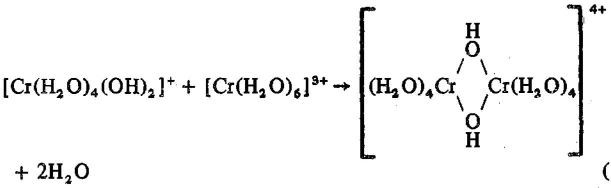
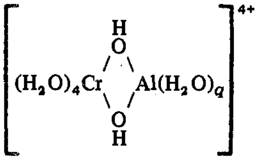
ecules readily lose hydrogen ions, which make the solution strongly acidic. Assuming that there are six water molecules in the complex, the reaction is written for chromium(III) as (1). The coordinated hydroxo group is a powerful complexing

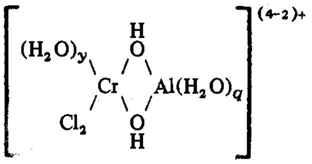
$$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H_3O^+ \rightleftharpoons [Cr(H_2O)_4(OH)_2]^+ + H_3O^+ \rightleftharpoons \text{etc.} \qquad (1)$$

agent and may displace a water molecule from an adjacent complex ion. This process is known as olation[5] (eq 2). There may be one, two, or three "ol bridges" between the two metal ions. If the remaining coordinated water molecules lose hydrogen ions, further olation can take place, leading to the formation of large aggregates, even up to colloidal dimensions.


(2)

The removal of aluminum from zeolites by chromium(III) chloride probably takes place through the formation of ol bridges in the pores of the zeolite. It is reasonable to picture the hydrated chromium(III) ion entering 5-Å pores (eight-membered rings) by temporary replacement of aquo groups. It is postulated that, once inside the pore, the aquochromium ion complexes with the hydrolyzed aluminum ions to form complexes of the type





which then diffuse out of the pore. Once outside the pore, olation with the excess chromium ions in the solution proceeds to the formation of particles containing five or six chromium ions for each aluminum ion. Aluminum removal must stop when all of the chromium is tied up in these large complexes or when the pH of the solution reaches a value which limits the number of hydroxo groups so much that olation no longer takes place.

Acknowledgment. The assistance of J. M. Crowley with much of the laboratory work and of G. T. Kokotailo with x-ray crystallinity studies is acknowledged with thanks.

Registry No. Erionite, 12510-42-8; clinoptilolite, 12173-10-3; phillipsite, 12174-18-4; aluminum hydroxide, 21645-51-2; chromium(III) chloride, 10025-73-7; chromium nitrate, 13548-38-4; potassium chromium sulfate, 10141-00-1; hydrochloric acid, 7647-01-0; EDTA, 60-00-4; Al, 7429-90-5.

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Reactions of Molybdates with Polyphosphates. 1. Spectrophotometric and Electron Paramagnetic Resonance Studies of Molybdenum(V)–Pyrophosphate Complexation

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In the course of a general study of mediation of biologically important phosphorylation and hydrolysis reactions by polyvalent transition metal–oxo ions, we have investigated the formation of complexes between pyrophosphate and Mo species. Previously, complex formation had been established, but neither formulations of the complexes nor oxidation states of the Mo had been settled. Treatment of $Mo_2O_4^{2+}$ with aqueous solutions of polyphosphate ions gives rise to complexes exhibiting an absorption peak in the near-ultraviolet region of the spectrum which fades away rapidly in the presence of oxidants such as oxygen, perchlorate ion, and nitrate ion. In the case of pyrophosphate ion, and thus far only in that case, an EPR signal is observed exhibiting ^{31}P hyperfine splitting. Isotopically enriched ^{95}Mo samples exhibit six hyperfine lines each split into five superhyperfine lines by the interaction of an unpaired d electron with four equivalent phosphorus atoms. Bis(pyrophosphate) complexes of $Mo_2O_4^{2+}$ are formed at pH 4.5 and dissociate to an extent of only 5% to form $MoO_2(P_2O_7)_2H_n^{n-7}$. Values are $g = 1.952$, $a(Mo)/g\beta = 56$ G, and $a(P)/g\beta = 10$ G at pH 4.5 and room temperature. Frozen solutions of ^{95}Mo complexes gave EPR spectra characterized by small g anisotropy and large hyperfine anisotropy. No ^{31}P hyperfine lines are observed in frozen solutions. Solutions containing complexes of $Mo_2O_4^{2+}$ with triphosphate ion, ATP, and ADP give no EPR signals under comparable conditions.

Introduction

Molybdenum in oxidation states VI, V, and IV is a powerful catalyst for the reduction of oxy ions such as nitrates and perchlorates[1,2] and of nitrogen[3] and also for the enzymatic reduction of NO_3^- and N_2 and oxidation of xanthine, purines, SO_3^{2-}, and aldehydes.[4,5] It also catalyzes the hydrolysis of ATP[6]. The nature and reactivity of complexes of Mo(IV), -(V), and -(VI) with oxy ions is thus of fundamental significance. Recently oxidations of VO^{2+} have been coupled directly to polyphosphate hydrolyses.[7] These observations have prompted us to investigate interactions of another d^1 species, Mo(V), with polyphosphates. A primary objective is to produce labile P(V) by increasing the electron density on phosphorus(V) atoms.

This report describes a complex of Mo(V) with pyrophosphate which exhibits interaction of the d^1 electron with the ^{31}P nucleus. Although polyphosphates form complexes with most metal ions[8–10] and electroanalytical studies[11,12] reveal complex formation of molybdenum and pyrophosphate in aqueous solution, formulas and metal oxidation states in

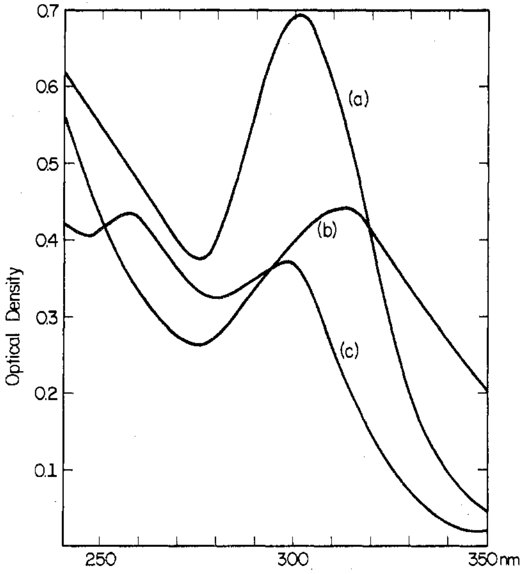

Figure 1. Uv spectra of aqueous Mo(V) species: (a) molybdenum(V) dimer–pyrophosphate system, $[\mathrm{Mo_2O_4}^{2+}] = 0.000\,20$ M, $[\mathrm{Na_4P_2O_7}]_0 = 0.003$ M, 25 °C, pH 4.5, $\mu = 0.1$ (NaCl); (b) hydrolysis product of the molybdenum(V) dimer, $[\mathrm{Mo_2O_4}^{2+}]_0 = 0.000\,20$ M, 25 °C, pH 4.5; (c) molybdenum(V) dimer in 1 N HCl, $[\mathrm{Mo_2O_4}^{2+}] = 0.000\,20$ M, 25 °C.

such complexes have not been determined. Moreover, we have seen reports of neither EPR studies on molybdenum(V)–pyrophosphate complexes nor ^{31}P superhyperfine splittings for molybdenum bound to phosphorus through an oxide bridge. Since the Mo(V) complexes reported here are particularly susceptible to oxidation and since common buffers form complexes with Mo(V),[13,14] all solutions were kept and handled under an argon atmosphere with only the pyrophosphate under study as a buffering agent. Rapid oxidation of the Mo(V) solutions with $\mathrm{ClO_4}^-$ and $\mathrm{NO_3}^-$ required use of HCl and NaCl to adjust pH and ionic strength. In such solutions $\mathrm{Mo_2O_4}^{2+}$ is still an aquo ion.[15,16]

Experimental Details

Argon gas (99.99%) scrubbed with boiled deionized water proved sufficient to prevent oxidation of Mo(V) in the solutions. All solutions were purged with argon and stored and used under an argon atmosphere. The pH, adjusted with 0.1 M HCl and NaOH solutions, was measured with a Model LSX Sargent-Welch pH meter. Electron paramagnetic resonance measurements employed a Varian E-9 spectrometer operating at ~9.5 GHz and 100-kHz modulation. Powder samples and frozen solutions at 77 K were contained in quartz EPR tubes of 3-mm bore. All liquid samples were contained in Varian flat quartz aqueous solution cells. Optical measurements employed a Cary 14RI spectrophotometer, usually with a specially designed optical cell having two sample vessels in which the solutions were deaerated by repeated freezings before mixing.

Molybdenum(V) dimer solutions were prepared by reduction of $\mathrm{Na_2MoO_4}$ by shaking it over $\mathrm{Hg^0}$ in 3 M HCl,[17] filtering off $\mathrm{Hg_2Cl_2}$ and Hg, and storing cold under Ar. The $\mathrm{Mo_2O_4}^{2+}$ purity was checked spectrophotometrically, principally by means of its well-characterized absorption maxima at 254 and 293 nm,[15] where ϵ is 1999 and 1727 (M cm)$^{-1}$, respectively. Oak Ridge National Laboratory supplied $^{95}\mathrm{MoO_3}$ (99%) used to enrich $\mathrm{Mo_2O_4}^{2+}$ in ^{95}Mo. Analytical grade $\mathrm{Na_3PO_4}$, $\mathrm{Na_4P_2O_7 \cdot 10H_2O}$, and $\mathrm{Na_5P_3O_{10}}$ were used without purification. Adenosine triphosphate (ATP) and adenosine diphosphate (ADP) were purchased from Nutritional Biochemicals.

Results

Absorption Spectra. In 3 M HCl $\mathrm{Mo_2O_4}^{2+}$ exhibits two peaks at 293 and 254 nm. As the pH is raised above 2.5, hydrolysis changes the spectrum to a single peak at 315 nm. Addition of pyrophosphate or tripolyphosphate to $\mathrm{Mo_2O_4}^{2+}$ solutions increases the ultraviolet absorbance dramatically as shown in Figure 1. The complex forms in the range $2 \leq \mathrm{pH} \leq 9$. At $\lambda_{\max}$ 302 nm, ϵ is 3.52×10^3 (M cm)$^{-1}$ for $\mathrm{Mo_2O_4(P_2O_7)_2}^{6-}$ where solutions obey Beer's law (Figure 2). Determination of the formula of the complex as $\mathrm{Mo_2O_4(P_2O_7)_2}^{6-}$ is illustrated in Figure 3. Despite all precautions and rigorous use of fresh solutions, poor precision was obtained at low $\mathrm{P_2O_7}^{4-}$; we infer that the aquo ion of $\mathrm{Mo_2O_4}^{2+}$ is less stable than the complex. The stability constant $K \equiv [\mathrm{Mo_2O_4(P_2O_7)_2}^{6-}]/[\mathrm{Mo_2O_4}^{2+}][\mathrm{P_2O_7}^{4-}]^2$ is approximately 10^{10} M^{-2} at 25 °C. The instability of $\mathrm{Mo_2O_4}^{2+}$ at high pH precluded a clear result from a Job plot.

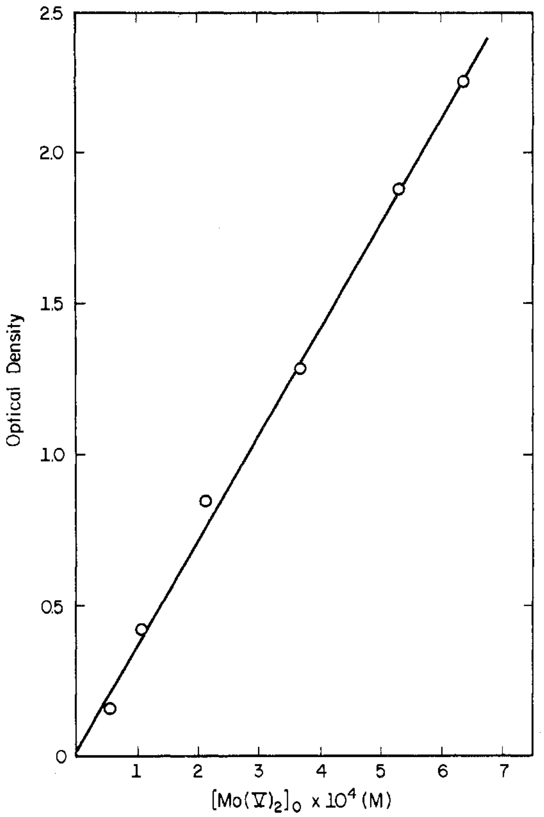

Figure 2. Absorbance change of the dimer complex at 300 nm with respect to the concentration of $\mathrm{Mo_2O_4}^{2+}$, at $[\mathrm{Na_4P_2O_7}]_0 = 0.0248$ M, 25 °C, $\mu = 0.1$ (NaCl), and pH 4.5; measured 10 min after preparaton.

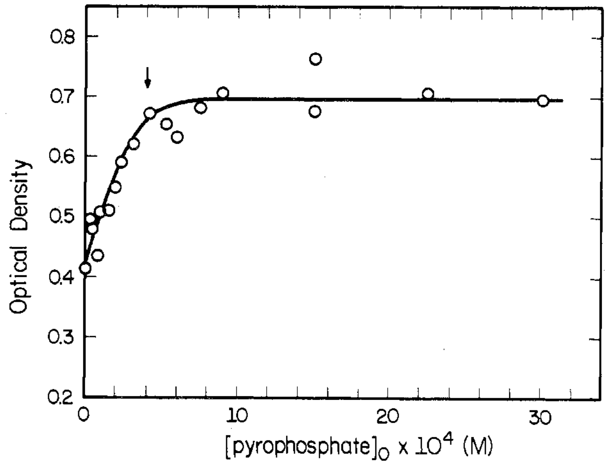

Figure 3. Absorbance of the dimer complex at 300 nm vs. concentration of pyrophosphate: mole ratio plot with $[\mathrm{Mo_2O_4}^{2+}]_0 = 0.0002$ M, at 25 °C, pH 4.5, and $\mu = 0.1$ (NaCl).

In the pH range used $\mathrm{Mo_2O_4}^{2+}$, which is stable at the low pH extreme, hydrolyzes in the absence of pyrophosphate (Figure 1) and forms a complex in the presence of pyro-

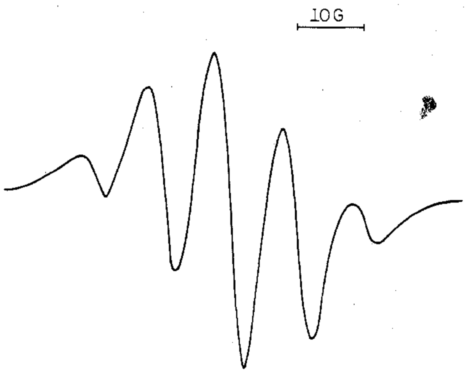

Figure 4. First-derivative EPR spectrum of the naturally occurring molybdenum(V)-pyrophosphate complex at room temperature, $[Mo_2O_4^{2+}] = 0.003$ M, $[Na_4P_2O_7] = 1.1 \times 10^{-1}$ M, and pH 4.5.

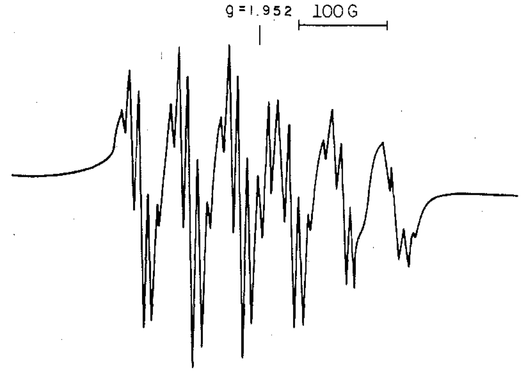

Figure 5. First-derivative EPR spectrum of the isotopically enriched molybdenum(V)-95-pyrophosphate complex at room temperature, $[^{95}Mo_2O_4^{2+}] = 0.0035$ M, $[Na_4P_2O_7] = 0.076$ M, and pH 4.5.

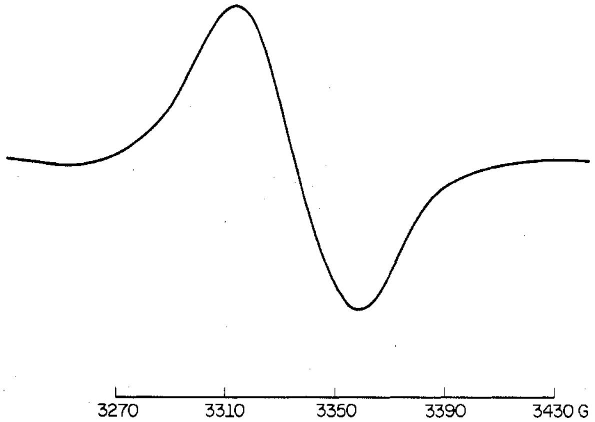

Figure 6. First-derivative EPR spectrum of the molybdenum(V)-pyrophosphate complex (natural isotopic abundance) at 77 K, $[Mo_2O_4^{2+}]_0 = 0.012$ M, and $[Na_4P_2O_7]_0 = 0.075$ M. pH is 4.5 when it is liquid.

phosphate. $H_2P_2O_7^{2-}$ is the principal uncoordinated pyrophosphate species present in solution over this range of pH. No attempt was made to determine the degree of protonation of the complex in question.

EPR Measurements. The Mo(V) dimer is diamagnetic and does not give an EPR signal in the range $1 \leq pH \leq 10$. Monomeric Mo(V) is paramagnetic but dimerizes very rapidly in this pH range.[18] Samples were prepared directly by mixing pyrophosphate and $Mo_2O_4^{2+}$ solutions under argon. The rate of complex formation is too fast to measure by a stopped-flow technique under these conditions. A five-line EPR signal appeared (Figure 4) for solutions of naturally occurring Mo(V) and pyrophosphate after the preparation of the samples at pH 4.5. The signal height developed with time, usually reaching a maximum after 20–60 min. Since the system is gradually oxidized by a trace amount of oxygen in the solution, the signal height then gradually decreased with time a few hours after preparation.

Signals were observed at between pH 2.4 and pH 8.0 but not at pH 1.0. At pH 10 some precipitation occurred, probably caused by hydrolysis of the molybdenum dimer. Maximum signals occurred around pH 4.5; at pH 8.0 the signal diminished during the course of a measurement. Hence, most of the experiments were carried out at pH 4.5. Quantitative intensity analysis of the signal employed an aqueous $VOSO_4$ solution as a standard solution;[19] it revealed the amount of Mo(V) monomer to be about 5%. That is, 2.5% of the molybdenum dimer complex dissociates at room temperature when $[Mo^{V}_2]_0 = 0.003$ M and $[P_2O_7^{4-}]_0 = 0.11$ M.

Although the EPR spectra of the solution gave five lines at room temperature, it was not clear whether the signal arose from a monomer or dimer complex. Naturally abundant molybdenum consists principally of isomers with zero nuclear spin. Magnetic isotopes ^{95}Mo and ^{97}Mo would be expected to produce six extra line groups but each would be very weak—<5% of the main line group intensity. However, rather than search for weak features we used labeled ^{95}Mo ($I = ^5/_2$) to differentiate between monomeric and dimeric complexes.

EPR-active dimers of Mo(V), tumbling rapidly in solution, would give 11-line signals like those of the molybdenum(V) dimer–glutathione complex.[19] A monomer would have a six-line spectrum.[20,21] Therefore, we prepared a sample solution of $Mo_2O_4(P_2O_7)_2^{6-}$ enriched in ^{95}Mo. Figure 5 shows that the hyperfine splitting of its EPR spectrum at room temperature consists of six lines with five superhyperfine lines superimposed on each. This result indicates that the complex which gives EPR signals is a molybdenum(V) monomer complex. The superhyperfine splitting can be ascribed to the electron spin coupling of Mo(V) and ^{31}P (nuclear spin $I = ^1/_2$) and suggests that four effectively equivalent phosphates are interacting with one molybdenum atom. At room temperature in a liquid solution, the species is characterized by a spin Hamiltonian

$$\mathcal{H} = \beta g \mathbf{B}\cdot\mathbf{S} + a_{Mo}\mathbf{I}_{Mo}\cdot\mathbf{S} + \sum_{P} a_P \mathbf{I}_P\cdot\mathbf{S}$$

with spin numbers $S = ^1/_2$, $I_{Mo} = ^5/_2$, and $I_P = ^1/_2$. From the solution EPR spectrum in Figure 5 we estimate an average g $(= ^1/_3(g_x + g_y + g_z))$ to be 1.95 and the hyperfine splitting parameters to be $a_{Mo}/g\beta = 56$ G and $(a_P/g\beta) = 10$ G. There are several papers which report the dissociation of the dimer complex with an oxygen atom at the coordination site as a ligand, but we find none which reports observation of phosphorus hyperfine interaction with Mo(V).[22]

To observe the EPR of a frozen solution prepared with naturally occurring Mo(V), we allowed the pH 4.5 solution with excess of pyrophosphate to stand in a 3-mm bore quartz cell for 20 min after preparation and then quickly dipped it into liquid nitrogen. The frozen sample gave a broad unresolved signal at $g = 1.95$ as shown in Figure 6.

Structure in the EPR spectrum (see Figure 7) of the corresponding frozen solution containing ^{95}Mo (99% purity) arises from partial resolution of both **g** and ^{95}Mo **A** anisotropy. The superhyperfine splitting owing to the four ^{31}P nuclei is evidenced only in the breadth of the individual metal hyperfine lines. To analyze the spectrum, we first selected probable assignments of certain features in the spectrum to estimate effective hyperfine splittings of 90, 55, and 24 G along the three principal molecular axes, respectively. Then, starting with these values for a first trial, we produced successive computer-generated simulations[23] with parameter adjustment

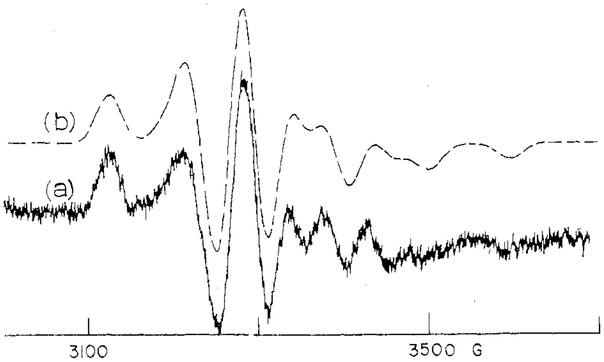

Figure 7. (a) First-derivative EPR spectrum of the isotopically enriched molybdenum(V)-95-pyrophosphate complex at 77 K, $[^{95}Mo_2O_4{}^{2+}] = 0.0035$ M, and $[Na_4P_2O_7] = 0.076$ M. pH is 4.5 when it is liquid. (b) Computer-generated simulation for comparison. $g_z = 1.9335, g_x = 1.9547, g_y = 1.9677$, $|A_z| = 0.0085$ cm^{-1}, $|A_x| = 0.0044$ cm^{-1}, $|A_y| = 0.0026$ cm^{-1}, frequency 9.088 GHz, line shape function is $\exp[-(B - B_0)^2/2W^2]$, and $W = 15$ G.

until the simulated and experimental spectra were in good agreement (see Figure 7). The best fit (subjectively judged) occurred for Gaussian line shapes of fixed, isotropic 30-G width (35-G full width at half-height; 30 G between turning points of the first derivative) and with parameters g_x, g_y, g_z, $|A_x|$, $|A_y|$, and $|A_z|$ of 1.9547, 1.9677, 1.9335, 0.0044 cm^{-1}, 0.0026 cm^{-1}, and 0.0085 cm^{-1}, respectively, in the spin Hamiltonian

$$\mathcal{H}_{\text{spin}} = (g_xB_x\beta + A_xI_x)S_x + (g_yB_y\beta + A_yI_y)S_y + (g_zB_z\beta + A_zI_z)S_z$$

The isotropic 30-G line width and the lack of further resolution are consistent with the proposition that the ^{31}P splitting just resolved in the isotropic solution spectrum of Figure 4 and 5 is perhaps somewhat but not strongly anisotropic; it is not possible to deduce whether the four phosphorus atoms are chemically equivalent.

The EPR signal intensity was measured quantitatively as a function of initial concentration of $Mo^V{}_2$ in excess pyrophosphate. Since the solution of $Mo^V{}_2$ and pyrophosphate is unstable to oxidation in the presence of a trace of air, the solution was frozen in liquid nitrogen 20 min after preparation for measurement of the quantity of monomer complex. The results (Figure 8) show that the concentration of monomer complex is almost proportional to the square root of the $[Mo^V{}_2]_0$. However, the straight line does not pass through the origin; the dissociation of the dimer complex may yet be incomplete after 20 min especially when the $Mo^V{}_2$ concentration is dilute, or some oxidation of Mo(V) may occur and lead to a positive intercept on the $[Mo(V)]^{0.5}$ axis.

The EPR signal (developed after 100 min) has also been measured as a function of pyrophosphate concentration. Figure 8 shows that the concentration of monomer is roughly proportional to $[H_2P_2O_7{}^{2-}]$, again with a positive intercept on the concentration axis. The slow rate of production of the monomer, coupled to uncertainty concerning oxidation of Mo(V) complexes, makes an accurate quantitative study of the monomer–dimer equilibrium unfeasible at this time. Nevertheless, the crude results depicted in Figure 8 do confirm the EPR evidence for formation of a bis(pyrophosphate)–molybdate(V) complex.

Reactions of $Mo_2O_4{}^{2+}$ with Other Phosphates. Immediately upon mixing ADP solutions with solutions of $Mo_2O_4{}^{2+}$ in 1 M HCl, we saw an orange precipitate which analysis showed to have an ADP:Mo_2O_4 ratio of 4:3. Dilute ADP and $Mo_2O_4{}^{2+}$, stirred vigorously, yielded hygroscopic precipitates containing a 1.1:1 ratio. Precipitates also resulted from addition of ATP to $Mo_2O_4{}^{2+}$ solutions, but they redissolved.

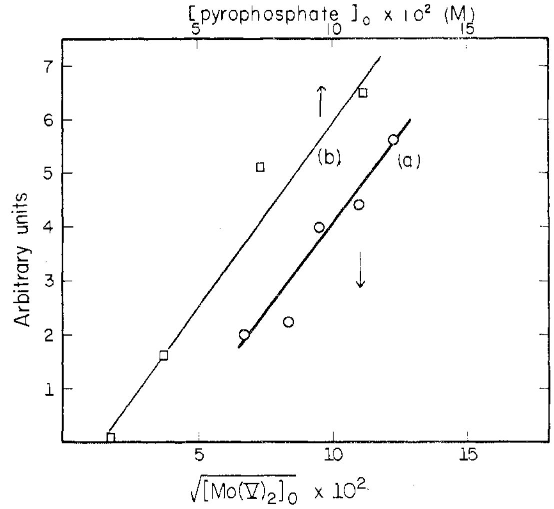

Figure 8. (a) Amount of monomer complex in frozen samples as determined by EPR measurement at 77 K and $[Na_4P_2O_7]_0 = 0.0075$ M. pH is 4.5 when it is liquid. (b) Amount of monomer complex in solution samples as determined by EPR measurement at room temperature, $[Mo_2O_4{}^{2+}]_0 = 0.0055$ M, and pH 4.5. Signals were measured at 100 min after preparation of solutions.

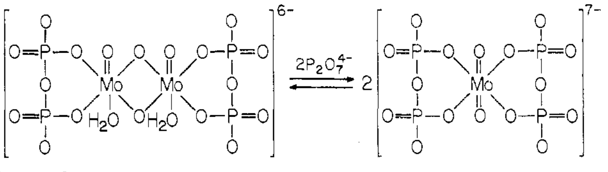

Figure 9. Formation of the molybdenum(V)-pyrophosphate monomer. The monomer structure is not necessarily precisely as shown: e.g., O=Mo=O could just as well be O=Mo–OH$_2$.

The ATP and ADP solutions and the two ADP powders exhibited no EPR activity and were not further examined in this study. Even though both pyrophosphate and tripolyphosphate solutions with $Mo_2O_4{}^{2+}$ have identical uv spectra, implying almost identical complex formation, the tripolyphosphate is unlike pyrophosphate but like ATP and ADP in giving Mo complexes with no EPR signal. Of all of the phosphates examined, only pyrophosphate appears to cleave $Mo_2O_4{}^{2+}$ to a discernible extent.

Discussion

The six-line hyperfine splitting for the molybdenum(V)-95–pyrophosphate complex strongly suggests the EPR-active complex to be monomeric. And since every main line is separated into five superhyperfine lines by interaction of Mo with the pyrophosphate, it is likely that two pyrophosphates are coordinating to Mo(V). We envisage a dissociation equilibrium like that shown in Figure 9.

The EPR data strongly imply the structure of the EPR-active species in solution to remain unchanged in frozen solution; the g and a_{Mo} values of the liquid solution are essentially identical with the averages $\langle g\rangle = (g_x + g_y + g_z)/3$ and $\langle A\rangle = (|A_x| + |A_y| + |A_z|)/3$ of the frozen solutions. We infer, too, that A_x, A_y, and A_z have the same signs. The anisotropies of both **g** and **A** are reasonable for a molecule of mainly axial geometry but with rhombic distortion, as one might propose for a monomer of the general sort depicted in Figure 9. The moderate ^{31}P superhyperfine structure, the substantial ^{95}Mo hyperfine splittings, and the quite substantial values of Δg ($g_{x,y,z} - 2.0023$), much like those found in compounds of VO^{2+} ion,[24,25] would all point to a spin distribution fairly well, but not entirely, localized on the metal center.

The tripolyphosphate complex with $Mo_2O_4{}^{2+}$ has no extra coordination site when two tripolyphosphates coordinate to

$Mo_2O_4^{2+}$. On the other hand, the pyrophosphate complex has two coordination sites where water can coordinate; see Figure 9. The mechanism for cleavage of the oxo bridge of the molybdenum dimer is not clear, but an attractive possibility is that another pyrophosphate ligand could use these extra sites to make a transient complex, which could then break at the oxo bridges to form monomers.

Several papers report the dissociation of $Mo_2O_4^{2+}$ dimers.[4] Two classes of dissociation mechanism appear possible. For molybdenum(V) complexes with cysteine,[20,21] aminoethanethiol, and ethanedithiol,[20] the dissociation of molybdenum(V) dimers occurs in moderately basic solution and the participation of OH^- in the breaking of oxygen bridges to form a paramagnetic monomer is proposed. On the other hand, the monomer complex forms in acidic solution by the simultaneous dissociation of the dimeric complex with proton catalysis. Tartaric,[14] gluconic, and citric[4] acids give small amounts of monomer at or near pH 7.0. These ligands coordinate to molybdenum through oxygen atoms. Spence[4] pointed out that complexes with these ligands have low *g* values, reflecting a much smaller degree of electron delocalization onto the ligands as opposed to thio ligands. The pyrophosphate system belongs to the second class if we use the criteria of oxygen ligation, low *g* values, and dissociation at low pH. However, the superhyperfine splitting by phosphorus ligands clearly indicates some electron delocalization onto the ligands. It appears also that cleavage of the oxo bridge of the pyrophosphate dimer complex is not by OH^- as is the cleavage of the cysteine dimer complex.

The sensitivity of polyphosphate complexes of $Mo_2O_4^{2+}$ to oxidation, combined with the labilization of the dioxo-bridge bond reported here, suggests that further study would be useful to ascertain whether monomers of Mo(V) polyphosphates are reactive species in redox processes as well as to obtain more precise information on the several equilibria present.

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Registry No. Mo, 7439-98-7; $H_4P_2O_7$, 2466-09-3.

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Nonempirical Valence-Electron Calculations on the Group 3B Monohalides

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The nonempirical valence-electron (NEVE) method for molecular orbital calculations on molecules containing heavy atoms has been extended to include fourth-row atoms in a minimum STO basis calculation. Unlike many MO methods in current use, the NEVE method allows comparisons down the periodic table. The present study illustrates this for the monohalides (F, Cl, Br, I) of the group 3B elements (B, Al, Ga, In). The results show trends in calculated properties which generally agree with the expectations of chemical intuition. The computational economy of the method, together with the good agreement with available all-electron ab initio results, indicates that the NEVE method should be of use in studies on a variety of inorganic systems.

Introduction

The development of valence-electron LCAO molecular orbital methods of reasonable economy and accuracy for use on molecules containing heavy atoms has not been rapid. The established semiempirical methods based on the EH and CNDO approximations have generally been unable satisfactorily to represent molecules containing atoms which differ markedly in characteristics such as atomic number or the number of valence electrons. This has meant that inorganic systems in particular have been poorly served by semiempirical calculations.

The need to account for core–valence interactions, both intra- and interatomic, is central in developments directed to these problems. Accurate model atomic potentials have recently been calculated by Bonifacic and Huzinaga[1] for use in molecular calculations. Klimenko and Dyatkina[2] have used a simple core pseudopotential and an orthogonalized AO basis in calculations on ClF. Horn and Murrell[3] have calculated effective atomic core charges as the basis of a simple model potential for valence-electron calculations on H_2S and SiH_4. Switalski and Schwartz[4] have used a simple valence-only atomic core potential model in calculations on polyatomic molecules containing first-row atoms. Ewig, Coffey, and Van Wazer[5] have used a similar method for calculations on the phosphorus halides, PF_3 to PI_3.

The NEVE Method

The nonempirical valence-electron (NEVE) method developed in this laboratory accounts for the core-valence interactions in a very simple manner. In earlier versions of the method,[6,7] this involved the addition of a core-correction energy