Two Heteropoly Anions Containing Organic Groups. Crystal and Molecular Structures of Ammonium Pentamolybdobis(methylphosphonate) Pentahydrate, $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$, and Sodium Tetramethylammonium Pentamolybdobis(ethylammoniumphosphonate) Pentahydrate, $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot5H_2O$

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The crystal and molecular structures of two stable organic derivatives of a heteropoly anion have been determined from three-dimensional x-ray data collected by counter methods. The pentamolybdomethylphosphonate compound, $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$, crystallizes in space group C_2^2-$P2_1$ of the monoclinic system with four formula units in a cell of dimensions $a = 10.597$ (2) Å, $b = 13.739$ (2) Å, $c = 19.901$ (2) Å; $\beta = 96.05$ (1)°. The observed and calculated densities are 2.48 (2) and 2.466 g/cm^3, respectively. The pentamolybdoethylammoniumphosphonate compound, $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot5H_2O$, crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four formula units in a cell of dimensions $a = 11.513$ (4) Å, $b = 20.146$ (6) Å, $c = 14.110$ (5) Å; $\beta = 95.25$ (4)°. The observed and calculated densities are 2.36 (2) and 2.354 g/cm^3, respectively. Both structures have been refined by least-squares techniques to final R factors on F of 0.032 for the methyl compound and 0.047 for the ethylammonium compound. The structures of both organo heteropoly anions are similar, consisting of rings of five MoO_6 octahedra joined by sharing edges, except for one pair which is joined by corner sharing. Each face of the Mo_5 ring is capped by a tetrahedral RPO_3 group ($R = CH_3$ or $C_2H_4NH_3^+$). The crystal structure of the methyl compound contains two independent $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions of the same chirality related by a pseudosymmetric B centering. The ammonium ions and water molecules form infinite hydrogen-bonded chains parallel to the b axis. In the ethylammonium crystal the $[(NH_3C_2H_5P)_2Mo_5O_{21}]^{2-}$ anions are loosely linked together as dimers by sodium ion–oxygen coordination. This is the first example of a zwitterionic heteropoly anion.

Introduction

Kwak, Pope, and Scully[1] have recently reported the synthesis and characterization of several 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-$CH_2c_6H_4NH_3^+$. These are the first heteropoly anions in which organic groups are covalently bonded to a phosphorus heteroatom. It seems probable that they represent a large class of compounds which may include a wide variety of anion types, heteroatoms, and organic moieties.[2] This combination of the unusual properties of heteropoly anions with the chemical versatility of organic functional groups is expected to produce new species with interesting chemical and physical properties, involving in some cases entirely new structural types.

The x-ray crystal structure determinations of two of these organophosphonate complexes, $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I) and $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot5H_2O$ (II), were undertaken to confirm the presence of the organic moieties in the heteropoly anions and to determine the effect of these organic substituents on the geometry of the anions. Knowledge of the structures of these complexes should help to provide information on the geometric requirements for the formation of new organo heteropoly anions.

Experimental Section

$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I). **Unit Cell and Space Group.** Crystals of I were kindly supplied by Professor M. T. Pope. A well-formed, colorless prism approximately 0.3 mm on an edge was mounted on a glass fiber with the $[\bar{1}01]$ direction coincident with the goniometer rotation axis. Preliminary Weissenberg and precession photographs exhibited monoclinic symmetry with systematic absences for $0k0$, $k \neq 2n$, indicating possible space groups C_2^2-$P2_1$ or C_{2h}^2-$P2_1/m$. The cell dimensions, $a = 10.597$ (2) Å, $b = 13.739$ (2) Å, $c = 19.901$ (2) Å, and $\beta = 96.05$ (1)°, were obtained using Mo Kα_1 radiation (λ 0.70926 Å) at 22 °C by a least-squares refinement to fit the $\pm2\theta$ values for 19 high-angle reflections centered on the Picker FACS-I four-circle diffractometer. The observed density of 2.48 (2) g/cm^3 obtained by flotation in CCl_4–$C_2H_2Br_4$ solutions agrees well with the calculated value of 2.466 g/cm^3 assuming $Z = 4$.

Collection and Reduction of Intensity Data. The same crystal used for the unit cell determination was used for data collection. Dif-

fractometer data were obtained using Zr-filtered Mo Kα radiation by the θ–2θ scan technique at a takeoff angle of 1.5°. The peaks were scanned at a rate of 1.0°/min from 0.5° on the low-angle side of the Kα_1 peak to 0.5° on the high-angle side of the Kα_2 peak. The diffracted beams were counted using a scintillation counter and were attenuated with zirconium foil whenever the count rate exceeded 8000 Hz. Stationary-crystal, stationary-counter background counts of 10 s were taken at each end of the scan.

A unique data set was collected to $2\theta = 50°$. The intensities of three reflections were monitored as standards every 100 reflections, and no loss in intensity was observed throughout the data collection. The intensities were corrected for background, and standard deviations were assigned according to the equations $I = C - 0.5(t_c/t_b)(B_1 + B_2)$ and $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ where C is the integrated peak count obtained in time t_c and B_1 and B_2 are the background counts obtained in time t_b, all corrected for scalar truncation. A value of 0.06 was used for p. The data were also corrected for Lorentz and polarization effects. No absorption correction was applied; the linear absorption coefficient of 22.9 cm^{-1} was calculated to give transmission coefficients ranging from 0.5 to 0.3. Of the 5332 unique data collected, only the 4864 reflections for which $I \geq 2\sigma(I)$ were used in the structure solution and refinement.

Solution and Refinement of the Structure. A Patterson function was computed[3] which clearly indicated (1) the correct choice of space group is $P2_1$ and (2) the two independent molecules in the unit cell are almost exactly separated by a pseudo B-centering translation of $^1/_2, 0, ^1/_2$. This pseudosymmetry results in an apparent 2_1 axis at $^1/_4, 0, ^1/_4$ which was originally (incorrectly) chosen as the cell origin. However, even with a correct choice of origin a model consisting of two identical rings each containing five MO atoms failed to refine satisfactorily. A careful reexamination of the Patterson map revealed a slight elongation in the w direction of one peak on the Harker plane at $v = ^1/_2$, indicating a breaking of the pseudosymmetry in the z direction for one pair of Mo atoms. Fortunately, a model assuming exact B centering except for this one z coordinate refined in seven cycles to give a reasonable geometry for both five-molybdenum rings. The asymmetric ring of anion I (see below) is rotated from that of anion I′, breaking the pseudosymmetry. The y coordinate of Mo(1) was fixed at 0.25 to define the origin of the unit cell, and an isotropic thermal parameter of 1.5 Å^2 was assumed for each of the 10 Mo atoms. The consistency indices R_1 and R_2 were 0.25 and 0.35, respectively, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. In this and succeeding refinements the function minimized
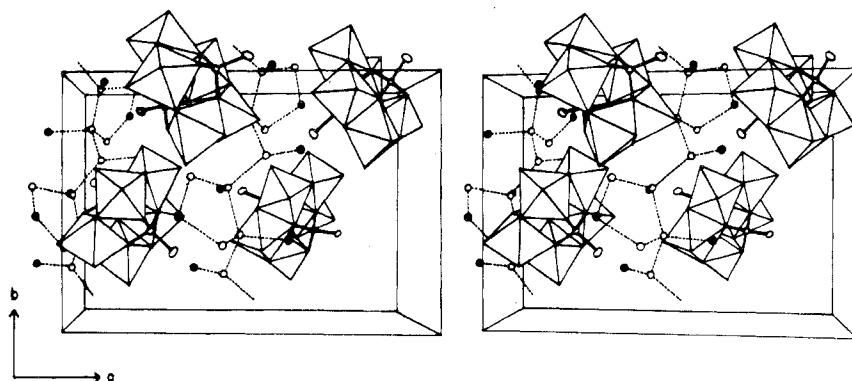
Figure 1. Stereoscopic view of the unit cell of $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I). The anions show MoO_6 octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. In the $H_2O-NH_4^+$ chains the probable N atoms have been shaded.

was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.

Two subsequent difference Fourier maps, interspersed with a least-squares refinement, led to the positions of all remaining nonhydrogen atoms. Four cycles of refinement assuming individual isotropic thermal parameters for all atoms led to values of 0.052 and 0.064 for R_1 and R_2. The atomic scattering factors used were those of Hanson et al.[4] while the values of the anomalous terms $\Delta f'$ and $\Delta f''$ were taken from Cromer.[5]

At this point in the solution of the structure a refinement with all x, y, z fractional coordinates converted to $\bar{x}, \bar{y}, \bar{z}$ failed to determine the polarity of the crystal, refining to essentially identical consistency indices. Hence 12 reflections were selected which calculations indicated should show the greatest differences between $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$. Using the same conditions as described above for data collection, the intensities of the (hkl), $(h\bar{k}l)$, $(\bar{h}\bar{k}\bar{l})$, and $(\bar{h}k\bar{l})$ reflections were recollected and processed as before, averaging the intensities of (hkl) with $(\bar{h}\bar{k}\bar{l})$. In each case, the observed inequality between $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ was in the same direction as the calculated inequality (Table I), consistent with a correct initial choice of crystal polarity.

In hopes of differentiating between the eight NH_4^+ cations and the ten water molecules, one cycle of anisotropic refinement, varying first three blocks of anisotropic thermal parameters followed by positional refinement of the 78 nonhydrogen atoms, was carried out. A difference Fourier map gave some indications of hydrogen positions; these peaks, together with an assumed $NH_4^+-NH_4^+$ contact distance of about 4 Å, resulted in the probable assignment reported. A final cycle of anisotropic refinement, in which no parameter shifted by more than its standard deviation, gave final values of $R_1 = 0.032$ and $R_2 = 0.042$, with a standard deviation in an observation of unit weight of 1.07. A difference Fourier map showed no peak greater than 0.7 $e/\text{Å}^3$, compared to an average value for oxygen of 5.0 $e/\text{Å}^3$.

Table II presents the positional and thermal parameters, along with the corresponding standard deviations. A table of the final values of $|F_o|$ and $|F_c|$ is available.[6]

$Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot5H_2O$ (II). Unit Cell and Space Group. Colorless crystals of II were supplied by Professor M. T. Pope. A crystal of approximate dimensions 0.2 × 0.3 × 0.3 mm was mounted parallel to the [100] direction and exhibited monoclinic symmetry in precession photographs. Systematic absences on the $hk0$, $h0l$, and $h1l$ nets for $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$, uniquely established the space group as $C_{2h}^5-P2_1/c$. The cell dimensions, obtained using Mo $K\bar{\alpha}$ radiation (λ 0.71069 Å) by centering 22 reflections at $\pm2\theta$ on the Picker FACS-I four-circle diffractometer, are $a = 11.513$ (4) Å, $b = 20.146$ (6) Å, $c = 14.110$ (5) Å, and $\beta = 95.25$ (4)° (at 22 °C). The calculated density of 2.354 g/cm³ for four formula units in the unit cell agrees well with the experimental value of 2.36 (2) g/cm³ obtained by flotation in $CCl_4-C_2H_2Br_4$ solutions.

Collection and Reduction of Intensity Data. The crystal used for unit cell determination was also used for data collection. A unique data set to $2\theta = 45°$ was collected using the same conditions as described for I, with the exception that the peaks were scanned from 0.75° below the $K\alpha_1$ peak to 0.75° above the $K\alpha_2$ peak. The intensities of three standard reflections, monitored every 100 reflections, remained essentially constant during data collection. The intensities were corrected for background and for Lorentz and polarization effects

Table I. Determination of Polarity of a Crystal of $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I)

Indices			F_o		$F_c{}^a$	
h	k	l	hkl	$\bar{h}\bar{k}\bar{l}$	hkl	$\bar{h}\bar{k}\bar{l}$
$\bar{2}$	5	2	62	54	74	65
3	4	3	35	41	32	37
0	5	4	83	92	68	79
$\bar{1}$	4	5	68	75	55	61
$\bar{1}$	1	7	42	37	46	41
$\bar{3}$	4	5	99	91	104	95
$\bar{3}$	1	5	64	70	66	71
4	3	0	93	88	97	91
7	3	7	56	51	59	54
$\bar{1}$	4	6	37	34	39	35
$\bar{4}$	2	6	75	73	79	74
5	5	7	34	38	28	32

a Based on final structure parameters.

as described for I. No absorption correction was applied; the linear absorption coefficient of 20.5 cm⁻¹ was estimated to give transmission coefficients ranging from 0.6 to 0.4. Of the 4279 reflections processed, 3541 were considered to be observed ($I \geq 2\sigma(I)$) and were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. Normalized structure factors were calculated, and the multiple-solution symbolic addition technique was applied utilizing the LSAM series of computer programs. A total of 395 reflections were selected for which $E \geq 1.50$; an E map was computed using the set of signs with the highest figures of merit, revealing the positions of the five Mo and two P atoms. Five cycles of least-squares refinement followed by a difference Fourier map gave the positions of the remaining nonhydrogen atoms. Five more cycles of refinement, assigning anisotropic thermal parameters to the five Mo atoms and isotropic thermal parameters to the remaining atoms, resulted in final values of $R_1 = 0.047$ and $R_2 = 0.070$, with a standard deviation in an observation of unit weight of 1.91.

A final difference Fourier map showed only one peak above 1.0 $e/\text{Å}^3$. This peak of 1.9 $e/\text{Å}^3$ corresponds to about 30% of the electron density found for solvent water and may be due to some disorder of the molecules of hydration. Some attempts to refine a possible disordered model were made, but the results were not significant.

The final positional and thermal parameters, along with the corresponding standard deviations, are presented in Table III. A table of the final values of $|F_o|$ and $|F_c|$ is available.[6]

Description of the Structures and Discussion

$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I). The crystal structure of I contains two crystallographically independent, essentially identical $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions (anion I and anion I'), nearly separated by a translation of $1/2, 0, 1/2$. The two anions are rotated about the Mo_5 ring axis relative to one another. The anions are chiral, and both possess the same handedness to give an optically pure crystal. The NH_4^+ cations and water molecules are in two independent chains, again separated by the $1/2, 0, 1/2$ translation, running parallel to the b axis. Figure 1 presents a stereoscopic view of the contents of the unit cell.

Table II. Final Positional and Thermal Parameters for $(NH_4)_4[(CH_3P)_2Mo_6O_{21}]\cdot 5H_2O$ (I)

Atom	Fractional coordinates			Anisotropic temperature factors $(\times 10^4)^a$					
	$\underline{x}$	$\underline{y}$	$\underline{z}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	1.09494(7)^b	0.25	0.63626(4)	39.4(7)	15.7(4)	9.6(2)	4.5(4)	0.7(3)	-2.0(2)
Mo(2)	1.23246(7)	0.45577(8)	0.73854(4)	36.3(7)	23.6(5)	9.4(2)	2.3(5)	-1.2(3)	-2.7(3)
Mo(3)	0.99310(7)	0.61630(8)	0.74526(4)	43.3(7)	14.8(4)	10.1(2)	1.6(4)	1.1(3)	-2.6(3)
Mo(4)	0.75471(7)	0.55058(8)	0.62870(4)	40.5(7)	16.7(4)	11.9(2)	6.3(5)	-2.2(3)	-0.8(3)
Mo(5)	0.82475(7)	0.33892(8)	0.55291(4)	43.1(7)	18.1(4)	9.5(2)	2.4(4)	-4.2(3)	-2.9(3)
Mo(1')^c	0.22694(7)	0.55228(8)	0.13608(4)	31.1(6)	15.6(4)	12.3(2)	2.6(5)	0.7(3)	0.0(3)
Mo(2')	0.32180(7)	0.33176(8)	0.04651(4)	35.6(7)	15.4(4)	10.4(2)	-1.1(4)	-2.3(3)	-1.4(2)
Mo(3')	0.59607(7)	0.25719(8)	0.13500(4)	36.1(7)	14.6(4)	11.5(2)	3.1(4)	-1.0(3)	0.9(2)
Mo(4')	0.70493(7)	0.44282(8)	0.23453(4)	32.5(6)	17.0(4)	9.9(2)	-0.2(5)	-0.7(3)	-0.4(2)
Mo(5')	0.49632(7)	0.63036(8)	0.22648(4)	38.7(7)	15.3(4)	10.6(2)	0.1(4)	0.2(3)	-1.9(3)
P(1)	1.0632(2)	0.5053(2)	0.5936(1)	42.4(21)	16.0(12)	7.6(6)	-1.2(13)	1.9(9)	0.9(7)
P(2)	0.9057(2)	0.3736(2)	0.7290(1)	35.3(20)	15.9(12)	8.9(6)	-0.6(13)	2.1(9)	-0.2(7)
P(1')	0.5373(2)	0.5022(2)	0.0824(1)	34.9(19)	15.9(12)	7.5(5)	-1.6(13)	2.6(8)	1.3(7)
P(2')	0.3882(2)	0.3827(2)	0.2253(1)	39.0(21)	18.1(13)	9.2(6)	-0.7(13)	2.9(9)	2.7(7)
O(1)	1.1860(6)	0.2453(5)	0.5696(3)	54(6)	32(4)	16(2)	8(4)	6(3)	-7(2)
O(2)	1.1207(6)	0.1385(5)	0.6713(3)	72(7)	22(4)	22(2)	17(4)	7(3)	1(2)
O(3)	1.2040(5)	0.3325(5)	0.6939(3)	42(6)	33(4)	12(2)	5(4)	-3(2)	0(2)
O(4)	0.9715(5)	0.2779(4)	0.7200(3)	52(6)	14(3)	12(2)	3(4)	7(3)	4(2)
O(5)	0.9258(6)	0.2322(4)	0.5917(3)	68(6)	18(3)	9(1)	4(4)	1(2)	-3(2)
O(6)	1.0144(6)	0.3982(4)	0.5866(3)	52(6)	21(4)	11(2)	-3(4)	-1(3)	-2(2)
O(7)	1.0051(5)	0.4535(5)	0.7438(3)	45(5)	23(4)	11(2)	0(4)	0(2)	1(2)
O(8)	1.1953(5)	0.5066(5)	0.6312(3)	50(6)	23(4)	13(2)	-7(4)	3(3)	-3(2)
O(9)	1.3870(6)	0.4755(5)	0.7309(3)	55(6)	37(4)	15(2)	-2(4)	2(3)	-5(2)
O(10)	1.2374(6)	0.4186(5)	0.8220(3)	56(6)	41(4)	11(2)	7(4)	-4(3)	0(2)
O(11)	1.1695(6)	0.5858(5)	0.7468(3)	41(6)	25(4)	15(2)	-9(4)	2(3)	-6(2)
O(12)	0.9821(6)	0.6270(5)	0.8305(3)	64(6)	32(4)	17(2)	0(4)	4(3)	3(3)
O(13)	0.9721(6)	0.5680(5)	0.6304(3)	54(6)	22(3)	11(2)	-2(4)	4(3)	-2(2)
O(14)	0.8158(6)	0.5866(5)	0.7191(3)	45(6)	27(4)	13(2)	4(4)	3(3)	-3(2)
O(15)	0.9979(7)	0.7350(5)	0.7185(4)	84(8)	22(4)	19(2)	-1(5)	2(3)	3(2)
O(16)	0.6015(6)	0.5200(6)	0.6379(4)	46(6)	45(5)	24(2)	4(4)	0(3)	-4(3)
O(17)	0.8163(5)	0.3981(4)	0.6650(3)	52(6)	18(4)	7(2)	3(4)	1(2)	1(2)
O(18)	0.7811(6)	0.4756(5)	0.5489(3)	70(6)	17(3)	11(2)	11(4)	-7(3)	2(2)
O(19)	0.7390(7)	0.6627(5)	0.5890(3)	86(7)	20(4)	20(2)	11(4)	-3(3)	4(2)
O(20)	0.8490(7)	0.3246(5)	0.4701(3)	109(8)	37(5)	13(2)	6(5)	1(3)	-3(2)
O(21)	0.6801(6)	0.2888(5)	0.5594(4)	55(6)	25(4)	23(2)	-1(4)	-6(3)	-1(2)
O(1')	0.2196(6)	0.6395(5)	0.0740(3)	58(7)	32(4)	17(2)	6(4)	-1(3)	7(2)
O(2')	0.0766(6)	0.5536(5)	0.1578(3)	48(6)	33(4)	23(2)	8(4)	7(3)	0(3)
O(3')	0.2303(5)	0.4410(5)	0.0775(3)	32(5)	19(3)	18(2)	3(4)	-5(2)	-1(2)
O(4')	0.2604(5)	0.4334(5)	0.2124(3)	47(5)	27(4)	10(2)	0(3)	7(2)	2(2)
O(5')	0.3131(5)	0.6224(5)	0.2108(3)	41(5)	23(4)	12(2)	4(4)	2(2)	1(2)
O(6')	0.4510(5)	0.5564(5)	0.1277(3)	34(5)	19(3)	11(2)	-3(4)	-3(2)	1(2)
O(7')	0.4180(5)	0.3274(4)	0.1605(3)	47(6)	17(3)	13(2)	-4(4)	-2(2)	2(2)
O(8')	0.4532(5)	0.4536(5)	0.0242(3)	49(5)	25(4)	9(2)	-13(4)	2(2)	0(2)
O(9')	0.2785(6)	0.3332(5)	-0.0381(3)	53(6)	39(4)	15(2)	-5(4)	-6(3)	-5(2)
O(10')	0.2270(6)	0.2411(5)	0.0727(3)	54(7)	25(4)	18(2)	-4(4)	1(3)	2(2)
O(11')	0.4829(6)	0.2659(5)	0.0516(3)	48(6)	25(4)	13(2)	8(4)	-2(3)	-5(2)
O(12')	0.5602(7)	0.1429(5)	0.1587(4)	84(7)	15(4)	25(2)	-7(4)	-7(3)	5(2)
O(13')	0.6212(5)	0.4278(5)	0.1235(3)	38(5)	20(3)	12(2)	-4(4)	-2(2)	2(2)
O(14')	0.6573(5)	0.3081(4)	0.2238(3)	41(6)	20(3)	14(2)	3(4)	-6(2)	2(2)
O(15')	0.7350(6)	0.2419(5)	0.0997(3)	48(6)	44(4)	15(2)	3(4)	0(3)	-6(2)
O(16')	0.7387(6)	0.4401(5)	0.3211(3)	86(7)	32(4)	10(2)	1(5)	-7(3)	1(2)
O(17')	0.4931(5)	0.4555(5)	0.2475(3)	44(5)	21(3)	10(1)	-5(4)	3(2)	0(2)
O(18')	0.6626(5)	0.5758(4)	0.2157(3)	37(5)	20(3)	15(2)	-3(3)	4(3)	3(2)
O(19')	0.8532(6)	0.4440(5)	0.2071(3)	58(6)	35(4)	15(2)	-2(4)	4(3)	-2(2)
O(20')	0.5212(6)	0.7417(5)	0.1951(4)	73(7)	21(4)	26(2)	-10(4)	-3(3)	3(2)
O(21')	0.5099(6)	0.6488(6)	0.3127(3)	73(7)	41(6)	17(2)	6(5)	-1(3)	-9(2)
C(1)	1.0643(10)	0.5517(8)	0.5097(5)	95(11)	32(6)	13(3)	-16(7)	1(5)	6(4)
C(2)	0.8142(10)	0.3630(7)	0.7989(5)	92(11)	20(5)	15(2)	3(6)	21(4)	1(3)
C(1')	0.6405(10)	0.5892(8)	0.0481(5)	75(10)	30(6)	19(3)	-19(6)	0(4)	8(3)
C(2')	0.3788(9)	0.2954(8)	0.2921(5)	67(10)	37(6)	14(3)	-3(6)	9(4)	11(3)
N(1)	0.0636(9)	0.4472(7)	0.3097(5)	113(11)	30(5)	29(3)	-3(7)	-7(5)	-1(4)
N(2)	0.4527(9)	0.3445(7)	0.6244(5)	112(11)	30(5)	27(3)	-6(6)	25(5)	-8(3)
N(3)	0.6778(8)	0.5625(7)	0.4292(4)	72(8)	44(6)	14(2)	-4(6)	3(4)	4(3)
N(4)	0.2704(9)	0.7152(7)	0.6485(4)	98(10)	35(5)	18(2)	-26(6)	-4(4)	2(3)
N(5)	0.5063(8)	0.4398(7)	-0.1210(4)	85(9)	36(6)	21(3)	-1(6)	-4(4)	4(3)
N(6)	1.0049(8)	0.3310(7)	0.1266(5)	59(8)	35(6)	29(3)	-9(6)	19(4)	-3(3)
N(7)	1.1931(10)	0.5465(7)	-0.0661(5)	145(11)	34(6)	17(2)	0(7)	10(4)	-2(3)
N(8)	0.8496(9)	0.7072(7)	0.1769(5)	88(10)	42(6)	22(3)	-31(6)	6(4)	-11(3)
Aq(1)	0.1161(8)	0.3304(6)	0.4283(4)	150(10)	44(5)	24(2)	24(6)	19(4)	5(3)
Aq(2)	0.3879(9)	0.3666(9)	0.4843(5)	138(12)	90(8)	34(3)	-1(8)	-9(5)	6(4)
Aq(3)	0.4110(7)	0.5631(7)	0.4478(4)	73(8)	76(7)	32(3)	7(6)	6(4)	10(4)
Aq(4)	0.2249(6)	0.6026(6)	0.3419(4)	54(7)	52(5)	29(2)	-5(5)	12(3)	-16(3)
Aq(5)	0.4633(8)	0.6979(7)	0.5611(4)	94(8)	59(5)	23(2)	27(5)	-3(4)	-7(3)
Aq(6)	0.6453(8)	0.3028(7)	-0.0470(4)	131(10)	57(6)	24(2)	42(6)	11(4)	10(3)
Aq(7)	0.8972(10)	0.3479(10)	-0.0097(5)	156(13)	106(9)	34(3)	-8(9)	15(5)	16(5)
Aq(8)	0.9383(9)	0.5373(9)	-0.0411(5)	149(12)	104(9)	37(3)	-11(9)	27(5)	4(5)
Aq(9)	0.7096(8)	0.5705(6)	-0.1503(5)	101(9)	37(6)	37(3)	-16(5)	29(5)	-7(3)
Aq(10)	0.9497(8)	0.6966(8)	0.0510(4)	98(8)	75(6)	31(3)	38(6)	10(4)	12(3)

^{a} The form of the anisotropic thermal ellipsoid is exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+2\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell)]$.

^{b} Numbers in parentheses in this and succeeding tables are estimated standard deviations in the least significant figures.

^{c} The primed atoms comprise the second anion ($\underline{I}'$), and are chemically equivalent to the unprimed atoms of the same number in the first anion ($\underline{I}$).

All intermolecular contacts are normal, with the shortest $NH_4^+-NH_4^+$ distance being 3.89 (1) Å between N(5) and N(7). There are no anion–anion contacts less than 3 Å, with the closest approach distances being 3.01 (1) and 3.05 (1) Å for O(10)–O(9') and O(2')–O(19'), respectively. (The primed atoms comprise anion I' and are chemically equivalent to the unprimed atoms of the same number in anion I.)

There appear to be no abnormally short hydrogen-bonded distances, either within the NH_4^+–water molecule chains or between these chains and the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions. Within the chains, the N–aq distances vary between 2.73 and 2.91 Å, while the aq–aq distances vary from 2.72 to 3.11 Å.

Table III. Final Positional and Thermal Parameters for Na[N(CH$_3$)$_4$][(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O (II)

	Fractional coordinates			Anisotropic temperature factors (x10^4)[a]					
Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.24564(8)	0.22407(4)	0.23308(6)	32.7(8)	9.5(3)	19.6(5)	-2.8(4)	4.6(5)	1.1(3)
Mo(2)	-0.07430(8)	0.21127(4)	0.23012(6)	32.0(8)	9.0(2)	17.5(5)	0.6(4)	5.6(5)	1.2(3)
Mo(3)	-0.12791(8)	0.05044(4)	0.28011(6)	35.7(8)	10.1(3)	20.6(5)	-4.4(4)	5.2(5)	0.7(3)
Mo(4)	0.11935(8)	-0.03873(4)	0.26704(6)	41.8(9)	8.8(3)	18.7(5)	-0.9(4)	2.2(5)	0.9(3)
Mo(5)	0.34086(8)	0.06588(5)	0.22484(6)	33.6(8)	11.0(3)	22.2(5)	0.8(4)	6.2(5)	0.7(3)

	Fractional coordinates			Isotropic thermal parameter (Å^2)
Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}$
P(1)	0.0668(2)	0.0989(1)	0.1165(2)	1.41(5)
P(2)	0.1351(2)	0.1173(1)	0.3804(2)	1.49(5)
Na	0.4929(5)	0.4296(3)	0.0870(4)	4.1(1)
O(1)	0.2708(7)	0.2456(4)	0.1190(5)	2.7(1)
O(2)	0.3018(6)	0.2898(2)	0.2991(5)	2.6(1)
O(3)	0.0811(6)	0.2431(3)	0.2277(4)	1.9(1)
O(4)	0.1972(6)	0.1835(3)	0.3780(5)	1.9(1)
O(5)	0.3645(6)	0.1584(3)	0.2623(5)	2.1(1)
O(6)	0.1827(6)	0.1224(3)	0.1713(4)	1.7(1)
O(7)	0.0133(6)	0.1240(3)	0.3243(4)	1.7(1)
O(8)	-0.0155(6)	0.1574(3)	0.1009(5)	1.9(1)
O(9)	-0.1542(6)	0.2624(3)	0.1514(5)	2.2(1)
O(10)	-0.1043(6)	0.2415(3)	0.3409(5)	2.4(1)
O(11)	-0.1734(6)	0.1342(3)	0.2218(5)	2.1(1)
O(12)	-0.1963(7)	0.0585(3)	0.3826(5)	2.7(1)
O(13)	0.0127(6)	0.0418(3)	0.1679(5)	1.8(1)
O(14)	-0.0100(6)	-0.0105(3)	0.3306(5)	2.0(1)
O(15)	-0.2175(7)	-0.0007(4)	0.2106(5)	2.8(2)
O(16)	0.1951(6)	-0.0812(4)	0.3579(5)	2.6(1)
O(17)	0.2049(6)	0.0590(3)	0.3422(4)	1.8(1)
O(18)	0.2386(6)	-0.0100(3)	0.1932(5)	2.2(1)
O(19)	0.0578(7)	-0.0996(4)	0.1950(5)	2.9(2)
O(20)	0.4033(7)	0.0667(4)	0.1183(5)	3.2(2)
O(21)	0.4410(7)	0.0283(4)	0.3044(5)	3.1(2)
N(1)	0.0949(8)	0.1824(4)	-0.0761(6)	2.8(2)
N(2)	-0.0777(8)	0.1585(4)	0.5095(6)	2.6(2)
N(3)	0.6233(8)	0.3642(5)	0.4755(7)	3.3(2)
C(1)	0.1063(9)	0.0699(5)	0.0025(7)	2.0(2)
C(2)	0.1736(10)	0.1222(5)	-0.0510(7)	2.3(2)
C(3)	0.1119(9)	0.0979(5)	0.5011(7)	2.3(2)
C(4)	0.0460(10)	0.1503(6)	0.5533(8)	2.6(2)
C(5)	0.7247(15)	0.3354(8)	0.4295(12)	6.3(4)
C(6)	0.5216(15)	0.3818(8)	0.4011(11)	6.0(4)
C(7)	0.6628(12)	0.4266(7)	0.5279(10)	4.4(3)
C(8)	0.5878(14)	0.3146(8)	0.5459(11)	5.7(4)
Aq(1)	0.6347(7)	0.4915(4)	0.0015(5)	3.2(2)
Aq(2)	0.3465(8)	0.4077(4)	0.1889(6)	4.5(2)
Aq(3)	0.6063(9)	0.3402(5)	0.1717(7)	5.8(2)
Aq(4)	0.4201(9)	0.3334(5)	-0.0106(7)	5.3(2)
Aq(5)	0.5927(11)	0.2122(7)	0.2776(9)	8.0(3)

[a] The form of the anisotropic thermal ellipsoid is exp[-($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell$)].
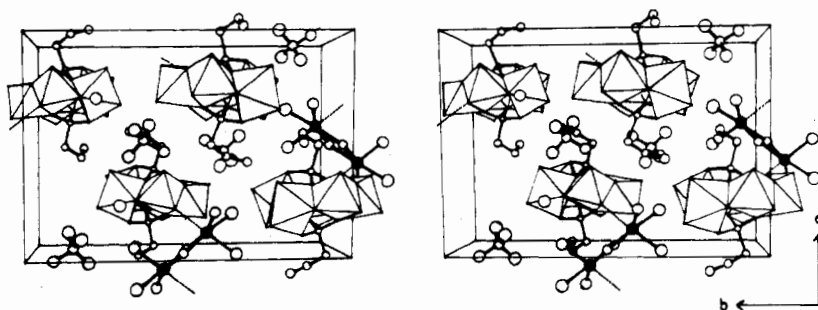

Figure 2. Stereoscopic view of the unit cell of Na[N(CH$_3$)$_4$][(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O (II). The anions show MoO$_6$ octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. The Na atoms of the [Na$_2$(H$_2$O)$_8$]$^{2+}$ cations have been shaded.

The shortest cation–anion and water–anion distances are 2.78 (1) Å for N(3)–O(18) and 2.75 (1) Å for aq(6)–O(1'), respectively.

Na[N(CH$_3$)$_4$][(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O (II). The crystal structure of II contains [(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]$^{2-}$ anions, N(CH$_3$)$_4^+$ cations, and [Na$_2$(H$_2$O)$_8$]$^{2+}$ cations. This is the first example of a zwitterionic heteropoly anion. A stereoscopic view of the unit cell is presented in Figure 2. It can be seen that the [Na$_2$(H$_2$O)$_8$]$^{2+}$ ion, which is located on a center of symmetry, consists of two octahedra joined on one edge by sharing two water molecules. The sixth coordination site of each Na atom is occupied by a terminal oxygen atom (O(21)) of the anion, resulting in dimeric units of two anions linked by the [Na$_2$(H$_2$O)$_8$]$^{2+}$ cation. There is, in addition, one water molecule (aq(5)) that is not coordinated to the sodium ion but occupies a hole in the packing structure.

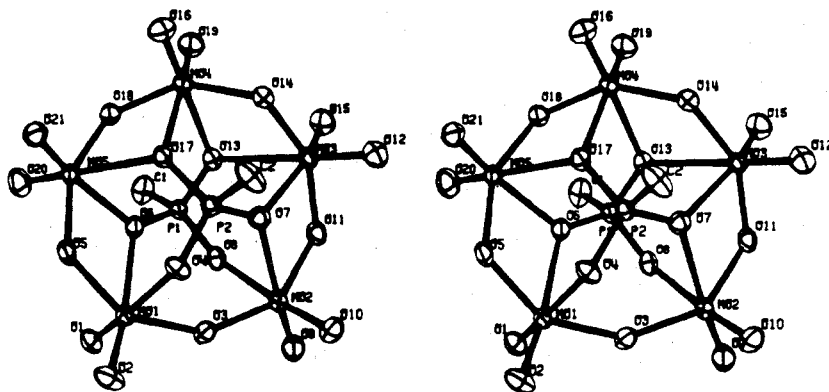All intermolecular contacts are normal, with the closest approach of anions being 3.19 Å between O(9) and O(16).

Figure 3. Stereoscopic view of the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anion (anion I), with vibrational ellipsoids drawn at the 50% probability level.

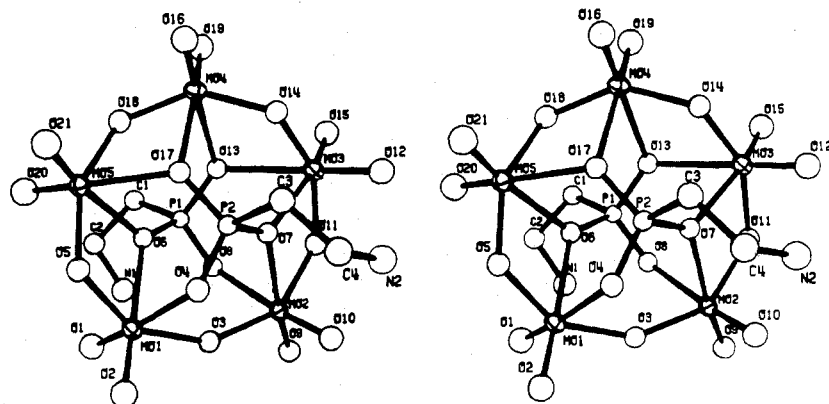**Figure 4.** Stereoscopic view of the $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anion (anion II). The vibrational ellipsoids are drawn at the 50% probability level.

The shortest water–anion distance is 2.83 Å between aq(2) and O(15) and between aq(5) and O(5), while the shortest water–water contact is 2.99 Å between aq(3) and aq(5). The distances between the positively charged NH_3^+ groups of the anion and the anion oxygens are expectedly shorter, with the closest approaches being 2.77 Å between N(2) and O(9) and 2.86 Å between N(1) and O(19).

Bond lengths and angles involving the two types of cations are given in Table IV. The $N(CH_3)_4^+$ group has the usual tetrahedral geometry, with C–N–C angles ranging from 107 to 112 (1)° and C–N distances ranging from 1.49 to 1.54 (2) Å. The coordination geometry about the sodium ion is that of a distorted octahedron, with sodium ion–water distances ranging from 2.36 to 2.48 (1) Å and the sodium ion–anion oxygen distance, Na–O(21), being 2.58 (1) Å. The Na–Na separation is 3.76 (1) Å.

Geometry of the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ Anions (Anion I and Anion I′) and the $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ Anion (Anion II). The anions I, I′, and II all possess the same basic structure, as seen in Figure 3 (anion I) and Figure 4 (anion II). The chemically equivalent molybdenum, phosphorus, and oxygen atoms in each anion have been numbered correspondingly. The geometry of each anion is similar to that reported for the $[P_2Mo_5O_{23}]^{6-}$ anion,[7] with a methyl or ethylammonium group replacing the terminal oxygens on phosphorus. Anions I and I′ nearly possess a twofold rotation axis running through Mo(4) and O(3), and in anion II this twofold symmetry is broken only by the ethylammonium groups. The anions can be considered to be composed of MoO_6 octahedra joined by sharing edges, except for Mo(1) and Mo(2) which share only a corner (Figure 5). Each face of the Mo_5 ring is capped by the tetrahedral RPO_3 groups, with two oxygen atoms each shared by two MoO_6 octahedra and one oxygen atom shared by only one octahedron (Mo(1) or Mo(2)). This results in the asymmetry of the Mo_5 ring previously noted.[7] Selected distances and

Table IV. Selected Distances (Å) and Angles (deg) for the Cations in $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ (II)

$[N(CH_3)_4]^+$

Distances

N(3)–C(5)	1.50 (2)	N(3)–C(7)	1.51 (2)
N(3)–C(6)	1.54 (2)	N(3)–C(8)	1.49 (2)

Angles

C(5)–N(3)–C(6)	112 (1)	C(6)–N(3)–C(7)	109 (1)
C(5)–N(3)–C(7)	109 (1)	C(6)–N(3)–C(8)	112 (1)
C(5)–N(3)–C(8)	107 (1)	C(7)–N(3)–C(8)	109 (1)

$[Na_2(H_2O)_8]^{2+}$

Distances

Na–aq(1)	2.457 (10)	Na–aq(4)	2.479 (11)
Na–aq(2)	2.355 (11)	Na–aq(1)^a	2.431 (9)
Na–aq(3)	2.468 (11)	Na–O(21)	2.582 (9)

Angles

aq(1)–Na–aq(2)	160.0 (4)	aq(2)–Na–O(21)	88.3 (3)
aq(1)–Na–aq(3)	105.2 (4)	aq(3)–Na–aq(4)	80.5 (4)
aq(1)–Na–aq(4)	109.3 (3)	aq(3)–Na–aq(1)^a	173.7 (4)
aq(1)–Na–aq(1)^a	79.3 (3)	aq(3)–Na–O(21)	99.2 (3)
aq(1)–Na–O(21)	74.2 (3)	aq(4)–Na–aq(1)^a	93.9 (3)
aq(2)–Na–aq(3)	86.8 (4)	aq(4)–Na–O(21)	176.5 (4)
aq(2)–Na–aq(4)	88.2 (4)	aq(1)^a–Na–O(21)	86.2 (3)
aq(2)–Na–aq(1)^a	90.2 (3)		

^{a} Symmetrically related to aq(1) by the center of inversion.

angles are presented in Table V. The Mo(1)–Mo(2) distances range from 3.689 to 3.707 (1) Å (average 3.696 Å) for the three anions (corner-shared MoO_6), while the remaining Mo–Mo distances range from 3.358 to 3.403 (1) Å (average 3.383 Å) for the edge-shared octahedra.

The P–C distances in anions I, I′, and II and the C–C and C–N distances in anion II also appear normal. The P–C bond lengths range from 1.78 to 1.81 (1) Å (average 1.796 Å), while in anion II the C–C distances are 1.55 (2) and 1.53 (2) Å and

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Table V. Selected Distances (Å) and Angles (deg) for the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ (I and I') and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ (II) Anions

Atoms	Mo-Mo, P-Mo, and P-P distances			Atoms	Mo-Mo, P-Mo, and P-P distances		
	Anion I	Anion I'	Anion II		Anion I	Anion I'	Anion II
Mo(1)-Mo(2)	3.693 (1)	3.707 (1)	3.689 (2)	P(1)-Mo(4)	3.470 (3)	3.444 (2)	3.512 (3)
Mo(2)-Mo(3)	3.375 (1)	3.394 (1)	3.385 (1)	P(1)-Mo(5)	3.440 (3)	3.431 (2)	3.442 (3)
Mo(3)-Mo(4)	3.368 (1)	3.358 (1)	3.385 (1)	P(2)-Mo(1)	3.330 (2)	3.295 (3)	3.325 (3)
Mo(4)-Mo(5)	3.394 (1)	3.388 (1)	3.403 (2)	P(2)-Mo(2)	3.628 (2)	3.621 (3)	3.600 (3)
Mo(5)-Mo(1)	3.382 (1)	3.384 (1)	3.376 (2)	P(2)-Mo(3)	3.467 (3)	3.448 (3)	3.492 (3)
P(1)-Mo(1)	3.616 (3)	3.269 (2)	3.561 (3)	P(2)-Mo(4)	3.433 (3)	3.443 (2)	3.523 (3)
P(1)-Mo(2)	3.302 (2)	3.296 (2)	3.288 (3)	P(2)-Mo(5)	3.551 (2)	3.589 (3)	3.529 (3)
P(1)-Mo(3)	3.529 (2)	3.562 (2)	3.501 (3)	P(1)-P(2)	3.776 (3)	3.772 (3)	3.753 (4)

Atoms	Mo-O and P-O distances			Atoms	Mo-O and P-O distances		
	Anion I	Anion I'	Anion II		Anion I	Anion I'	Anion II
				Terminal Oxygen			
Mo(1)-O(1)	1.722 (6)	1.717 (7)	1.717 (7)	Mo(3)-O(15)	1.718 (7)	1.720 (6)	1.703 (7)
Mo(1)-O(2)	1.694 (7)	1.694 (6)	1.712 (7)	Mo(4)-O(16)	1.705 (6)	1.722 (6)	1.712 (7)
Mo(2)-O(9)	1.683 (6)	1.699 (6)	1.718 (7)	Mo(4)-O(19)	1.732 (7)	1.718 (6)	1.705 (7)
Mo(2)-O(10)	1.733 (6)	1.716 (6)	1.741 (7)	Mo(5)-O(20)	1.706 (7)	1.683 (7)	1.725 (8)
Mo(3)-O(12)	1.720 (6)	1.695 (7)	1.716 (7)	Mo(5)-O(21)	1.698 (7)	1.725 (7)	1.710 (8)
				Oxygen Doubly Shared by Two Mo Atoms			
Mo(1)-O(5)	1.930 (6)	1.920 (6)	1.921 (7)	Mo(3)-O(14)	1.940 (6)	1.948 (6)	1.918 (7)
Mo(1)-O(3)	1.912 (6)	1.926 (6)	1.927 (7)	Mo(4)-O(14)	1.912 (6)	1.924 (6)	1.895 (7)
Mo(2)-O(3)	1.921 (7)	1.923 (6)	1.903 (7)	Mo(4)-O(18)	1.938 (6)	1.909 (6)	1.889 (7)
Mo(2)-O(11)	1.921 (7)	1.925 (6)	1.924 (7)	Mo(5)-O(18)	1.934 (6)	1.948 (6)	1.956 (7)
Mo(3)-O(11)	1.912 (6)	1.946 (6)	1.929 (7)	Mo(5)-O(5)	1.928 (6)	1.937 (6)	1.950 (7)
				Oxygen Doubly Shared by One Mo Atom and One P Atom			
Mo(1)-O(4)	2.257 (6)	2.233 (6)	2.317 (7)	P(1)-O(8)	1.516 (6)	1.537 (6)	1.515 (7)
Mo(2)-O(8)	2.242 (6)	2.251 (6)	2.278 (7)	P(2)-O(4)	1.508 (6)	1.520 (6)	1.516 (7)
				Oxygen Triply Shared by Two Mo Atoms and One P Atom			
Mo(1)-O(6)	2.382 (6)	2.398 (5)	2.316 (7)	Mo(5)-O(17)	2.384 (6)	2.440 (7)	2.385 (7)
Mo(2)-O(7)	2.423 (6)	2.387 (6)	2.372 (6)	Mo(5)-O(6)	2.207 (6)	2.220 (6)	2.221 (7)
Mo(3)-O(7)	2.240 (7)	2.225 (6)	2.246 (7)	P(1)-O(6)	1.560 (6)	1.542 (6)	1.553 (7)
Mo(3)-O(13)	2.369 (6)	2.374 (6)	2.373 (7)	P(1)-O(13)	1.535 (7)	1.534 (6)	1.524 (7)
Mo(4)-O(13)	2.313 (6)	2.303 (6)	2.404 (7)	P(2)-O(7)	1.529 (7)	1.558 (6)	1.552 (7)
Mo(4)-O(17)	2.288 (6)	2.294 (6)	2.404 (7)	P(2)-O(17)	1.543 (6)	1.525 (6)	1.547 (7)

Anion I		Anion II		Anion I		Anion II	
Atoms	Additional distances	Atoms	Additional distances	Atoms	Additional distances	Atoms	Additional distances
P(1)-C(1)	1.790 (10)	P(1)-C(1)	1.808 (10)	P(2')-C(2')	1.802 (10)	C(3)-C(4)	1.527 (15)
P(1')-C(1')	1.802 (10)	P(2)-C(3)	1.791 (10)			C(2)-N(1)	1.537 (14)
P(2)-C(2)	1.784 (9)	C(1)-C(2)	1.546 (15)			C(2)-N(2)	1.509 (14)

Atoms	Angles about Mo			Atoms	Angles about Mo		
	Anion I	Anion I'	Anion II		Anion I	Anion I'	Anion II
O(1)-Mo(1)-O(2)	101.8 (3)	101.7 (3)	103.1 (3)	O(11)-Mo(3)-O(15)	98.7 (3)	98.0 (3)	99.0 (3)
O(1)-Mo(1)-O(3)	97.6 (3)	96.9 (3)	99.4 (3)	O(12)-Mo(3)-O(13)	165.3 (3)	166.7 (3)	164.4 (3)
O(1)-Mo(1)-O(4)	172.1 (3)	172.6 (3)	172.4 (3)	O(12)-Mo(3)-O(14)	96.8 (3)	98.3 (3)	96.4 (3)
O(1)-Mo(1)-O(5)	102.1 (3)	100.9 (3)	101.4 (3)	O(12)-Mo(3)-O(15)	103.4 (3)	103.2 (4)	104.0 (4)
O(1)-Mo(1)-O(6)	85.3 (3)	84.5 (3)	86.8 (3)	O(13)-Mo(3)-O(14)	72.1 (2)	72.7 (2)	72.4 (3)
O(2)-Mo(1)-O(3)	103.2 (3)	103.9 (3)	100.9 (3)	O(13)-Mo(3)-O(15)	88.2 (3)	88.3 (3)	89.2 (3)
O(2)-Mo(1)-O(4)	86.0 (3)	85.4 (3)	84.4 (3)	O(14)-Mo(3)-O(15)	100.1 (3)	101.3 (3)	101.4 (3)
O(2)-Mo(1)-O(5)	100.2 (3)	100.4 (3)	100.9 (3)	O(13)-Mo(4)-O(14)	73.9 (2)	74.8 (2)	72.0 (2)
O(2)-Mo(1)-O(6)	168.4 (3)	169.1 (3)	168.1 (3)	O(13)-Mo(4)-O(16)	169.1 (3)	167.6 (3)	166.1 (3)
O(3)-Mo(1)-O(4)	79.4 (2)	79.6 (2)	77.8 (3)	O(13)-Mo(4)-O(17)	80.8 (2)	80.3 (2)	82.6 (2)
O(3)-Mo(1)-O(5)	145.5 (3)	146.1 (2)	145.4 (3)	O(13)-Mo(4)-O(18)	80.6 (2)	80.7 (2)	80.2 (3)
O(3)-Mo(1)-O(6)	84.8 (2)	84.0 (2)	83.6 (3)	O(13)-Mo(4)-O(19)	87.9 (3)	88.2 (3)	88.6 (3)
O(4)-Mo(1)-O(5)	77.2 (2)	79.2 (2)	78.0 (3)	O(14)-Mo(4)-O(16)	101.2 (3)	96.6 (3)	99.4 (3)
O(4)-Mo(1)-O(6)	87.2 (2)	88.7 (2)	85.8 (3)	O(14)-Mo(4)-O(17)	83.3 (2)	80.6 (2)	81.5 (3)
O(5)-Mo(1)-O(6)	69.1 (2)	69.4 (2)	70.4 (3)	O(14)-Mo(4)-O(18)	147.7 (3)	147.7 (2)	144.2 (3)
O(3)-Mo(2)-O(7)	84.3 (2)	84.0 (2)	84.7 (3)	O(14)-Mo(4)-O(19)	101.9 (3)	102.2 (3)	101.4 (3)
O(3)-Mo(2)-O(8)	80.3 (2)	80.0 (2)	78.3 (3)	O(16)-Mo(4)-O(17)	89.1 (3)	89.5 (3)	85.4 (3)
O(3)-Mo(2)-O(9)	102.0 (3)	102.5 (3)	103.6 (3)	O(16)-Mo(4)-O(18)	100.2 (3)	103.7 (3)	102.8 (3)
O(3)-Mo(2)-O(10)	99.8 (3)	98.0 (3)	99.3 (3)	O(16)-Mo(4)-O(19)	102.8 (3)	102.6 (3)	104.0 (3)
O(3)-Mo(2)-O(11)	145.2 (2)	145.5 (2)	145.5 (3)	O(17)-Mo(4)-O(18)	73.2 (2)	74.8 (2)	72.7 (3)
O(7)-Mo(2)-O(8)	88.2 (2)	89.7 (2)	87.3 (2)	O(17)-Mo(4)-O(19)	165.7 (3)	167.0 (3)	169.5 (3)
O(7)-Mo(2)-O(9)	171.0 (3)	170.4 (3)	168.8 (3)	O(18)-Mo(4)-O(19)	96.6 (3)	97.6 (3)	100.1 (3)
O(7)-Mo(2)-O(10)	83.4 (3)	84.2 (3)	82.3 (3)	O(5)-Mo(5)-O(6)	73.1 (2)	73.2 (2)	72.1 (3)
O(7)-Mo(2)-O(11)	69.6 (2)	69.5 (2)	69.9 (3)	O(5)-Mo(5)-O(17)	87.7 (2)	86.6 (2)	87.2 (3)
O(8)-Mo(2)-O(9)	86.5 (3)	84.5 (3)	87.1 (3)	O(5)-Mo(5)-O(18)	151.1 (3)	149.7 (3)	151.1 (3)
O(8)-Mo(2)-O(10)	171.6 (3)	173.7 (3)	169.5 (3)	O(5)-Mo(5)-O(20)	99.5 (3)	100.7 (3)	99.7 (3)
O(8)-Mo(2)-O(11)	76.4 (2)	78.2 (3)	77.6 (3)	O(5)-Mo(5)-O(21)	97.4 (3)	98.4 (3)	100.1 (3)
O(9)-Mo(2)-O(10)	101.7 (3)	101.8 (3)	103.4 (3)	O(6)-Mo(5)-O(17)	73.3 (2)	72.3 (2)	72.3 (3)
O(9)-Mo(2)-O(11)	102.0 (3)	101.7 (3)	99.4 (3)	O(6)-Mo(5)-O(18)	82.0 (2)	80.8 (2)	82.2 (3)
O(10)-Mo(2)-O(11)	99.7 (3)	100.8 (3)	99.9 (3)	O(6)-Mo(5)-O(20)	96.4 (3)	96.6 (3)	95.3 (3)
O(7)-Mo(3)-O(11)	74.0 (2)	72.9 (2)	72.7 (3)	O(6)-Mo(5)-O(21)	158.1 (3)	159.3 (3)	158.8 (3)

Table V *(Continued)*

Atoms	Angles about Mo			Atoms	Angles about Mo		
	Anion I	Anion I'	Anion II		Anion I	Anion I'	Anion II
O(7)–Mo(3)–O(12)	96.2 (3)	96.8 (3)	94.6 (3)	O(17)–Mo(5)–O(18)	71.0 (2)	70.7 (2)	72.1 (3)
O(7)–Mo(3)–O(13)	73.0 (2)	72.6 (2)	73.3 (2)	O(17)–Mo(5)–O(20)	165.3 (3)	164.6 (3)	163.4 (3)
O(7)–Mo(3)–O(14)	80.9 (2)	81.2 (2)	81.3 (3)	O(17)–Mo(5)–O(21)	86.8 (3)	88.6 (3)	88.0 (3)
O(7)–Mo(3)–O(15)	160.0 (3)	159.2 (3)	160.7 (3)	O(18)–Mo(5)–O(20)	97.6 (3)	97.5 (3)	95.6 (3)
O(11)–Mo(3)–O(12)	99.8 (3)	99.1 (3)	98.6 (3)	O(18)–Mo(5)–O(21)	100.6 (3)	100.6 (3)	99.2 (3)
O(11)–Mo(3)–O(13)	86.9 (2)	85.5 (2)	87.4 (3)	O(20)–Mo(5)–O(21)	104.8 (3)	103.6 (4)	105.4 (4)
O(11)–Mo(3)–O(14)	151.1 (3)	150.2 (3)	150.9 (3)				

Atoms	Angles about P			Atoms	Angles about P		
	Anion I	Anion I'	Anion II		Anion I	Anion I'	Anion II
O(6)–P(1)–O(8)	109.6 (3)	108.5 (3)	109.5 (4)	O(4)–P(2)–O(7)	109.3 (3)	109.8 (3)	108.5 (4)
O(6)–P(1)–O(13)	110.7 (3)	110.8 (3)	111.3 (4)	O(4)–P(2)–O(17)	110.1 (3)	111.0 (4)	113.5 (4)
O(6)–P(1)–C(1)	106.7 (4)	108.8 (4)	105.5 (4)	O(4)–P(2)–C(2)^a	108.5 (4)	108.1 (4)	109.0 (4)
O(8)–P(1)–O(13)	110.6 (3)	111.7 (4)	112.3 (4)	O(7)–P(2)–O(17)	110.7 (3)	110.8 (3)	111.3 (4)
O(8)–P(1)–C(1)	111.1 (4)	109.3 (4)	109.0 (4)	O(7)–P(2)–C(2)^a	109.2 (4)	108.5 (4)	107.3 (4)
O(13)–P(1)–C(1)	108.1 (5)	107.6 (4)	109.0 (4)	O(17)–P(2)–C(2)^a	109.0 (4)	108.5 (4)	107.1 (4)

Atoms	Angles about C (anion II)	Atoms	Angles about C (anion II)	Atoms	Angles about C (anion II)	Atoms	Angles about C (anion II)
P(1)–C(1)–C(2)	113.1 (7)	C(1)–C(2)–N(1)	109.9 (8)	P(2)–C(3)–C(4)	115.6 (8)	C(3)–C(4)–N(2)	111.8 (9)

^{a} Corresponds to C(3) in anion II.
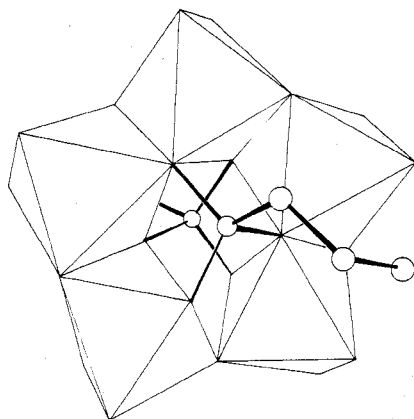
Figure 5. The $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anion (anion II) showing the MoO$_6$ octahedra.

the C–N distances are 1.54 (1) and 1.51 (1) Å. The P–C–C and C–C–N angles range from 110 to 116 (1)°.

The Mo–O and P–O bond lengths are consistent with those previously reported,[7] with average distances and ranges given in Table VI. It can be seen that the Mo–O distance increases considerably as the sharing of oxygen atoms increases, with average values of 1.71 Å for terminal Mo–O bonds to 2.33 Å for Mo–O bonds in which the oxygen atom is shared by two Mo atoms and one P atom. The increase in P–O bond lengths is not nearly so marked, with average values of 1.52 Å for P–O bonds in which the oxygen atom is shared by one P atom and one Mo atom to 1.54 Å for Mo–O bonds with the oxygen atom shared by one P atom and two Mo atoms. These distances can be compared to the average values for P–O bond lengths of 1.50, 1.52, and 1.56 (1) Å reported for terminal, doubly shared, and triply shared oxygen atoms, respectively, in the $[P_2Mo_5O_{23}]^{6-}$ anion.[7] Table V also shows that, whereas the MoO$_6$ octahedra exhibit large angular variations from the ideal octahedral geometry, the RPO$_3$ tetrahedral angles remain close to the predicted value, ranging from 106 to 112°. Thus it appears that the organophosphonate portion of the anion retains its original structure insofar as possible, while the MoO$_6$ octahedra are considerably distorted in forming the heteropoly anion. This retention of geometry by the phosphate or organophosphonate moiety might account for the inability to

Table VI. Average Mo–O and P–O Bond Distances (Å)

Atoms	No. aver- aged	Type of oxygen atom	Range	Average
Mo–O	30	Terminal	1.683–1.741^a	1.712
Mo–O	30	Doubly shared by two Mo atoms	1.889–1.946	1.926
Mo–O	6	Doubly shared by one Mo atom and one P atom	2.233–2.317	2.263
Mo–O	24	Triply shared by two Mo atoms and one P atom	2.207–2.440	2.332
P–O	6	Doubly shared by one P atom and one Mo atom	1.508–1.537	1.519
P–O	12	Triply shared by one P atom and two Mo atoms	1.524–1.560	1.542

^{a} Average estimated standard deviations are 0.006 Å for Mo–O and 0.007 Å for P–O.

isolate the corresponding As$_2$Mo$_5$ ions,[8] with arsenic in place of phosphorus. The larger covalent radius of arsenic (1.22 Å vs. 1.10 Å for phosphorus[9]) might sterically inhibit the formation of heteropoly ions of this type with molybdenum.

Registry No. I, 57820-87-8; II, 57951-45-8.

Supplementary Material Available: Listings of structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) See, for example, the structure of [C(NH$_2$)$_3$]$_2$[(CH$_3$)$_2$AsMo$_4$O$_{14}$(OH)]: K. M. Barkigia and C. O. Quicksall, Abstracts, 25th Anniversary Meeting of the American Crystallographic Association, Charlottesville, Va., No. J19.
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programs, Johnson's ORTEP plotting program, and the LSAM series by Main, Woolfson, and Germain.

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Trigonal-Prismatic vs. Octahedral Coordination in a Series of Tris(benzene-1,2-dithiolato) Complexes. 1. Crystal and Molecular Structure of Tris(benzene-1,2-dithiolato)molybdenum(VI), Mo(S2C6H4)3[1]

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The structure of $Mo(S_2C_6H_4)_3$ has been determined crystallographically and consists of four discrete molecules of the complex in the unit cell (space group *Pnam*, a = 16.093 (3) Å, b = 10.177 (1) Å, c = 11.906 (2) Å). Observed and calculated densities are 1.74 (2) and 1.75 g cm^{-3}, respectively. The molybdenum atoms occupy the 4(c) special positions and the molecules therefore have site symmetry m. On the basis of 1050 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ the structural data were refined by full-matrix, least-squares techniques to R = 0.035 and R_w = 0.034. The molybdenum atoms are each surrounded by six sulfur atoms in an almost perfect trigonal-prismatic coordination, with the two triangular faces of the prism being related by the crystallographic mirror plane. The dithiolene ligands span the three edges of the prism connecting the two triangular faces. The complex is distorted from ideal D_{3h} symmetry because of bending of the S_2C_6 ligand planes from the corresponding MoS_2 planes by 13.1, 21.1, and 30.0°. Some relevant average molecular parameters are Mo–S = 2.367 (6) Å, S–S(intraligand) = 3.110 (8) Å, S–S(interligand) = 3.091 (15) Å, and S–C = 1.727 (6) Å.

Introduction

The discovery of trigonal-prismatic (TP) coordination in a series of 1,2-dithiolene[2] complexes, ReS6C6Ph6[3] (Ph = C6H5), MoS6C6H6,[4] and VS6C6Ph6,[5] heralded the first examples of nonoctahedral coordination being displayed by six-coordinate molecular complexes. Although TP coordination had been observed much earlier in MoS2 and WS2,[6] and later in NiAs,[7] these latter compounds were infinitely extended lattices and molecular packing was believed responsible for their unusual geometry.[8] It therefore was of interest to determine what factors were responsible for the preference of TP over octahedral coordination in these dithiolene complexes. In all three dithiolene prisms an amazing constancy in prism dimensions was observed with all having inter- and intraligand S–S distances of ca. 3.08 and 3.06 Å, respectively, and M–S (M = metal) distances of ca. 2.33 Å. The shortness of these "nonbonded" S–S contacts led to the conclusion that S–S bonding was involved in stabilizing the prism.[9,10] The similarity in the M–S distances, although the covalent and ionic radii of molybdenum and rhenium were 0.07 Å greater than those of vanadium, was thought to be a consequence of the S–S bonding.

In an attempt to explain the trigonal-prism stability Gray et al. proposed a molecular orbital scheme in which they attributed the prism stability to two features.[10] The first, overlap of the sulfur π_h orbitals (sulfur sp^2 hybrid orbitals at 120° to the M–S and S–C σ orbitals) with the metal d_{z^2} orbitals, gives rise to a stable $2a_1'$ orbital, which is always filled, and an empty antibonding $3a_1'$ orbital. The second interaction, between the ligand π_v orbitals (perpendicular to the ligand plane) and the metal $d_{x^2-y^2}$ and d_{xy} orbitals, gives rise to the stable $4e'$ orbital, which is also occupied, and the empty $5e'$ antibonding level. It was the occupancy of these stable orbitals to which Gray attributed the prism stability.

The subsequent structural determinations of [Me4N]2-[VS6C6(CN)6][11] (Me = CH3) and [Ph4As]2[MoS6C6-(CN)6][12] showed non-trigonal-prismatic coordination and both in fact had geometries approximately midway between the TP and octahedral limits. In the molybdenum dianion the double occupancy of the $3a_1'$ molecular orbital, which is antibonding relative to prism stability, was believed to be an important factor in the distortion from TP coordination. In the vanadium dianionic complex the distortion was much more irregular and not readily predictable by Gray's scheme. However reversals in several of the molecular orbital levels have been considered[13,14] and these may account for the distortion. In addition, the anion in [Ph4As]2[FeS6C6(CN)6][18] was found to have an almost undistorted octahedral coordination. In this anion the destabilization of the prism can again be attributed to population of the antibonding $3a_1'$ level. The octahedral coordination is further stabilized relative to the TP because of additional occupancy of the $5e'$ level which is also antibonding with respect to the prism.

The dianionic tris(dithiolenes) therefore lend support to Gray's hypothesis that the ligand π_h and metal d_{z^2} interaction is significant in stabilizing the prism. However no structural evidence was available testing the importance of the ligand π_v and metal d_{xy}, $d_{x^2-y^2}$ interaction. It seemed reasonable to expect that, in view of the proximity in energy of the $4e'$ molecular orbital and the metal d orbitals, the $4e'$ level would be sensitive to changes in d-orbital energies. Thus destabilizing the metal d orbitals might be expected to destabilize the resulting $4e'$ level with a resulting decrease in prism stability. In this respect the series of compounds to be reported in this and the following two papers—Mo(S2C6H4)3, [Ph4As]-[Nb(S2C6H4)3], and [Me4N]2[Zr(S2C6H4)3]—is especially useful. The molybdenum and niobium complexes have electronic spectra[16,17] similar to those observed in previous TP complexes and this type of spectrum was believed characteristic of TP coordination. The spectrum of the zirconium complex,[17] however, is vastly different, implying a non-trigonal-prismatic coordination. Thus it was believed possible to test the importance of the $4e'$ molecular orbital level in prism stability since in this isoelectronic series, from a molecular orbital viewpoint, only the metal d-orbital energies are changing, and this change in d-orbital energies seemed to be strongly influencing prism stability as witnessed by the differing electronic spectra. The determination of the structures of the three