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Crystal Structures of α-$[Co^{II}W_{12}O_{40}]^{6-}$ and Its Heteropoly Blue 2e Reduction Product, α-$[Co^{II}W_{12}O_{40}]^{8-}$. Structural, Electronic, and Chemical Consequences of Electron Delocalization in a Multiatom Mixed-Valence System

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Abstract: This paper reports for the first time X-ray crystal structures for a parent heteropoly complex and for its heteropoly blue reduction product. The potassium salt of the former complex, α-$[Co^{II}W_{12}O_{40}]^{6-}$, is ordered in space group $P6_222$; and the potassium salt of its two-electron heteropoly blue reduction product, α-$[Co^{II}W_{12}O_{40}]^{8-}$, is disordered in space group $Pm3m$. The structures were refined to $R(\text{on } F) = 0.034$ and $R(\text{on } F) = 0.044$, respectively. Except for a shortening of each central $Co–O_{tet}$ distance, by 0.03 Å, and a consequent corresponding increase in $W–O_{tet}$ distances, the reduction caused remarkably little change in interatomic distances within the complex. Very slight lengthening of W–W distances between edge-sharing WO_6 octahedra, upon reduction, and a corresponding contribution toward slight shortening of the W–W distances through corner-sharing between WO_6 groups, as suggested by previous data, were near the limits of statistical significance. On the other hand, the reduction apparently creates sizable new energy barriers to atomic displacements for both W's and O's. The displacement parameters for all of those atoms in the heteropoly complex decrease markedly, upon its reduction, while such parameters remain unchanged for all of the atoms not in the complex (H_2O's and K^+'s). The attendant significantly enhanced rigidity of the reduced complex is consistent with increased kinetic stability of heteropoly blue products to substitution and to degradation by base. The increased resistance to atom displacements in the heteropoly blue species may be seen as a consequence of the additional energy factor involved in maintaining favorable orbital overlaps for the delocalization of the added electrons. While the delocalization of the "blue" electrons presumably does involve thermal hopping of those electrons among W atoms, the greatly decreased displacement parameters, observed for the O's as well as the W's, suggest the importance of a ground-state delocalization mechanism involving partial "blue" electron residency in molecular orbitals that involve oxygen atoms. The increase in negative charge on bridging O atoms is consistent with their increased nucleophilicity and with the above-cited changes in $Co–O_{tet}$ and $W–O_{tet}$ distances. Those changes imply that the central $Co^{II}O_4$ tetrahedron is slightly more isolated from the rest of the W–O framework in the reduced species. This is consistent with a pronounced decrease, upon reduction, in the magnitude of the large isotropic shift for the ^{183}W NMR signal.

Background

Heteropoly complexes resemble discrete fragments of metal oxide structures of definite sizes and shapes.[1-6] They maintain their identities in aqueous and nonaqueous solutions as well as in ionic crystals. Many heteropoly complexes can be made which contain various combinations of d-transition metals at specific sites.[6,7] Numerous heteropoly complexes (Pope's "Type I")[6] can be reversibly reduced by addition of various specific numbers of electrons. The reduction products, which typically retain the general structures of their oxidized parents and are frequently deep blue in color, comprise a large and potentially very important group of complexes generally known as the "heteropoly blues". The added ("blue") electrons are "delocalized", according to various time scales, usually over numerous atoms in the heteropoly structure. Heteropoly blues are usually regarded as class II systems in the Robin and Day[8] treatment of mixed-valence compounds.

Heteropoly complexes and heteropoly blues are therefore especially valuable for study of divers important interrelated areas of current interest including (a) catalysis, (b) intermolecular and intramolecular electron transfer,[9-11] (c) mixed metal oxide conductivity,[12,13] (d) different types, mechanisms,[6,14] and pathways[12-17] for mixed-valence electron delocalization and for extensive d-electron spin delocalization,[18,19] (e) theory of multinuclear NMR chemical shifts,[13,18,20-24] (f) electron-spin couplings,[9,12,15,25-27] and (g) isolated paramagnetic spin-coupled systems.[15,25-29]

Electron delocalization in heteropoly blue complexes is viewed as operating through two mechanisms: a thermally activated electron hopping process from one addendum (e.g., W or Mo) atom to the next and a ground-state delocalization (gsd)[6] pre-

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sumably involving π-bonding through bridging oxygen atoms from the reduced metal atom to its neighbors. Heretofore attention has focused primarily on the thermal hopping,[6] but the existence of gsd is required to account for intervalence charge-transfer bands. A preponderance of evidence indicates that when a heteropoly blue tungstate contains an even number of added "blue" electrons, their spins are characteristically paired via multiroute superexchange even when the individual electrons are hopping among addenda atoms that are well-separated.[12,13,15]

The present paper is one of a continuing series aimed at further elucidation of the roles played by blue electrons and by unpaired electrons in determining properties and structures of heteropoly complexes and their blue reduction products.[7,9,10–13,15,16,18,20–22,24–29]

Experimental Section

Preparations. All reagents used were Analytical Grade. $K_6[Co^{II}W_{12}O_{40}]\cdot nH_2O$ was prepared as described by Simmons[28] and Baker.[30] Recrystallization from acidified water gave well-formed green prisms. The visible spectrum,[28] cyclic voltammogram,[31,32] ^{183}W NMR spectrum,[18,22] and magnetic susceptibility at room temperature[28] agreed with those reported in the literature. Six K^+ ions per complex are found in the crystal structure. The crystal system is hexagonal (as in the case of the Co(III) isomorph, $K_5[Co^{III}W_{12}O_{40}]\cdot qH_2O$[1,28,30,33]).

The potassium salt of the 2e blue reduction product, $[Co^{II}W_{12}O_{40}]^{8-}$, a new crystalline compound, was prepared as follows. A 0.05 M solution of $K_6[Co^{II}W_{12}O_{40}]$ in N_2-swept (O_2-free) 1 M sodium citrate buffer (pH = 3) was reduced electrolytically under pure N_2 atmosphere. The constant applied potential was −0.69 V vs SCE. A double junction Ag/AgCl electrode with 1 M $LiNO_3$ in the outer compartment was the reference electrode, and carbon cloth was the working electrode. The anodic cell consisted of a Pt wire in a solution of the same buffer. The reduction was monitored coulometrically, and when current flow became minimal (the rest potential having been reached), the ratio of experimentally versus theoretically required Coulombs was 1.00.[34] An equal volume of deoxygenated saturated KCl solution was added to the electrolysis solution, and the mixture was allowed to stand overnight under argon. Shiny, extremely dark blue (essentially black) crystals separated. These were filtered off, washed with cold deoxygenated water, and dried in a stream of argon, using Schlenck glassware. The reversible cyclic voltammogram of the reduced complex is identical with that of the oxidized Co(II) species. Samples of the dark crystals exposed to air for 6 months showed only a 10% change in the degree of reduction. The salt crystallized with a primitive cubic unit cell.

Waters of Crystallization and Counterions.[35] There are frequently substantial amounts of water of crystallization in heteropoly salts, occupying the interstices and channels between the large anions. Often much of this water is zeolytic in nature, and the formulas used for hydrates generally represent analyses that reflect different degrees of drying. Thus air-dried crystals of $K_6[Co^{II}W_{12}O_{40}]\cdot nH_2O$ analyzed to show $n \simeq 3.1$ in this work, but freshly grown crystals, promptly sealed in glass capillaries to minimize efflorescence, had $n \simeq 11$. Further, some of the water molecules and frequently one or more (but usually not most) of the counterions (e.g., K^+'s) in such salts are fairly commonly sufficiently disordered in the interstices between the complexes that they cannot be individually crystallographically identified in the unit cell. Fortunately, within very broad limits this situation does not affect the positions of the complex anions, the atoms they contain, or their thermal parameters. The disorder of some H_2O's and occasionally solvated counterions is a consequence of the very weak nature of the H bonds characteristically formed by the outer oxygens of heteropoly complexes. The addenda (e.g., W(VI) or Mo(VI)) atoms have relatively small radii for octahedral coordination with oxygen, and so they move far off-center in their MO_6 octahedra toward the exterior oxygens of the complex, which heavily polarizes those O's toward the center of the complex and very greatly vitiates the strengths of the H bonds they can form. The large ion-to-induced dipole attractions between addenda and exterior O's hold the addenda in these off-center sites.

Analyses. Tungsten was determined in both salts by the method of Hayashi and Moffat,[36] after precipitation of cobaltic hydroxide with 6 M NaOH and Br_2 and boiling. Potassium was determined as its tetraphenylborate.[37] The extent of reduction of the blue complex was determined by adding weighed amounts to excess standard deoxygenated $K_2Cr_2O_7$ solution followed by potentiometric back-titration with standardized Mohr's salt solution. This showed the reduction had added 1.77 (3) electrons per complex. This closely checks the analytical atomic ratio of 7.77 K atoms per 12.00 W atoms. The formula of the blue-black crystals can then be represented as $K_{7.77}[Co^{II}W_{12}O_{40}]^{8-}{}_{0.885}$-$[Co^{II}W_{12}O_{40}]^{6-}{}_{0.115}\cdot mH_2O$. The W and K analyses each then show that $m \simeq 9.7$ in this sample.

The fact that no 1e reduction product is present in the dark crystals is confirmed not only by observed disproportionation upon precipitation of the 1e species but by magnetic susceptibility measurements on the blue-black compound in both the solid state and solution.[15] The paramagnetism of the oxidized species is decreased appropriately, upon its electrolytic reduction (to the expected extent within experimental error), by the ring current effect[12] in the 2e reduction product. This excludes the presence of any 1e heteropoly blue, which would very substantially *increase* paramagnetism.

The dark blue crystals may therefore be regarded as the potassium salt of the 2e heteropoly blue complex, $[Co^{II}W_{12}O_{40}]^{8-}$, doped with 11.5% of the isomorphous unreduced species occupying sites in the cubic crystal structure of the reduced species rather than with an impurity of occluded unreduced complex. This is consistent with the homogeneity in size and morphology of crystals in the bulk sample. No increase in apparent atomic displacement parameters, caused by the presence of the oxidized complex, was detectable in view of the great decrease in those parameters, upon reduction, caused by other factors and described below. The reduced complex has a framework that is very similar to, but not identical with, that of the oxidized complex.

Crystal Structure Analysis. The two structures were determined from data collected at room temperature on a Picker FACS I automatic diffractometer with graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation with θ/2θ scans (2.0 deg/min) and data collection software from NRC-Canada (E. Grabe). Three standard reflections were measured every 100 reflections and showed no significant intensity change in the case of either compound. Lorentz and polarization corrections were applied to the intensity data, which were subsequently analyzed with the Structure Determination Package (SDP) from B.A. Frenz and Associates and Enraf-Nonius. Empirical absorption corrections were applied to the raw data for each case. Data from more than one independent section of the reciprocal lattice having been collected for the heteropoly blue, equivalent reflections were averaged after absorption correction ($R_{int}(F^2) = 0.045$ for $P\bar{4}3m$ giving 617 data and $R_{int}(F^2) = 0.027$ for $Pm3m$ giving 348 data).

$K_6[Co^{II}W_{12}O_{40}]\cdot 11H_2O$. A newly recrystallized elongated prism was truncated to make the three crystal dimensions nearly equal, and it was sealed in a glass capillary to minimize efflorescence. Precession photo-

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Table I. Crystal Data and Procedures for Its Collection for $K^+_6[Co^{II}W_{12}O_{40}]^{-6}\cdot nH_2O$ and $K^+_{7.77}[Co^{II}W_{12}O_{40}]^{8-}_{0.885}[Co^{II}W_{12}O_{40}]^{6-}_{0.115}\cdot mH_2O$ (where $n = 11$ and $m = 9.7$)

	oxidized species	2e reduced heteropoly blue
formula weight	3338	3384
space group	$P6_222$	$Pm3m$
a, Å	19.110 (7)	10.665 (2)
c, Å	12.483 (3)	
V, Å^3	3947 (5)	1213.1 (7)
Z	3	1
density calc, g/mL	4.21	4.63
density obs, g/mL	4.7 (1)[a]	4.7 (1)
crystal color	green-blue, clear	extremely dark blue, opaque
shape and dimns	prism, ca. 0.25, 0.10, 0.10 mm, sealed in glass capillary	cube, ca. 0.1 mm, sealed in glass capillary
linear abs coeff, cm^{-1}	275.8	299.8
transmission factors, %	60.9–93.5 (empir corr)	69.0–90.4 (empir corr)
takeoff angle, deg	2.4	2.4
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	2.0	2.0
scan range, deg	$3.0 < 2\theta < 60.0$	$3.0 < 2\theta < 75.0$
sin θ/λ limits, Å^{-1}	0.0369–0.705	0.0369–0.857
data collected	$+h,+k,+l$ and $-h,-k,-l$ plus $50.0 < 2\theta$, $+h,-k,+l$	$+h,+k,+l$ and $-h,-k,-l$ with $h > k > l$ and $k > h > l$
total no. of reflcns	9505	4111
no. of unique data	3137	706
no. of unique data with $F_o^2 > 5\sigma F_o^2$	2061	348
	Final Least-Squares Refinement	
reflcns used	$F_o^2 > 5\sigma F_o^2$	$F_o^2 > 5\sigma F_o^2$
sin θ/λ limits, Å^{-1}	0.15–0.705	0.20–0.857
p ($w = KI/[\sigma^2_{\text{count.}} + (pI)^2]$)	0.050	0.060
data/parameter	1726/92	348/27
extinction coeff	not refined	not refined
final R (R_w)	0.0336 (0.0420)	0.0444 (0.0539)

[a] The experimental density for the oxidized compound was taken on the air-dried sample for which $n = 3.1$.

graphs showed hexagonal symmetry with systematic absences uniquely consistent[38] with space group $P6_222$. Unit cell dimensions and other features of data collection and refinement are given in Table I.

The structure was solved by direct methods (MULTAN 82) and developed with successive difference Fourier syntheses and refinements. At convergence $R = 0.0336$ ($R_w = 0.040$). The residual electron density observed in the final difference Fourier map had a maximum of 1.90 e/Å^3 and went down to a general background value of ~1.34 e/Å^3. Typical electron densities for water oxygens in this structure were 10–16 e/Å^3, and for K$^+$'s they were ~45 e/Å^3. The anion has crystallographically imposed D_2—222 symmetry.

The atomic parameters, their standard deviations, and the isotropic equivalents of the atomic displacement factors are available in the supplementary material. Six K$^+$ sites per complex were found, each fully occupied. Of 16 H_2O sites per complex, 6 were fully occupied and each of the others was partially occupied.

$K^+_{7.77}[Co^{II}W_{12}O_{40}]^{8-}_{0.885}[Co^{II}W_{12}O_{40}]^{6-}_{0.115}\cdot 9.7H_2O$: Two cubic crystals were sealed in separate argon-flushed capillaries. Data were collected for both crystals and refined independently, yielding the same solution.

Precession photographs showed cubic symmetry and no systematic absences, consistent[38] with five possible cubic space groups: $P23$, $Pm3$, $P\bar{4}3m$, all having tetrahedral symmetry, and $P432$ or $Pm3m$, both with octahedral symmetry. The last two space groups would imply disorder of the anion. The high symmetry observed indicated that no isomerization of the complex to the β form had occurred upon reduction. Crystal data, collection procedures, and refinement parameters are given in Table I.

The structure was solved with MULTAN 82. Given the sharpness of the diffraction peaks, there was no reason initially to suspect the presence of disorder of the complexes. Refinements were conducted in space group $P\bar{4}3m$, corresponding to the complex's intrinsic symmetry. The cleanness of successive refinements and low atomic displacement parameters appeared to confirm the absence of disorder for the 2e blue complexes, except that the geometry indicated for the Keggin ion was unusually distorted.

At convergence, $R(F)$ and $R_w(F)$ were 0.0422 and 0.053 (617 data, 29 variables), respectively. In each of the difference Fourier maps, a ghost of the oxygen atom tetrahedrally disposed around the cobalt in position *4e* (x,x,x) appeared at the alternative position $(x,x,\bar{x})$. This corresponds to a 90° rotation of the Keggin ion around its $\bar{4}$ axis. With the exception of this oxygen atom, rotation by 90° leaves other oxygen and tungsten atoms approximately superimposed, although the W atom in the $P\bar{4}3m$ refinement has rather anisotropic root-mean-square components of displacement of 0.081, 0.114, and 0.201 Å.

Refinement was therefore performed in space group $Pm3m$, after averaging of equivalent data, with the Keggin ion statistically disordered by a 90° rotation.

A similar situation was identified by Björnberg and Hedman[39] for Keggin structure $K_6[V(V_2Mo_{10})O_{40}]\cdot 13H_2O$. They, however, chose to refine a disordered structure in $P\bar{4}3m$, with unfortunate results since the pairs of atoms are hopelessly correlated.

Placement of the tungsten at site *12i* with *mm* symmetry leads to an elongated atomic displacement ellipsoid (root-mean-square components 0.081–0.201 Å), metrical values outside the range observed for α-Keggin ions, and slightly higher values for R and R_w (0.046 and 0.058, respectively). Placing the W atom at site *24m* with *m* symmetry led to a more nearly isotropic W atom (root-mean-square components 0.086–0.133 Å) and lower values for R and R_w (0.044 and 0.053, respectively). It also allowed the extraction of a Keggin ion of more typical stereochemistry. (One could also extract a Keggin ion with nearly the same unusual stereochemistry as that which had been revealed by refinement in $P\bar{4}3m$.)

Potassium ion K2 was initially refined at half occupancy since it lies close to a symmetry element. However, its temperature factor is high, and therefore the degree of occupancy was refined also. In that way the total number of K$^+$ ions accounted for comes to 6.6. The total number of sites per complex occupied by K$^+$'s is 9, of which 3 are fully occupied and 6 are partially occupied. Thirteen H_2O sites are identified, of which 12 are half-occupied and one fully occupied, accounting for a total of 7 H_2O's.

The residual electron density in the final difference Fourier map was greater, averaging 3.3 e/Å^3, than that for the oxidized structure. Typical electron densities for O atoms were 9–20 e/Å^3 and for K$^+$ ions ~27 e/Å^3. The high noise may have its origins in the presence of ~11.5% of the oxidized material dispersed through the crystal. Alternatively, it cannot be excluded that the crystal structure might be more accurately described as a twin in $P\bar{4}3m$ (hkl and $hk\bar{l}$ superimposed). The R_{int} value would then indicate equal contributions. That is, the disorder imposed by space group $P\bar{4}3m$ may be less than randomly distributed throughout

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[38] *International Tables for X-Ray Crystallography*; Vol. 1, Kynoch Press: Birmingham, England, 1965.

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Table II. Most Relevant Interatomic Distances and Angles for Oxidized and 2e Reduced Blue 12-Tungstocobaltates(II)[a]

	oxidized complex	blue complex	other α-Keggin tungstates
		Distances, Å	
Co–O_{tet}	1.895 (12)	1.859 (9)	1.53–1.92[b]
W–O_{tet}	2.13–2.18	2.19	2.14–2.44
W–O_{term}	1.68–1.73	1.71	1.68–1.71
Co–O_{term}	5.13–5.18	5.18	
Co–O_{cor}	3.25–3.33	3.31	
Co–O_{ed}	4.08–4.12	4.14	
W–O_{ed}	1.89–1.99	1.99	
W–O_{corr}	1.88–1.95	1.91	
W–W(O_{ed} linked)	3.253, 3.262, 3.286 (3.267 av)	3.295	3.25–3.42
W–W(O_{cor} linked)	3.697, 3.700, 3.714 (3.704 av)	3.702	3.68–3.73
Co–W	3.482, 3.487, 3.495 (3.488 av)	3.501	
O_W–O_{ed}	2.92–3.06	2.90	
O_W–O_{term}	2.99–3.36	3.43	
O_W–O_{cor}	3.06–3.12	3.64	
K–O_{ed}	2.73	2.82	
K–O_{term}	2.74	2.63, 2.83	
K–O_{cor}	3.93	2.87	
O_{term}–O_{term}	5.38–5.45	5.46	in W_3O_{13} triplet (edge sharing)
	4.83–4.98	4.89	between W_3O_{13} triplets
O_{ed}–O_{ed}	2.73–2.75	2.83	in W_3O_{13} triplet
O_{cor}–O_{cor}	2.59–2.65	2.58	
O_{term}–O_{ed}	2.70–2.75	2.75	same WO_6
	4.72–4.75	4.79	same W_3O_{13} triplet
O_{term}–O_{cor}	2.78–2.82	2.82	same WO_6
O_{ed}–O_{cor}	2.66–2.74	2.74	
		Angles, deg	
O_{tet}–Co–O_{tet}	107.8–111.2	109.5	
O_{tet}–W–O_{term}	164.9–166.4	166.4	
O_{tet}–W–O_{ed}	72.5–74.4	75.0	
O_{term}–W–O_{ed}	93.5–98.9	95.7	
O_{tet}–W–O_{cor}	86.5–89.3	87.9	
O_{term}–W–O_{cor}	99.9–114.3	102.0	
O_{ed}–W–O_{cor}	85.3–93.4	89.4	
	159.0–162.0	162.2	
O_{ed}–W–O_{ed}	89.0–89.6	90.8	
O_{cor}–W–O_{cor}	86.6–87.6	85.1	
W–O_{tet}–W	98.1–99.3	97.7	
W–O_{ed}–W	113.2–114.5	112.3	
W–O_{cor}–W	148.6–154.3	152.3	

[a] Estimated standard deviations in W–O or Co–O separations are 0.01–0.02 Å for the oxidized complex and 0.007–0.009 Å for the 2e reduced complex. For the Co–W and W–W separations the standard deviations are 0.001 and 0.006 Å respectively for the oxidized and reduced complexes. For the O–W–O and W–O–W angles the estimated standard deviations are 0.5–0.9° and 0.4–0.9°, respectively. [b] Central atom to O_{tet} distances.

the entire crystal subjected to X-ray diffraction. Neither source of the noise will have a significant influence on the metrical details of the 2e-reduced species, however.

The resulting structure was also refined in space group *P*23, with less satisfying results, so there was no reason to maintain that lower symmetry.

Lists of atomic positions, their standard deviations, and equivalent isotropic atomic displacement factors are available in the supplementary material.

Comparative Isotropic Atomic Displacement Parameters. These parameters were refined isotropically for all atoms, except that the refinements were anisotropic for all the W atoms, for the Co in the oxidized complex, and for the K's in the reduced complex. For the atoms refined anisotropically, the equivalent isotropic displacement parameters were calculated from the following definition: $(^4/_3[a^2(B(1,1) + b^2(B(2,2)) + c^2(B(3,3)) + ab(\cos\gamma)(B(1,2)) + ac(\cos\beta)(B(1,3)) + bc(\cos\alpha)(B(2,3))]$. The isotropic atomic displacement parameters, *B*(iso) (A^2) values, for the non-reduced compound were the following: Co, 1.5 (1); W's, 2.26 (2), 2.17 (1), 2.21 (2), av 2.21 (2); O_{cor}, 2.0 (3), 2.4 (3), 2.5 (3), av 2.3 (3); O_{ed}, 2.5 (3), 2.5 (3), 2.8 (3), av 2.6 (3); O_{tet}, 1.62 (2); O_{term}, 2.7 (3), 3.3 (3), 2.7 (3), av 2.9 (3); K's, 2.9 (1); O_w's, 2.9 (4), 5.5 (4), 4.9 (6), 15 (5), 8 (1), 5 (1), av 6.9. For the reduced compound the values were the following: Co, 0.99 (1); W's, 0.9 (1); O_{cor}, 1.3 (2); O_{ed}, 1.4 (3); O_{tet}, 1.3 (5); O_{term}, 1.8 (3); K's, av 3.1 (2); O_w's, 7 (2), 7.1 (9), av 7.0.

Discussion

Figure 1 shows a polyhedral representation of an idealized α-Keggin structure. Both $\alpha\text{-}[\mathrm{Co^{II}W_{12}O_{40}}]^{6-}$ and $\alpha\text{-}[\mathrm{Co^{II}W_{12}O_{40}}]^{8-}$ have α-Keggin structures. Figure 2 shows an ORTEP view of the oxidized complex. An ORTEP view of the reduced complex, when plotted on the same scale, would not be detectably different from Figure 2 with respect to atomic positions, but it would have very much smaller atomic displacement ellipsoids. Table II summarizes the most relevant interatomic distances and angles for both complexes. A much more extensive listing is available in the supplementary material.

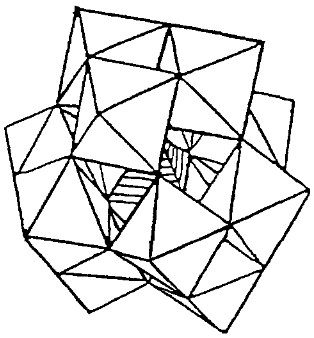

Figure 1. The α-Keggin 12-tungstate heteropoly structure (idealized). Each vertex of a polyhedron locates the center of an oxygen atom. Each white octahedron contains a W atom, displaced far off-center toward its unshared O atom. The interior (hatched) tetrahedron contains the heteroatom (Co in the present work).

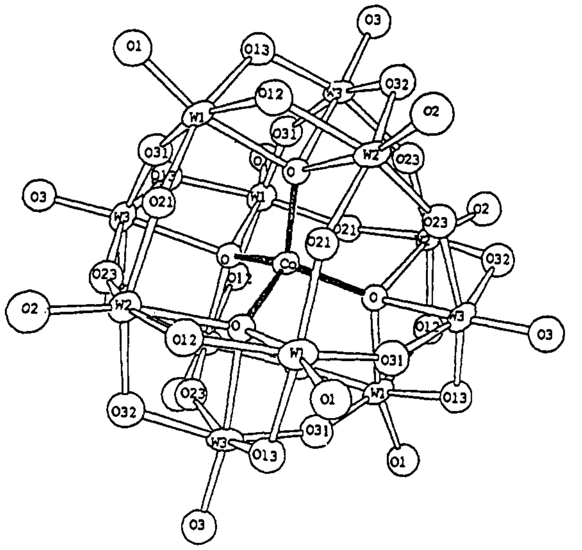

Figure 2. Perspective ORTEP diagram for oxidized species α-$[Co^{II}W_{12}O_{40}]^{6-}$. Except for much smaller atomic displacement elipsoids, an ORTEP diagram for the reduced species α-$[Co^{II}W_{12}O_{40}]^{8-}$ would not show atomic positions that are detectably different from those for this oxidized species when drawn on this scale.

Most striking is the fact that the reduction caused only very small differences in average interatomic separations and angles between the oxidized and the reduced complexes.

There are four structural types of O atoms in a Keggin complex. See Figure 1. Atoms designated O_{tet} are part of the central CoO_4 tetrahedron and each is also bonded to three W atoms. The exterior unshared terminal oxygen of each WO_6 octahedron is designated O_{term}. The oxygens which link WO_6 octahedra by corner-sharing are categorized as O_{cor} while each outer O involved in joining WO_6's by edge-sharing is O_{ed}. Each oxygen of a water of crystallization is denoted O_w.

Atomic Displacement Parameters, Rigidity of Complexes, and Chemical Properties. Comparisons of atomic displacement parameters are often subject to systematic errors that can create doubts about their physical significance. In the present case, however, the large decreases of the displacement parameters for all of the atoms in the complex, upon reduction, appear to be quite real (see last paragraph of Experimental Section above). There are no such decreases in the displacement parameters for the atoms (O_w's and K^+'s) *not* in the complex in these crystals. Even after scaling to the point where the central Co atoms in each complex have identical equivalent atom displacement parameters, the average displacement parameters for the other atoms in the reduced complex are substantially lower than those in the oxidized species.

It is postulated that the sizable decrease in the complex's atomic displacement parameters, upon reduction, and an attendant significantly increased overall rigidity of the reduced complex[40] result from the additional energy required to displace the W and shared O atoms from equilibrium positions which are most favorable to the delocalization of the added blue electrons. That is, in balance with all the other forces acting on each atom, the reduction introduces new forces, only marginally present in the relatively flexible oxidized species,[18] which (1) slightly displace the atoms toward positions most favorable for those W-O orbital overlaps that most facilitate the delocalization and (2) thus act to impose additional energy requirements for any displacements of the atoms away from those positions.

The fact that the displacement parameters of the complex's O atoms (as well as of its W atoms) are decreased, upon reduction, emphasizes the essential major participation in the electron delocalization by those oxygens which are shared between WO_6 octahedra and the consequent increased electron density on shared oxygens in blue complexes. This explains the increased nucleophilicity of those oxygens in heteropoly blues, and it is consistent with our group's recent interpretations of NMR chemical shifts in oxidized[18,20] and reduced[15] paramagnetic heteropoly complexes. It is also consistent with Racah parameters which indicate an unusually pronounced nephelauxetic effect for the Co's d electrons in the oxidized complex.[28] With respect to the unshared O_{term} atoms, each is tightly attached to a W via a double bond and by an unusually strong ion-induced dipole attraction, so that the damping of each W's displacements also damps those of its unshared O_{term}.

Other Structural Changes. Additional structural evidence for increased negative charge on the bridging O atoms in the reduced complex is provided by the stronger H bond between O_{ed} and H_2O and the shortened distance between O_{cor} and the neighboring K^+. The O_{cor}-K^+ distance (2.87 Å) in the reduced compound is within the usual range of O coordinated to K^+, but the corresponding distances in the oxidized compound (~3.93 Å) are well outside that range.

Other structural evidence may be cited for the overall flexibility of the framework of the oxidized complex relative to the rigidity of the reduced species. For the oxidized complex the crystallographically imposed symmetry is D_2—222, leading to three crystallographically independent W atoms. The W-W separations through edge-sharing WO_6 octahedra range from 3.253 (1) to 3.286 (1) Å while W-to-shared-O separations and O-W-O angles show considerable variations. (See Table IV, supplementary material.) This reflects the significant influence of crystal packing upon the relatively flexible internal framework of the oxidized heteropoly species. The W-O_{term} linkages (double bonded and with very strong ion-induced dipole attraction) are nearly invariant. In other words, for the oxidized complex the energy required for distortion from equilibrium geometry, with T_d—$\bar{4}3m$ symmetry, is not great.

For the 2e reduced complex, T_d—$\bar{4}3m$ symmetry is imposed crystallographically upon the individual anions, although in space group $Pm3m$ the anions are disordered at sites of O_h—$m3m$ symmetry, leading to only a single crystallographically independent W atom and its associated O atoms of each chemical type.

Chemical Consequences. Heteropoly blue complexes are well-known to be stronger Bronsted bases and more stable to degradations by base (e.g., stable at higher pH's) than their oxidized parents. Although the increase in negative charge on the structures' shared O atoms provides the explanation for these thermodynamic effects, the effect of the increased rigidity of the blue species is probably very important for kinetic stability to attack by base and to substitution rates, both of which involve mechanisms requiring considerable distortion of the polyanion framework.

The Importance of Rigidity. Although Mo(VI) and W(VI), both d^0 and from periodic group VIB, are generally assigned essentially identical ionic radii, it is well-known that polymolybdates generally establish their equilibria very rapidly while polytungstates generally react very slowly. Keggin structure polymolybdates exchange radioactive Mo(VI) rapidly with paramolybdate, while exchanges of tungstate with Keggin structure polytungstates are very slow.[41] The same difference has been demonstrated for Anderson-Evans structure 6-molybdonickelate(II) versus its isomorph 6-tungstonickelate(II).[42] The only obvious explanation for the many cases of this sort of difference seems to lie in the fact that the force constants for W(VI)-O linkages are slightly larger than those for corresponding

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(40) The rigidity of the oxygen framework of the reduced complex is probably increased even somewhat more than indicated by the calculated decrease of the oxygen atoms' displacement parameters, owing to the dominance of the heavy W's in the refinement procedures. Also, the real atomic displacement parameters of the reduced complex are probably even somewhat smaller than those calculated because the presence of ~11.5% of the oxidized complex doped into the crystal structure of the reduced salt would tend to increase apparent displacement parameters.

(41) (a) Spitsyn, V. I.; Torchenkova, E. A. *Dokl. Akad. Nauk. S.S.S.R.* **1954**, *95*, 289. (b) Spitsyn, V. I. *Rocz. Chem.* **1955**, *29*, 218. (c) Spitsyn, V. I.; Bykoukaia, I. I. *Dokl. Akad. Nauk. S.S.S.R.* **1955**, *104*, 256.

(42) Lee, K.-H. *Doctoral Dissertation*, Georgetown University, 1970; *Diss. Abstr. Int.* **1971**, *31B*, 5240.

Mo(VI)–O attachments. Although the difference is quite small for a given linkage, the cumulative effect of many slightly stronger attachments must make the polytungstate frameworks considerably more rigid. Similarly, $[Fe^{III}O_6Mo_6O_{18}H_6]^{3-}$ exchanges Mo(VI) rapidly while its isomorph $[Cr^{III}O_6Mo_6O_{18}H_6]^{3-}$ exchanges Mo(VI) two orders of magnitude more slowly.[42,43] The difference, in view of the necessary mechanism, has been attributed to the CFSE stiffening of the d^3 CrO_6 central octahedron, which imparts rigidity to the whole complex, while the d^5 high-spin $Fe^{III}O_6$ octahedron, having no CFSE, allows the molybdate framework to be more flexible. The thermodynamic stabilities of the two complexes are essentially identical.[43]

Co–O_{tet} Distances. The Co–O_{tet} distance is slightly shorter (by 0.03 (1) Å) in the reduced complex. This reflects a slightly greater negative charge, in the reduced complex, on O_{tet}, which is close to the Co and relatively far from the nearest W's, the latter being displaced far off-center in their WO_6 octahedra, toward the exterior of the complex. The change in the Co–O_{tet} distance upon reduction implies that the central $Co^{II}O_4$ tetrahedron is slightly more isolated from the rest of the heteropoly framework in the reduced species. The increased isolation of the paramagnetic $Co^{II}O_4$ tetrahedron is sensitively reflected in the decrease in the magnitude of the chemical shift of the ^{183}W NMR signal at room temperature from −888 ppm for the oxidized complex upfield to −550 ppm for the 2e blue.[15,18] This 338-ppm difference springs primarily from a decrease in the isotropic shift and contrasts with the 60–70-ppm decrease observed and calculated[16] upon 2e reduction of diamagnetic isomorphs such as α-$[SiW_{12}O_{40}]^{4-}$.

W–W Distances. In 1985 Barrows, Jameson, and Pope[14] reported the X-ray crystal structure of an acid-salt of the 4e heteropoly blue of β-12-molybdophosphate. The β isomer differs from the α-Keggin structure by a 60° rotation of one edge-sharing Mo_3O_{13} group about its 3-fold axis. See Figure 1. The rotated Mo_3O_{13} group is joined together only by edge-sharing and is attached to a belt of six alternately edge- and corner-sharing MoO_6 octahedra in a way which differs from that in the α-Keggin structure. Since oxidized β-12-molybdophosphate has never been reported, comparisons were made with the structure of oxidized β-12-tungstosilicate[45] complex, which very probably has very similar structural dimensions to a hypothetical oxidized β-12-molybdophosphate despite the different heteroatom and different addenda atoms. On this basis, it was observed that the 4e reduction, which concentrates the delocalized electrons mainly in the 6 Mo belt, had clearly lengthened the Mo–Mo distances between edge-sharing octahedra and shortened the Mo–Mo distances between corner-sharing octahedra in the 6 Mo belt. It was argued that the anion was probably protonated at outer oxygen atoms of shared edges between the belt MoO_6 octahedra.

It is to be noted that shortening of Mo–Mo distances through shared MoO_6 corners is to be expected, upon reduction, on the grounds that it increases overlaps of appropriate unfilled d orbitals of the Mo with filled p orbitals of the O_{cor}'s, facilitating delocalization of the blue electrons. The overlaps through shared MoO_6 edges are less favorably oriented, and so a lower energy state for the blue complex is reached by shortening Mo–Mo through corners at the expense of lengthening Mo–Mo through edges. This is consistent with the significantly greater $^2J_{WOW}$ nuclear coupling constants through shared WO_6 corners, in which W–O–W is more linear, as contrasted with those through shared edges, as revealed by ^{183}W NMR spectroscopy of oxidized species,[46] and it is especially consistent with our group's recent determination[13] of relative residency times of the blue electrons on various W atoms.

In the structure of the 4e heteropoly blue, β-$[PMo_{12}O_{40}]^{7-}$, four blue electrons are delocalized primarily over just six MoO_6 octahedra,[14] and so these changes in Mo–Mo distances are more pronounced than those in the present case of α-$[Co^{II}W_{12}O_{40}]^{8-}$, wherein only two blue electrons are delocalized over twelve WO_6 octahedra. Nevertheless, the new crystal structures indicate changes in the two kinds of W–W distances that are in the expected directions and probably just within the limits of statistical significance. The average W–W distance through shared WO_6 edges increases by 0.028 Å while the average W–W distance through O_{cor} appears to decrease by only 0.002 Å. However, it must be noted that the radius of the whole complex increased a little upon reduction. The average Co–W distance went from 3.488 to 3.501 Å, which expansion alone would account for 0.014 Å of the increase of W–W through edges while nullifying by the same amount any inherent W–O_{cor}–W decreases. Applying these corrections indicates that tendencies to achieve more effective orbital overlaps made contributions equivalent to net decreases of W–O_{cor}–W distances by 0.016 Å and net increases in W–W distances through shared edges equivalent to 0.014 Å.

A Previous Study. In 1966 Tourné and Souchay[47] reported an approximate crystal structure, determined from 33 powder lines, for the potassium salt of the isopoly 2e blue, $[H_2W_{12}O_{40}]^{8-}$, which has the same W–O framework as the Keggin structure. The error limits for their W–W distances are so large that conclusions about the structural changes upon reduction are not warranted, and a meaningful comparison with the results of the present work is not possible.

Ground-State Delocalization of Blue Electrons. In considering electron delocalization in heteropoly blue polytungstates, emphasis on thermal hopping of the blue electrons from W to W, and the residency of those electrons on the W's, is common. The reduction's apparent lowering of the displacement parameters of the complex's *oxygen* atoms and the accumulation of negative charge on bridging O's emphasize the role of the oxygens and suggest increased emphasis on the importance of an interpretation of gsd based on molecular orbitals that cover the entire region of electron delocalization. Also, polytungstates with even numbers of delocalized electrons, which are always spin paired, may not necessarily behave in just the same fashion as 1e blues. It has thus far been impossible to observe the structural changes derived from 1e reduction. For example, no solid salt of 1e $[CoW_{12}O_{40}]^{7-}$ has been obtained. Although that complex exists in solution, disproportionation accompanies crystallization. The few reported crystalline 1e blues have all been much too unstable for X-ray diffraction.[15] The much greater chemical stability of the 2e heteropoly blue tungstates compared to the 1e species may be indicative of fundamental differences in electronic structure and dynamics.

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Supplementary Material Available: Tables of atomic coordinates, estimated standard deviations, isotropic atomic displacement parameters, and detailed interatomic distances and angles and stereoscopic views of components of the unit cell of $K_6[Co^{II}O_6W_{12}O_{40}]\cdot 11H_2O$ (8 pages). Ordering information is given on any current masthead page.

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