agreement with the qualitative trend in electronegativities reported earlier.[26,27]

A final point of interest relates to the sensitivity of the various series of mercurials, RHgR′, to alkyl substitution. In Figure 5, the ionization potentials of a series of dialkylmercury compounds R–Hg–R′ have been plotted against the oxidation potentials of the corresponding Grignard reagent (representing a common scale). The slopes decrease in the order R′HgMe > R′HgEt > R′Hg-*i*-Pr > R′Hg-*t*-Bu. We attribute this result to the fact that partial delocalization of charge by the first R group in the molecular ion diminishes the effect of the second group R′; or, stated alternatively, there is less charge remaining to be delocalized. The apparent intercept at about 7.2 eV (disregarding the experimental scatter in the highly substituted compounds) represents a limiting example, in which one group, extremely effective at delocalizing charge, completely nullifies the effect of the second group.

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Registry No. $(CH_3)_2Hg$, 593-74-8; $(CH_3)(C_2H_5)Hg$, 29138-86-1; $(C_2H_5)_2Hg$, 627-44-1; $(CH_3)(i\text{-}C_3H_7)Hg$, 29138-88-3; $(CH_3)(i\text{-}C_4H_9)Hg$, 59643-44-6; $(CH_3)(t\text{-}C_4H_9)Hg$, 59049-78-4; $(C_2H_5)(i\text{-}C_3H_7)Hg$, 59049-79-5; $(n\text{-}C_3H_7)_2Hg$, 628-85-3; $(i\text{-}C_3H_7)_2Hg$, 1071-39-2; $(C_2H_5)(t\text{-}C_4H_9)Hg$, 59049-80-8; $(i\text{-}C_3H_7)(t\text{-}C_4H_9)Hg$, 59049-81-9; $(n\text{-}C_4H_9)_2Hg$, 629-35-6; $(i\text{-}C_4H_9)_2Hg$, 24470-76-6; $(t\text{-}C_4H_9)_2Hg$, 23587-90-8; $(i\text{-}C_4H_9)(neo\text{-}C_5H_{11})Hg$, 59643-45-7; $(neo\text{-}C_5H_{11})_2Hg$, 10284-49-8.

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Low-Temperature Electron Spin Resonance Spectra of Heteropoly Blues Derived from Some 1:12 and 2:18 Molybdates and Tungstates

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X-Band ESR spectra of nine reduced heteropoly anions (heteropoly blues) have been recorded at temperatures between 4.2 K and room temperature. The spectrum of $PMo^VMo_{11}O_{40}^{4-}$ is isotropic ($g = 1.945$) at all temperatures and exhibits hyperfine structure (six lines) below 64 K, with $\langle a \rangle = 55 \times 10^{-4}$ cm^{-1}. The intensity of the hyperfine spectrum relative to the central (nonmagnetic) line increases as the temperature is lowered. The spectra of five reduced 1:12 tungstates are rhombic at low temperatures, with $g_1 = 1.848–1.852$, $g_2 = 1.805–1.827$, and $g_3 = 1.759–1.79$. Above 50–80 K, depending on the anion, the spectra appear isotropic[1] due to line broadening. The spectra of reduced α-$P_2W_{18}O_{62}^{6-}$ and α-$As_2W_{18}O_{62}^{6-}$ remain rhombic at higher temperatures, with $g_1 = 1.905$, $g_2 = 1.85$, and $g_3 = 1.81$. The spectrum of the reduced β isomer of $P_2W_{18}O_{62}^{6-}$ is isotropic ($g = 1.852$) at all temperatures down to 13 K. All of the ESR spectra are discussed in terms of weakly trapped Mo(V) or W(V) valences. The rate of intraionic electron delocalization in $PMo^VMo_{11}O_{40}^{4-}$ at 6 K must be greater than ca. 10^8 s^{-1} implying a much lower activation energy than predicted by the Hush model for mixed valence compounds. The source of the rhombic crystal field for tungsten atoms in the 1:12 (Keggin) structure is discussed and the major differences between the spectra of 1:12 and 2:18 anions are rationalized. Two-electron heteropoly blues appear diamagnetic, probably through antiferromagnetic coupling of electrons localized on adjacent metal atoms.

Introduction

Heteropoly and isopoly oxo anions of vanadium, molybdenum, or tungsten are reducible to mixed-valence heteropoly "blue" isomorphs if they have structures in which the metal atoms are each bound to one, as opposed to two, *terminal* oxygen atoms.[2]. Although there are several such (type I) structures known for polyanions, most studies of heteropoly blues have been made on anions with the 1:12, $XZ_{12}O_{40}$ (Keggin), and 2:18, $X_2Z_{18}O_{62}$, structures. Optical spectra of reduced "mixed" anions, e.g., $PV^{IV}W_{11}O_{40}^{5-}$ and $PMo^VW_{11}O_{40}^{4-}$, are similar to those of "real" heteropoly blues, $PW^{V,VI}{}_{12}O_{40}^{4-}$, etc., yet according to ESR spectroscopy the valences are trapped as indicated by the above formulas.[3-5] There have been relatively few attempts to record ESR spectra of heteropoly blues, and the results have not been very conclusive. A few years ago we reported spectra for a number of reduced 1:12 and 2:18 tungstates at temperatures down to 77 K.[6] The spectra for the 1:12 anions were isotropic at 77

K and were anomalously weak for $PW_{12}O_{40}^{4-}$ and $SiW_{12}O_{40}^{5-}$ anions. Stonehart et al.[7] have also noted weak isotropic spectra for reduced tungstophosphate solutions. Spectra for $SiMo_{12}O_{40}^{4-}$ that had been reduced by one, two, three, and four electrons were briefly reported by Rabette, Ropars, and Grivet.[8] Some of these spectra were said to exhibit hyperfine structure at 77 K, but no details were given, nor has this work been published in final form.

With the availability of appropriate equipment and with improved synthetic procedures, we have been able to extend ESR measurements of heteropoly blues to the temperature range 77–4.2 K. The results of this work, reported below, tend to confirm a model for heteropoly blues in which the unpaired electron undergoes a rapid "hopping" delocalization.[6] Some of the results for reduced 12-molybdophosphate anion have been the subject of a preliminary communication.[9]

Experimental Section

Preparation of Compounds. The syntheses of alkali salts of most of the heteropoly tungstates have been described in previous papers.[10,11] Potassium 12-tungstoborate and 12-tungstogermanate were prepared from the corresponding heteropoly acids.[12,13] Tetrabutylammonium salts of the reduced anions $PMo_{12}O_{40}^{4-}$ and $PMoW_{11}O_{40}^{4-}$ were isolated as described elsewhere.[9,14]

Electrochemistry. Cyclic voltammograms were recorded on 0.5–1.0 mM solutions of the heteropoly anions in appropriate supporting electrolytes (see below) using a wax-impregnated graphite electrode and Heath components.[15] A Wenking potentiostat, Model 70TS1, and a Koslow Scientific coulometer, Model 541, were used for controlled-potential electrolytic reduction of the heteropoly anions.

Spectroscopy. X-Band ESR spectra were recorded on a JEOL MES-3X spectrometer. The magnetic field was calibrated with a Newport Instruments NMR magnetometer and the microwave frequency determined using DPPH. Variable-temperature spectra from 298 to about 6 K were obtained using an Air Products liquid-transfer Heli-Tran refrigerator, Model LTD-3-110, which had been modified to place the cold junction of the copper–constantan thermocouple as close as possible to the sample. Immersion Dewars were used for 77- and 4.2-K spectra. Samples for the reduced heteropolytungstates were frozen water–ethylene glycol glasses with concentrations ranging from 0.5 to 20 mM. The reduced tungstates are highly sensitive to reoxidation by air and were handled under nitrogen. The heteropolymolybdate spectra were recorded in acetonitrile solution or as dilute polycrystalline samples in $(Bu_4N)_4SiW_{12}O_{40}$. ESR spectra were simulated using a program (RESLIN) designed for calculating magnetic resonance spectra of polycrystalline samples or glasses. The program solves the appropriate spin Hamiltonian to second order using perturbation theory.

Results and Discussion

Electrochemical Reduction of Heteropolytungstates. In almost all previous electrochemical studies of heteropolytungstates a mercury electrode has been used.[7,10,11,16,17] The reduced anions are frequently strongly adsorbed on mercury so that a clean electrolytic reduction is not always possible. Furthermore "hydrolytic disproportionation" reactions such as

$$2PW_{12}O_{40}^{4-}\ \text{(one-electron blue, paramagnetic)}$$
$$\xrightarrow{OH^-} PW_{12}O_{40}^{5-}\ \text{(two-electron blue, diamagnetic)}$$
$$+\ PW_{11}O_{39}^{7-} + \text{isopolytungstate}$$

can occur very rapidly under certain conditions. Such reactions probably account for inconsistencies in the literature regarding the stoichiometry of reduction of an anion such as $PW_{12}O_{40}^{3-}$ and almost certainly account for the anomalously weak ESR spectra of some blues that we noted previously.[6,7]

In the present work we have used a wax-impregnated graphite electrode for cyclic voltammetry[15] and a graphite cloth cathode (Union Carbide Co., X2010) for bulk electrolyses. Highly satisfactory cyclic voltammograms could be obtained for all of the heteropoly anions studied; see Figure 1 for an example. Voltammetric data are summarized in Table I and the separations of 60–80 mV between cathodic and anodic peak potentials show that the reductions are close to reversible. Typical results of controlled-potential bulk electrolyses using a graphite cloth cathode are shown in Table II. As these results show, it was possible to add one electron to each of the heteropoly anions and in most cases subsequently to add a second electron. The added electrons could be removed by controlled-potential oxidation. All of the one-electron reduced anions gave ESR signals of comparable intensity at 77 K, in contrast to previous results.[6] Since hydrolytic disproportionation of $PMo^{V,VI}{}_{12}O_{40}^{4-}$ cannot take place in acetonitrile, we conclude that little disproportionation of the tungstates occurred.

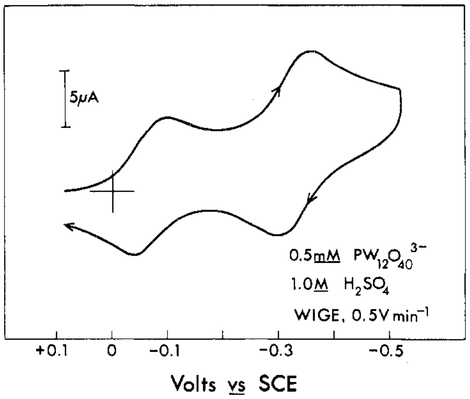

Figure 1. Cyclic voltammogram of 0.5 mM $PW_{12}O_{40}^{3-}$ in 1.0 M H_2SO_4 using a wax-impregnated graphite electrode.

Table I. Voltammetric Data[a] for Heteropolytungstates Using a Wax-Impregnated Graphite Electrode

Anion	Medium	E_{p_a}, V	E_{p_c}, V
$PW_{12}O_{40}^{3-}$	1 *M* H_2SO_4	−0.04	−0.10
		−0.30	−0.36
$SiW_{12}O_{40}^{4-}$	1 *M* H_2SO_4	−0.24	−0.30
		−0.46	−0.52
$GeW_{12}O_{40}^{4-}$	1 *M* H_2SO_4	−0.21	−0.27
		−0.40	−0.46
$BW_{12}O_{40}^{5-}$	1 *M* H_2SO_4	−0.55	−0.61
		−0.66	−0.73
$H_2W_{12}O_{40}^{6-}$	pH 8[b]	−0.58	−0.66
		−0.75	−0.85
$P_2W_{18}O_{62}^{6-}$ (α isomer)[d]	pH 5[c]	+0.02	−0.05
		−0.16	−0.22
		−0.55	−0.61
		−0.68	−0.75
$P_2W_{18}O_{62}^{6-}$ (β isomer)[d]	pH 5[c]	+0.05	−0.01
		−0.13	−0.20
		−0.51	−0.58
		−0.65	−0.71
$As_2W_{18}O_{62}^{6-}$	pH 5[c]	+0.06	−0.02
		−0.13	−0.19
		−0.51	−0.59
		−0.64	−0.69

[a] Anion concentration 1.0 mM; sweep rate 0.5 V min⁻¹; all reductions are one-electron processes. [b] Tris(hydroxymethyl)aminomethane buffer. [c] Acetate buffer. [d] In earlier papers α and β isomers were referred to as B and A forms, respectively

ESR Spectroscopy. 12-Molybdophosphate and Molybdo-11-tungstophosphate Anions. The ESR spectrum of $PMo^VMo_{11}O_{40}^{4-}$ could be observed only in frozen solutions or, more conveniently, as dilute polycrystalline samples in $(Bu_4N)_4SiW_{12}O_{40}$ host. The spectrum between 298 and 77 K consisted of a single isotropic line the width of which varied with temperature as shown in Figure 2. The line shape was approximately Lorentzian at the higher temperatures, but below 140 K a Gaussian component could be detected. At

Table II. Controlled-Potential Electrolysis of Heteropolytungstates Using a Graphite Cloth Electrode

Anion[a]	Applied potential,[b] V	Mode[c]	No. of equiv/mol
$PW_{12}O_{40}^{3-}$ [d]	−0.22	R	1.00
	−0.50	R	0.93
	+0.15	O	1.87
$SiW_{12}O_{40}^{4-}$	−0.40	R	0.99
	−0.57[e]	R	1.04
	−0.40	O	0.87
	−0.02	O	1.12
$GeW_{12}O_{40}^{4-}$	−0.28	R	0.97
	−0.45	R	1.16
	0.00	O	2.4
$BW_{12}O_{40}^{5-}$	−0.63	R	0.97
	−0.55	O	0.98
$H_2W_{12}O_{40}^{6-}$	−0.71	R	1.00
	−0.50	O	0.98
	−0.87	R	*f*
α-$P_2W_{18}O_{62}^{6-}$	−0.10	R	0.89
	−0.30	R	0.84
	−0.10	O	0.86
	+0.15	O	0.90
β-$P_2W_{18}O_{62}^{6-}$	−0.08	R	1.00
	−0.26	R	0.93
$As_2W_{18}O_{62}^{6-}$	−0.04	R	0.99
	−0.20	R	1.03
	−0.04	O	0.96
	+0.14	O	0.97

[a] Supporting electrolytes as in Table I; anion concentration 0.5–20 mM. [b] Potentials for each anion are shown in the sequence in which they were applied. [c] Key: R, reduction; O, oxidation. [d] For this anion alone NaCl–agar salt bridges were used to avoid precipitation of insoluble $K_3PW_{12}O_{40}$. [e] Slight precipitation noted. [f] Decomposition.

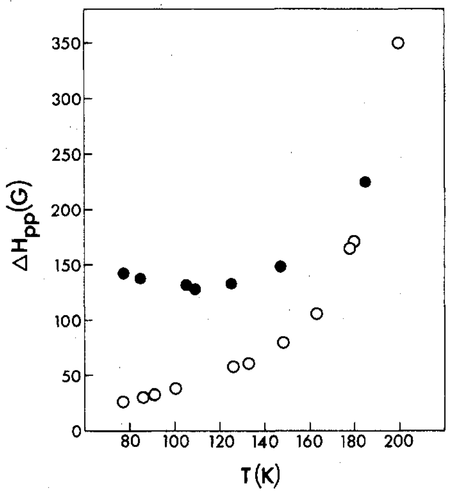

Figure 2. Temperature variation of peak-to-peak line widths of ESR spectra of $PMo^VMo_{11}O_{40}^{4-}$ in polycrystalline $(Bu_4N)_4SiW_{12}O_{40}$: open circles, sample with natural isotopic distribution; closed circles, sample enriched with 98% ^{95}Mo.

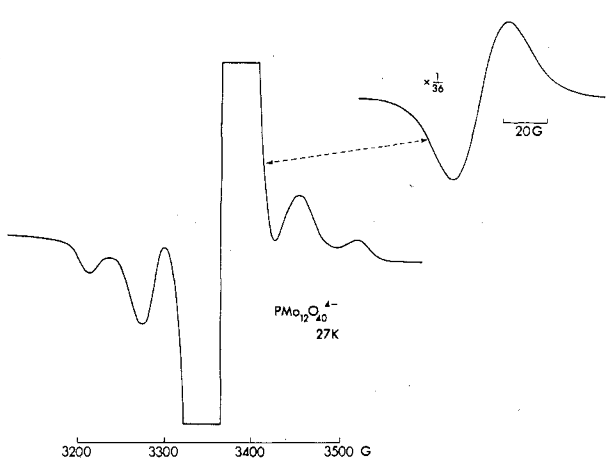

Figure 3. Polycrystalline ESR spectrum of $PMo^VMo_{11}O_{40}^{4-}$ in $(Bu_4N)_4SiW_{12}O_{40}$ at 27 K.

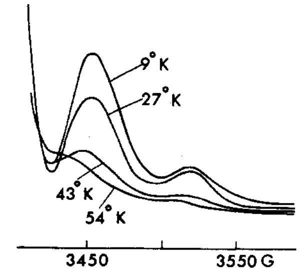

Figure 4. Temperature variation of high-field hyperfine lines in the spectrum of $PMo^VMo_{11}O_{40}^{4-}$.

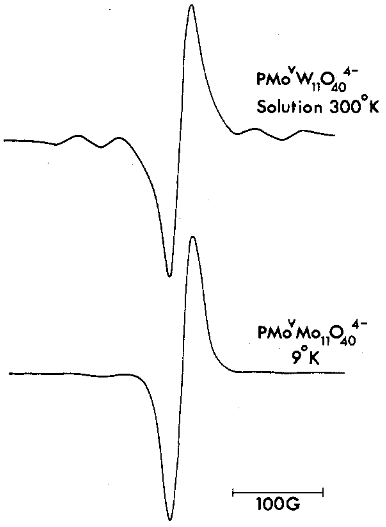

Figure 5. ESR spectra of acetonitrile solutions of $(Bu_4N)_4$-$PMo^VW_{11}O_{40}$ at 300 K (top) and of $PMo^VMo_{11}O_{40}^{4-}$ in polycrystalline $(Bu_4N)_4SiW_{12}O_{40}$ at 9 K (bottom).

77 K the line was about 26 G peak to peak[18] and 25% Gaussian. In the range 77–163 K the line width varied approximately as T^3. No further changes were seen in line shape or width at temperatures between 77 and 4.2 K, but below ca. 64 K hyperfine satellites appeared and these grew in intensity as the temperature was further lowered. The full spectrum at 27 K is shown in Figure 3 and the variation of the intensity of the high-field lines with temperature is shown in Figure 4. At 9 K the spectrum is comparable to a solution spectrum of $(Bu_4N)_4PMo^VW_{11}O_{40}$ in acetonitrile at room temperature (see Figure 5) although as can be seen in this figure the hyperfine lines are weaker than anticipated for the natural abundance (25.3%) of the molybdenum isotopes with $I = ^5/_2$. Based on the 9-K spectrum, $\langle g \rangle = 1.945$ and $\langle a \rangle = 55 \times 10^{-4}$ cm^{-1}. The corresponding parameters[5] for $PMo^VW_{11}O_{40}^{4-}$ are $\langle g \rangle = 1.926$ and $\langle a \rangle = 47.1 \times 10^{-4}$ cm^{-1}.

The spectrum of the isotopically enriched (98% ^{95}Mo, $I = ^5/_2$) anion $PMo^VMo_{11}O_{40}^{4-}$ also consists of an isotropic line at temperatures above ca. 110 K. As can be seen from Figure 2, the line width is greater than that of the nonenriched material and below 110 K actually appears to increase (from 128 to 142 G peak to peak) as the temperature is lowered to 77 K. The apparent increase in line width is caused by the gradual resolution of six hyperfine lines. The hyperfine components are first clearly detectable at ca. 61 K and at 6 K are as shown in Figure 6. Also shown in Figure 6 for the purpose of comparison is the spectrum of isotopically enriched

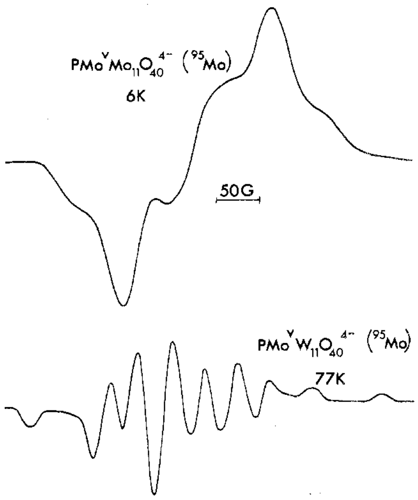

Figure 6. ESR spectra of isotopically enriched (98% ^{95}Mo) $PMo^VMo_{11}O_{40}^{4-}$ and $PMo^VW_{11}O_{40}^{4-}$ in polycrystalline $(Bu_4N)_4$-$SiW_{12}O_{40}$.

$PMo^VW_{11}O_{40}^{4-}$ at 77 K which shows well-resolved parallel and perpendicular components. The positions of the hyperfine lines in Figure 6 agree with the corresponding ones in Figure 3 but are somewhat broader for the enriched sample, possibly because of unresolved superhyperfine interactions with neighboring ^{95}Mo atoms. The spectrum of the enriched material can be simulated only if a broad (ca. 185 G) line is mixed with the hyperfine components. The relative intensities of the hyperfine spectrum and underlying line varied somewhat with temperature but accurate measurements were not possible since the hyperfine line widths may also have been changing with temperature.

The metal atoms in the Keggin structure adopted by $PMo_{12}O_{40}^{3-}$ and $PMoW_{11}O_{40}^{3-}$ occupy equivalent sites of approximately C_{4v} symmetry. The spectrum of $PMo^VW_{11}O_{40}^{4-}$ shown in Figure 6 is entirely consistent with a tetragonal site symmetry for Mo(V) and we have analyzed the ESR spectrum of this anion elsewhere.[5] For the spectrum of $PMo^{V,VI}_{12}O_{40}^{4-}$ in a polycrystalline solid to appear isotropic, it must follow that the unpaired electron is hopping rapidly from one molybdenum atom to the next. The 12 metal atoms in the Keggin structure occupy the corners of a cuboctahedron and are oriented so that their individual pseudofourfold (z) axes are directed approximately toward the center of the anion. Consequently a rapid intraionic electron delocalization constitutes a pseudotumbling of the heteropoly anion. Interaction of the unpaired electron with 12 equivalent ^{95}Mo nuclei would be expected to give 61 lines with intensities 1, 12, ..., 12, 1, and a splitting of about 60/12 = 5 G. The experimental spectrum of $PMo^{V,VI}_{12}O_{40}^{4-}$ has only six hyperfine lines and a broad (185 G) underlying signal at 6 K. The possibility that the 185-G line is the unresolved envelope of 61 hyperfine components can be shown to be implausible by computer simulation.[19] Within the constraints of the simple model that we have adopted we can conclude that the intramolecular electron-transfer (pseudotumbling) rate in $PMo_{12}O_{40}^{4-}$ must be $>10^8$ s^{-1} in order to yield an isotropic spectrum, but we are unable to account satisfactorily for the six-line spectrum which would seem to indicate a slower rate.

Heteropolytungstates. Five 1:12 tungstates, all isostructural with the molybdates discussed above, and three 2:18 tungstates have been studied. Both 1:12 and 2:18 anions are known to exist as so-called α and β isomers and the structures of all four anion types are known.[20] We have restricted the present study to the thermodynamically stable α (Keggin) isomers of the 1:12 anions but have included both isomers of $P_2W_{18}O_{62}^{6-}$. In our earlier papers[6,11,21] we referred to these isomers as A and B forms, following Wu's[22] nomenclature. To be consistent and utimately to minimize confusion with the corresponding 2:18 molybdate isomers[23,24] we now endorse renaming the B form (which is the thermodynamically stable structure) as the α isomer, and the A form as the β isomer.[25] Arguments supporting the change in nomenclature are presented elsewhere.[20]

Table III. ESR Parameters of Reduced Polytungstates

Anion	Temp, K	g_1	g_2	g_3	$\langle g \rangle$
$PW_{12}O_{40}^{4-}$	14		1.827[a]		
$SiW_{12}O_{40}^{5-}$	22	1.85	1.822	1.79	1.821
$GeW_{12}O_{40}^{5-}$	26	1.848	1.816	1.779	1.814
$BW_{12}O_{40}^{6-}$	14	1.854	1.823	1.773	1.817
$H_2W_{12}O_{40}^{7-}$	16	1.852	1.805	1.759	1.805
α-$P_2W_{18}O_{62}^{7-}$	26	1.906	1.854	1.814[b]	1.858
α-$As_2W_{18}O_{62}^{7-}$	12	1.905	1.849	1.810	1.854
β-$P_2W_{18}O_{62}^{7-}$	77[c]		1.852[c]		

[a] Almost isotropic spectrum. [b] A previously reported[6] value for g_3 (1.845) had been incorrectly computed from the experimental spectrum. The present results agree with the earlier ones obtained at 77 K. [c] Below 77 K the spectrum appears to be that of a mixture; see the text.

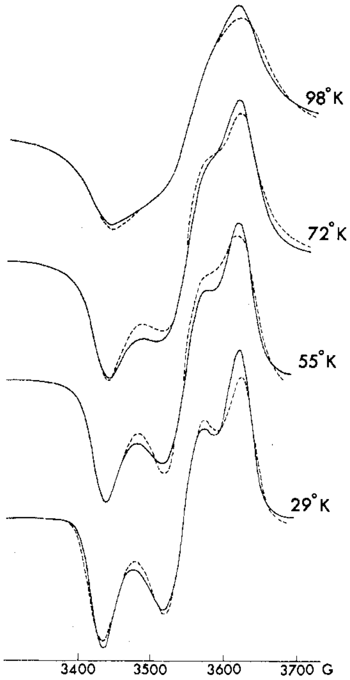

Figure 7. ESR spectra (water–ethylene glycol glasses) of As_2-$W^VW_{17}O_{62}^{7-}$ at various temperatures: solid lines, experimental spectra; broken lines, simulated spectra.

The ESR spectra of all the polytungstates, with the exception of β-$P_2W_{18}O_{62}^{7-}$ which is discussed separately later, were rhombic at the lowest temperatures studied. The g values measured at these temperatures are listed in Table III. As the temperature was raised for each sample, the lines broadened and the spectrum passed through an "axial" form before appearing to be wholly isotropic.[1] A typical set of spectra, of $As_2W_{18}O_{62}^{7-}$, is shown in Figure 7. The spectral changes could be simulated for each compound, by keeping the three g values constant and varying the component line widths. As found for reduced molybdophosphate, a significantly better simulation was achieved if Gaussian lines were used at the lower temperatures and Lorentzians at the higher temperatures. In Figure 7 the two lower spectra were simulated with 17.5- and 20.0-G Gaussian lines, and the two upper spectra were simulated with 50- and 90-G Lorentzian lines. Spectra of the 1:12 anions became more "isotropic" at lower temperatures than did those of α-$P_2W_{18}O_{62}^{7-}$ and $As_2W_{18}O_{62}^{7-}$.

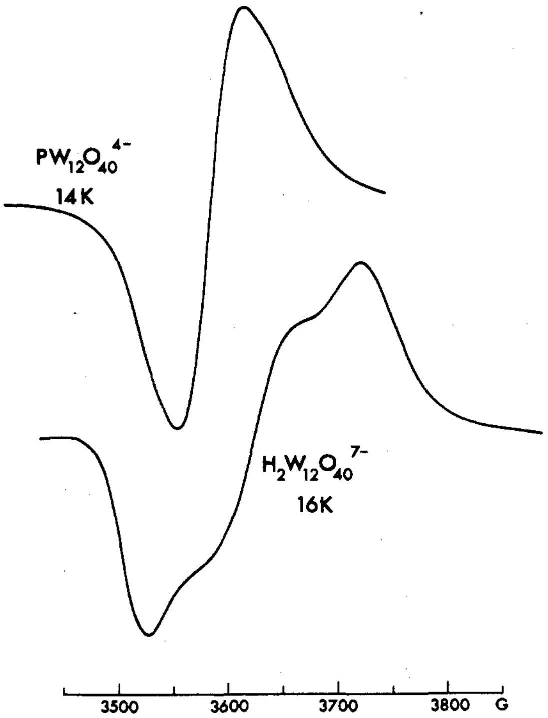

Figure 8. ESR spectra of $PW^VW_{11}O_{40}^{4-}$ and $H_2W^VW_{11}O_{40}^{7-}$.

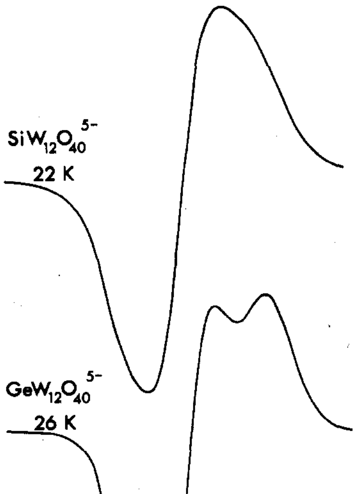

Figure 9. ESR spectra of $SiW^VW_{11}O_{40}^{5-}$ and $GeW^VW_{11}O_{40}^{5-}$.

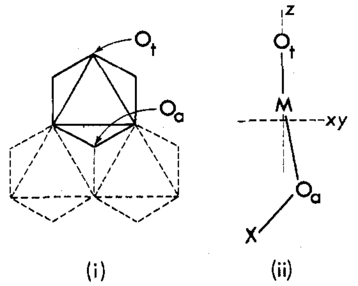

Figure 10. Representation of rhombic distortion of MO_6 octahedra in Keggin and related structures: (i) edge-shared M_3O_{13} group showing location of axial oxygen atoms O_a (directly bound to central atom X) and O_t (terminal, unshared oxygen) (rhombic distortion is produced by moving O_a vertically up out of the plane of the paper); (ii) relative positions of metal and axial oxygen atoms with respect to the plane of equatorial oxygens.

1:12 Tungstates. There was a significant variation in the magnitude of the anisotropy and in the $\langle g \rangle$ values for the Keggin (1:12) anions. This variation is most clearly illustrated in Figure 8 which shows the spectra of $PW_{12}O_{40}^{4-}$ and $H_2W_{12}O_{40}^{7-}$ taken at comparable temperatures, and it is also apparent in the spectra of anions with the same overall charge; see Figure 9. The observation of a rhombic spectrum indicates that at low temperatures ($<\sim 60$ K) electron hopping from tungsten atom to tungsten atom (pseudotumbling) occurs at a rate slower than ca. $3 \times 10^8\ s^{-1}$. The variation in resolution of the rhombic components may indicate slight differences in rates of electron delocalization for the different anions. In none of the tungstate spectra were we able to detect hyperfine structure. This is not surprising in view of the low natural abundance of the magnetic isotope of tungsten (^{183}W, 14.28%, $I = {}^1/_2$) and the expected magnitude of the splitting (ca. 150 G).[26] The g values observed for the 12-tungstates are within the range found for axial oxo complexes of tungsten(V). As the temperature rises, the two low-field components are the first to merge, suggesting that g_1 and g_2 could be viewed as g_{xx} and g_{yy} ("$g_\perp$") and g_3 as g_{zz} ("$g_\parallel$"). Thus $g_\perp > g_\parallel$ which is also found to be the case for WOF_5^{2-} (1.767, 1.589)[27] and $WO(NCS)_5^{2-}$ (1.819, 1.775)[28] but is the reverse of that found for $WOCl_5^{2-}$ (1.758, 1.804)[26] and $WOBr_5^{2-}$ (1.775, 1.940).[26] As is evident from Figure 7, the two *high*-field components merge first for the 2:18 tungstate spectra, indicating that $g_\parallel > g_\perp$ for these anions, a point to which we shall return later.

The small but real diminution of $\langle g \rangle$ from $PW_{12}O_{40}^{4-}$ (1.827) to $H_2W_{12}O_{40}^{7-}$ (1.805) probably reflects the increasing deviation from axial symmetry of individual tungsten atoms in these anions. We shall now consider the source of this deviation. The following discussion is based on a neutron diffraction study[29] of α-$K_4SiW_{12}O_{40}\cdot 17H_2O$, which results in more reliable oxygen positions than the numerous x-ray studies of polytungstates, and on a recent x-ray structure determination of $H_3PMo_{12}O_{40}\cdot(29-31)H_2O$.[30] The relevant dimensions are illustrated in Figure 10 which shows one of the four groups of three edge-shared MO_6 octahedra in the Keggin structure. As has been noted before, the metal atoms in each octahedron are displaced toward the terminal oxygen atoms, O_t. Bond lengths are $W-O_t = 1.68$, $W-O_a(Si) = 2.38$, $Mo-O_t = 1.68$, and $Mo-O_a(P) = 2.43$ Å. Such a displacement puts the metal atom 0.3–0.4 Å above the plane of the four equatorial oxygen atoms which themselves define the corners of a quite good "square" (sides ranging from 2.61 to 2.68 Å for the molybdate and from 2.60 to 2.72 Å for the tungstate). The metal–equatorial oxygen bond lengths are 1.91–1.92 Å for the molybdate and 1.91–1.95 Å for the tungstate. The departure from axial symmetry can be blamed upon the displacement of atom O_a from the pseudo-fourfold axis as shown in Figure 10. The angle O_t-M-O_a is 170.5° in the tungstate[29] and 170.8° in the molybdate (computed from the data in Strandberg's paper[30]). The displacement of O_a results in a slight trapezoidal distortion of the "square" of the four equatorial oxygen atoms.

Inspection of Figure 10 reveals that the rhombic distortion should become greater as the central atom $(X)-O_a$ bond length becomes larger (Si vs. Ge) or as X becomes less polarizing (P vs. H). Such an argument would account for the variation of the spectra shown in Figures 8 and 9. Structural evidence for an increased rhombic distortion as the size of X increases is provided by O_t-W-O_a angles of 177.4 and 162.5° for $PW_{12}O_{40}^{3-}$ and $H_2GaW_{11}O_{40}^{9-}$, respectively, that we have calculated from the data given in Evans' review.[31] While the uncertainties in these angles, based as they are on early or unrefined x-ray data, are doubtless quite large, there is clearly a significant difference in the expected direction.

Figure 11. Central portion (due to nonmagnetic molybdenum isotopes) of ESR spectrum of $PMo^VW_{11}O_{40}^{4-}$ at 4.2 K (left) and 77 K (right) showing loss of axial symmetry at the lower temperature.

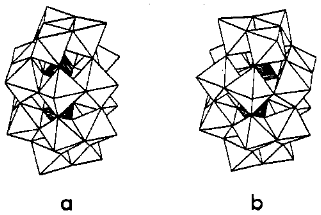

Figure 12. (a) Structure of α-$P_2W_{18}O_{62}^{6-}$ (Dawson[32]) and α-$P_2Mo_{18}O_{62}^{6-}$ (Strandberg[24]). (b) Structure of β-$P_2W_{18}O_{62}^{6-}$ (Matsumoto and Sasaki[25]).

Although, as we have pointed out above, a metal ion in the Keggin structure has only rhombic symmetry, the development of fully rhombic ESR spectra appears to be restricted to 5d species in the tungstates, e.g., $PRe^{VI}W_{11}O_{40}^{3-}$ [14] and the anions described in this paper. We have examined the ESR spectrum of the $3d^1$ case, $PV^{IV}W_{11}O_{40}^{5-}$, at 4.2 K and find no evidence of other than axial symmetry for the V(IV) ion. The situation for a 4d ion appears to be intermediate, and in Figure 11 is shown the central portion (due to the nonmagnetic isotopes of Mo) of the spectrum of $PMo^VW_{11}O_{40}^{4-}$ at 77 and 4.2 K. The spectrum appears to be changing from an "axial" to a "rhombic" form. The different types of spectra for $PXW_{11}O_{40}$ anions can be traced ultimately to the large increase in spin–orbit coupling parameters and hence to larger ranges of g values, as X varies from a 3d to a 5d ion. Consequently we do not view the difference between the rhombic tungstate spectra and the isotropic spectrum of $PMo^VMo_{11}O_{40}^{4-}$ as indicating a major difference in electron delocalization rates.

2:18 Tungstates. The spectra for the α 2:18 anions differ from those of the 1:12 anions in three respects. The anisotropy persists to much higher temperatures (ca. 150 K), values of $\langle g\rangle$ are significantly larger (Table III), and, as noted above, g_2 and g_3 merge before g_1, suggesting that "$g_\parallel$" > "$g_\perp$". Unlike the Keggin structure in which each of the metal atoms occupies an equivalent site, the α 2:18 structure[32] has six metal atoms of one kind and twelve of another. The group of six metals occupies two ("polar") edge-shared M_3O_{13} groups at either end of the anion and the remaining twelve metal atoms form two rings of six alternately edge- and corner-shared MO_6 octahedra in an approximately "equatorial" position (see Figure 12). Quite recently Strandberg[24] has reported a detailed structure of α-$P_2Mo_{18}O_{62}^{6-}$ and this work provides more reliable bond lengths and angles than the earlier study of Dawson[32] on the corresponding tungstate. A major difference between the detailed structures of the 1:12 and 2:18 anions as revealed by Strandberg's results is the prevalence of unsymmetrical Mo–O–Mo bridges in the α 2:18 structure. The six oxygen atoms that link the halves of the anion are displaced alternately about 0.2 Å on either side of an equatorial plane. As we have pointed out elsewhere, these displacements by themselves confer a chirality on the whole structure.[20] The chirality is reinforced by further displacements induced in the other Mo–O–Mo bridges via trans effects in individual MoO_6 octahedra. The structure of the whole anion contains three loops of trans-related O–Mo–O–Mo bond sequences that have alternately "long" (ca. 2.1 Å) and "short" (ca. 1.8 Å) Mo–O bonds. As a result of this alternation in bond lengths, which affects the equatorial Mo–O bonds of individual MoO_6 octahedra, the symmetry of each metal is much reduced from axial (C_{4v}). Whereas in the Keggin structure the equatorial Mo–O bond lengths are all between 1.91 and 1.92 Å, the corresponding bonds in α-$P_2Mo_{18}O_{62}^{6-}$ range from 1.75 to 2.14 Å. Since several salts of α-$P_2W_{18}O_{62}^{6-}$ and α-$As_2W_{18}O_{62}^{6-}$ are isomorphous with the corresponding molybdates, it is reasonable to conclude that similar distortions occur in the tungstates.[33] The distortions away from C_{4v} symmetry for each of the metal atoms in the α 2:18 structure may account for the differences between the ESR parameters of the 1:12 and 2:18 anions that were noted at the beginning of this section.

The ESR spectrum of β-$P_2W_{18}O_{62}^{7-}$ is isotropic at 77 K. Changes in the spectrum that occurred on cooling to 13 K indicated that a small amount of the α isomer (5–10%, undetectable by polarography) was present in the sample but that there was no further resolution of the main signal. The spectrum of β-$P_2W_{18}O_{62}^{7-}$ is thus similar to that of α-$PW_{12}O_{40}^{4-}$. Very recently, Matsumoto and Sasaki[25] have reported the structure of β-$P_2W_{18}O_{62}^{6-}$; it is illustrated in Figure 12b. As we have pointed out elsewhere, the β structure is a meso combination of two chiral PW_9 units. No metal–oxygen bond length data are yet available for this structure, but on the basis of the ESR spectrum we speculate that pronounced rhombic distortions of the WO_6 octahedra are not present in the β isomer.

Conclusions

The ESR data show that "one-electron" heteropoly blues contain weakly trapped Mo(V) or W(V) valences and that the trapping becomes tighter as the metal atom site symmetry diminishes; cf. $PW^VW_{11}O_{40}^{4-}$, $H_2W^VW_{11}O_{40}^{7-}$, and α-$P_2W^VW_{17}O_{62}^{7-}$. The increased degree of valence trapping seems to be paralleled by an increase in the energy of the lowest intervalence charge-transfer (IVCT) bands, which range from 8000 to 11 000 cm^{-1} for these particular anions.[6] According to the widely accepted Hush model[34] for mixed-valence compounds, the activation energy for *thermal* electron transfer should be approximately one-fourth the energy of the *optical* band. It is evident that this relationship, which for the heteropoly blues implies an activation energy for thermal electron delocalization of at least 6 kcal/mol, is incompatible with the "isotropic" ESR spectra observed here. Although it is not possible to determine activation energies from the present work,[35] it is clear that they are much smaller than predicted from the Hush model.

Further reduction of the heteropoly blues described in this paper leads to the "two-electron" blues which have no observable ESR spectra and which are diamagnetic at room temperature.[6] Subsequent reduction to "six-electron" blues in one- or two-electron steps is evident from polarographic studies.[10,11,17,36] A feature of the polarograms of these anions is the presence of two-electron reductions in acidic media and one-election reductions under conditions where the anions are not protonated. When one-electron reductions are observed, the half-wave potentials are closely spaced for the first and second, third and fourth, etc. waves. This behavior, coupled with the observed diamagnetism of the two-electron blues leads us to propose that the second, fourth, and sixth electrons are antiferromagnetically paired with the first, third, and fifth electrons. Moreover it seems likely that the paired electrons are localized on adjacent metal atoms, in contrast to the highly mobile odd electron in the one-, three-, and five-electron blues.

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Registry No. $PW_{12}O_{40}^{4-}$, 12534-78-0; $SiW_{12}O_{40}^{5-}$, 12504-06-2; $GeW_{12}O_{40}^{5-}$, 59965-05-8; $BW_{12}O_{40}^{6-}$, 39326-57-3; $H_2W_{12}O_{40}^{7-}$, 12501-12-1; $P_2W_{18}O_{62}^{7-}$, 12504-08-4; $As_2W_{18}O_{62}^{7-}$, 59965-04-7; $PMo^{V}W_{11}O_{40}^{4-}$, 12776-99-7; $PMo^{V}Mo_{11}O_{40}^{4-}$, 53850-86-5; $P^{95}Mo^{V95}Mo_{11}O_{40}^{4-}$, 59965-02-5; $P^{95}Mo^{V}W_{11}O_{40}^{4-}$, 59965-03-6; $PW_{12}O_{40}^{3-}$, 12534-77-9; $SiW_{12}O_{40}^{4-}$, 12363-31-4; $GeW_{12}O_{40}^{4-}$, 37369-87-2; $BW_{12}O_{40}^{5-}$, 12513-03-0; $H_2W_{12}O_{40}^{6-}$, 12207-61-3; $P_2W_{18}O_{62}^{6-}$, 12269-70-4; $As_2W_{18}O_{62}^{6-}$, 12267-69-5.

References and Notes

(1) The words "isotropic", "axial", and "rhombic" are used in this paper to describe the *appearance* of an ESR spectrum and do not necessarily imply that the species responsible for the spectrum is respectively isotropic, axial, or rhombic. As will become apparent, all of the complexes under discussion have rhombic symmetries but give "axial" or "isotropic" spectra when exchange broadening increases the line widths beyond the separation of the rhombic components.

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A Cobalt-59, Indium-115, Gallium-69, Gallium-71, Bromine-79, Bromine-81, and Chlorine-35 Nuclear Quadrupole Resonance Study of Structure and Bonding in Four-Coordinate Gallium and Indium Compounds Containing Metal–Metal Bonds

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Pure nuclear quadrupole resonance spectra are reported for a series of four-coordinate gallium and indium compounds having as ligands $Co(CO)_4$, Br, Cl, THF, acac, and $(C_6H_5)_3PO$. The ^{59}Co, ^{115}In, ^{69}Ga, ^{71}Ga, ^{79}Br, ^{81}Br, and ^{35}Cl NQR parameters when taken together and separately lead to qualitative structural inferences and a coherent picture of the ground-state electron distribution in these molecules. The ^{59}Co and ^{115}In coupling constants and the ^{115}In asymmetry parameters suggest that ligand angle changes in the In(III) coordination sphere account for some of the trends. ^{59}Co asymmetry parameters suggest cobalt–indium (gallium) π bonding is not a major factor in these compounds. The presence of bridging and terminal halogens can be determined using ^{79}Br, ^{81}Br, and ^{35}Cl NQR frequencies. The halogen frequency shifts are consistent with orbital population changes on indium as evidenced by the ^{115}In coupling constants. The number of examples is limited but partial quadrupole splitting values for ligands derived from Sn(IV) Mössbauer spectra appear to predict the trends in In(III) coupling constants. The EFG trends and carbonyl ir frequency shifts in $Co(CO)_4$–In(Ga) bonds compared to $(CO)_4Co$–Sn(Ge) bonds are entirely consistent but show ν_{CO} to be much less sensitive than the electric field gradient to substitutions.

Introduction

Cobalt-59 nuclear quadrupole resonance spectra for a large number of M–$Co(CO)_4$ molecules have been obtained and analyzed on the basis of the effect of M on the cobalt electric field gradient (EFG).[1-10] In most cases M has been a group 4A or group 5A atom based moiety with Si, Ge, Sn, Pb, and P at the bonding site. Although many interesting inferences about σ- and π-bonding character have been extracted from these data, none of these group 4A and 5A elements bound to $Co(CO)_4$ possesses quadrupolar nuclei in the ground state. Hence it has not been possible to probe both ends of the metal–metal bond by NQR spectroscopy. In providing an