sented as Figure 4 shows that ratios of quadrupole coupling constants in the same chain have a regular dependence on the methyl substitution of the ammonium counterion. For Figure 4A the ratios of splittings $(\Delta\nu_1/\Delta\nu_{10})$ and $(\Delta\nu_2/\Delta\nu_{10})$ from the decylsulfate chain in these nematic phases show a maximum value for the dimethylammonium counterion and rather similar minimum values for the ammonium and tetramethylammonium counterions. As seen in Figure 4B the magnitude of the ratio is always larger for the decanol chain but again a maximum in the ratio occurs with two methyl groups. In Figure 4C the ratios $(\Delta\nu_2/\Delta\nu_1)$ and $(\Delta\nu_4/\Delta\nu_1)$ are much smaller but also illustrate a maximum at two methyl groups in the substituted ammonium counterion. An increase in these ratios with the counterion is interpreted in terms of greater structure building ability and penetration of the counterion into the surface and hydrophobic regions. It is suggested that the ammonium ion itself has unprotected positive charge and hence is very hydrophilic while the tetramethylammonium ion is too bulky to penetrate efficiently into the tight structurally bound superstructure. The balance between hydrophobic methyl groups and the charged $-^{+}NH_2$ group of the dimethylammonium ion appears to represent an optimization of the structure building properties and therefore it interacts most efficiently with the double layer interface. The difference in the decanol and decylsulfate chain motions is quite clear in this counterion effect. In terms of the absolute magnitude of the quadrupole couplings the largest values at the initial carbons of a chain occur with the dimethylammonium counterion. This implies a structure building capacity for this ion with respect to other counterions. Actual magnitudes of couplings may be misleading when compared between phases since they are often sensitive to small variations in composition and temperature. This sensitivity, however, may turn out to be very useful for the investigation of such parameters.

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Stable Organic Derivatives of Heteropoly Anions, Pentamolybdobisphosphonates

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Abstract: Heteropoly molybdates containing covalently bound organic moieties have been prepared and characterized by chemical analysis and spectroscopic measurements. Salts of the anions $(RP)_2Mo_5O_{21}^{4-}$. where R = H, CH_3, C_2H_5. C_6H_5. $C_2H_4NH_3^+$, and p-$CH_2C_6H_4NH_3^+$, are stable in aqueous solution at pH 2.5-5. The new complexes have a structure related to that of $P_2Mo_5O_{23}^{6-}$ and are not reducible to heteropoly blue species. The amino derivatives are the first examples of zwitterionic heteropoly complexes. Applications of organic derivatives of heteropoly complexes, of which the molybdophosphonates are the first examples, are briefly considered.

Heteropoly oxoanions of the transition metals of groups V and VI form a large class of complexes with a number of unusual properties.[1] To a large extent these discrete inorganic complexes may be viewed as fragments of close-packed metal oxide lattices, and they provide well-defined models for examining many of the properties of such lattices including magnetic interactions, electron delocalization,[2] and heterogeneous catalysis. We have for some years been interested in the possibility of synthesizing heteropoly complexes containing organic groups. It seemed to us that such species would have several interesting properties and potentially important applications.

Table I. Analytical Results for $(RP)_2Mo_5O_{21}{}^{4-}$ Anions

	R, cation $(nH_2O)^b$						
	H, $NH_4{}^+$ (7)	CH_3, $NH_4{}^+$ (6)	C_2H_5, $NH_4{}^+$ (0)	C_6H_5, Me_4N^+ $(8)^c$	$C_2H_4NH_3{}^+$, $Me_4N^+Na^{+\,a}$ $(5)^d$	$C_2H_4NH_3{}^+$, $Bu_2NH_2{}^+$ (1)	$pCH_2C_6H_4NH_3{}^+$, Me_4N^+ (9)
% C, found	0.04	2.16	4.22	21.29	8.31	19.18	18.83
calcd	0	2.21	4.76	22.83	8.32	19.21	18.84
% H, found	2.70	2.79	3.03	4.40	3.16	4.70	4.12
calcd	2.97	3.13	2.58	5.03	3.20	4.84	4.31
% N, found	5.31	5.29	5.35	3.28	3.69	4.41	4.05
calcd	5.20	5.15	5.57	3.81	3.72	4.48	4.00
% P, found	5.77	5.85	5.87	4.19	5.65	4.94	4.46
calcd	5.75	5.70	6.14	4.21	5.37	4.96	4.42
% Mo, found	44.73	44.19	47.64	32.58	41.21	38.40	34.20
calcd	44.51	44.10	47.61	32.60	41.11	38.37	34.21
Mo/P, found	2.50	2.45	2.60	2.50	2.35	2.50	2.50

[a] Double salt. Sodium detected by flame test and confirmed by X-ray crystal structure analysis (ref 9). [b] Number of molecules of water of crystallization. [c] % H_2O found, 7.86; calcd, 7.78. [d] % H_2O found, 1.78; calcd, 1.44.

Since heteropoly and isopoly anions are exceedingly weak bases, direct alkylation is not likely to lead to particularly stable products, although preliminary work with methyl fluorosulfonate has been encouraging.[3] In this paper we report the first results from a different approach, namely, the synthesis of new heteropoly anions using heteroatoms with covalently-attached organic groups. We have chosen the hydrolytically stable alkyl and aryl phosphonates, $RPO_3{}^{2-}$, for the initial experiments. Apart from descriptions of molybdophosphite complexes by Rosenheim et al.[4,5] there have been no previous reports of heteropoly metallophosphonates.

Experimental Section

Preparation of Complexes. Ammonium Pentamolybdobismethylphosphonate. Sodium molybdate (85 g, 0.35 mol) was added to a solution of 11.5 g (0.12 mol) of methylphosphonic acid in 60 ml of water and the pH adjusted to 5.5. After the solution had been boiled for 15 min, traces of a white precipitate were removed by filtration, and 9.3 g (0.12 mol) of ammonium acetate was dissolved in the filtrate. The pH of the resulting solution was readjusted to 5.4 with 1:1 sulfuric acid. After 4 days at room temperature large colorless crystals had separated. These were recrystallized from water at pH 5.5 and air-dried. Yield ca. 35%. Analytical results are given below.

Ammonium Pentamolybdobisethylphosphonate. This salt was prepared in a similar fashion to the methyl derivative. It was recrystallized from water at pH 4.6. Yield ca. 30%.

Tetramethylammonium Pentamolybdobisphenylphosphonate. A solution of sodium molybdate (12.1 g, 0.05 mol) and phenylphosphonic acid (7.9 g, 0.05 mol) in 60 ml of water was boiled for 10 min and filtered to remove traces of insoluble material. Eleven grams (0.1 mol) of tetramethylammonium chloride was dissolved in the filtrate, the pH adjusted to 6.7 with 1:1 perchloric acid, and the solution was boiled for a further 10 min. The colorless crystals which separated after the solution had been allowed to evaporate for 5 days at room temperature were twice recrystallized from water.

Tetramethylammonium Sodium Pentamolybdobis(2-aminoethylphosphonate). A solution of 2-aminoethylphosphonic acid (0.5 g, 4.0 mmol) and sodium molybdate (2.42 g, 10 mmol) in 20 ml of water adjusted to pH 4 with 1 *M* sulfuric acid was boiled until the volume had been reduced to 10 ml. A solution of 0.88 g (8 mmol) of tetramethylammonium chloride in 10 ml of water, pH 4.5, was added to the hot solution, and the final pH adjusted to 4. After the solution had been allowed to evaporate at room temperature for several days the resulting crystals were separated by filtration, washed with cold water, and recrystallized from water at pH 4. Ammonium and tetraethylammonium salts of the above anion were prepared in an analogous fashion. Di-*n*-butylammonium and *tert*-butylammonium salts were precipitated directly from the reaction mixture by addition of the solutions of the appropriate alkylammonium chloride. These salts were recrystallized from hot water.

Tetramethylammonium Pentamolybdobis(*p*-aminobenzylphosphonate). The phosphonic acid (0.37 g, 2 mmol) was dissolved in a solution of 1.21 g of sodium molybdate in 70 ml of water. After the pH of the resulting solution had been adjusted to 3, it was boiled for 10 min, filtered, and 0.22 g of tetramethylammonium chloride (2 mmol) was added. After 5 min the precipitated heteropoly salt was filtered off, washed with water, and air-dried. The salt could be recrystallized with difficulty from water. Unrecrystallized and recrystallized products gave identical ir spectra. The analytical results listed below are for the unrecrystallized product.

Ammonium Pentamolybdodiphosphite. This salt was prepared by a modification of the method of Rosenheim and Schapiro. Molybdic acid (14.4 g, 0.1 mol) was added to a boiling solution of 13.7 g of 30% phosphorous acid (0.05 mol) and 7 ml of 15 *M* ammonia (0.1 mol) in 70 ml of water. After 30 min most of the molybdic acid had dissolved, the resulting solution was filtered and boiled to reduce its volume to 30 ml. During the process of concentration about 5 drops of 15 *M* NH_3 was added. Crystals of the product separated from the concentrated solution upon cooling: they were filtered off and washed thoroughly with cold water.

Analyses. Carbon, hydrogen, nitrogen, and phosphorus analyses were carried out by Galbraith Laboratories, Inc, Knoxville, Tenn. Molybdenum was determined spectrophotometrically as the complex with TIRON (1,2-dihydroxybenzene-3,5-disulfonic acid) at pH 7. The complex has a molar absorptivity of ca. 2500 M^{-1} cm^{-1} at 475 nm, and its formation is unaffected by the presence of the phosphonate anions.

Physical Measurements. Spectroscopic and electrochemical measurements were made as described in previous papers.[6,7] Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-1B instrument.

Results and Discussion

Stoichiometry and Structure. The molybdophosphonate complexes are readily formed in aqueous solution at pH 4–5. Analytical data for the crystalline salts are in good agreement with the empirical formula $(RP)_2Mo_5O_{21}{}^{4-}$; see Table I.

The 2:5 stoichiometry is reminiscent of the $P_2Mo_5O_{23}{}^{6-}$ anion, the structure of which was first reported by Strandberg.[8] In this structure two PO_4 tetrahedra span either side of a ring of five edge- and corner-shared MoO_6 octahedra (see Figure 1). Although the whole structure is dissymmetric, the PO_4 tetrahedra are related by a twofold axis and each tetrahedron has one unshared oxygen. It seems reasonable to expect that the phosphonate complexes would have the organic group, or a hydrogen atom, in this position. X-Ray crystallographic structure analysis[9] of the methyl- and 2-aminoethyl derivatives has confirmed this suggestion.

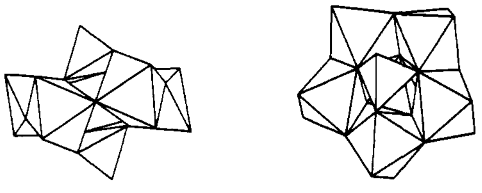

Figure 1. Two views of the structure of the $P_2Mo_5O_{23}^{6-}$ ion (R. Strandberg, *Acta Chem. Scand.*, 27, 1004 (1973)) showing arrangement of PO_4 tetrahedra and MoO_6 octahedra.

Proton NMR spectra of the complexes where R = H, CH_3, C_2H_5, and C_6H_5 are similar to, but shifted slightly downfield (0.1-0.2 ppm) from, those of the free phosphonic acids. Chemical shifts (relative to Tiers' salt) and coupling constants, $J_{\text{P-H}}$, are (values for uncomplexed acids in parentheses) R = H, 7.15 (6.91) ppm, 683 (679) Hz; R = CH_3, 1.68 (1.52) ppm, 16.9 (16.1) Hz; R = C_2H_5, complex multiplet 0.76-2.21 (0.79-2.11) ppm; R = C_6H_5, multiplets at 7.50 (7.47) and 7.75 (7.85) ppm. The NMR spectrum of the molybdophosphite complex, which was originally formulated by Rosenheim, Weinberg, and Pinsker[4] as $2(NH_4)_2O{\cdot}P_2O_3{\cdot}5MoO_3{\cdot}5H_2O$ confirms the phosphonate (P-H) composition for this anion. Further evidence for a common structure for the phosphite, phosphonate, and phosphate complexes is provided by their infrared spectra which show similar features in the metal-oxygen stretching region; see Table II and Figure 2.

The molybdophosphonate complexes do not appear to be reducible to mixed valence heteropoly blue species as is the case for some other polyanions. A polarogram (dropping mercury electrode) of the methyl derivative (2.5×10^{-4} *M*, pH 4.5 acetate buffer) showed a single irreversible wave at −0.56 V vs. SCE, the height of which corresponded to the addition of about 15 electrons per anion and probably signified complete decomposition. No reversible features were observed in the cyclic voltammogram (wax-impregnated graphite electrode) of the same complex. The nonreducibility of the molybdophosphonate complexes is consistent with the presumed "type II"[10] structure (Figure 1). We have pointed out earlier[10] that polyanion structures in which the metal atoms are bound to two (cis) terminal oxygen atoms are not reduced to heteropoly blues.

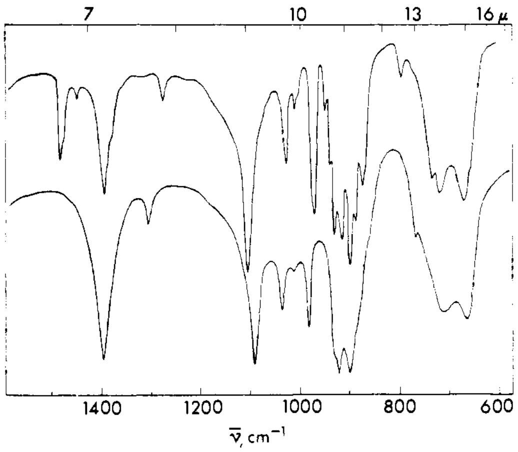

Figure 2. Infrared spectra of $Na(CH_3)_4N[(H_3NC_2H_4P)_2Mo_5O_{21}]{\cdot}5H_2O$ (upper) and $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]{\cdot}6H_2O$ (lower).

Stability. All the complexes were formed at pH 4-5, and appear from spectroscopic measurements (uv and NMR) to be stable within the range pH 2.5-5. Typical uv spectra measured at pH 4.5 are shown in Figure 3, and positions of band maxima are given in Table III. Slight negative deviations from Beer's law were observed in solutions more dilute than 1.0 m*M* indicating partial hydrolytic degradation. Potentiometric titrations of solutions of the complexes with sodium hydroxide gave poorly defined end points (pH ca. 8) after the addition of 10 ± 0.5 equiv of base in accordance with the reaction

$$(RP)_2Mo_5O_{21}^{4-} + 10OH^- \rightarrow 5MoO_4^{2-} + 2RPO_3^{2-} + 5H_2O$$

The amino derivatives therefore remain protonated

Table II. Infrared Absorption Frequencies (cm^{-1}) for $(RP)_2Mo_5O_{21}^{4-}$ Anions

R							Tentative assignment
H	CH_3	C_2H_5	C_6H_5	$C_2H_4NH_3^+$[a]	$CH_2C_6H_4NH_3^+$	O^-[b]	
2450 (w[c])							ν(P–H)[d]
2420 (w)							
			1439 (w)				ν(P–C)[f]
	1310 (m)						
		1270 (w)	1286 (w)	1280 (w)			
		1230 (w)			1246–1115[e]		
1130 (sh)	1090 (s,b)	1088 (s,b)	1132 (s)	1106 (s)	1090 (s)	1115 (m)	ν(P–O)
1120 (s)			1118 (s)		1080 (s)		
			1105 (sh)				
1048 (m)	1038 (m)	1040 (s)	1050 (s)	1033 (m)	1035 (m)	1036 (s)	
1025 (sh)							
986 (m)	982 (s)	990 (sh)	992 (w)	976 (s)	976 (s)	985 (w)	
		980 (sh)					
		970 (s)					
940 (sh)	930 (sh)	915 (s)	943 (sh)	952–878[g]	924 (s)		$\nu(Mo{-}O_{terminal})$
925 (s)	920 (s)	900 (s,b)	927 (sh)		915 (sh)		
909 (s)	900 (s)	874 (sh)	910 (s)		895 (s)	895 (s,b)	
890 (sh)			902 (s)		884 (sh)	865 (sh)	
	770 (w)	790 (w)	755 (w)	802 (w)			δ(P–C)[f]
				734 (w)			
690 (s,b)	715 (s,b)	705 (sh)	726 (sh)	723 (s)	698 (s,b)	680 (s,b)	$\nu(Mo{-}O_{bridging})$
	660 (s,b)	680 (s,b)	685 (s,b)	674 (s)	680 (s)		

[a] Sodium tetramethylammonium salt. [b] Sodium salt of the pentamolybdodiphosphate anion prepared according to ref 8. [c] Key: w, weak; m, medium; s, strong; b, broad; sh, shoulder. [d] D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 493 (1954); C. Duval and J. Lecompte, *C. R. Acad. Sci.*, 240, 66 (1955); M. Tsuboi, *J. Am. Chem. Soc.*, 79, 1351 (1957). [e] Four bands. [f] E. Steger and K. Lunwitz, *Naturwissenschaften*, 48, 522 (1961); L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, 21, 1905 (1965); C. N. R. Rao, J. Ramachandran, and D. Balasubramian, *Can. J. Chem.*, 39, 171 (1961); L. A. Harrah, M. I. Ryan, and C. Tamborski, *Spectrochim. Acta*, 18, 21 (1962). [g] Eight bands.

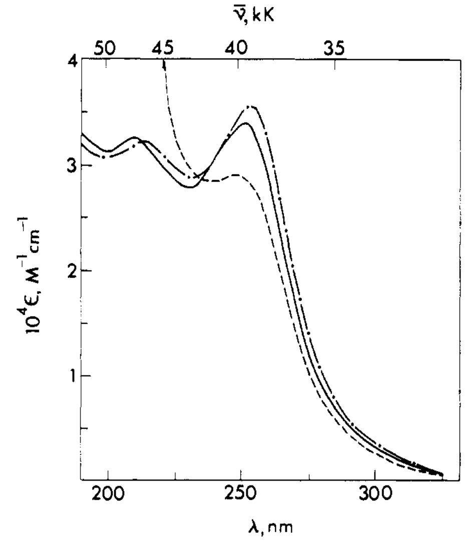

Figure 3. Absorption spectra of $[(CH_3P)_2Mo_5O_{21}]^{4-}$ (—), $[(C_6H_5P)_2Mo_5O_{21}]^{4-}$ (- - -), and $[(H_3NC_2H_4P)_2Mo_5O_{21}]^{2-}$ (-·-·-).

Table III. Uv Spectral Data[a] for $(RP)_2Mo_5O_{21}{}^{4-}$ Anions

R	Maxima, nm (10^4 absorbance, M^{-1} cm^{-1})	
H	245 (3.1)	213 (3.2)
CH_3	251 (3.4)	211 (3.2)
C_2H_5	252 (3.2)	210 (3.2)
C_6H_5	248 (2.9)	208 (5.1)
$C_2H_4NH_3{}^+$	252 (3.5)	213 (3.2)
p-$CH_2C_6H_4NH_3{}^+$	245 (3.0)	210 (5.5)

[a] Ca. 0.7 mM solutions at pH 4.5.

throughout the whole range of existence of the polyanions[11] and must exist in solutions as zwitterionic species with a novel quadrupolar charge distribution, e.g., $H_3{}^+NC_2H_4PO_3(Mo_5O_{15})^{2-}O_3PC_2H_4N^+H_3$. In view of the flexibility of the ethylene chain it is likely that the $-NH_3{}^+$ groups are hydrogen bonded to the oxygen atoms of the pentamolybdate moiety. The multiplicity of Mo-O vibrations in the infrared spectrum of $Na(CH_3)_4N[(H_3NC_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ (Figure 2) suggests that such intra- or intermolecular hydrogen bonding occurs in the solid state.

The thermal stability of the solid heteropoly complexes was studied by differential scanning calorimetry, coupled with infrared spectroscopy. The hydrates showed endotherms with maxima at the following temperatures (±2°): R = H, 56°; CH_3, 48°, 64°, 72°; C_6H_5, 50°, 60°; $C_2H_4NH_3{}^+$, 75°, 101°, 128° (Na-TMA salt); $CH_2C_6H_4NH_3{}^+$, 117°.

With the exception of the phosphite complex which had decomposed completely at 180°, only slight decomposition, according to infrared spectroscopy, could be detected in those salts which had been heated to 200-250°.

Conclusions

The existence of a potentially very large class of heteropoly oxometalate derivatives of alkyl and aryl phosphonic acids has been demonstrated. There appears to be no fundamental reason why other heteroelements should not function in a similar way to give rise to an extensive field of organometal oxide complexes. We have, for example, recently reinvestigated some organoarsenic molybdate complexes originally reported by Rosenheim[12] and have shown that some, at least, have new and unusual polyanion structures.[13] The chemical possibilities afforded by complexes with both metal oxide and organic functionalities would appear to be pertinent to many fields. For example, new kinds of inorganic and coordination polymers are certainly possible. If such polymers incorporate type I[10] polyanion structural units they should undergo facile reduction and serve as electron exchange materials and as redox catalysts. In another area, heteropoly complexes are widely used as electron microscope "stains" on account of their concentration of heavy atoms. It now becomes possible to imagine synthesizing heavy metal complexes that can be used to label specific functional groups or active sites in macromolecules. We shall explore some of these possibilities in future papers.

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