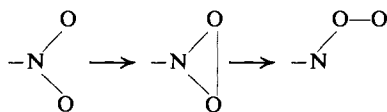


The present study, then, centered about a series of non-empirical self-consistent-field computations, with electron configurations 1, 2, and 3 representing the three expected isomers. A helpful qualitative discussion of the analogous states of ozone has been given by Goddard and coworkers.¹⁵

One important qualitative conclusion may be drawn prior to the calculations. This concerns the possible interconversion of the "normal" and peroxy forms of NO_2^- . The most likely pathway for this conversion would be (schematically)



In fact, such a path is highly improbable, since the ring state has three occupied π (or a'') orbitals ($1b_1$, $2b_1$, and $1a_2$) while the normal and peroxy forms have only two occupied π orbitals. Thus, orbital symmetry suggests that there should be a substantial barrier preventing access to the ring state from either direction.

The structure of each isomer has been predicted by minimizing the total energy with respect to the various geometrical parameters. The results are summarized in Table I. Note first that the expected ground state

Table I. Geometries, Energies, and Mulliken Populations for Three Isomers of NO_2^- ^a

Property	Isomer		
	Normal	Peroxy	Ring
$r(\text{N-O})$	1.264	1.245	1.502
$r(\text{O-O})$		1.493	
θ (deg)	117.0	118.5	58.5
E (hartrees)	-204.0336	-203.9161	-203.8736
E (eV)	0.00	3.20	4.35
Atomic populations			
N	6.83	7.21	7.24
O ₁	8.58	8.22	8.38
O ₂	8.58	8.57	8.38

^a Bond distances are in Å. O₁ is the central atom in the peroxy isomer.

geometry is indeed remarkably close to that of ozone, the difference in bond angles being less than 1° . The difference in bond distances is less than 0.02 Å, another indication of the validity of isoelectronic arguments.¹⁶ Finally, this geometry agrees quite well with the experimental structure of the NO_2^- ion in crystalline sodium nitrite.¹⁷ The peroxy form has a similar bond angle, 118° , and NO bond distance, 1.25 Å. However, the O-O bond distance is much longer than in ozone. In fact, the O-O distance is slightly greater than in hydrogen peroxide,¹⁸ 1.475 Å. Thus the labeling of this second isomer as the peroxy form is quite appropriate. The peroxy form lies 3.20 eV above the

normal isomer. The ring isomer is indeed very nearly an equilateral triangle, the ONO bond angle being 58° . The NO bond distance is 1.50 Å, or 0.05 Å longer than the predicted bond distance¹² for the comparable isomer of O_3 . However, the ring isomer is seen to lie much higher (4.4 eV) for the NO_2^- system than for O_3 (1.6 eV). Thus our isoelectronic analogy is not very accurate in this particular regard.

Since it has been suggested³ that the anomalous NO_2^- is the result of a weak electrostatic interaction between NO and O^- , we report in Table I Mulliken populations for the three isomers. There it is seen that the terminal oxygen is indeed the most negatively "charged," in a simple picture. However, the other two atoms account for nearly half of the ion's -1 charge.

In conclusion, the peroxy form of NO_2^- corresponds to a well-defined minimum in the potential energy surface. Consequently, its postulation by experimentalists is given substantive theoretical support. Moreover, the fact that the peroxy and normal forms of NO_2^- do not appear²⁻⁴ to interconvert can be understood in terms of the relatively high energy of the ring state, the superficially logical intermediate for such an interconversion.

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Synthesis of Heteropoly Anions in Aprotic Solvents. Tungstoselenates(V), -(VI), and -(VII)

Sir:

The characterization of "substituted" heteropoly Keggin anions, $\text{XMZ}_{11}\text{O}_{40}^{n-}$, where X is the central tetrahedrally coordinated atom, Z is molybdenum or tungsten, and M is a second heteroatom occupying one of the 12 equivalent "octahedral" sites, was first reported by Baker, *et al.*¹ Numerous examples of such complexes have since been described.² When M is in a high formal oxidation state (+5, +6), further substitution is possible and it is difficult to isolate pure

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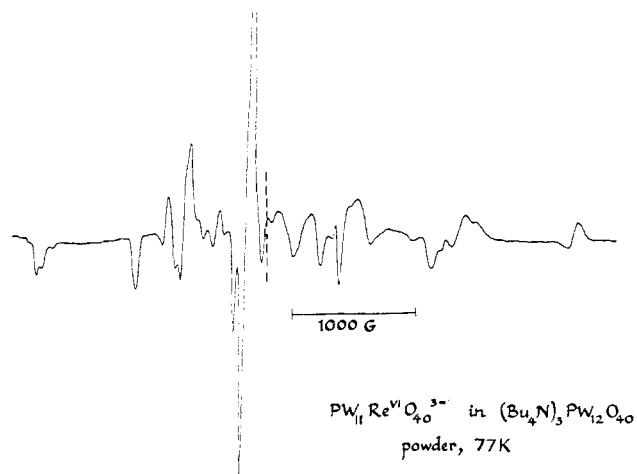


Figure 1. Polycrystalline X-band esr spectrum of $\text{PRe}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$ as a 1% solution in $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$, recorded at 77°K. The dashed line indicates the position of DPPH. The spectra of frozen solutions in acetonitrile or propylene carbonate are similar.

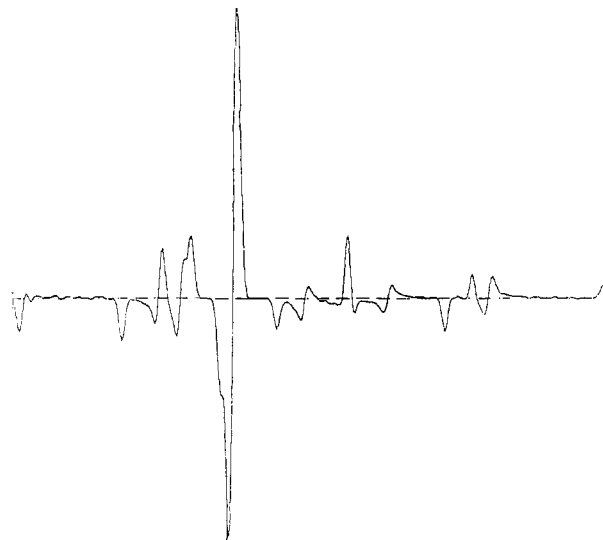


Figure 2. Computer simulation of the experimental spectrum shown in Figure 1.

complexes.^{3,4} We have made use of the solubility of many Keggin anions in polar nonaqueous solvents to develop a rational and efficient synthesis of such 1:1:11 anions where M is molybdenum(V) or rhenium(V). These complexes can be oxidized to the corresponding Mo(VI), Re(VI), and Re(VII) species.⁵

The synthesis involves adding tetrabutylammonium hydroxide (5 mol) to a solution of tetrabutylammonium 12-tungstophosphate, $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$, or the corresponding molybdate (1 mol), in acetonitrile or propylene carbonate. To the solution of the $\text{PW}_{11}\text{O}_{39}^{7-}$ ion thus formed is added $\text{Bu}_4\text{N}[\text{MoOCl}_4]$ or $\text{Bu}_4\text{N}[\text{ReOCl}_4]$, and the intense color of the substituted anion forms immediately. The yield is essentially quantitative. Tetrabutylammonium salts of the anions $\text{PMo}^{\text{V}}\text{W}_{11}\text{O}_{40}^{4-}$ (dark green-blue), $\text{PMo}^{\text{V}}\text{W}_{11}\text{O}_{40}^{4-}$ (red-purple), $\text{PRe}^{\text{V}}\text{W}_{11}\text{O}_{40}^{4-}$ (red-purple), and $\text{SiW}_{12}\text{O}_{40}^{4-}$ (white) are anisolvates⁶ and are isomorphous by crystal morphology and X-ray powder diffraction. The esr spectra of the Mo(V) anions are reported elsewhere.^{4,7} Oxidation with bromine leads to $\text{PMo}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$ (pale yellow), $\text{PRe}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$ (dark green), and $\text{PRe}^{\text{VII}}\text{W}_{11}\text{O}_{40}^{2-}$ (pale yellow). Salts of the -3 anions are isomorphous with $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ but not with those of the other charge types, and this property permits easy separation.

A cyclic voltammogram of $(\text{Bu}_4\text{N})_3\text{PReW}_{11}\text{O}_{40}$ in propylene carbonate, using a graphite electrode, shows the reversible $\text{Re}(\text{V}) \rightarrow \text{Re}(\text{VI})$ and $\text{Re}(\text{VI}) \rightarrow \text{Re}(\text{VII})$ oxidations at -0.10 and $+0.44$ V *vs.* sce, respectively (anodic peak potentials, 0.1 M Bu_4NClO_4 supporting electrolyte). The crystalline salts are indefinitely stable in air, as are solutions of the molybdates and rhenates-(V) and -(VI). The color of solutions of $\text{PRe}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$

O_{40}^{2-} in wet solvents fades after an hour or so indicating hydrolysis to ReO_4^- .

The three isostructural tungstohexates form an unusual, if not unique, redox series. The symmetry for rhenium in the Keggin structure is approximately C_{4v} , and the oxidations involve stepwise removal of formally nonbonding d_{xy} electrons. The optical spectrum of $\text{PRe}^{\text{V}}\text{W}_{11}\text{O}_{40}^{4-}$ has maxima at 14.0, 19.5, and 25.3 kK (ϵ 950, 2000, and 1000 $M^{-1} \text{cm}^{-1}$, respectively) and these are probably intervalence ($\text{Re}^{\text{V}} \rightarrow \text{W}^{\text{VI}}$) transitions. The spectrum of $\text{PRe}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$ has a shoulder at 25 kK (ϵ 490) and a maximum at 21.5 kK (ϵ 340) with an extremely broad tail that obscures the ligand field region.

The X-band esr spectrum of a polycrystalline sample of $\text{PRe}^{\text{VI}}\text{W}_{11}\text{O}_{40}^{3-}$ (1% in $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$) at 77°K is shown in Figure 1. No further resolution was observed at 6°K, although the spectrum began to deteriorate at 90°K and was unobservable above *ca.* 200°K. Since the rhenium atom is almost certainly disordered over the 12 equivalent tungsten sites in the Keggin structure, *cf.* V(IV) in $\text{PVW}_{11}\text{O}_{40}^{5-}$,⁸ no advantage is gained from measurements on single crystals. The spectrum was analyzed in terms of the rhombic spin Hamiltonian ($I = 5/2$ for ^{185,187}Re)

$$\mathcal{H} = [g_x H_x + g_y H_y + g_z H_z] + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z$$

and the approximate values for the g and hyperfine parameters determined by computer simulation. The best fit⁹ parameters are

$$\begin{aligned} g_x &= 1.75 \pm 0.02 & A_x &= 415 \pm 20 \text{ G} \\ g_y &= 1.67 \pm 0.02 & A_y &= 470 \pm 20 \text{ G} \\ g_z &= 1.790 \pm 0.002 & A_z &= 860 \pm 5 \text{ G} \end{aligned}$$

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A typical simulated spectrum (in this case with $g_x = 1.775$, $g_y = 1.690$, $g_z = 1.790$, $A_x = 425$ G, $A_y = 485$ G, $A_z = 865$ G) is shown in Figure 2.

Of the handful of rhenium esr spectra that have been reported previously, two are of axial rhenium(VI) species. Garif'yanov¹⁰ reported $g_{\perp} = 1.77$, $g_{\parallel} = 1.90$, $A_{\perp} = 400$, and $A_{\parallel} = 480$ G for ReOCl_4 (frozen solution) and Mertis, *et al.*,¹¹ give $g_{\perp} = 1.94$ and $g_{\parallel} = 2.25$ for $\text{ReO}(\text{CH}_3)_4$. The g values for the heteropoly anion are similar to those for ReOCl_4 and we have noted that g values for other d^1 species, V(IV),⁵ Mo(V),⁷ and W(V),¹² in Keggin anions are comparable with, but generally slightly smaller than, those for the corresponding oxopentachloro complexes.

The hyperfine parameters for the heteropoly anion are the largest that have been observed for any transition metal ion. The very large value for A_z in particular results in partial resolution, observable in the lowest field hyperfine line, of the two magnetic isotopes of rhenium, ¹⁸⁵Re (37.07%) and ¹⁸⁷Re (62.93%). This is the first esr resolution of isotopic nuclei whose magnetic moments differ by only 1%.

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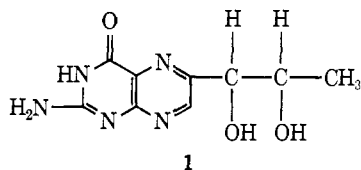
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An Unequivocal Total Synthesis of L-erythro-Biopterin¹

Sir:

L-erythro-Biopterin (1), apparently in its 5,6,7,8-tetrahydro form, is a wide-spread naturally occurring



enzyme cofactor identified in the phenylalanine-to-tyrosine² and tyrosine-to-dopa^{3,4} conversions, in melanin synthesis,^{5,6} and in tryptophan⁷⁻¹⁰ and dihydro-

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rotic acid¹¹ hydroxylation. It has furthermore been implicated in a broad spectrum of other biological oxidation reactions including the conversion of long chain alkyl ethers of glycerol to fatty acids and glycerol, the 17- α -hydroxylation of progesterone, and the biosynthesis of the prostaglandins.^{2,12} In addition, indirect evidence supports the suggestion that tetrahydrobiopterin and/or closely related tetrahydropterins play a critical role in cellular electron transport, including photosynthesis.² Biopterin itself appears to be a ubiquitous natural product, found in microorganisms, insects, algae, amphibia, and mammals,^{2,18} and is the most abundant of the naturally occurring pterins found in human urine.¹⁴

As a consequence of this apparent wide-spread utilization of biopterin (or reduced biopterin) in metabolic processes, there has been considerable contemporary interest in its synthesis. Most approaches involve the condensation of 2,4,5-triamino-6-hydroxypyrimidine with a suitable sugar intermediate,¹⁵⁻¹⁸ and, as a consequence, give mixtures of 6- and 7-isomers which then must be separated by laborious, and often destructive, chromatographic techniques. The only unequivocal synthesis of biopterin appears to be that of Andrews, Barber, and Tong,¹⁹ which involves the condensation of 2-amino-4-chloro-5-nitro-6-hydroxypyrimidine with the appropriate α -aminoketone prepared from 5-deoxy-L-arabinose, followed by reductive cyclization. A later synthesis developed by Viscontini appears to be much less satisfactory.²⁰

We describe in this communication a new total synthesis of pure L-erythro-biopterin which, because of the complete absence of the 7-isomer, eliminates the extensive purification procedures which have plagued most previous attempts to prepare this enzyme cofactor. As with the Andrews, Barber, and Tong route,¹⁹ our synthesis also commences with 5-deoxy-L-arabinose (5), for which we have developed a much improved synthesis. Thus, L-rhamnose (2) was converted to its dithioacetal (3) (85%) by acid-catalyzed reaction with ethyl mercaptan essentially according to the procedure of Zisis and Richtmyer.²¹ Oxidation to L-rhamnose bissulfone (4) has previously been described²² utilizing aqueous perpropionic acid, which gave a mixture of the desired bissulfone 4 and a vinyl sulfone. By contrast,

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