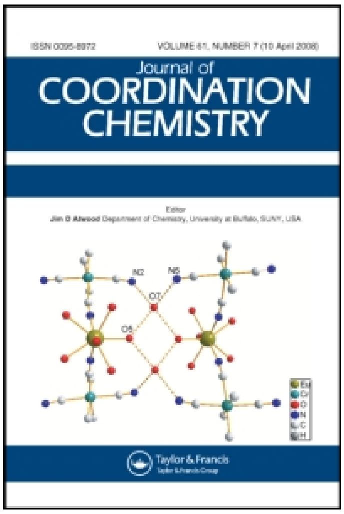

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CRYSTAL AND ELECTRONIC STRUCTURE OF A PROTONATED IMIDAZOLE DIPHOSPHOPENTAMOLYBDENUM(VI) POLYOXOMETALATE: $(C_4H_7N_2)_4[HP_2Mo_5O_{23}]\cdot H_3O\cdot 4.5H_2O$

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The protonated imidazole diphosphopentamolybdenum polyoxometalate $(C_4H_7N_2)_4[HP_2Mo_5O_{23}]\cdot H_3O\cdot 4.5H_2O$ has been synthesized and its structure has been determined by single-crystal X-ray diffraction. This compound crystallizes in the triclinic crystal system, space group $P(-1)$, $a = 10.171(2)$, $b = 11.839(2)$, $c = 20.170(4)$ Å, $\alpha = 75.69(3)$, $\beta = 84.56(3)$, $\gamma = 64.90(3)^\circ$, $V = 2130.8(7)$ Å^3, $Z = 2$ and $R = 0.0329$. The compound is composed of $[HP_2Mo_5O_{23}]^{5-}$ clusters and $C_4H_7N_2^+$ and H_3O^+ cations as well as water of crystallization, and forms a supramolecular network structure through hydrogen bonds. The monoprotonated polyanions are held together by two strong hydrogen bonds [$d_{O\cdots O} = 2.582(7)$ and $2.581(8)$ Å]. Density functional theory (DFT) calculation has been carried out to investigate the electronic properties of the $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ ($n = 0, 1, 2$) polyanions. Mulliken charges for all atoms have been analyzed. The results show that the negative charges delocalize over all types of oxygen atoms, and molybdenum and phosphorus atoms accept electrons from the oxygen atoms. The protonation affects the charge distribution, redox properties and relative stability of the polyanion; the non-protonated polyanion $[P_2Mo_5O_{23}]^{6-}$ can be more easily reduced.

Keywords: Organoammonium; Diphosphopentamolybdate; X-ray diffraction; Hydrogen bond; Density functional theory

INTRODUCTION

Contemporary interest in inorganic oxides stems from the ubiquity and diversity of the composition and structure that endow these materials with special physical properties giving rise to applications in many fields extending from heavy construction to

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microelectronics [1]. The interactions of the polyoxometalates with organic functional compounds have attracted growing attention since polyoxometalates and their compounds have been successfully applied to fields such as medicine, biology, catalysis and molecular materials [2,3]. The phosphorus–molybdenum oxides are an important subclass of the oxides including binary and ternary oxides and isopoly- and heteropolyoxoanion clusters [4–6]. The structures of heteropolyoxoanions, such as $Na_6[P_2Mo_5O_{23}] \cdot 13H_2O$, $Na_4[H_2P_2Mo_5O_{23}] \cdot 10H_2O$ and $(NH_4)_5[HP_2Mo_5O_{23}] \cdot 3H_2O$, have been determined [7–9]. A polymeric nickel complex with formula $(NH_4)_8Ni[(HP_2Mo_5O_{23})_2] \cdot 12H_2O$ and a diphosphopentamolybdate cage $[P_2Mo_5O_{21}]^{2-}$ have been synthesized [10].

There is interest in how these molecules and ions are organized in the solid state to form novel materials with improved electronic, optical, magnetic or catalytic properties. The study of Aranzabe *et al.* on the geometrical characteristics of $(C_4H_{12}N)_4[H_2P_2Mo_5O_{23}] \cdot 5H_2O$, $Al(C_4H_{15}N_3)_4[HP_2Mo_5O_{23}]Cl \cdot 10H_2O$ and $(C_5H_7N_2)_6[P_2Mo_5O_{23}] \cdot 5H_2O$ revealed several relationships between the protonated state and topological changes in the heteropolyanions [11]. This work is of particular importance in the field of polyoxometalate chemistry, as the organic cations play an important role not only in the formation of the crystal structure but also in their catalytic properties such as particle size, porosity and thermal stability [12].

Organoamine bases were chosen because of the ability of the amino groups to form strong hydrogen bonds to the oxygen atoms of heteropolyanions and to stabilize the crystal structure of this kind of compound. Although there have been theoretical studies on packing interactions in simple organic systems, to date very few reports have dealt with high-level theoretical calculations on crystal packing of polyoxometalate anions because of the large size of these species. Recently, DFT methods have been applied to interpret polyanions properties [13–15] with convincing results. In this article, we present the synthesis, crystal structural analysis and first theoretical studies of the polyanion $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ ($n = 0, 1, 2$) using the DFT method.

EXPERIMENTAL

Synthesis

The title compound was synthesized by hydrothermal reaction under autogenous pressure. A mixture of MoO_3 (0.8641 g), 2-methylimidazole (0.0822 g), H_3PO_4 (0.04 cm^3, 85%) and H_2O (10 cm^3) in a molar ratio 1 : 1 : 2 : 90 was sealed in a 20-cm^3 Teflon-lined stainless steel autoclave and heated at 180°C for 5 days. After cooling to room temperature, pale pink block crystals were isolated by filtration and washed with distilled water. Yield: 15%. Calcd. for $C_{16}H_{41}Mo_5N_8O_{28.5}P_2$: C, 14.34; H, 3.03; N, 8.36; P, 4.62; Mo, 35.85. Found: C, 14.29; H, 3.01; N, 8.54; P, 4.67; Mo, 35.89. Magana 560 FT-IR (KBr pellets, cm^{-1}): 1100s, $\nu(P–O_t)$; 1065s, $\nu(P–O_b)$; 930vs, $\nu(Mo–O_t)$; 900vs, $\nu(Mo–O_b)$; breathing of polyanion 700vs(br).

Structural Determination and Analysis

A suitable pale pink crystal of the compound with approximate dimensions of 0.46 × 0.37 × 0.32 mm was mounted on a glass fibre. Diffraction intensities for this

TABLE I Crystal data and structure refinement for the title compound

Empirical formula	$C_{16}H_{41}Mo_5N_8O_{28.5}P_2$
Formula weight	1343.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P(-1)$
Unit cell dimensions	
a (Å)	10.171(2)
b (Å)	11.839(2)
c (Å)	20.170(4)
α (°)	75.69(3)
β (°)	84.56(3)
γ (°)	64.90(3)
Volume (Å^3)	2130.8(7)
Z	2
Calculated density (mg m^{-3})	2.094
Absorption coefficient (mm^{-1})	1.606
$F(000)$	1322
Crystal size (mm)	0.46 × 0.37 × 0.32
θ range for data collection (°)	1.95–27.48
Limiting indices	$-13 \le h \le 13$ $-15 \le k \le 15$ $-25 \le l \le 26$
Reflections collected/unique	15687/9619 ($R_{\mathrm{int}} = 0.0186$)
Completeness to $\theta = 27.48$	98.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9619/18/595
Goodness-of-fit on F^2	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0329$, $wR_2 = 0.0995$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1044$
Largest diff. peak and hole (e Å^{-3})	1.277 and–0.996

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]$.

complex were collected on a Rigaku RAXIS-RAPID image plate diffractometer using ω scan technique with MoKα radiation ($\lambda = 0.71073$ Å) at 193(2) K. Absorption corrections were applied using the multiscan technique [16]. The structure was solved with the direct method of SHELXS-97 [17] and refined with full-matrix least-squares techniques using the SHELXL-97 program [18]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located. Analytical expression of neutral-atom scattering factors was used and anomalous dispersion correction incorporated [19]. The crystallographic data for the compound are given in Table I. Selected bond lengths and angles are given in Table II.

Theoretical Calculation

The geometry of $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ ($n = 0, 1, 2$) heteropolyanion was fully optimized by DFT methods [20] with the ADF2.3 program [21]. The Vosko–Wilk–Nusair [22] (VWN) form was used to local density approximation (LDA), and Becke's 1988 [23] exchange and Perdew's 1986 [24] correlation were corrected to LDA. Triple-ζ plus polarization Slater basis sets were used to describe the valence electrons of P and O atoms; for molybdenum a frozen core composed of 1s to 3spd shells was described by the Triple-ζ plus polarization basis set.

TABLE II Selected bond lengths (Å), bond angles and selected torsion angles (°) for the title compound

Parameter	*X-ray*	*DFT calculation*	*Parameter*	*X-ray*	*DFT calculation*
Bond lengths					
P(1)–O(19)	1.577(3)	1.54631	Mo(2)–O(8)	2.315(3)	2.38977
P(1)–O(12)	1.528(3)	1.55804	Mo(3)–O(13)	1.711(3)	1.77621
P(1)–O(3)	1.537(3)	1.57637	Mo(3)–O(14)	1.712(3)	1.77094
P(1)–O(22)	1.567(3)	1.72342	Mo(3)–O(11)	1.896(3)	1.96251
P(2)–O(4)	1.527(3)	1.58516	Mo(3)–O(7)	1.929(3)	1.95492
P(2)–O(8)	1.561(3)	1.62061	Mo(3)–O(12)	2.364(3)	2.45943
P(2)–O(16)	1.566(3)	1.63905	Mo(3)–O(8)	2.310(3)	2.32681
P(2)–O(23)	1.508(3)	1.53049	Mo(4)–O(17)	1.718(3)	1.77762
Mo(1)–O(5)	1.700(3)	1.78052	Mo(4)–O(18)	1.694(3)	1.76758
Mo(1)–O(6)	1.717(3)	1.77556	Mo(4)–O(11)	1.932(3)	1.96037
Mo(1)–O(1)	1.962(3)	2.00084	Mo(4)–O(15)	1.911(3)	1.97528
Mo(1)–O(2)	1.927(3)	1.96888	Mo(4)–O(12)	2.437(3)	2.68910
Mo(1)–O(3)	2.323(3)	2.54974	Mo(4)–O(16)	2.178(3)	2.20856
Mo(1)–O(4)	2.258(3)	2.14337	Mo(5)–O(20)	1.707(3)	1.77789
Mo(2)–O(9)	1.698(3)	1.77505	Mo(5)–O(21)	1.719(3)	1.77038
Mo(2)–O(10)	1.724(3)	1.78306	Mo(5)–O(2)	1.887(3)	1.95334
Mo(2)–O(1)	1.915(3)	1.94640	Mo(5)–O(15)	1.925(3)	1.97610
Mo(2)–O(7)	1.954(3)	1.98731	Mo(5)–O(16)	2.338(3)	2.41166
Mo(2)–O(3)	2.235(3)	2.31941	Mo(5)–O(19)	2.300(3)	2.36220
Bond angles					
O(19)–P(1)–O(12)	112.36(16)	114.298	O(1)–Mo(1)–O(3)	71.07(11)	66.647
O(19)–P(1)–O(3)	108.85(17)	113.388	O(1)–Mo(2)–O(7)	152.81(11)	152.431
O(19)–P(1)–O(22)	110.04(16)	104.604	O(1)–Mo(2)–O(3)	73.90(11)	72.329
O(3)–P(1)–O(22)	107.62(16)	100.687	O(3)–Mo(2)–O(7)	82.44(11)	84.353
O(12)–P(1)–O(22)	105.75(16)	105.935	O(8)–Mo(2)–O(7)	72.27(11)	69.365
O(12)–P(1)–O(3)	112.07(16)	115.905	O(11)–Mo(3)–O(7)	145.23(12)	146.304
O(23)–P(2)–O(4)	111.26(17)	112.556	O(8)–Mo(3)–O(7)	72.81(11)	71.260
O(23)–P(2)–O(8)	109.70(17)	112.890	O(11)–Mo(3)–O(12)	74.11(11)	72.236
O(8)–P(2)–O(4)	108.92(15)	107.140	O(15)–Mo(4)–O(11)	150.72(12)	149.993
O(23)–P(2)–O(16)	111.90(16)	113.029	O(11)–Mo(4)–O(12)	71.78(11)	67.002
O(16)–P(2)–O(4)	106.02(16)	103.831	O(15)–Mo(5)–O(19)	77.26(12)	78.910
O(8)–P(2)–O(16)	108.93(15)	106.758	O(19)–Mo(5)–O(16)	87.88(10)	83.718
O(1)–Mo(1)–O(2)	145.73(12)	145.542	P(1)–O(22)–H(22)	109.50	100.003
O(1)–Mo(1)–O(4)	76.00(11)	79.208			

RESULTS AND DISCUSSION

Crystal Structure of $(C_4H_7N_2)_4[HP_2Mo_5O_{23}]\cdot H_3O\cdot 4.5H_2O$

The isolation of the polyanion from a solution can be achieved by addition of alkylamines or aromatic amines as counterions. These counterions not only provide groups that may participate in formation of hydrogen bonding with the oxygen atoms either from the polyanions or from water molecules, but also play an important role in the photochemical properties [11]. An asymmetrical unit in the crystal contains four 2-methylimidazole cations, four and a half water molecules, one oxonium ion and one diphosphopentamolybdate(VI) anion. The diphosphopentamolybdate anion $[HP_2Mo_5O_{23}]^{5-}$ consists of five MoO_6 octahedra and two PO_4 tetrahedra (Fig. 1). The octahedra form a pentagonal ring by sharing with four edges and one corner, and the PO_4 tetrahedra are attached to two sides of the ring by sharing three oxygen atoms (Fig. 2). Each octahedron has four bridge oxygen atoms and two terminal oxygen atoms. The Mo–O bonds can be divided into three types: (i) short terminal

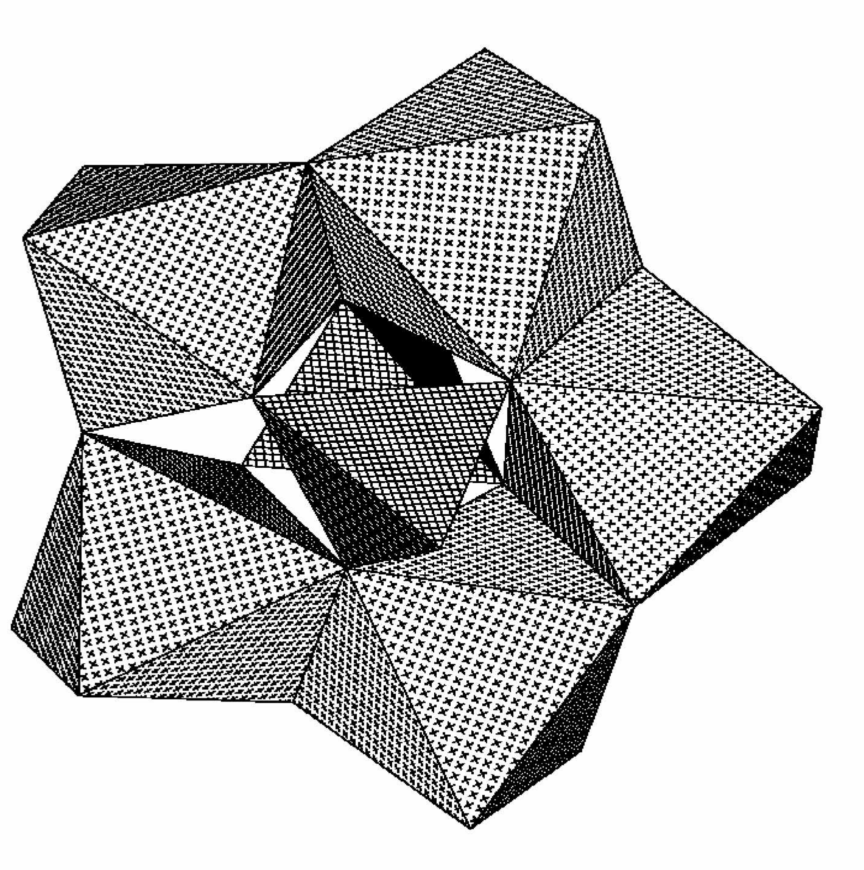

FIGURE 1 Polyhedral representation of the structure of $[P_2Mo_5O_{23}]^{6-}$.

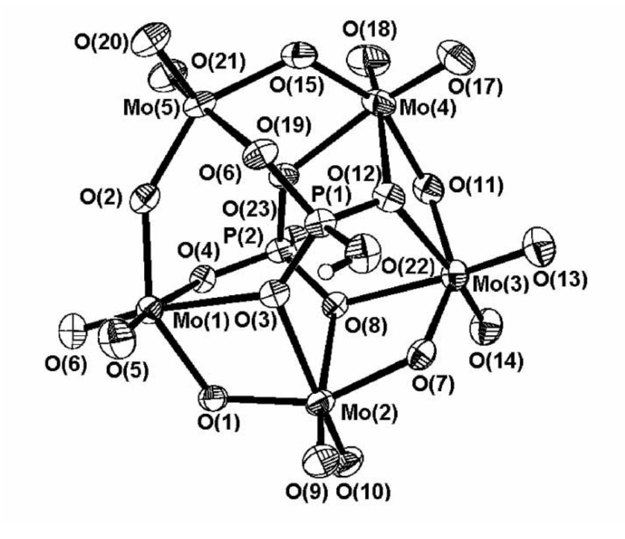

FIGURE 2 Structure and numbering scheme for $[HP_2Mo_5O_{23}]^{5-}$.

oxygen bonds, Mo–O$_t$ 1.694–1.724 Å; (ii) medium bridge oxygen bonds, Mo–O$_{b1}$ (oxygen atoms are shared by two molybdenum atoms) 1.887–1.962 Å; and (iii) long bonds Mo–O$_{b2}$ (oxygen atoms are between phosphorus and molybdenum atoms), 2.178–2.437 Å. Each molybdenum atom is coordinated by two O$_t$, two O$_{b1}$ and two O$_{b2}$ atoms. The tetrahedral PO$_4$ are almost regular with the P–O distance ranging between 1.508 and 1.577 Å, consistent with the results in the literature [11]. In the non-protonated phosphorus oxygen tetrahedron of the polyanion, P(2)–O(23) (O$_t$) (1.508 Å) is shorter than those involving the oxygen atoms shared by the molybdenum atoms P(2)–O(8) (1.561 Å), P(2)–O(16) (1.566 Å); in the protonated PO$_4$, the oxygen atom is protonated and the distance P(1)–O(22) (O$_t$) (1.567 Å) is longer than those of P(1)–O(3) (1.537 Å) and P(1)–O(12) (1.528 Å). X-ray diffraction shows that the maximal residual difference peak lies beside the heavy metal, rather than the phosphorus without the hydroxyl group. There is no residual difference peak around the phosphorus atom. On the basis of these facts an anionic formula $[HP_2Mo_5O_{23}]^{5-}$ is derived. In order to balance the charge, there must be an oxinium in the compound. Each $[HP_2Mo_5O_{23}]^{5-}$ anion is joined with the two adjacent polyanions by means of strong hydrogen bond contacts of the type O–H···O(22)···O(9) = 2.582 and O(22)···O(8) = 2.596 Å, and four protonated 2-methylimidazole molecules as counter-ions constructing the strong hydrogen bonds with the oxygen atoms of the polyanions N–H···O, stabilizing the crystal structure of the compound (Fig. 3). The different hydrogen bonds within the structure are showed in Table III.

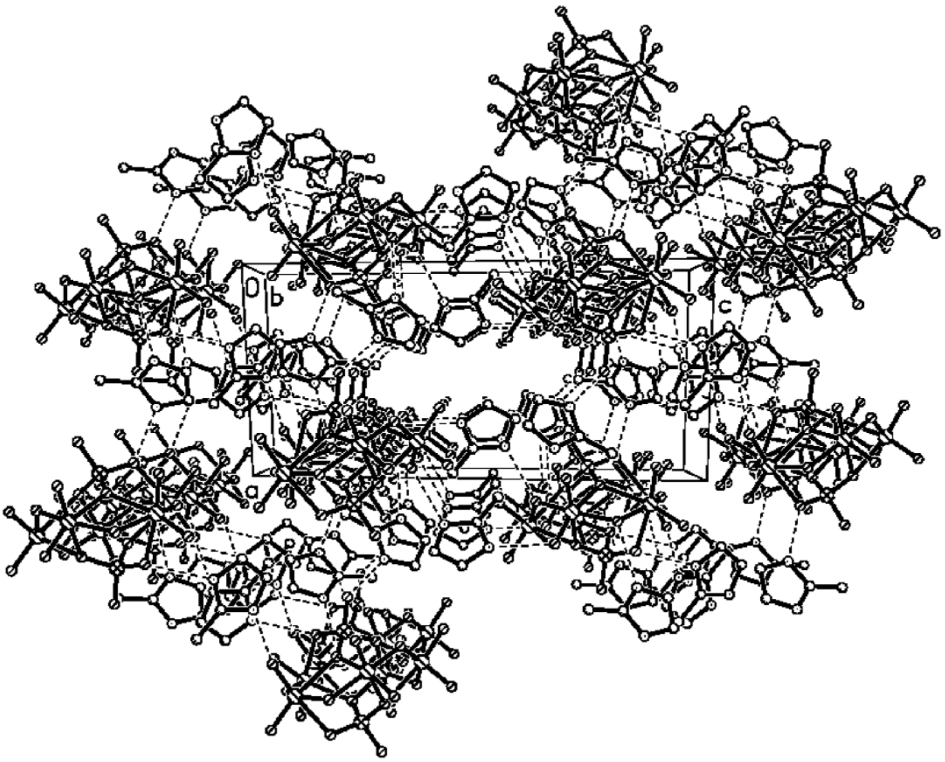

FIGURE 3 Packing arrangement of the compound along the *b*-axis.

TABLE III Hydrogen bonds for the title compound (Å and °)

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*∠(DHA)*
O(22)–H(22)···O(2W)	0.82	1.78	2.585(8)	167.4
O(22)–H(22)···O(3W) #3	0.82	1.80	2.578(8)	158.3
N(1)–H(1A)···O(6) #8	0.90	2.47	3.151(5)	133.2
N(1)–H(1B)···O(4) #8	0.90	2.32	2.811(5)	114.0
N(1)–H(1B)···O(21) #8	0.90	2.37	3.069(5)	134.6
N(5)–H(5B)···O(23)	0.90	2.19	2.662(6)	111.8
N(7)–H(7A)···O(7)	0.90	2.14	2.755(5)	124.8
N(7)–H(7A)···O(9)	0.90	2.44	3.154(5)	135.9
N(7)–H(7B)···O(22)	0.90	2.64	3.310(5)	131.6

Symmetry transformations used to generate equivalent atoms: #1: $-x-1$, $-y+2$, $-z+1$; #2: $-x$, $-y+3$, $-z$; #3: $-x+1$, $-y+1$, $-z$; #4: $x+1$, y, z; #5: $-x-1$, $-y+2$, $-z+1$; #6: $-x$, $-y+2$, $-z+1$; #7: x, $y-1$, z; #8: $-x+1$, $-y+1$, $-z$.

Calculation

The electronic properties of $[HP_2Mo_5O_{23}]^{5-}$ with one protonated oxygen atom, O(22), and $[H_2P_2Mo_5O_{23}]^{4-}$ with two protonated oxygen atoms, O(22) and O(23), can be compared to $[P_2Mo_5O_{23}]^{6-}$. A structural scheme of polyanion $[HP_2Mo_5O_{23}]^{5-}$ with atom labelling is presented in Fig. 2, in which $[P_2Mo_5O_{23}]^{6-}$ and $[H_2P_2Mo_5O_{23}]^{4-}$ show similar structures. Calculated bond lengths and bond angles for $[HP_2Mo_5O_{23}]^{5-}$ are partially given in Table II. The experimental and theoretical values are, in general, in good agreement, and the slight differences between them may result from the isolated gas-phase system used in the theoretical calculation without considering the counterions and crystal environment.

The differences of Mulliken net charges are much more useful, although in some cases they have little meaning [25]. Mulliken charges for atoms in systems $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ ($n=0,1,2$) are given in Table IV. The results show that the charges of molybdenum, phosphorus and hydrogen are all smaller in systems $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ than the ones in their formal oxidation states and the charges of the oxygen atoms are all larger than their formal valence state, implying that Mo, P and H atoms accept electrons from their adjacent O atoms. The protonation affects the charge distribution on the polyanions, and the degree of protonation leads to the different character of the charge distribution. In $[HP_2Mo_5O_{23}]^{5-}$, protonated oxygen atom O(22) donates electrons to hydrogen, so that the O(22) atom has the smallest charge and the charges of the P atoms increase. The diprotonated polyanion $[H_2P_2Mo_5O_{23}]^{4-}$ has a different charge character. The charges of the Mo and P atoms are higher than the corresponding atoms of the non-protonated anions; the charges of the terminal oxygen atoms decrease and the charges of the bridge oxygen atoms O_{b1} shared by two Mo atoms increase. In $[H_nP_2Mo_5O_{23}]^{(6-n)-}$, the charges of the bridge oxygen atoms O_{b1} are larger, but the charges of the terminal oxygen atoms O_t and bridge oxygen atoms O_{b2} are smaller. In general, the oxygen atom having the larger charge participates in nucleophilic reactions, and the oxygen atom having the smaller charge tends to be involved in electrophilic reactions [26–28]. Based on the results of the calculation, it can be proposed that the nucleophilic oxygen sites of $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ concentrate on O_{b1}, and the electrophilic oxygen sites concentrate on terminal oxygen atoms O_t. Although the bridge oxygen atoms

TABLE IV Mulliken charges for all of the atoms in the polyanions studied

Atom	$[P_2Mo_5O_{23}]^{6-}$	$[HP_2Mo_5O_{23}]^{5-}$	$[H_2P_2Mo_5O_{23}]^{4-}$
Mo1	2.096	2.130	2.131
Mo2	2.140	1.619	2.144
Mo3	2.156	2.189	2.172
Mo4	2.148	2.180	2.157
Mo5	2.096	1.456	2.123
P1	1.061	1.377	1.318
P2	1.109	1.143	1.321
O1	−0.913	−0.905	−0.907
O2	−0.930	−0.947	−0.936
O3	−0.818	−0.830	−0.825
O4	−0.731	−0.708	−0.707
O5	−0.778	−0.786	−0.741
O6	−0.807	−0.776	−0.739
O7	−0.903	−0.933	−0.924
O8	−0.801	−0.805	−0.802
O9	−0.789	−0.775	−0.752
O10	−0.807	−0.747	−0.752
O11	−0.931	−0.911	−0.954
O12	−0.752	−0.742	−0.754
O13	−0.795	−0.796	−0.739
O14	−0.812	−0.788	−0.760
O15	−0.918	−0.923	−0.916
O16	−0.835	−0.849	−0.823
O17	−0.794	−0.792	−0.733
O18	−0.808	−0.781	−0.755
O19	−0.732	−0.715	−0.713
O20	−0.810	−0.754	−0.741
O21	−0.784	−0.725	−0.736
O22	−0.7840	−0.432	−0.435
O23	−0.773	−0.733	−0.452
H1		0.059	0.094
H2			0.138

O_{b2} have smaller charges, it is more difficult for O_{b2} to participate in the reaction than O_t due to steric hindrance of O_{b2}. Furthermore, the higher degree of protonation leads to higher electrophilic and nucleophilic reactivity.

The Mulliken charges of the reduced polyanions $[HP_2Mo_5O_{23}]^{6-}$ were calculated using the same method and basis sets. The charges of the oxygen atoms O_b increase in $[HP_2Mo_5O_{23}]^{6-}$ compared to those in $[HP_2Mo_5O_{23}]^{5-}$ and the charges of the O_t atoms of Mo(2) and Mo(5) in $[HP_2Mo_5O_{23}]^{6-}$ decrease. The values are −0.7746, −0.7467, −0.7537 and −0.7251 for O(9), O(10), O(20) and O(21), respectively, and these become electrophilic active sites.

Eigenvalue diagrams for the occupied and unoccupied valence levels of $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ are given in Fig. 4. These figures are entirely qualitative and intended to show the distributions of energy levels [29,30] and the differences between $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ polyanions. The highest occupied molecular orbital (HOMO) is contributed by bridge-oxygen 2p and the lowest unoccupied molecular orbital (LUMO) is characterized by participation of molybdenum atoms 3d and bridge-oxygen 2p in the protonated and non-protonated polyanions. The energy gap between the HOMO and LUMO increases from $[P_2Mo_5O_{23}]^{6-}$ to $[H_2P_2Mo_5O_{23}]^{4-}$. The lower energy gap in the polyanions means that they can be more easily reduced. The higher

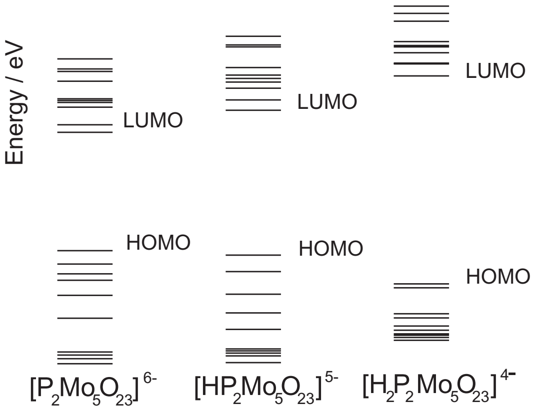

FIGURE 4 Qualitative molecular orbital diagram of $[P_2Mo_5O_{23}]^{6-}$, $[HP_2Mo_5O_{23}]^{5-}$ and $[H_2P_2Mo_5O_{23}]^{4-}$.

the degree of protonation, the larger the energy gap, and consequently, the more stable the polyanion is. Hence, $[P_2Mo_5O_{23}]^{6-}$ is more easily reduced than the protonated polyanions.

CONCLUSION

A hydrothermal technique has been used in the synthesis of the imidazole diphosphopentamolybdate $(C_4H_7N_2)_4[HP_2Mo_5O_{23}]\cdot H_3O\cdot 4.5H_2O$ and its structure has been determined by X-ray diffraction. The structure is composed of $[HP_2Mo_5O_{23}]^{5-}$ clusters and $C_4H_7N_2^+$ and H_3O^+ cations, as well as water of crystallization linking through hydrogen bonding into a network.

The influences of protonation on the charge distribution and on the reactive active sites of $[H_nP_2Mo_5O_{23}]^{(6-n)-}$ have, for the first time, been investigated using DFT calculation. The population results show that negative charge is distributed over all types of oxygen atoms. For $[H_nP_2Mo_5O_{23}]^{(6-n)-}$, the nucleophilic active sites concentrate on O_{b1}, and the electrophilic active sites concentrate on O_t, and the charges of the terminal oxygen atoms decrease with increasing degree of protonation, so the electrophilic activity of terminal O is enhanced. The polyanion $[P_2Mo_5O_{23}]^{6-}$ with a small energy gap between the HOMO and LUMO is more easily reduced than protonated polyanions.

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