Very Strong Centrosymmetric [O...H...O]+ and Asymmetric [O-H…O]+ Hydrogen Bonds In a New POM-Based Hybrid Material

M. Pourayoubi[a,b] and A.R. Mahjoub[b,]*

aDepartment of Chemistry, Ferdowsi University of Mashhad, Mashhad, 91779, Iran
bDepartment of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

A specific assembly process, driven by coexisting X-H…O hydrogen bonding and X…O short intermolecular contacts (X = C, N, O) is described, in which the pseudo-*Keggin* polyoxoanion and two types of molecule...cation pairs (with C_1 and C_i symmetries) were assembled to the programmed supramolecular architecture. Cooperation of the positive-charge, resonance effect and the O=C…O$_{terminal}$ intermolecular contact led to the short and strong symmetrical [O…H…O]+ hydrogen bond (O…O = 2.449(13) Å) in one of the molecule…cation pairs $[C_4H_9NO…H…ONC_4H_9]^+$ with the H-bonded proton in the center of inversion. The other $[C_4H_9NOH…ONC_4H_9]^+$ molecule…cation pair (non-centrosymmetric) was formed through a very strong asymmetric [O.H.O]+ hydrogen bond of 2.431(13) Å in length which was created *via* the synergistic effect between the minor N-H…O secondary interaction, +CAHB (positive-charge-assisted hydrogen bond) and RAHB (resonance assisted hydrogen bond) mechanisms.

INTRODUCTION

Hydrogen bonds (HBs) are involved in numerous important contexts; they play a vital role to stabilize supramolecular aggregates and have been a key issue in natural sciences [1]. Gilli *et al.* have classified hydrogen bonds as positive or negative charge-assisted hydrogen bonds (±CAHBs), resonance-assisted hydrogen bonds (RAHBs), polarization-assisted hydrogen bonds (PAHBs), and isolated hydrogen bonds (IHBs) [2]. Familiarity with the nature of hydrogen bonds and other short intermolecular contacts is crucial for the elucidation of forces stabilizing materials in solid state. Crystal engineering shows great interest in the non-covalent forces and in accumulating the different classes of

molecules or clusters in its approach to the design of the programmed supramolecular architecture [3-5].

There are numerous recent examples involving different molecular entities: organic molecules, proteins, peptides, DNA and others in molecular self-assembly [6,7]. The resulting hybrid materials exhibit cooperative properties of different building blocks [8,9]. In this paper, we present a new POM-based hybrid material containing two symmetrically independent organic molecule cation pairs (with C_1 and C_i symmetries). The cooperation between the positive-charge-assisted hydrogen bond with the resonance-assisted hydrogen bond mechanisms and the minor secondary interactions (C…O short intermolecular contact and N-H…O hydrogen bond) resulted in some very strong homoconjugated [O.H.O]+ hydrogen bonds in the title hybrid material.

*Corresponding author. E-mail: mahjouba@modares.ac.ir

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were purchased commercially and used without further purification. ^1H, ^{13}C and ^{31}P NMR spectra were determined on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS, and ^{31}P chemical shift relative to 85% H_3PO_4 as external standard. Infrared (IR) spectrum was recorded on a Shimadzu model IR-60 spectrometer. The elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. The thermal behavior was measured with PLSTA 1500 apparatus. UV-Vis spectrum was recorded on a double-beam Shimadzu 2550 spectrophotometer. X-ray structural analysis on single crystal of title compound was carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å).

Synthesis of $[CH_3CH_2C(OH)NHCH_3]_3[PMo_{12}O_{40}]\cdot 3CH_3CH_2C(O)NHCH_3$

A solution of N-methyl propionamide (0.429 g, 4.92 mmol) in HCl (10 ml, 1 M) was added dropwise to a solution of $H_3PMo_{12}O_{40}$ (1.5 g, 0.82 mmol) in H_2O (90 ml) and stirred (1.5 h) at room temperature. The solution was filtered and kept until the yellow crystals were obtained. IR (KBr) frequencies (cm^{-1}): 3450m, 1643m, 1593m, 1453m, 1398m, 1347m, 1288m, 1153m, 1111m, 1059 (P-O_a), 956s (Mo-O_d), 874s (Mo-O_b-Mo), 790vs (Mo-O_c-Mo), 683m, 633m, 563m, 496m, 461m. ^{31}P NMR ((D$_6$)DMSO): -3.85. ^1H NMR ((D$_6$)DMSO): 0.98 (t, $^3J(H,H)$ = 7.6 Hz, 18H, 6CH$_3$), 2.05 (q, $^3J(H,H)$ = 7.6 Hz, 12H, 6CH$_2$), 2.55 (s, 18H, 6CH$_3$), 8.12 (b, 9H, 6NH & 3OH$^+$). ^{13}C NMR ((D$_6$)DMSO): 174.0, 28.4, 25.4, 9.8. UV-Vis (4.3 × 10^{-4} M in water, λ_{max}): 237.5 nm and 307.5 nm. Anal. Calcd. for $C_{24}H_{57}Mo_{12}N_6O_{46}P_1$: C, 12.28; H, 2.45; N, 3.58. Found: C, 12.09; H, 2.39; N, 3.50.

RESULTS AND DISCUSSION

The hybrid material $[CH_3CH_2C(OH)NHCH_3]_3[PMo_{12}O_{40}]\cdot 3CH_3CH_2C(O)NHCH_3$ was obtained by the reaction of 12-molybdophosphoric acid with N-methylpropionamide (1:6 ratios) in acidic (HCl) solution.

IR Spectroscopy

The IR spectrum of hybrid material contains the characteristic bands at 790 cm^{-1} (Mo-O_c-Mo), 874 (Mo-O_b-Mo), 956 (Mo-O_d) and 1059 cm^{-1} (P-O_a) which demonstrate the pseudo-*Keggin* structure of the Mo atom. The O_a, O_b, O_c and O_d atoms are the oxygen atoms which bonded to P and Mo, the corner-shared oxygen atoms of MoO$_6$ octahedra, the edge-shared oxygen atoms of MoO$_6$ octahedra and the terminal oxygen atoms, respectively. The band at 1643 cm^{-1} is assigned to C=O.

NMR Spectroscopy

Phosphorus-31 NMR spectrum shows one signal at -3.85 ppm demonstrating the pseudo-*Keggin* polyoxoanion of Mo. ^1H NMR spectrum indicates three signals in aliphatic region (triplet at 0.98 ppm for CH$_3$, quartet at 2.05 ppm for CH$_2$ and singlet at 2.55 ppm for the CH$_3$ which linked to the N atom). The lines at 9.8, 25.4 and 28.4 ppm in ^{13}C NMR spectrum are related to CH$_3$, CH$_2$ and the CH$_3$ (which linked to N) carbon atoms. The C=O signal appears at 174.0 ppm.

UV-Vis Spectrum

UV-Vis absorbance spectrum (Fig. 1) in water solution of $[CH_3CH_2C(OH)NHCH_3]_3[PMo_{12}O_{40}]\cdot 3CH_3CH_2C(O)NHCH_3$ (4.3 × 10^{-4} M) shows the absorption peaks at 237.5 nm and 307.5 nm.
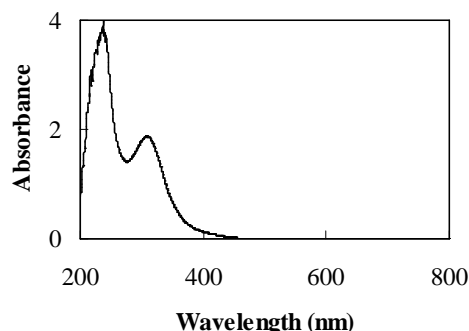
Fig. 1. UV-Vis absorbance spectrum of $[CH_3CH_2C(OH)$ $NHCH_3]_3[PMo_{12}O_{40}]\cdot 3CH_3CH_2C(O)NHCH_3$ in water (4.3 × 10^{-4} M), λ_{max} = 237.5 nm and 307.5 nm.

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Thermogravimetric and Differential Thermal Analysis (TG-DTA)

TGA and DTA for the compound were measured at 30-750 °C. The DTA diagram (Fig. 2) shows endothermal peaks at 109, 130, 191, 236, 427, 508, 532, 555, 583 and 596 °C, and exothermal peaks, with maxima at 333 and 455 °C. The endothermal peaks may be ascribed to the release of 1-(methylamino)propylidene oxonium cations and physisorbed H-bonded N-methyl propionamide molecules. The exothermal peaks may be assigned to pseudo-*Keggin* anion decomposition to yield a very stable metal oxide, MoO$_3$. The TG (Fig. 2) analysis shows that the title compound underwent a loss of 26.3% (calcd: 26.4%), corresponding to the solvated molecules, the organic cations and polyoxoanion decomposition (loosing 0.5 mol P$_2$O$_5$ and 1.5 mol H$_2$O and the remaining MoO$_3$). The thermal behavior of the compound may be largely attributed to the effect of the organic cations, the solvated molecules, the non-covalent interactions and the hydrogen-bonds and strong covalent bonds.

Description of the Crystal Structure

Single crystals of the hybrid compound were obtained from an aqueous acidic solution after a slow evaporation at room temperature. The crystal data and the details of X-ray analysis are given in Table 1. The selected bond lengths and angles are listed in Table 2.

In the crystal structure of the hybrid compound, the simple peptide molecule, R^{1}NHC(O)R^2 and its cation, [R^{1}NHC(OH)R^2]$^+$ (R^1 = CH$_3$, R^2 = C$_2$H$_5$), were subjected to self-assembly process with pseudo-*Keggin* polyoxoanion *via* X-H…O hydrogen bonds and X…O short intermolecular contacts (X = C, N, O). The hybrid compound is made of PMo$_{12}$O$_{40}$$^{3-}$ polyoxoanion, three [CH$_3$NHC(OH)CH$_2$CH$_3$]$^+$ cations and three H-bonded CH$_3$NHC(O)CH$_2$CH$_3$ molecules. The [PMo$_{12}$O$_{40}$]$^{3-}$ anion has a pseudo-*Keggin* structure and the central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. The P atom lies across an inversion center instead of the tetrahedral symmetry observed for the α-*Keggin* anion (Evans & Pope, 1984) [10]. This can be interpreted as an orientational disorder of normal α-*Keggin* anion over two positions related by an inversion center (Attanasio *et al.*, 1990) [11]. The PO$_4$ group is disordered over two sites with the P-O distances ranging from 1.511(11) to
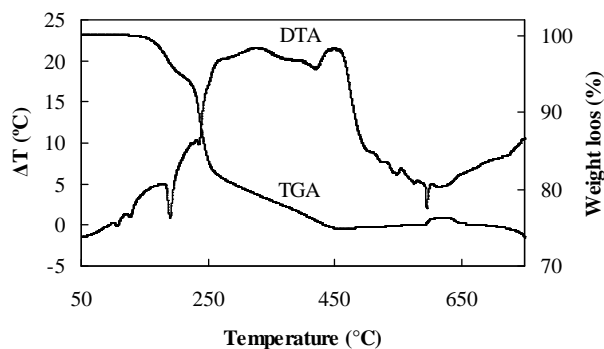

Fig. 2. The TGA-DTA curve of hybrid material.

1.563(11) Å. There are alternating 'short' and 'long' Mo-O$_b$-Mo-O$_b$ bonds in the polyoxoanion. For instance, in the belt of Mo4-O7-Mo5-O8-Mo6-O9-Mo4-O7-Mo5-O8-Mo6-O9-Mo4, the bond distances are 1.989(10), 1.809(10), 1.992(10), 1.817(10), 1.980(10), 1.803(10) Å (and again repeating these values due to the symmetry of anion), owing to a slight displacement of Mo atoms from the mirror planes of the Mo$_3$O$_{13}$ triplets. The ORTEP view of the asymmetric unit is shown in Fig. 3. Two types of molecule...cation pairs exist in the crystal network. The first [C$_4$H$_9$NOH…ONC$_4$H$_9$]$^+$ (non-centrosymmetric) with the hydrogen located near oxygen (O24) is bonded through a very strong asymmetric O.H.O hydrogen bond of 2.431(13) Å in length (O24-H24O...O23, Table 3). This molecule…cation pair is involved in minor secondary PMo$_{12}$O$_{39}$O$_t$$^{3-}$…[C$_4H_9$NOH…ONC$_4H_9$]$^+$… PMo$_{12}O_{39}O_t$$^{3-}$ (O$_t$ = O$_{terminal}$) interactions in the centrosymmetric rings array *via* O$_t$(= O15)…N2 electrostatic force and O$_t$(= O14)…H3N-N3 hydrogen bond (Table 3). Another pair, [C$_4$H$_9$NO…H…ONC$_4$H$_9$]$^+$, causes the hydrogen atom to be statistically distributed among O25 and O25#3 (#3 -x, -y, -z+1) base on the short distance between two oxygen atoms (2.449(13) Å). The H25O atom is located at the center of inversion to form a homoconjugated centrosymmetric cationic system [C$_4$H$_9$NO…H…ONC$_4$H$_9$]$^+$ with a short and symmetrical O…H…O hydrogen bond. Because the hydrogen bonded C$_4$H$_9$NO molecules are symmetrically equivalent, the (C$_4$H$_9$NO)$_2$H$^+$ cation is similar to the type A acid salts of carboxylic acid [12], HF$_2$$^-$ anion (F…F = 2.27 Å in LiHF$_2$) [13], bis(homarine) hydrogen perchlorate [14] and

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Table 1. Crystal Data and Structure Refinement for $[CH_3CH_2C(OH)NHCH_3]_3[PMo_{12}O_{40}].3CH_3CH_2C(O)NHCH_3$

Empirical formula	$C_{24}H_{57}Mo_{12}N_6O_{46}P$
Formula weight	2348.01
Temperature	120(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 11.6338(16)$ Å, $b = 11.7319(16)$ Å, $c = 13.8981(19)$ Å, $\alpha = 108.900(5)°$, $\beta = 95.151(5)°$, $\gamma = 119.585(5)°$
Volume (Å^3)	1487.0(4)
Z	1
Density (calculated)	2.622 g cm^{-3}
Absorption coefficient	2.578 mm^{-1}
F(000)	1130
Crystal size	$0.24 \times 0.21 \times 0.18$ mm^3
Theta range for data collection	2.04 to 30.06°
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-19 \le l \le 19$
Reflections collected	17441
Independent reflections	8615 [R(int) = 0.0214]
Completeness to θ	98.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.620 and 0.540
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8615/6/308
Goodness-of-fit on F^2	1.012
Final R indices [for 7978 rfln with I > 2σ(I)]	R1 = 0.0812, wR2 = 0.1644
R indices (all data)	R1 = 0.0862, wR2 = 0.1672
Largest diff. peak and hole	2.914 and -2.892 e Å^{-3}

Table 2. Selected Bond Lengths and Angles for $[CH_3CH_2C(OH)NHCH_3]_3[PMo_{12}O_{40}].3CH_3CH_2C(O)NHCH_3$

P(1)-O(20)	1.533(12)	O(24)-C(5)	1.280(11)
P(1)-O(19)	1.546(11)	O(23)-C(9)	1.266(12)
P(1)-O(19)#1	1.546(11)	O(25)-C(1)	1.302(12)
P(1)-O(21)	1.563(11)	N(1)-C(1)	1.303(15)
P(1)-O(22)	1.511(11)	N(1)-C(4)	1.452(17)
Mo(2)-O(14)	1.665(10)	N(2)-C(5)	1.304(12)
Mo(3)-O(15)	1.659(10)	N(3)-C(9)	1.316(12)
P(1)-O(19)-Mo(3)	123.1(6)	O(25)-C(1)-N(1)	115.6(9)
O(22)#1-P(1)-O(22)	180.0(19)	N(1)-C(1)-C(2')	113.4(17)
O(22)-P(1)-O(20)	111.3(7)	O(25)-C(1)-C(2)	114.9(9)
O(20)-P(1)-O(21)	108.6(7)	O(24)-C(5)-N(2)	118.2(9)
C(9)-N(3)-C(12)	123.6(9)	O(23)-C(9)-N(3)	119.0(9)

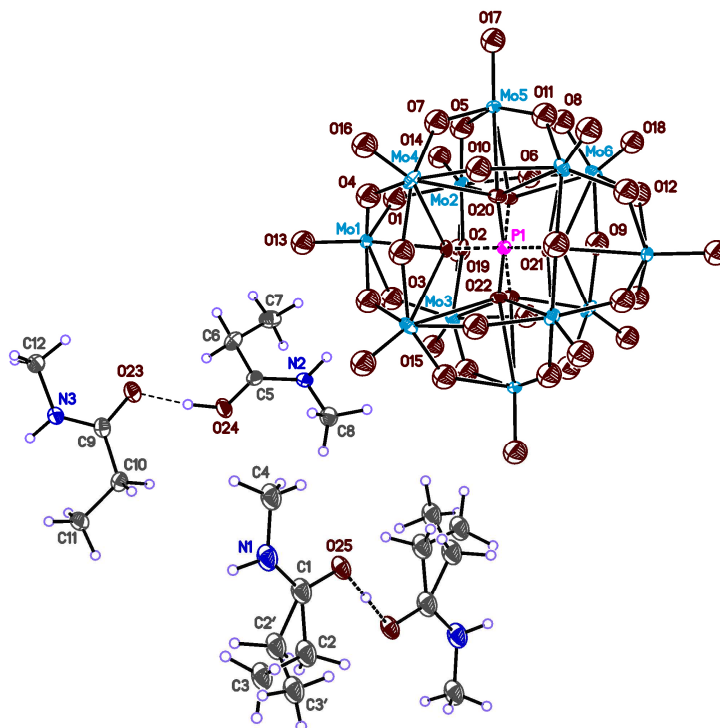Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z.

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Fig. 3. ORTEP view (50% probability level) of polyoxoanion and the molecule...cation pairs [C$_4$H$_9$NO.H.ONC$_4$H$_9$]$^+$. Only symmetrically independent atoms are labeled. In molecule…cation C1O25, the hydrogen bonded H atom is located at the center of inversion. Symmetry codes to generate equivalent atoms in polyoxoanion and [C$_4$H$_9$NO.H.ONC$_4$H$_9$]$^+$ are, respectively, -x+1, -y, -z and -x, -y, 1-z.

Table 3. Hydrogen Bonds and Short Intermolecular Contacts for [CH$_3$CH$_2$C(OH)NHCH$_3$]$_3$[PMo$_{12}$O$_{40}$]. 3CH$_3$CH$_2$C(O)NHCH$_3$

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
N(1)-H(1N)...O(13)#1	0.88	2.61	3.165(13)	122
N(1)-H(1N)...O(4)#1	0.88	2.66	3.534(13)	175
N(2)-H(2N)...O(3)	0.88	2.28	3.126(15)	160
N(3)-H(3N)...O(14)#2	0.88	2.45	3.061(14)	127
O(24)-H(24O)...O(23)	0.97	1.47	2.431(13)	170
O(25)-H(25O)...O(25)#3	1.22	1.22	2.449(13)	180
C(6)-H(6A)...O(5)#4	0.99	2.58	3.134(14)	115
O(15)...O(15)#5			2.794(13)	
O(15)...N(2)#5			2.925(14)	
O(15)...C(8)#5			3.049(14)	
C(1)...O(14)#6			3.197(13)	
C(3)...O(17)#7			3.172(13)	

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

Table 4. Very Strong Symmetric and Asymmetric Hydrogen Bonds

Compound	O…O	Molecule…cation symmetry	Ref.
$(HOM)_2HClO_4$	2.480(3)	Centrosymmetric	[14]
$(PB)_2H.ClO_4$	2.456(5)	Centrosymmetric	[15]
$(TRG)_2H.Cl.H_2O$	2.456(4)	Non-centrosymmetric	[16]
$(TRG)_2H.ClO_4.H_2O$	2.484(3)	Non-centrosymmetric	[17]
$(MIN)_2H.Cl.H_2O$	2.456(3)	Non-centrosymmetric	[18]
$(QB)_2H.ClO_4$	2.453(3)	Non-centrosymmetric	[19]
$[H_3PMo_{12}O_{40}][CO(NH_2)_2]_3.5H_2O$	[a]2.557	Non-centrosymmetric	[20]
$\alpha\text{-}H_3PMo_{12}O_{40}.6DMA.CH_3CN.0.5H_2O$	[a]2.411, 2.420, 2.458	Non-centrosymmetric	[21]
$[(TMU)_2H]_3[PW_{12}O_{40}]$	[a]2.45, 2.47, 2.33	Centrosymmetric	[22]
$[(TMU)_2H]_3[PMo_{12}O_{40}]$	[b]-	[b]-	[23]

HOM = homarine, PB = pyridine betaine, TRG = trigonelline, MIN = 1-methylisonicotinate, QB = quinoline betaine, DMA = N,N-dimethylacetamide, TMU = 1,1,3,3-tetramethylurea; [a]esd was not determined in Refs. [20-22]; [b]was not discussed in Ref. [23].

bis(pyridine betaine) perchlorate [15] (Table 4). Moreover, there are many examples of very strong asymmetric hydrogen bonds (with C_1 symmetry) in the literature [16-19] (Table 4). In an earlier work, the short $[H_2O\text{-}H…OC(NH_2)_2]^+$ hydrogen bond (O…O = 2.557 Å) was reported in the structure of $[H_3PMo_{12}O_{40}][CO(NH_2)_2]_3.5H_2O$ hybrid compound [20]. Williamson and co-workers have reported the structure of α-$H_3PMo_{12}O_{40}.6DMA.CH_3CN.0.5H_2O$, where, although the hydrogen atoms could not be located directly, several structural features suggested strongly that they were associated with the six DMA (N,N-dimethylacetamide) solvate molecules as three strongly hydrogen bonded pairs, $[DMA\text{-}H\text{-}DMA]^+$ [21] (Table 4). Similarly, the $[(TMU)_2H]_3[PW_{12}O_{40}]$ hybrid compound contained six TMU (1,1,3,3-tetramethylurea) molecules as three hydrogen-bonded pairs, in one of which, *i.e.*, the $[(TMU)_2H]^+$ pair, the hydrogen atom was located [22].

The very strong hydrogen bonds in the title compound are among the shortest known O.H.O hydrogen bonds. It was interesting to notice that the packing map of the hybrid compound showed the weak intermolecular electrostatic C1…O14 contact (3.197(13) Å) which was shorter than the sum of van der Waals radii, 3.22 Å). The C…O interaction is attributed to the overlap between the non-bonding electrons of polyoxoanion terminal oxygen atom and π^* of the organic

component, resulting in the increase of O25-C1 bond distance (1.302(12) Å) and the charge density on O25 oxygen atom relative to O24-C5 (1.280(11) Å) and O23-C9 (1.266(12) Å). Such an assumption is supported by the fact that the longest Mo-$O_{terminal}$ is Mo2-O14 (1.665(10) Å) due to the decrease of back-bonding from O14 lone pair to Mo2 (the lone pair of O14 is only slightly involved in C…O interaction).

This short symmetric strong hydrogen bond belongs to the positive-charge assisted and the resonance-assisted (the effect of nitrogen atom lone pair) hydrogen bond which cooperates with the C…O intermolecular contact (Fig. 4). For asymmetric molecule…cation pair, besides the +CAHB and RAHB mechanisms, the minor secondary N-H…O interaction is responsible for the creation of the short distances between the hydrogen-bonded oxygen atoms (Fig. 5). It seems that the formation of N3-H3N…O14 hydrogen bond causes the weakening of N3-H3N bond strength and increases the electron density on N3 atom whose resonance, *via* the C=O π system, increases the possibility of the H atom to be accepted by this carbonyl oxygen atom (hydrogen bond-assisted hydrogen bond).

In the centrosymmetric molecule…cation pair, CH_3-CH_2 moiety is disordered over two positions (C2 & C2', C3 & C3' and their corresponding hydrogen atoms). Figure 6 shows the

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Very strong hydrogen bond

C...O electrostatic intermolecular contact
in a short-contact assisted hydrogen bond

Resonance-assisted

Positive charge and resonance-assisted hydrogen bond
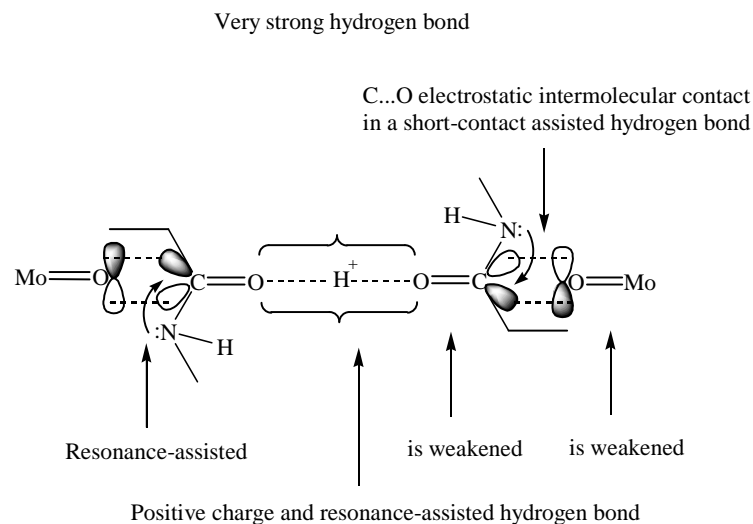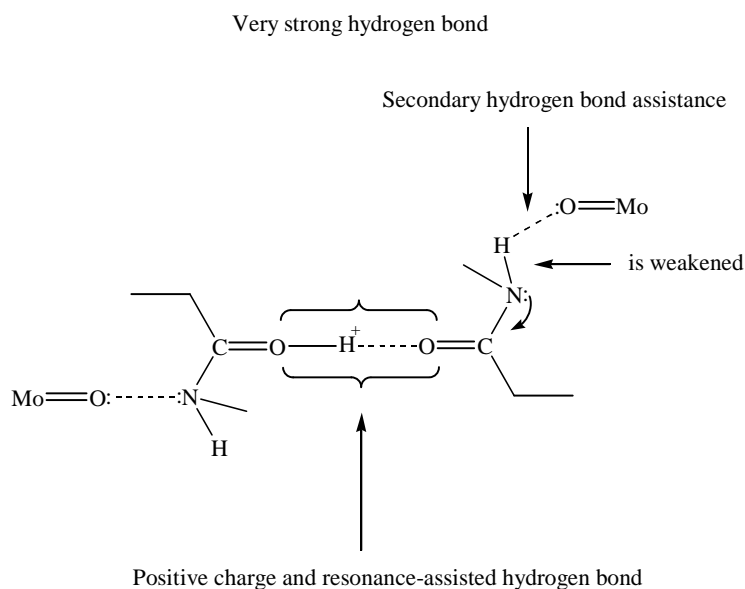
is weakened   is weakened

Fig. 4. Cooperation of positive-charge assisted hydrogen bond and resonance-assisted hydrogen bond mechanisms with C…O short intermolecular contact in the symmetric very strong [O…H…O]$^+$ hydrogen bond, the C…O interaction is produced by weak overlapping between the non-bonding electrons of polyoxoanion terminal oxygen atom and π* of the organic component.

Very strong hydrogen bond

Secondary hydrogen bond assistance

is weakened

Positive charge and resonance-assisted hydrogen bond

Fig. 5. Cooperation of positive-charge assisted hydrogen bond and resonance-assisted hydrogen bond mechanisms with secondary minor N-H…O interaction in the asymmetric very strong [O-H…O]$^+$ hydrogen bond (the nitrogen atom in left side of figure is involved in N…O electrostatic force).

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X-H…O hydrogen bonds and X…O electrostatic interactions (X = N, O) in the crystal lattice. Furthermore, the *PLATON* analysis (Spek, 2003) [24] suggests the existence of weak C-H...O hydrogen bonding between the cation and anion (Fig. 7, Table 3). The N1 atom makes a bifurcated hydrogen bond with the terminal O13 and the bridged O4 atoms. The N2 and N3 atoms form the H-bonds with O3 bridged and O14 terminal atoms, respectively. The O15…O15 electrostatic force occurs between the neighboring heteropolyanions *via* the terminal oxygen atoms. In the crystal structure, non-centrosymmetric molecule...cation pairs [$C_4H_9NOH…ONC_4H_9$]$^+$ and polyoxoanions are connected *via* the intermolecular N3-H3N…O14, O24-H24O…O23 hydrogen bonds and the N2…O15 interaction to form infinite chains of centrosymmetric rings (each ring contains two inorganic anions and two non-centrosymmetric [$C_4H_9NOH…ONC_4H_9$]$^+$ pairs). Connection of these chains *via* O…O electrostatic interaction and N2-H2N…O3 hydrogen bonds leads to a 2-D array (Fig. 8). Furthermore, the weaker H-bonds N(1)-H(1N)**...**O(13)#1 and N(1)-H(1N)**...**O(4)#1 are formed to complete the crystal packing (the packing of the molecule...cation pairs is shown in Fig. 9). Unit cell packing with polyhedra representation for the polyoxoanions and ball and stick for the organic components is shown in Fig. 10.

Supplementary Material

CCDC 296875 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via*: www.ccdc.cam.ac.uk/data-request/cif.
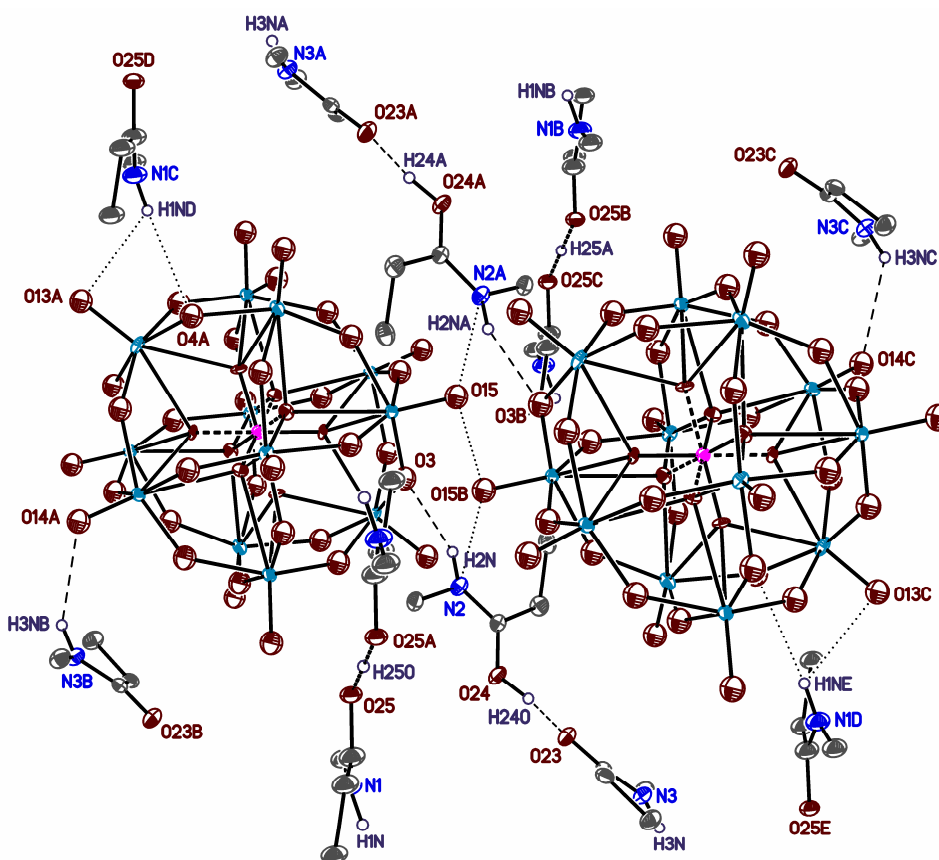

Fig. 6. A view of N-H…O and O-H…O hydrogen bonds and N…O and O…O electrostatic interactions.

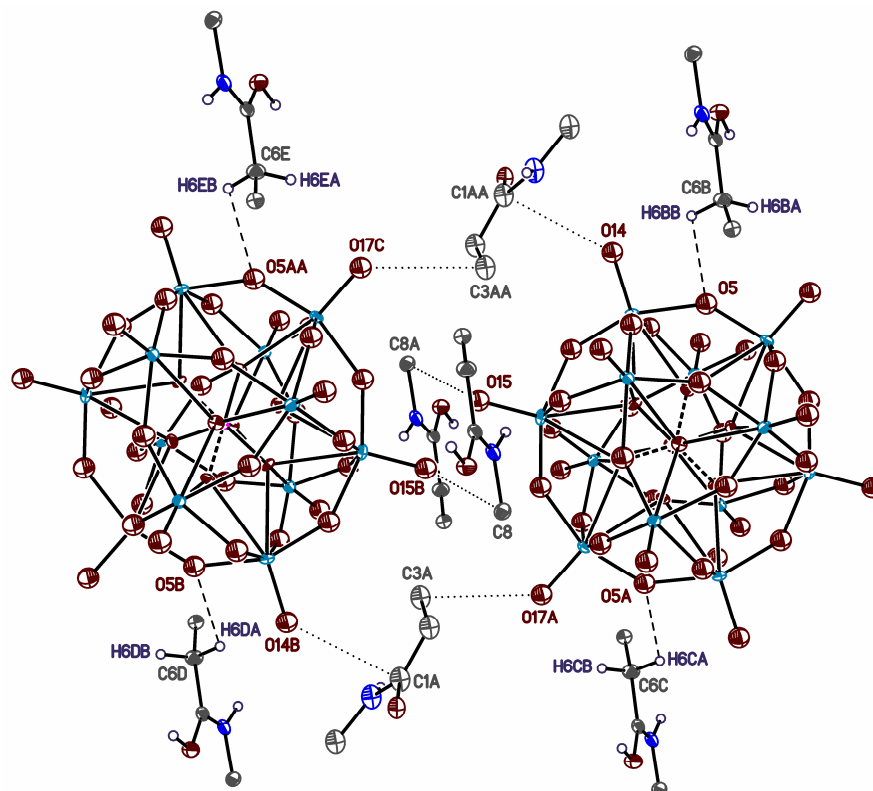Very Strong Centrosymmetric [O...H...O]⁺ and Asymmetric [O-H…O]⁺ H-Bonds

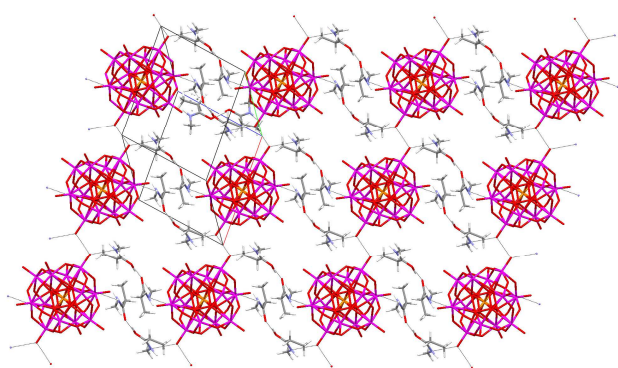**Fig. 7.** A view of C-H…O hydrogen bonds and C…O short intermolecular contacts.

Fig. 8. 2-D array of centrosymmetric rings containing polyoxoanions and non-centrosymmetric molecule…cation pairs [C₄H₉NOH…ONC₄H₉]⁺ which is produced by connecting 1-D chains of centrosymmetric rings *via* O…O electrostatic interaction and N-H…O hydrogen bond.
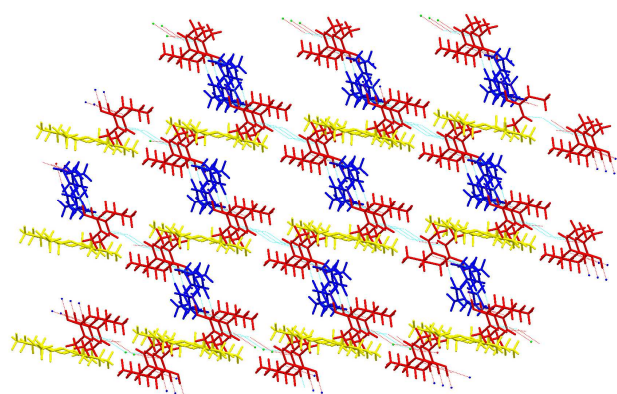

Fig. 9. A view of molecule…cation pairs packing; centrosymmetric molecule…cation pairs are shown with yellow color, non-centrosymmetric as blue and red, the vacancies are the places of polyoxoanions.
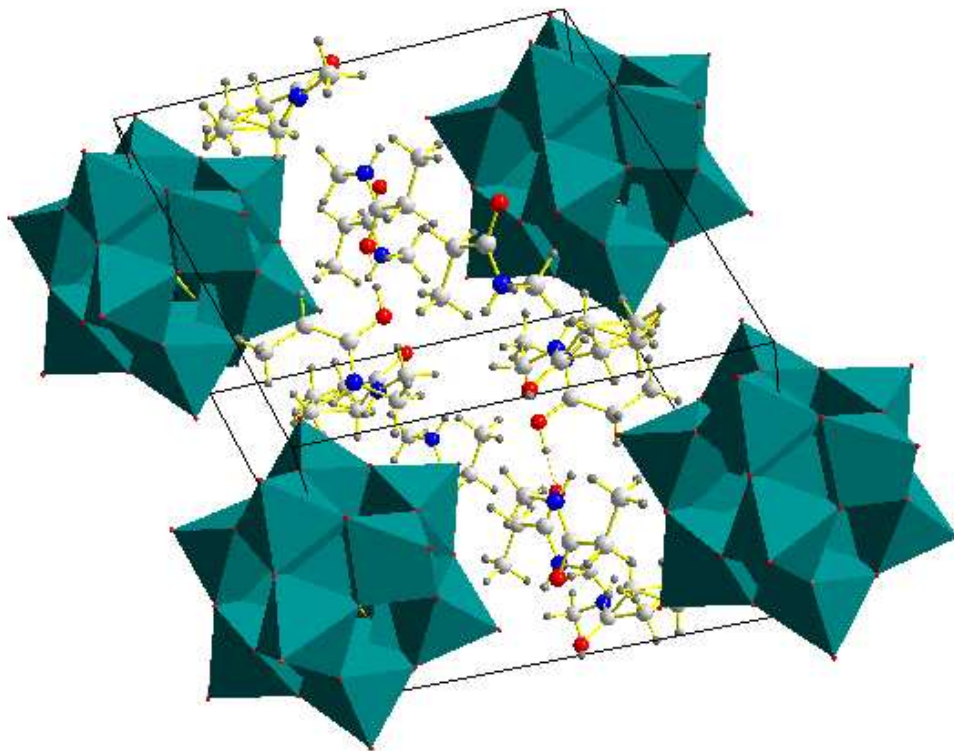
Fig. 10. A view of crystal packing of hybrid material, pseudo-*Keggin* polyoxoanions are represented as polyhedra, organic components as ball and stick forms.

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