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Stabilization and magnetic resonance characterization of the one-electron heteropoly blue derivative of the molybdophosphate $[P_2Mo_{18}O_{62}]^{6-}$. Slow intramolecular proton exchange of the two-electron blue in acetonitrile solution*

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Abstract

Reduction of the heteropolyanion α-$[P_2Mo_{18}O_{62}]^{6-}$ (α**0**) in acetonitrile, followed by the addition of $[(n\text{-}C_4H_9)_4N]OH$, leads to cyclic voltammograms showing two initial one-electron redox features ($\Delta E = 150$ mV) and the possibility of generating solutions that contain the paramagnetic anion α-$[P_2Mo_{18}O_{62}]^{7-}$ (α**I**), the existence of which had earlier been doubted. Solutions of α**I** are most conveniently prepared by comproportionation of α**0** and deprotonated α-$[P_2Mo_{18}O_{62}]^{8-}$ (α**II**) in acetonitrile solution. Such solutions are ESR-active at room temperature ($g \sim 1.94$; linewidth 80 G) and yield a single ^{31}P NMR resonance at +13.4 ppm (linewidth 220 Hz). The transient existence of α**I** in aqueous solution is demonstrated by the observation of the ^{31}P NMR signal in a rapidly-alkalinized solution of α**II**. Based on comparison of the ESR parameters of α**I** ($g_\perp$, 1.945; $g_\parallel$, 1.965) with those for the two isomers of α-$[P_2W_{17}Mo^VO_{62}]^{7-}$, it is concluded that the reduction of α**0** has occurred at one of the equatorial molybdenum sites, but that there is substantial delocalization (or rapid hopping) to the mirror-related molybdenum atom. The electronic absorption spectrum shows intervalence transitions at 9710 and 12 190 cm^{-1}. Intermolecular electron transfer between α**0**, α**I** and α**II** is slow on the NMR timescale. In acetonitrile solution the ^{31}P NMR spectra of diprotonated and unprotonated α**II** consist of single narrow lines consistent with effective D_{3h} symmetry for the reduced Dawson structure. However the *monoprotonated* anion has a two-line spectrum that undergoes coalescence as the temperature is raised. This is attributed to a slow intramolecular exchange ($k \sim 1$ s^{-1}) of the proton between O(---Mo^V) atoms on either side of the equatorial plane of the Dawson structure. Based on the spectral changes between 297 and 333 K, the activation energy for this process is 5.9 kcal mol^{-1}.

Introduction

The reduction of heteropolymolybdates and -tungstates to mixed-valence 'blues' has attracted the attention of several groups over the past 30 years or so [1]. Polyanions in which the Mo or W atoms each are coordinated to a single terminal oxygen atom (Type 1) [2] exhibit polarograms with reversible one- or two-electron reductions. The latter processes are pH-dependent and in almost all cases eventually become pH-independent one-electron steps under conditions of pH (or in aprotic solvents) where protonation of the reduced species is not possible. This behavior has especially been documented for dozens of polyoxoanions with Keggin ($XM_{12}O_{40}$) and Dawson ($X_2M_{18}O_{62}$) structures, with the notable exception of $[P_2Mo_{18}O_{62}]^{6-}$ and $[As_2Mo_{18}O_{62}]^{6-}$ †. It was early shown that, in contrast to the behavior of $[P_2W_{18}O_{62}]^{6-}$ and $[PMo_{12}O_{40}]^{3-}$, polarograms of $[P_2Mo_{18}O_{62}]^{6-}$ displayed only two-electron reductions, even at high pH [3]. In a more complete study of $[As_2Mo_{18}O_{62}]^{6-}$, the only evidence for an odd reduction state was for the 5-electron product, **V**, and then only in an equilibrium mixture with the 4- and 6-electron reduced species, **IV** and **VI** [4]. Explanations proposed for the apparent instability of **I** (i.e. a high comproportionation constant for **0** + **II**) have been based upon the chirality of the oxidized anion (**0**) or on the deformability of Mo–O–Mo bonds [5]. Subsequently, Jeannin *et al.* showed that **I** could be partially stabilized in dimethylformamide in the absence of Na$^+$ cations [6], and Papaconstantinou and Hoffman have reported

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†Both molybdates exist as α and β isomers with very similar properties, as do the corresponding tungstates. The structures of the less-stable β isomers of the molybdates are not known, but it is often presumed that they correspond to those of the β-tungstate isomers (see ref. 1b).

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a partial electronic spectrum (500–800 nm) of a short-lived species, alleged to be that of **I** in aqueous solution, by pulse-radiolysis [7].

We have re-examined the electrochemistry of α-$[P_2Mo_{18}O_{62}]^{6-}$ in acetonitrile solution and have demonstrated that the reduced species **I** can be readily attained and is not susceptible to disproportionation. We report the characterization of **I** by electronic, NMR and ESR spectroscopy, and the observation of slow intramolecular proton exchange in the monoprotonated two-electron blue.

Experimental

Preparation of compounds

α-$K_6[P_2Mo_{18}O_{62}]\cdot nH_2O$ and α_1-$K_6[P_2W_{17}MoO_{62}]\cdot nH_2O$ were prepared by literature methods [8]. The latter species was contaminated by *c.* 10% of the α_2 isomer and 10% of the lacunary species α_1-$[P_2W_{17}O_{61}]^{10-}$ according to ^{31}P NMR as has been noted previously [9].

*α-$[(n\text{-}C_4H_9)_4N]_5H[P_2Mo_{18}O_{62}]$ (α**0**-H)*

Five grams of the potassium salt (1.7 mmol) and 3.2 g $(n\text{-}C_4H_9)_4NBr$ (QBr, 10.0 mmol) were separately dissolved into 50 ml 0.1 M HCl. After addition of a drop of Br_2 to oxidize fully the heteropolyanion solution (green to yellow) the solutions were mixed and the resulting precipitate filtered off, stirred into 75 ml 0.1 M HCl, refiltered, washed with water and allowed to dry. The crude product was recrystallized by dissolving it in 35 ml boiling acetonitrile and reducing the volume to 25 ml. To the hot solution was added 25 ml methanol containing 2 ml conc. HCl, and the solution allowed to cool slowly with constant stirring. The bright yellow crystals were filtered off and washed with methanol. *Anal.* Calc.: C, 24.06; H, 4.57; N, 1.75; P, 1.55; Mo, 43.24. Found: C, 23.86; H, 4.59; N, 1.72; P, 1.54; Mo, 43.29%. ^{31}P (CD_3CN), δ ($\Delta\nu_{1/2}$), −0.1 (0.44).

*α_1-$[(n\text{-}C_4H_9]_4N]_5H[P_2W_{17}MoO_{62}]$ (α_1**0**-H)*

The above preparation was repeated using 5.0 g of the potassium salt (1.1 mmol) and 2.1 g (6.6 mmol) of QBr. The pale yellow product was recrystallized from acetonitrile as described for α**0**-H. *Anal.* Calc.: C, 17.51; H, 3.32; N, 1.28; P, 1.13; W, 56.94; Mo, 1.75. Found: C, 17.67; H, 3.00; N, 1.36; P, 1.06; W, 55.68; Mo, 2.24%. ^{31}P (CD_3CN), δ ($\Delta\nu_{1/2}$), −8.6 (1.2), −9.3 (1.4). A cyclic voltammogram in acetonitrile with 0.1 M $QClO_4$ showed reduction waves at +0.10, −0.45 and −1.13 V. The product contained *c.* 10% impurities of the α_2 isomer and the α_1 lacunary anion. A solution containing the one-electron reduced derivative of α_1**0** was prepared by electrolytic reduction of an acetonitrile solution (0.1 M $QClO_4$) at +0.10 V (the most positive cyclic voltammetric peak). Electrolysis was continued to about 90% stoichiometry to ensure that no α_2 isomer (present as impurity, and with a more negative reduction potential) was reduced.

Potentiometric titrations were carried out using acetonitrile solutions (0.2 M) of $(n\text{-}C_4H_9)_4OH$ (QOH) and CF_3COOH, which had been prepared by diluting methanolic QOH (*c.* 1 M) or 11.0 M acid under argon or nitrogen. Most operations involving the reduced species were carried out with syringe/septum techniques, or in a Vacuum Atmospheres glovebox.

^{31}P NMR spectra were recorded at 121.496 MHz on a Bruker AM-300WB spectrometer using a wide-band tunable multinuclear probe with 10-mm tubes. The pulse width was 11 μs. Chemical shifts, determined by the sample replacement method, are reported with reference to 85% H_3PO_4, a positive sign denoting a shift to high frequency. ESR spectra were recorded at X-band on a Varian E-4 instrument using a TM_{110} cavity, and were simulated using CURHEPR [10]. Electrochemical measurements were made on an assembly of McKee-Pederson Modules and a Houston Instruments XY recorder. Glassy carbon, platinum and saturated calomel reference electrodes were used in a conventional three-electrode arrangement. All potentials are reported with reference to aqueous SCE. Controlled potential electrolyses were carried out using a Brinkmann-Wenking 70 TST potentiostat, a Koslow Scientific Company model 541 coulometer, and a platinum gauze working electrode.

Results and discussion

Identification of one-electron reduced α-$[P_2Mo_{18}O_{62}]^{6-}$

The cyclic voltammogram of α**0**-H in acetonitrile and 0.1 M $QClO_4$ reveals several overlapping redox processes (Fig. 1(a)) as a result of the presence of different protonated species. Electrolytic reduction by one equivalent per mole, followed by the addition of *c.* 1.5 mmol QOH (a slight excess) yields the voltammogram shown in Fig. 1(b) which shows separation of the initial reduction process into two one-electron steps. A similar voltammogram, Fig. 1(c), was recorded on a solution prepared by two-equivalent electrolytic reduction of α**0**-H in acetonitrile and 0.1 M $QClO_4$ to yield α**II**-H_2 (α-$[H_2P_2Mo_{18}O_{62}]^{6-}$) followed by addition of two equivalents of QOH. Voltammetric scans initiated at the point of zero charge confirmed that the electroactive species in Fig. 1(b) and (c) were the one- and two-electron reduced anions, respectively. It proved convenient to prepare solutions of α**I** for spectroscopic purposes by means of a comproportionation procedure. This was carried out in the glovebox by combining an

TABLE 1. Electronic spectral features of reduced molybdodiphosphates in acetonitrile solution

Anion	E_{op} (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	$\Delta\nu_{1/2}$ (obs.)	$\Delta\nu_{1/2}$ (calc.)[a]	α[b]
α**I**	9710	5500	4980	4710	0.29
	12190 (sh)	4100			
α**II**	8750 (sh)	4350	3080	4480	0.21
	12580	11600			
α_1**I**	14710	2400			
	20500 (sh)	1550			

[a] $\Delta\nu_{1/2} = \sqrt{16kT\ln(2)E_{op}} = \sqrt{2312E_{op}}$ at 300 K. [b] $\alpha^2 = 4.24\times10^{-4}\,\frac{\epsilon_{max}\Delta_{1/2}}{E_{op}d^2}$, d = metal–metal distance (Å).

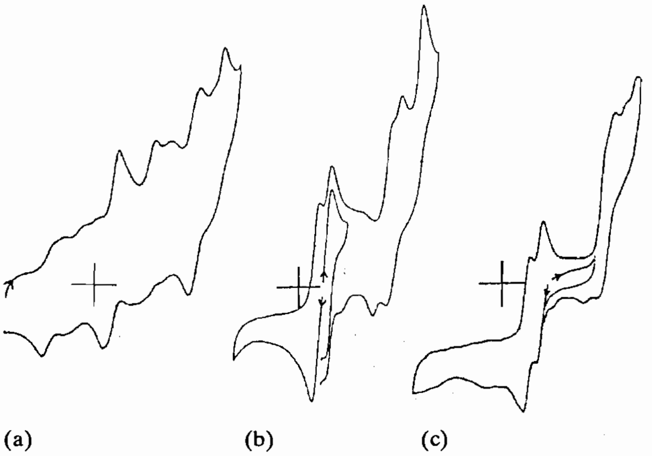

Fig. 1. Cyclic voltammograms recorded on a glassy carbon electrode in acetonitrile solution, 0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$, 2.0 V min^{-1}. Positive ordinates denote cathodic currents. The directions of initial sweeps are denoted by the arrows. 0.0 V vs. SCE is indicated. The horizontal scale bars correspond to 500 mV. (a) 1.0 mM α**0**-H; (b) 4.0 mM α**I**; (c) 1.0 mM α**II**. Solutions prepared as described in the text.

aliquot of a solution of α**II**-H_2, prepared as above, with an equimolar amount of solid α**0**-H. Addition of 1.8 equiv. of QOH (a slight excess) caused the dark blue solution to assume the dark green color of the α**I** species.

Electronic and NMR spectroscopy

Electronic spectral data for the reduced anions are summarized in Table 1, and the spectra of α**I** and α**II** are shown in Fig. 2. The spectra of heteropoly blue anions have been discussed elsewhere [1a, b] in terms of the Robin-Day Class II formalism. If the lowest energy absorption is taken to be the intervalence transition, the conventional analysis [11] leads to the values of the α (the valence delocalization coefficient), listed in Table 1.

^{31}P NMR spectra of α**I** and α_1**I** in acetonitrile solution are shown in Fig. 3, and chemical shifts and linewidths for these and related species are summarized in Table 2. Only one line (in addition to residuals of the starting

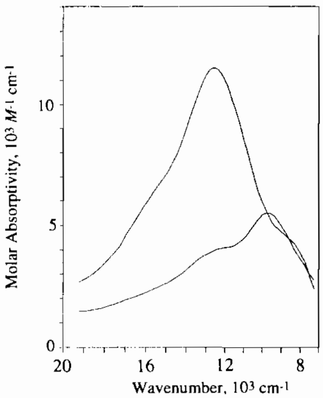

Fig. 2. Electronic absorption spectra of acetonitrile solutions of (a) 0.11 mM α**I**, 6.0 mM $QClO_4$; (b) 0.06 mM α**II**, 3.0 mM $QClO_4$.

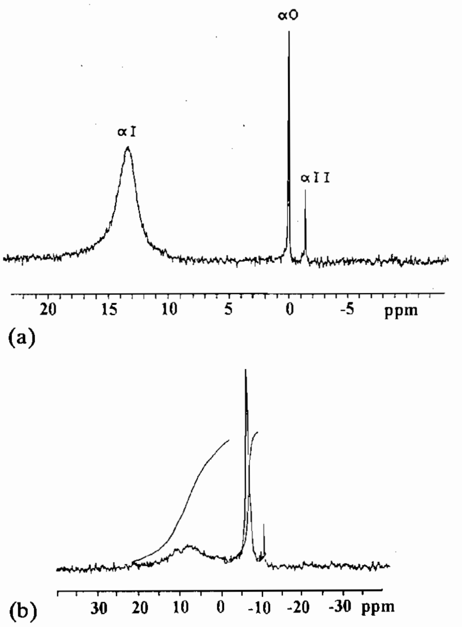

Fig. 3. (a) ^{31}P NMR spectrum of a solution prepared by comproportionation of α**0** and α**II**-H_2 in CD_3CN, followed by addition of 1.8 equiv. of 0.2 M QOH in 20% CH_3OH, 80% CH_3CN. Approximate concentration of α**I** produced is 9.6 mM. Temperature 297 K. (b) ^{31}P NMR spectrum of 2.5 mM α_1**I**, 0.1 M $QClO_4$ in CD_3CN. Temperature 297 K.

TABLE 2. ^{31}P NMR data for related molybdodiphosphates in aqueous and acetonitrile solutions at 297 K

Anion	Solvent[a]	Chemical shift (ppm) [linewidth (Hz)]	Reference
$[HP_2Mo_{18}O_{62}]^{5-}$ (α**0**-H)	AN	−0.1 [0.44]	this work
(α**0**)	AN	+0.1 [0.37]	this work
(α**0**)	aq	−3.4	13
	aq[b]	−2.8	14
	aq	−3	15
(α**I**)	AN	+13.4 [220]	this work
(α**II**-H_2)	AN	−1.9 [13]	this work
(α**II**-H)	AN	−1.3 [14], −2.3 [14]	this work
(α**II**)	AN	−1.4 [14]	this work
(α**II**-H_2)	aq[c]	−4.0 [1.8]	this work
	aq[d]	−3.8 [10]	this work
	aq[b]	−4.6	14
α_1-$[HP_2W_{17}MoO_{62}]^{5-}$ (α_1**0**-H)	AN	−8.6 [1.2], −9.3 [1.4]	this work
(α_1**0**)	aq	−11.4 [1.5], −12.3 [1.5]	1d
	aq	−12.2, −13	13
(α_1**I**-H)	AN	+3.8 [500], −5.7 [170]	this work
(α_1**I**)	AN	+8.4 [900], −6.6 [90]	this work
	aq	+6.3 [900], −9.2 [80]	1d

[a] AN, CD_3CN; aq, D_2O. [b] 323 K. [c] pH 0. [d] pH 9.6.

materials α**0** and α**II**) is observed for α**I** and its width is two orders of magnitude greater than that for the corresponding one-electron reduced $[PMo_{12}O_{40}]^{4-}$ Keggin anion (2.6 Hz at 297 K) [12]. The two-line spectrum for α_1**I** is similar to that previously reported for aqueous solutions [1d]. Chemical shifts and linewidths are affected by protonation as indicated in Table 2. Kozik *et al.* [1d] have demonstrated that the ^{31}P relaxation mechanism in aqueous solutions of α_1**I** and α_2**I** is dipolar in character since the ratio of the linewidths in the spectrum of each anion is approximately equal to the ratio of the two P...Mo^V distances raised to the sixth power. The correlation time, τ_c, for the dipolar interaction (at the limiting conditions $\omega_s^2\tau_c^2 \gg 1$, where ω_s is the Larmor precession frequency of the electron, *c.* 10^{12} for the 300 MHz spectrometer) [16] is given by the following equation

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{7}{15}\left(\frac{h}{2\pi}\right)^2 S(S+1)\gamma_s^2\gamma_I^2\tau_c r^{-6}$$

where $\mu_0 = 4\pi \times 10^{-7}$ kg m s^{-2} A^{-2}, $\gamma_s = -1.76 \times 10^{11}$ rad s^{-1} T^{-1}, $\gamma_I = 10.83 \times 10^7$ rad s^{-1} T^{-1} and $r = 3.459 \times 10^{-10}$ m. The rate of intramolecular electron hopping in α**I**, $\tau^{-1}_{(hopping)}$ is given by the difference between τ_c^{-1} for α**I** and α_1**I**, and is found to be 1.2×10^{10} s^{-1}. Since the ^{31}P NMR linewidths for α_1**I** in acetonitrile are similar to those in aqueous solution, it is possible to compare the electron hopping rate of α**I** in acetonitrile with that of the analogous tungstate, α-$[P_2W_{18}O_{62}]^{7-}$, in aqueous solution. The latter rate was determined by Kozik *et al.* [1d] to be 1.7×10^{11} s^{-1}, i.e. an order of magnitude faster than for the molybdate.

In an attempt to determine whether α**I** could be produced in aqueous solution a sample of a solution of α**II**-H_2 was generated by electrolysis in 0.1 M HCl. Aliquots of this solution were then transferred into 1.0 M $NaHCO_3$–NaOH buffer, pH 9.6, and cyclic voltammograms and ^{31}P NMR spectra were immediately recorded. The voltammograms showed no splitting of the initial two-electron redox wave of P_2Mo_{18}, but the NMR spectrum, recorded within 15 min, showed a broad resonance at +10.1 ppm as well as lines from α**II** (−3.8) and HPO_4^{2-} (+3.6), see Fig. 4. The same solution after 3 h showed only the HPO_4^{2-} resonance together with an unidentified line at −11.6 ppm. The transitory resonance at +10.1 ppm is attributed to α**I** (formed by partial oxidation) on the basis of linewidth and chemical shift, since it has been shown that apparent chemical shifts in acetonitrile are 3.1±0.1 ppm down-

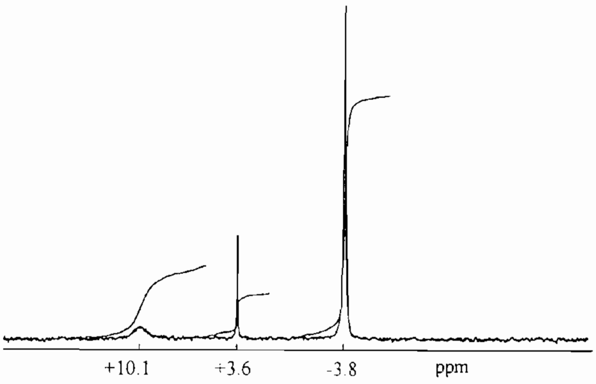

Fig. 4. ^{31}P NMR spectrum of a solution prepared by diluting 20 mM α**II**-H_2 into 1.0 M $NaHCO_3$/NaOH/D_2O buffer, pH 9.6. Spectrum recorded within 15 min after solution preparation. The resonances, in order of increasing chemical shift, are assigned to α**II**, HPO_4^{2-} and α**I**.

field from those of the same species in aqueous solution [12].

Sequential deprotonation of α**II**-H_2 in acetonitrile via addition of stoichiometric amounts of QOH permits observation of NMR spectra of α**II**-H and α**II**. As shown in Table 2, not only does δ diminish upon deprotonation, but the spectrum of α**II**-H consists of a symmetrical pair of lines, indicating a protonation-induced loss of the equatorial mirror plane of the Dawson structure (Fig. 5) for this species. A solution containing α**0**, α**I** and α**II**-H was prepared by electrolytic reduction of α**0** by two electrons, followed by addition of two equivalents of QOH, and reoxidation of the resulting solution by one electron. The ^{31}P NMR spectra of this solution were recorded at three temperatures and are shown in Fig. 6. These spectra demonstrate three significant points. First, the chemical shift and linewidth of the α**I** resonance are temperature-dependent as expected. The linewidth is 700 Hz at 252 K and 175 Hz at 333 K; δ decreases by *c.* 0.04 ppm deg^{-1} over the same temperature range. Second, the linewidth and chemical shift of the resonance for α**0** are unchanged between 252 and 333 K indicating that *inter*molecular electron transfer between α**I** and α**0** is slow, as observed earlier for the corresponding PMo_{12} species [13]. Third, the two resonances for α**II**-H are partially coalesced at 297 and 333 K. This behavior is interpreted in terms of a slow *intra*molecular proton transfer from one side of the anion's equator to the other. Kazansky and Fedotov [14] have argued on the basis of ^{17}O NMR that the two added electrons in α**II**(aq) occupy adjacent Mo sites on either side of the equatorial plane. We suggest that the proton in α**II**-H is bound to one of the oxygen atoms attached to an Mo^V atom, probably at an edge-shared junction as directly observed for β-$[H_6PMo_{12}O_{40}]^-$ [17]. The linewidth data can be analyzed to determine an approximate rate and activation energy for the proton transfer. A 297 and 333 K, $k \approx 0.8$ and 2.3 s^{-1}, respectively, and $E_a \approx 5.9$ kcal mol^{-1}. These values are the first to be determined for proton transfer on an oxometalate surface.

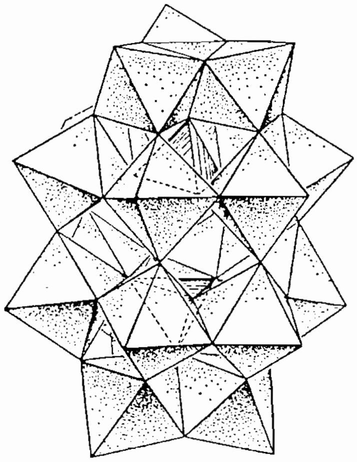

Fig. 5. Polyhedral representation (PO_4 tetrahedra and MoO_6 octahedra) of the Dawson structure observed for α-$[P_2Mo_{18}O_{62}]^{6-}$. Assuming D_{3h} symmetry (which is not strictly true, see ref. 5a), there are two types of molybdenum atoms, six axial (or 'cap') and twelve equatorial (or 'belt').

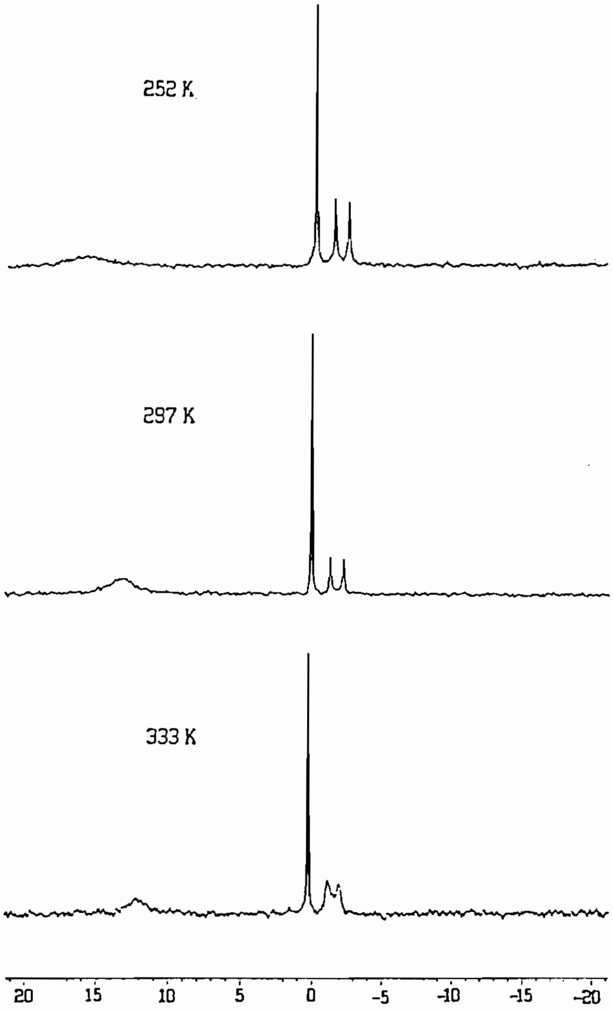

Fig. 6. ^{31}P NMR spectra of a mixture of α**0**, α**I** and α**II**-H, in CD_3CN (0.1 M $QClO_4$), recorded at three temperatures. Total heteropolyanion concentration 2.5 mM.

ESR spectroscopy

The ESR spectra of acetonitrile solutions of α**I** and α_1**I** at different temperatures are shown in Figs. 7 and 8, and parameters for these and related species are summarized in Table 3. Observation of an intense, relatively narrow ESR spectrum for α**I** at room temperature is unprecedented for a heteropoly blue species and indicates that intramolecular electron transfer is relatively slow, and that the electron is localized, although no hyperfine structure could be detected at 297 or 77 K. The orthorhombic spectra of α_1**I** and α_1**I**-H

TABLE 3. ESR parameters for some molybdate heteropoly blue species[a]

Anion	Temp. (K)	g	A (G)	$g_{\perp} > g_{\parallel}$	Ref.
α-$[P_2Mo_{18}O_{62}]^{7-}$	77	1.945($\perp$)		no	this work
(α**I**)		1.965($\parallel$)			
	297	1.940			
α_1-$[HP_2W_{17}MoO_{62}]^{6-}$	77	1.867(x)		no	this work
(α_1**I**-H)		1.897(y)			
		1.927(z)			
α_1-$[P_2W_{17}MoO_{62}]^{7-}$	77	1.888(x)	46	no	this work
(α_1**I**)		1.900(y)	46		
		1.933(z)	87		
	297	1.905	60		
α_2-$[P_2W_{17}MoO_{62}]^{7-}$	?	1.940($\perp$)	34.3	yes	18
(α_2**I**, aqueous soln)		1.919($\parallel$)	73.2		
	?	1.932			
α-$[PMo_{12}O_{40}]^{4-}$	10	1.949($\perp$)	27.2	yes	19
		1.938($\parallel$)	60.7		
α-$[PW_{11}MoO_{40}]^{4-}$	297	1.940($\perp$)	34.3	yes	20
		1.914($\parallel$)	73.1		
$[Mo_6O_{19}]^{3-}$	77	1.930($\perp$)	34.5	yes	21
		1.919($\parallel$)	80.5		
$[MoW_5O_{19}]^{3-}$	10	1.924($\perp$)	39.7	yes	19
		1.917($\parallel$)	85.2		

[a] As tetra-n-butylammonium salts in acetonitrile solution, except where noted.

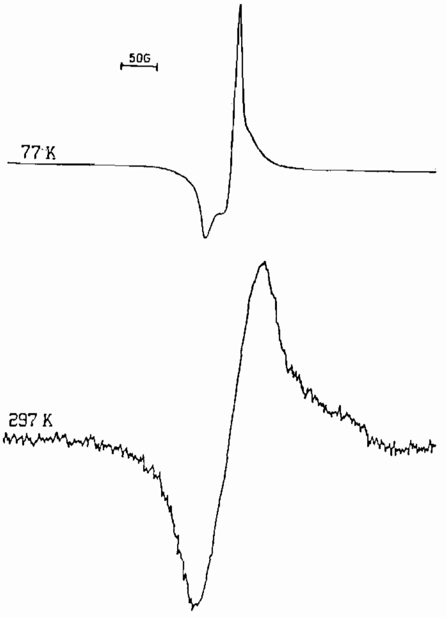

Fig. 7. X-band ESR spectra of 9.6 mM α**I** in acetonitrile, 0.1 M $QClO_4$ recorded at 297 and 77 K.

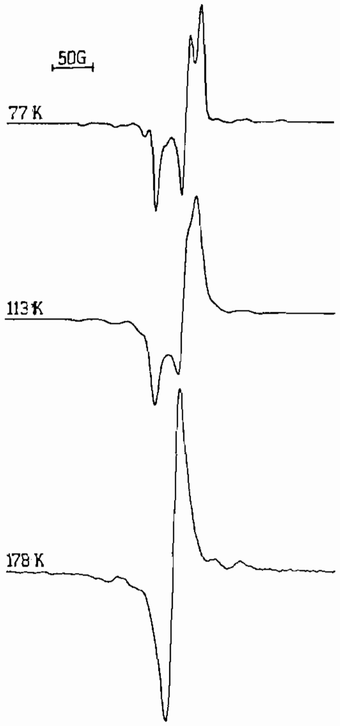

Fig. 8. X-band ESR spectra of 2.5 mM α_1**I** in acetonitrile recorded at 77, 113 (isopentane/liquid nitrogen) and 178 (toluene/liquid nitrogen) K.

at 77 K show that the central and upfield lines move closer together upon deprotonation. The proton is most probably bonded to an edge-sharing oxygen of the Mo^VO_6 octahedron. If g_z is assumed to be aligned with the terminal Mo---O bond, removal of a proton will mainly affect g_x and g_y. Accordingly, the most downfield line is assigned to g_z and the remaining two to g_x and g_y. These assignments are confirmed by the temperature variation of the spectrum of α_1**I** which shows coalescence into an axial spectrum ($g_x + g_y \rightarrow g_{\perp}$) at *c.* 113 K. The g and hyperfine parameters of α_1**I**, determined by simulation and reported in Table 3, may be used to determine the extent of electron delocalization using the following equation

$$\beta_2{}^2 = \frac{7}{6}\,\frac{A_\perp - A_\parallel}{P} - \frac{7}{6}(2.0023 - g_\perp) + \frac{5}{12}(2.0023 - g_\parallel)$$

where $P = 2.0023\beta_e g_n \beta_n \langle r^{-3}\rangle = -55\times10^{-4}$ cm^{-1} and the orbital coefficient β_2 is defined by

$$|B_2\rangle = \beta_2|\mathrm{d}_{xy}\rangle - \beta_2{}'|\phi_{\mathrm{b}2}\rangle$$

and $\phi_{\mathrm{b}2}$ is a linear combination of ligand (oxygen) orbitals of appropriate symmetry. The value of β calculated in this way is 0.84, identical with that found for α-$[\mathrm{PW_{11}Mo^VO_{40}}]^{4-}$ [19].

Che *et al.* [21] have compared the relative magnitudes of $g_\perp > g_\parallel$ for Mo^V complexes and have noted (and rationalized) that $g_\perp > g_\parallel$ when all the ligands are bonded through oxygen. As shown in Table 3, this is true for the reduced polyoxomolybdates, with the exception of α**I** and α_1**I**. Since the Mo^V atom in α_1**I** occupies an equatorial site, we conclude that α**I** is reduced at an equatorial molybdenum atom also. An analogous conclusion, reduction at an equatorial site, has previously been drawn for α-$[\mathrm{P_2W_{18}O_{62}}]^{7-}$ [1d].

Note that in contrast to α_1**I**, the g and A parameters for α_2**I** and α-$[\mathrm{PW_{11}MoO_{40}}]^{4-}$ are virtually identical, in keeping with the very similar site-symmetries for Mo in the last two anions.

Conclusions

Protonation-driven disproportionation, i.e.

$$2\alpha\mathbf{I} + 2\mathrm{H}^+ \rightarrow \alpha\mathbf{0} + \alpha\mathbf{II}\text{-}\mathrm{H}_2$$

is a common feature of heteropolyanion–heteropoly blue chemistry. Effective disproportionation constants, K_{disp}, can be derived from the differences between the first and second reduction potentials of the heteropolyanion under conditions where none of the reduced species is believed to be protonated. These conditions can normally be achieved by raising the pH to a level beyond which the reduction potentials no longer change. Table 4 compares data for α**0** with those for other polyoxometalates. We note that disproportionation becomes more favorable as the anion charge (basicity) increases and, for species of the same charge and structure, is less favored for tungstates. The apparent disproportionation constant for α-$[\mathrm{PMo_{12}O_{40}}]^{4-}$ is notably solvent- (or counter cation-) dependent and indicates that the simple proton-driven equation above is an over-simplification. Preferential solvation or ion-pairing* involving the two-electron reduced species cannot be excluded from consideration, especially when the anion charge is high. That the existence of α**I** in aqueous solution cannot be demonstrated by electrochemical measurements at high pH (even though its transient presence in such solutions is shown by NMR) should come as no surprise considering the small K_{disp} observed in acetonitrile.

TABLE 4. Apparent disproportionation constants for one-electron heteropoly blues derived from electrochemical data

Anion	Solvent	ΔE (V)^a	K_{disp}	Reference
α-$[\mathrm{PMo_{12}O_{40}}]^{4-}$	H$_2$O/diox^b	0.21	3×10^{-4}	22
	CH$_3$CN	0.44	3×10^{-8}	10
α-$[\mathrm{PW_{12}O_{40}}]^{4-}$	CH$_3$CN	0.52	1×10^{-9}	this work
α-$[\mathrm{P_2Mo_{18}O_{62}}]^{7-}$	CH$_3$CN	0.15	3×10^{-3}	this work
$[\mathrm{Mo_6O_{19}}]^{3-}$	CH$_3$CN	0.85	3×10^{-15}	21
$[\mathrm{W_6O_{19}}]^{3-}$	CH$_3$CN	$>0.55^c$	$<5\times10^{-10}$	23

^{a}Difference between the first and second one-electron reduction potentials. ^{b}50% water, 50% *p*-dioxane. Counter cation not specified, but presumably Na$^+$ from buffer. ^{c}Second reduction step not observed.

For a one-electron reduced heteropoly blue species the ^{31}P NMR linewidth of α**I** is relatively large and its ESR linewidth is relatively narrow at room temperature. These factors are of course correlated, and indicate that the unpaired electron is not relaxing quickly, and is more tightly trapped than is the electron of $[\mathrm{PMo_{12}O_{40}}]^{4-}$. The presence of a single NMR line and the magnitudes of the ESR g values suggest that the electron is delocalized (or is rapidly hopping) between a mirror-plane-related pair of equatorial molybdenum atoms of the Dawson structure, and presumably undergoes much slower hopping to other equatorial molybdenums.

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*Partial stabilization of α**I** was first noted in dimethylformamide solution in the *absence* of Na$^+$ cations [6].

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