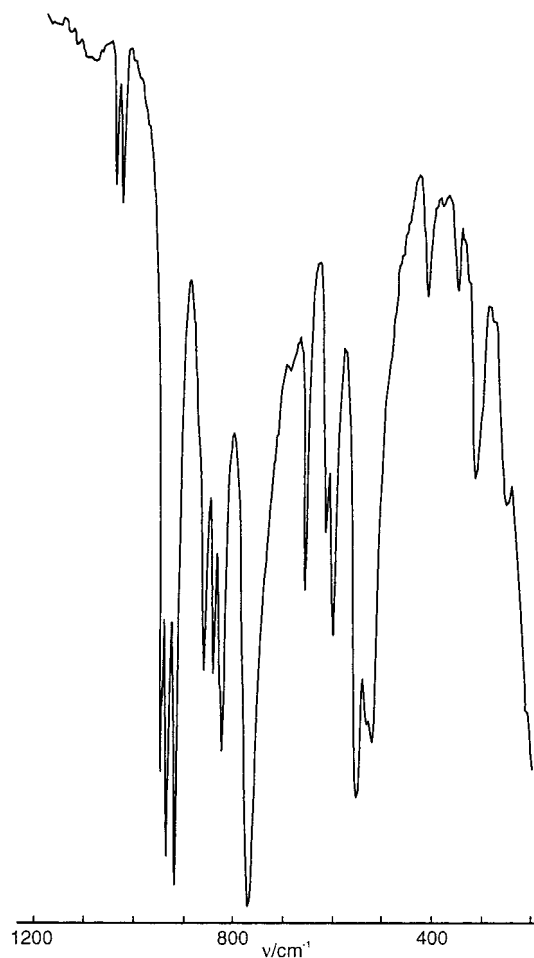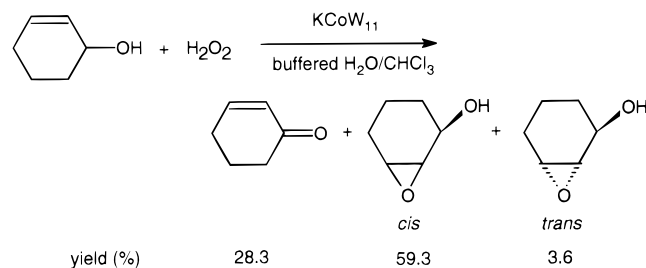
Figure 7. IR spectrum of the crystalline material obtained from the reaction of $XW_{11}O_{39}{}^{n-}$ (X = P^{5+}, Si^{4+}, Ga^{3+}, and Fe^{3+}) with H_2O_2.

cm^{-1}, which can be confidently assigned to the O−O streching of a superoxide complex, since they are exactly in the same region of $1020-1080$ cm^{-1} found in other superoxides.[32d,34] (3)-The crystalline white materials obtained from the reaction of H_2O_2 with SiW_{11}, PW_{11}, GaW_{11}, and FeW_{11} have identical IR and ESR spectra. Obviously, these results imply the loss of parent heteropoly structure, as well as the absence of the precursor heteroatom (P^{5+}, Si^{4+}, Ga^{3+}, or Fe^{3+}) in the product. This has been confirmed by elemental analysis and ^{31}P NMR. Further work is currently in progress to isolate good-quality crystals adequate for X-ray structural analysis. Efforts are also being made to characterize the species in solution by [183]W NMR studies.

Polyoxometalate-Catalyzed Oxidation of Olefins and Alcohols with Hydrogen Peroxide. To obtain a first estimate of the potential of **1** as a catalyst for the oxidation of organic substrates, 2-cyclohexenol was treated with hydrogen peroxide in the presence of a catalytic amount of **1** in a heterogeneous biphase medium (1 M pH 5 acetic buffer/$CHCl_3$), using a substrate:H_2O_2:**1** molar ratio of 250:400:1. Rather than using a preformed sample of **1**, it is more convenient to prepare it in situ from its parent $KCoW_{11}$ (the *precursor* of **1**), as described in the Experimental Section. That the active oxygen-to-substrate transfer agent is **1** is evidenced by the development of its

characteristic blue color in the aqueous phase upon addition of hydrogen peroxide. This blue color remains after the complete conversion of the substrate. The results confirm **1** as a remarkably efficient catalyst for the oxidation of olefins and alcohols, as demonstrated herein by the essentially complete (91.2%) conversion of the substrate to cyclohexenone and epoxide with high turnovers (ca. 230 or greater) at room temperature, according to the following chemical equation and yields based on substrate charged (the use of preformed **1** gave identical results):

It is worth noting the product diastereoselectivity shown by **1**. While *cis-* and *trans-*epoxides are produced in essentially a 1:1 ratio when dimethyloxirane is used as the oxidant in an uncatalyzed process,[35] oxidation with hydrogen peroxide catalyzed by **1** affords the *cis-*epoxide as the major product, with a *cis:trans-*epoxide ratio of 16.5. It is also worth mentioning that catalysis by **1** favors conversion to epoxide vs enone, with an epoxide:enone ratio of 2.2. The fact that the reaction gives the enone and the epoxide as separated products, but no keto-epoxide, is not surprising, since the first-step oxidation products, either the enone or the epoxyalcohol, are less reactive toward the oxygen atom transfer agent than the starting substrate. This is also in line with the well-known fact that α,β-unsaturated carbonyl compounds show even lower reactivity toward electrophilic epoxidation than simple olefins.[36]

Thus, our results clearly demonstrate the catalytic activity of **1**, with excellent efficiency and product stereoselectivity, which compares well and probably betters the results obtained with other related systems. Further work is currently in progress using a variety of substrates under different conditions, to examine in detail the catalytic activity of **1**, so that stereocontrol and product control could be achieved by appropriate modulation of such variables as pH, temperature, and solvent composition.[35,37]

Conclusions

The major findings of this work are as follows:

(1) Addition of hydrogen peroxide to buffered aqueous solutions of lacunary heteropolyoxotungstates of the 1:11 series ($XW_{11}O_{39}{}^{n-}$) leads to the formation of novel dioxygen derivatives containing peroxo and/or superoxo moieties.

(2) According to X-ray crystal analysis, application of this procedure to α-$[Co^{3+}W_{11}O_{39}]^{9-}$ yields salts of the tetraperoxo anion β_3-$[(CoO_4)W_{11}O_{31}(O_2)_4]$.[10-]

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(3) The new heteropolyoxotetraperoxotungstate is a remarkably effective catalyst for the epoxidation and oxidation of 2-cyclohexenol with hydrogen peroxide. The reaction yields *cis*- and *trans*-epoxyalcohols and cyclohexenone (yields are 59.3%, 3.6%, and 28.3%, respectively; turnovers 230 or better).

(4) IR and ESR spectra reveal that addition of H_2O_2 to buffered aqueous solutions of other undecatungstates, $XW_{11}O_{39}{}^{n-}$ ($X = P^{5+}$, Si^{4+}, Ga^{3+}, and Fe^{3+}) yields instead a polytungstate containing superoxo moieties, whose structure and composition is independent of the heteroatom present in the lacunary precursor.

Experimental Section

Starting Materials. Samples of the lacunary parent salt K_9-$[Co^{3+}W_{11}O_{39}]$ were prepared according to a procedure recently reported by us.[16] Other XW_{11} salts were synthesized according to well-established procedures.[38,39] Deionized water was used throughout this work. All other reagents used were of analytical grade.

Instrumentation. Infrared spectra were recorded in the $4000-200$ cm^{-1} region on a Perkin-Elmer 843 spectrophotometer with solid samples in KBr pellets. UV and visible spectra were recorded using Hewlett-Packard 8451A and Perkin-Elmer LAMBDA 15 spectrophotometers. near-IR spectra were recorded in the $600-2600$ μm region using Cary 14 and Hitachi recording spectrophotometers. All NMR spectra were obtained using a Bruker AM 300 WB spectrometer, operating at 7.05 T (300.13 MHz for protons) and equipped with an Aspect 300 computer, using precision NMR tubes 5, 10, or 20 mm in width, as stated in the text. Magnetic moment determinations in solution (modified Evans method)[26] used a pair of concentric NMR tubes, the outer one being a standard 5 mm tube and the inner one (available from Wilmad Glass, catalog no. WGS-5BL) being 2 mm wide inside the outer tube. The outer and inner tubes contain the sample and reference solutions, respectively. All NMR spectra were taken on solutions in deuterium oxide having a minimum isotopic purity of 99.7 atom % D. EPR spectra were obtained with a Bruker RSE 200 ER spectrometer on polycrystalline powdered samples at temperatures between 3 and 270 K. Single-crystal structural data were obtained using a Buerger precision camera and a four-circle Picker FACS-I spectrometer. Gas chromatography was performed on a Fisons 9000 capillary gas chromatograph, using a flame ionization detector, a fused silica SPB5 capillary column (25 m × 1.0 mm; film thickness 0.25 μm), and He as the carrier gas. GC–MS spectra were obtained using a Fisons Trio 1000 quadrupolar mass spectrometer linked to a Fisons CE–8000 gas chromatograph.

Analyses. Elemental analyses of tungsten, cobalt, and potassium were performed following well-established procedures.[22,39] Peroxide content was determined, in the absence of air, by addition of a known excess of a standarized solution of $(NH_4)_2SO_4\cdot FeSO_4\cdot 6H_2O$ (Mohr salt) and back-titration with potassium dichromate in 0.5 N H_2SO_4.[39] Water content was determined by TGA after subtraction of peroxide content.

Syntheses of Salts of the Title Heteropoly Anion, β_3-$[Co^{2+}W_{11}O_{35}$-$(O_2)_4]^{10-}$ (1). A ca. 6.0 g sample of (ocherous) $K_9[Co^{3+}W_{11}O_{39}]\cdot 12H_2O$ (1.8 mmol) was dissolved in the minimum volume of 1 M pH 5 acetic buffer. Addition of 30% p/v hydrogen peroxide (6 mL, 59 mmol) yielded a blue solution to which solid KCl was slowly added until the appearance of a slight turbidity. After filtration, slow cooling in the refrigerator afforded bright-blue prismatic crystals which were recrystallized from warm (45 °C) pH 5 acetic buffer. Anal. Calcd. for K_{10}-$[Co^{2+}W_{11}O_{35}(O_2)_4]\cdot 7H_2O$ ($M_r = 3286.3$): K, 11.90; Co, 1.79; W, 61.54; active O_2, 3.89; H_2O, 3.83. Found: K, 10.60; Co, 1.92; W, 61.06; active O_2, 3.87; H_2O, 3.96. Density, 4.42 g/mL. Magnetic moment, $\mu_{eff} = 4.18 \pm 0.05$ μ_B. The synthesis of the potassium–ammonium double salt, $(NH_4)_9K[Co^{2+}W_{11}O_{35}(O_2)_4]\cdot 5H_2O$, used for X-ray crystal analysis, followed the same procedure as above, except that ammonium chloride was used as the precipitant instead of potassium chloride. Density, 4.16 g/mL.

X-ray Data Collection, Structure Determination, and Refinement. The crystal structure analysis of the title heteropolyanion **1** was performed on its potassium–ammonium double salt, owing to the better quality of the crystals. A suitable blue prismatic crystal ($0.20 \times 0.15 \times 0.10$ mm^3) was selected, attached to a glass fiber by silicon grease, mounted on the goniometer head, and placed inside a Buerger precision camera, using zirconium-filtered Mo $K\alpha$ radiation for crystal alignment and determination of cell parameters. Monoclinic symmetry and systematic absences consistent with space groups $P2_1$ or $P2_1/m$ were established by single-crystal precision photography. Intensity data were collected on a Picker FACS-I four-circle diffractometer, equipped with a graphite monochromator of Mo K ($\lambda = 0.7107$ nm) radiation, under the control of the NRC-Canada software (E. Gabe). Crystal mosaicities as determined by ω scans were ca. 0.14°, typical of high-quality crystals. Crystal stability was controlled during data adquisition by monitoring every 50 measurements the intensities of three representative reflections (0,4,0; 0,0,5; −5,0,2). Data collection proceeded smoothly until the crystal rapidly disassembled after ca. 24 h of X-ray exposure, as indicated by a sudden decay in the intensities of the above-mentioned reference reflections and a crystal color change from blue to green. Eventually, after several unsuccessful attempts, a crystal survived long enough to collect ψ-scan data for an empirical correction as well as an adequate data set for crystal structure determination. What was subsequently diagnosed as an intermittently failing power supply in the interface led to spurious transmission of some intensity data from the diffractometer to the computer. About 200 reflections seriously affected, easily recognizable by a $|F_o|-|F_c| \approx 50$, were eliminated at a late stage in the refinement.[40]

The tungsten framework was identified using direct methods. MULTAN82 programs incorporated in the Structure Determination Package (B. A. Frenz and Associates and Enraf-Nonius) installed on a PDP11/44 computer were used. The data were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum, minimum, and weighted values for the transmission factors were 0.997, 0.413, and 0.758, respectively). As the subsequent difference Fourier maps contained many artifacts, structure solution and refinement proceeded slowly and cautiously. Isotropic thermal parameters were first applied to all atoms, followed by application of anisotropic thermal parameters to tungsten atoms. Key crystal and refinement parameters are given in Table 3. An unsuspected 8-coordinate potassium cation was identified in a difference Fourier map and confirmed by chemical analysis. Although unequivocal assignments of water and ammonium moieties are not possible, this does not significantly affect the structure results concerning the *heteropoly anion*. The assignments of atomic parameters (see the Supporting Information) are chemically reasonable (no ammonium cations coordinated to potassium or adjacent to one another, etc.). With the anion and most of the cation and solvate moieties included in the model, the worst 50 *bad* reflections all had $|F_o| \gg |F_c|$. In addition, several O atoms in the anion had negative temperature factors and chemically equivalent bond distances had statistically significant differences. Successive removal of many of the spuriously recorded data led to more stable refinements, eliminated negative temperature factors, and removed discrepancies among chemically equivalent bond parameters. In addition, the final difference Fourier map was flat and featureless, with the biggest peak (1.69 e/$Å^3$) located near a tungsten atom. While this process of elimination was aesthetically distasteful, the precision and accuracy of the structure reported herein stay uncompromised by spurious data (some of which had been flagged by the diffractometer's error detection routines). Refinements of the structure in space group $P2_1$ prior to data rejection were unsuccessful with chemically unreasonable bond parameters resulting from high correlation among pseudosymmetrically related

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(40) Unfortunately, we have been unsuccessful in all attempts thus far on our part to grow new X-ray-quality crystals sufficiently stable under the X-ray for structure determination. It is well-known that polyoxoanion chemistry is plagued with difficulties in structure determination and refinement (often a "crystallographer's nightmare"),[40a] as a result of disorder, ghost electron density near heavy atoms, inability to locate counterions and solvent molecules, crystal instability, etc. For some recent examples see: (a) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235 and refs 13 and 14 therein. (b) Hayashi, Y.; Müller, F.; Lin, Y.; Miller, S. M.; Anderson, O. P.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11401.

Table 3. Summary of X-ray Crystallographic Data

empirical formula	$W_{11}CoO_{48}KN_9H_{46}$
fw	3060.78
crystal shape	multifaceted prism
crystal system	monoclinic
space group	$P2_1/m$
a (Å)	10.8607(2)
b (Å)	17.437(3)
c (Å)	16.268(3)
β (deg)	123.32(2)
V (Å^3)	2514.0(2)
Z	2
density (calcd) (g/cm^3)	4.04 (4.16)
crystal size (mm)	$0.20 \times 0.15 \times 0.10$
radiation	Mo Kα ($\lambda = 0.7107$ Å)
temperature (K)	293(2)
absn coeff μ (cm^{-1})	261.2
trans coeff (mean)	0.413−0.997 (0.758)
range θ collected (deg)	1−21
no. of reflns colld	2404
no. of obsd reflns	1824 ($I > 10\sigma_I$)
no. of parameters refined	181
goodness-of-fit on F^2	1.21
R^a	0.042
$R_w{}^a$	0.058
max peak in diff map (e/Å^3)	1.69

[a] $R = \sum(F_o - F_c)/\sum(F_o)$; $R_w = [\sum[w(F_o - F_c)^2]/\sum[w(F_o)^2]]^{1/2}$.

parameters. We find no indication in the final structure that the real symmetry should be *I* not *m*. The final R (R_w) value was 0.042 (0.058). Additional crystallographic tabulations are in the *Supporting Information.* Despite the numerous diffractometer problems encountered during data adquisition, we can be completely confident that, once the problems were correctly diagnosed and the spurious data deleted, the final result is satisfactory in terms of accuracy and precision, so that all the atom connectivities within the heteropolyanion as well as its structure are unequivocally established.[40]

Susceptibility Measurements in Solution. Determinations of magnetic susceptibility were carried out at room temperature with the Evans method,[26] using deaerated sample and reference solutions of essentially identical densities accurately measured in a 2 mL pycnometer. The outer NMR tube contained a sample solution of the paramagnetic compound, $K_{10}[Co^{2+}W_{11}O_{35}(O_2)_4]$ (ca. 10^{-2} M) in pH 5 D$_2$O acetic buffer. The inner tube contained a reference solution (also ca. 10^{-2} M) of the diamagnetic $K_8[SiW_{11}O_{39}]$ in pH 5 D$_2$O acetic buffer. A 2% v/v solution of *tert*-butyl alcohol was added to both sample and reference solutions as the ^{1}H NMR-active solute. Details concerning calculations following the Evans method as modified for a superconducting magnet are described elsewhere.[26]

Reaction of H$_2$O$_2$ with Other Lacunary $XW_{11}O_{39}{}^{x-}$ **(X = P^{5+}, Si^{4+}, Fe^{3+}, and Ga^{3+}) Complexes.** Potassium salts of the four listed undecatungstates, differing only in the heteroatom, were each treated with H$_2$O$_2$ according to the following procedure. $K_{10}SiW_{11}O_{39}$ (8.0 g, 2.6 mmol) was dissolved in 100 mL of 1.5 M pH 5 acetic buffer. After

filtration of turbidity, 30% H$_2$O$_2$ (18 mL, 176 mmol) was slowly added with continuous stirring. After 1 day of storage in the refrigerator, slow addition of 8.0 g of potassium chloride afforded 7.0 g of a white precipitate of prismatic crystals which were filtered and dried in a desiccator. Similar procedures were applied to the potassium salts of $PW_{11}O_{39}{}^{9-}$, $FeW_{11}O_{39}{}^{11-}$, and $GaW_{11}O_{39}{}^{11-}$. The white crystalline materials obtained in all four cases studied have identical ESR (Figure 6) and IR (Figure 7) spectra. Anal. Found: K, 7.70%; W, 54.20%; active O$_2$, 7.6 mequiv/g. The absence of heteroatom (P, Si, Fe, and Ga) in the product was confirmed in each case by elemental analysis and, in the $PW_{11}O_{39}{}^{9-}$ system, by its solution being ^{31}P NMR silent.

General Procedure for the Catalytic Oxidation with H$_2$O$_2$. To a solution of KCoW$_{11}$ (0.055 g, 0.026 mmol) in 2.5 mL of 1 M pH 5 acetic buffer was added 15 mL of a solution of 2-cyclohexenol (0.64 mL, 6.5 mmol) in CHCl$_3$. Hydrogen peroxide (30%, 1.2 mL, 10.6 mmol) was added, and the resulting mixture stirred at room temperature in the dark for 12 h. The organic phase was then extracted, washed three times with water, dried under MgSO$_4$, and analyzed by GC and GC−MS. The products were identified by comparing chromatographic and mass spectral data with literature values[35,41] and with those of separate runs using authentic samples (cyclohexenone and *cis-* and *trans*-epoxides) obtained by oxidation of 2-cyclohexenol with dimethyloxirane.[35] *trans*-2,3-Epoxycyclohexan-1-ol was identified by its GC parameters and on the basis of the following MS data: (EI, 70 eV) *m/z* 98 (M$^+$ − 16, 0.2), 95 (5), 70 (100), 67 (12), 58 (48), 58 (47), 57 (85), 41 (30), 39 (25), 29 (28). *cis*-2,3-Epoxycyclohexan-1-ol was also identified by its GC parameters and on the basis of the following MS data: (EI, 70 eV) *m/z* 98 (M$^+$ − 16, 0.2), 95 (5), 71 (15), 70 (100), 67 (14), 58 (46), 57 (90), 55 (18), 41 (29). 2-Cyclohexen-1-one was similarly identified: MS (EI, 70 eV) *m/z* 96 (M$^+$, 31), 68 (100), 67 (4), 55 (6), 42 (9), 40 (18), 39 (22).

Supporting Information Available: Complete tables of crystallographic data (Table S1), final atomic coordinates and equivalent isotropic (Table S2) and anisotropic (Table S3) thermal parameters, bond distances (Table S4), and bond angles (Table S5) and ORTEP diagram for the unit cell (Figure S1) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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