Synthesis and structures of two novel one-dimensional mixed-valence iron molybdophosphate matrices

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Two composite solids consisting of one-dimensional mixed-valence iron and molybdenum phosphates with metal complexes, $[(C_{10}H_8N_2)_3Fe^{II}]_3Fe^{II}{}_2Fe^{III}{}_2Mo^{V}{}_{24}(H_2PO_4)_8(HPO_4)_4(PO_4)_4O_{48}(OH)_{12}(H_2O)_4\cdot 12H_2O$ (**1**) and $[(C_{10}H_8N_2)_3Fe^{II}]_2Fe^{II}Fe^{III}Mo^{V}{}_{12}(H_2PO_4)_2(H_{2-x}PO_4)(H_{1+x}PO_4)(HPO_4)_2(PO_4)_2O_{24}(OH)_6(H_2O)_2\cdot 9H_2O$ ($x = 0$–1) (**2**), in which the one-dimensional inorganic anions are constructed of alternating $[Fe^{II}(P_8Mo_{12})]$ units and Fe^{III} ions, were synthesized by hydrothermal reaction of MoO_3, H_3PO_4, $Fe_2(C_2O_4)_3\cdot 5H_2O$, 2,2′-bipyridine, $H_2C_2O_4\cdot 2H_2O$ and H_2O, and characterized by elemental analysis and single-crystal X-ray diffraction. Though the non-hydrogen atomic ratios among Mo, Fe, P, O in the anionic chains are the same, the protonation of the PO_4 groups is different in **1** and **2**, with the result that the anionic chains carry different charges and subsequently give rise to different numbers of Fe^{II}(2,2′-bipyridine)$_3$ per $\{Fe^{III}{}_2[Fe^{II}{}_2(P_{16}Mo^{V}{}_{24})]\}$ unit.

The rapid growth of research in the area of inorganic solids possessing extended architectures is due to their potential applications in the areas of catalysis, sorption, molecular electronics and energy storage.[1,2] Typical examples are the cooperative assembly of organic components and transition metal oxides including vanadium oxides,[3–5] molybdenum oxides,[6,7] reduced molybdenum phosphates,[8,9] iron phosphates,[10,11] vanadium phosphates[2,12] and iron molybdenate.[13] Recently, a new class of octahedral-octahedral frameworks, based on the M–Mo–P–O system (M = transition metal cation) and showing great structural diversity and potential applications in catalysis and molecule sorption, has received a great deal of attention.[14–19] In this paper, two novel composite solids consisting of one-dimensional mixed-valence iron and molybdenum phosphates, $[(C_{10}H_8N_2)_3Fe^{II}]_3Fe^{II}{}_2Fe^{III}{}_2Mo^{V}{}_{24}(H_2PO_4)_8(HPO_4)_4(PO_4)_4O_{48}(OH)_{12}(H_2O)_4\cdot 12H_2O$ (**1**) and $[(C_{10}H_8N_2)_3Fe^{II}]_2Fe^{II}Fe^{III}Mo^{V}{}_{12}(H_2PO_4)_2(H_{2-x}PO_4)(H_{1+x}PO_4)(HPO_4)_2(PO_4)_2O_{24}(OH)_6(H_2O)_2\cdot 9H_2O$ ($x = 0$–1) (**2**), synthesized by the hydrothermal reaction of MoO_3, H_3PO_4, $Fe_2(C_2O_4)_3\cdot 5H_2O$, 2,2′-bipyridine, $H_2C_2O_4\cdot 2H_2O$ and H_2O, are reported for the first time.

Experimental

Syntheses

Compound **1** was prepared from a mixture containing MoO_3 (0.213 g), H_3PO_4 (0.37 ml), $Fe_2(C_2O_4)_3\cdot 5H_2O$ (0.23 g), 2,2′-bipyridine (0.09 g), $H_2C_2O_4\cdot 2H_2O$ (0.19 g) and H_2O (6 ml). The final mixture, with an approximate composition of 2.9 : 15.5 : 1 : 1.2 : 3 : 667 of the respective reactants, was sealed in a 23 ml PTFE-lined stainless steel autoclave and heated at 160 °C for 4 days. After cooling to room temperature, a crop of black–red block-shaped crystals of **1** were isolated by suction filtration, washed with deionized water and dried at room temperature (0.38 g, 85% yield based on Mo). Anal. calc. for $C_{90}H_{36}Fe_7Mo_{24}N_{18}O_{140}P_{16}$: C, 15.65; H, 1.97; N, 3.65; found: C, 15.59; H, 1.93; N, 3.12%.

Compound **2** was obtained similarly, with the mol ratio being 5.7 : 21.5 : 1 : 2.2 : 5.8 : 1278 for the same reactants, after heating at 180° for 4 days (0.27 g, 58% yield based on Mo). Anal. calc. for $C_{60}H_{85}Fe_4Mo_{12}N_{12}O_{73}P_8$: C, 19.12; H, 2.26; N, 4.46; found: C, 19.25; H, 2.16; N, 4.08%.

X-Ray crystallography

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction. Data was collected using a SMART 1-K CCD diffractometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan mode. The data collection covered a hemisphere of reciprocal space using a combination of three sets of exposures; each set has a different ϕ angle (0, 88 and 180°) for each crystal, and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing was $-35°$. Coverage of the unique set is over 99% complete. Crystal decay, monitored by repeating 30 initial frames at the end of the data collection and analyzing the duplicate reflections, was found to be negligible. The unit cell parameters were determined using SMART.[20] The three sets of data collected for **1** and **2** were each reduced using the program SAINT.[21] Absorption corrections were applied using the program SADABS.[22] The structures were solved by direct methods using the program SHEXLTL,[23] which readily established the heavy atom (P, Mo, Fe, P) sites and most of the light atom (O, C, N) positions. Full-matrix least-squares refinement against $|F^2|$ was carried out using SHEXTL. For the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode except those attached to oxygen atoms. The final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. The relevant details of the structure determination and some selected bond lengths

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Table 1 Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{90}H_{36}Fe_7Mo_{24}N_{18}O_{140}P_{16}$	$C_{60}H_{85}Fe_4Mo_{12}N_{12}O_{73}P_8$
Formula weight	6899.20	3764.84
T/K	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	13.9348(1)	13.5955(2)
b/Å	25.2744(3)	19.1463(1)
c/Å	27.6186(4)	21.4573(3)
α/°	98.360(1)	95.668(1)
β/°	94.318(1)	91.353(1)
γ/°	92.105(1)	99.809(1)
U/Å^3	9585.21(19)	5472.19(11)
Z	2	2
μ/mm^{-1}	2.275	2.068
Collected/unique reflections	64 073/43 441 [R(int) = 0.0713]	39 933/26 244 [R(int) = 0.0528]
Reflections with $I > 2\sigma(I)$	22 065	22 374
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0795$, $wR_2 = 0.2004$	$R_1 = 0.0522$, $wR_2 = 0.1354$
R indices (all data)	$R_1 = 0.1545$, $wR_2 = 0.2502$	$R_1 = 0.0627$, $wR_2 = 0.1424$

and angles of **1** and **2** are presented in Tables 1, 2 and 3, respectively.

CCDC reference numbers 155192 and 155193. See http://www.rsc.org/suppdata/nj/b1/b102903g/ for crystallographic data in CIF or other electronic format.

Results and discussion

The asymmetric unit of **1** consists of 295 non-hydrogen atoms that are crystallographically independent. There are 7 Fe, 24 Mo, 140 O, 16 P, 90 C and 18 N atoms. For **2** the number of non-hydrogen atoms that are crystallographically independent in the asymmetric unit is 169. There are 4 Fe, 12 Mo, 73 O, 8 P, 60 C and 12 N atoms. $H_2C_2O_4$ is not incorporated into the structures of **1** and **2**, but it is necessary to maintain the pH of the reaction. The pH values are 1.5 and 2.0 for **1** and 1.5 and 2.1 for **2**, before and after the reaction, respectively. The most important role of $H_2C_2O_4$ is that it acts as a reducing agent.

For **1**, based on the results from bond valence calculations,[24,25] all molybdenum atoms have bond valence values in the range 4.86–5.15, indicating that all Mo atoms have a +5 oxidation state. The values for the Fe1, Fe2 and Fe3 atoms are in the range 1.86–1.88, while the values for Fe4 and Fe5 are 3.27 and 3.28, respectively, indicating that the three former irons have a +2 oxidation state and the two latter ones have a +3 oxidation state. All P atoms have values in the range 4.88–5.16, indicating that all P atoms have a +5 oxidation state. O1, O9, O16, O18, O22, O26, O28, O31, O34, O44, O46, O48, O49, O52, O56, O57, O58, O61, O71, O74, O83, O88, O93, O99, O105, O114, O121, O122, O124, O125 and O127 are OH oxygen atoms, as determined by their bond valence values in the range 1.00–1.34, while O24, O29, O39 and O66 are water oxygen atoms based on their bond valence

Table 2 Selected bond lengths (Å) and angles (°) for **1**[a]

Mo(3)–O(5)	1.651(9)	Mo(22)–O(67)	2.330(8)
Mo(3)–O(112)	1.940(8)	Mo(4)–O(103)	1.941(8)
Mo(3)–O(116)	1.966(8)	Mo(4)–O(87)	1.965(9)
Mo(3)–O(75)	2.071(9)	Mo(4)–O(90)	2.077(10)
Mo(11)–O(111)	2.301(8)	Mo(12)–O(72)	2.040(8)
Fe(1)–O(6)	2.170(7)	Fe(2)–O(81)	2.189(8)
Fe(1)–O(87)#1	2.239(8)	Fe(2)–O(78)	2.209(8)
Fe(3)–O(107)	2.208(8)	Fe(4)–O(24)	2.091(10)
Fe(3)–O(107)#2	2.208(8)	Fe(4)–O(39)	2.146(11)
Fe(5)–O(11)	1.887(9)	Fe(5)–O(29)	2.094(10)
Fe(5)–O(51)	1.896(8)	Fe(5)–O(66)	2.159(10)
P(2)–O(89)	1.505(10)	P(6)–O(98)	1.523(9)
P(2)–O(79)	1.561(10)	P(6)–O(18)	1.565(9)
P(3)–O(3)	1.523(8)	P(7)–O(90)	1.507(10)
P(4)–O(106)	1.524(9)	P(8)–O(9)	1.558(10)
P(9)–O(58)	1.617(11)	P(14)–O(15)	1.472(9)
O(93)–Mo(3)–O(85)	71.6(3)	O(93)–Mo(4)–O(85)	72.6(3)
O(71)–Mo(5)–O(100)	72.1(3)	O(114)–Mo(6)–O(7)	72.6(3)
O(5)–Mo(3)–O(85)	171.5(4)	O(86)–Mo(5)–O(100)	169.7(4)
O(89)–Mo(5)–O(71)	83.7(3)	O(116)–Mo(3)–O(75)	159.9(4)
O(116)#1–Fe(1)–O(6)#1	82.9(3)	O(80)–Fe(2)–O(8)	96.2(3)
O(119)–Fe(3)–O(119)#2	180.0(4)	O(60)–Fe(4)–O(24)	83.4(4)
O(13)#2–Fe(3)–O(107)	82.7(3)	O(73)–Fe(4)–O(39)	83.6(4)
O(3)–Fe(5)–O(29)	84.5(4)	O(37)–Fe(4)–O(39)	175.0(4)
O(109)–Fe(5)–O(29)	82.5(4)	O(37)–Fe(4)–O(60)	99.8(4)
O(109)–P(1)–O(85)	107.5(5)	O(123)–P(2)–O(79)	109.1(6)
O(15)–P(14)–O(14)	116.6(6)	O(46)–P(2)–O(79)	105.2(6)
O(3)–P(3)–O(108)	110.4(4)	O(60)–P(4)–O(100)	112.3(5)
O(67)–P(3)–O(108)	108.0(5)	O(60)–P(4)–O(106)	111.9(5)
O(121)–P(9)–O(58)	100.3(7)	O(100)–P(4)–O(106)	108.2(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y-1, -z$; #2 $-x+1, -y+1, -z+1$.

Table 3 Selected bond lengths (Å) and angles (°) for **2**[a]

Mo(3)–O(59)	2.287(4)	Mo(4)–O(34)	1.667(4)
Mo(5)–O(16)	1.970(4)	Mo(6)–O(58)	2.057(4)
Mo(5)–O(5)	2.095(4)	Mo(6)–O(62)	2.103(4)
Mo(7)–O(38)	2.095(4)	Mo(12)–O(33)#1	2.343(4)
Mo(7)–O(49)	2.302(4)	Mo(8)–O(11)#1	2.294(4)
Fe(1)–O(19)#2	2.123(4)	Fe(3)–O(28)	1.910(6)
Fe(1)–O(19)	2.123(4)	Fe(3)–O(57)	1.939(5)
Fe(1)–O(4)#2	2.196(4)	Fe(3)–O(21)#1	2.004(4)
Fe(1)–O(15)	2.203(4)	Fe(3)–O(26)	2.162(4)
Fe(2)–O(16)	2.234(4)	Fe(2)–O(13)	2.202(3)
P(4)–O(21)	1.522(4)	P(5)–O(44)	1.524(5)
P(4)–O(11)	1.538(4)	P(5)–O(30)	1.596(5)
P(4)–O(40)#1	1.543(4)	P(5)–O(42)#1	1.517(5)
P(6)–O(39)	1.525(5)	P(7′)–O(22)	1.296(9)
P(8A)–O(31)	1.496(7)	P(8B)–O(20)	1.614(8)
O(8)–Mo(1)–O(40)	71.57(14)	O(64)–Mo(12)–O(33)#1	171.24(18)
O(10)–Mo(5)–O(40)	83.27(15)	O(46)–Mo(6)–O(12)	106.3(2)
O(8)–Mo(5)–O(40)	71.93(14)	O(63)–Mo(10)–O(6)	105.2(2)
O(41)–Mo(11)–O(17)	105.8(2)	O(64)–Mo(12)–O(2)#1	99.2(2)
O(38)–Mo(11)–O(49)	72.61(14)	O(7)–Mo(12)–O(2)#1	153.51(17)
O(14)–Fe(2)–O(14)#1	180.000(19)	O(19)#2–Fe(1)–O(4)	82.45(14)
O(4)#2–Fe(1)–O(4)	180.000(1)	O(21)#1–Fe(3)–O(26)	83.79(19)
O(19)#2–Fe(1)–O(4)	82.45(14)	O(14)#1–Fe(2)–O(13)#1	85.15(14)
O(50)–Fe(3)–O(32)	85.08(19)	O(28)–Fe(3)–O(26)	174.1(2)
O(22)–P(7)–O(23)	98.9(4)	O(31)–P(8B)–O(27B)	81.3(9)
O(31)–P(8B)–O(51)	127.0(6)	O(28)–P(3)–O(58)	113.8(3)
O(5)–P(2)–O(56)	105.9(2)	O(28)–P(3)–O(45)	110.6(3)
O(11)–P(4)–O(33)#1	108.1(2)	O(44)–P(5)–O(30)	105.4(3)
O(40)#1–P(4)–O(33)#1	109.2(2)	O(61)–P(6)–O(24)	107.2(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x-3$, $-y+1$, $-z$; #2 $-x-3$, $-y+2$, $-z+1$.

values in the range 0.33–0.40. All other oxygen atoms in the inorganic anion framework have values very close to 2, showing that they are not protonated.

For **2**, based on the bond valence results,[24,25] the bond valence values for all the molybdenum and phosphorous atoms are in the ranges 4.87–5.03 and 5.03–5.25, respectively, indicating that all Mo and P have a +5 oxidation state. Fe1, Fe2 and Fe3 have values of 1.93, 1.86 and 2.97, respectively, such the Fe1 and Fe2 have a +2 oxidation state and Fe3 has a +3 oxidation state. The values for O2, O3, O8, O9, O22, O23, O24, O27, O29, O30, O35, O38, O56 and O62 are in the range 0.99–1.34, indicating that they are OH oxygens, while O26 and O32 have values of 0.33 and 0.34, respectively, indicating that they are water oxygens; except for O31 and O44, all other oxygen atoms have values very close to 2. The valence sums in the case of O31 and O44 are 1.39 and 1.31,

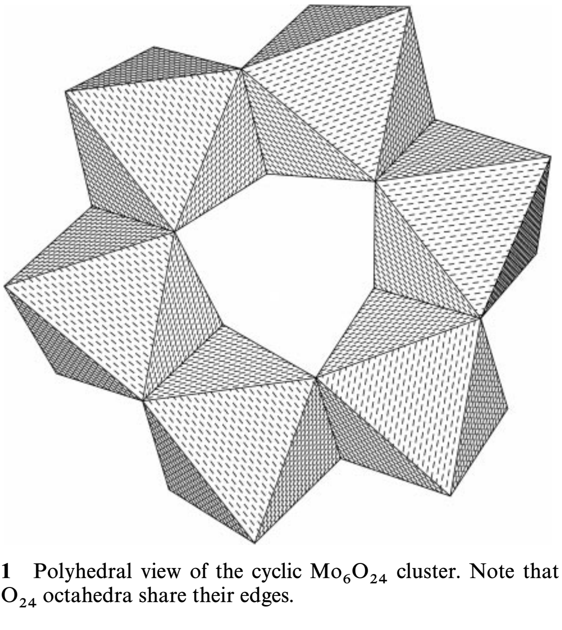
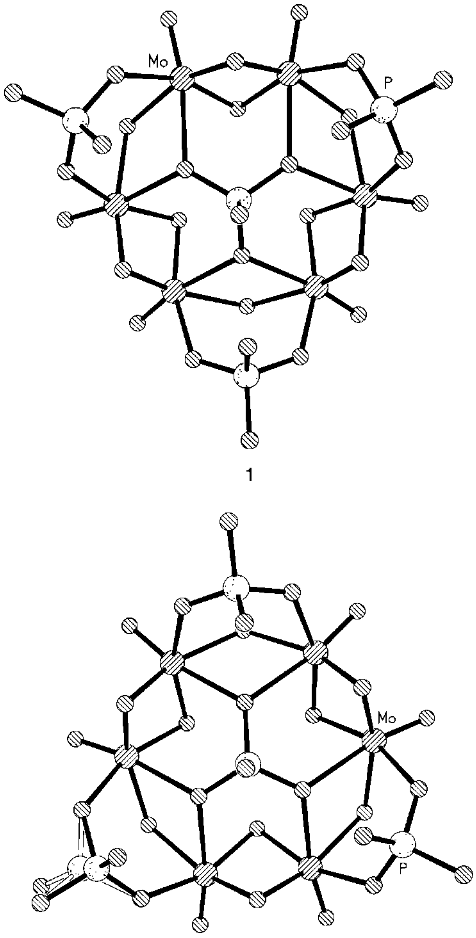


Fig. 1 Polyhedral view of the cyclic Mo_6O_{24} cluster. Note that the Mo_6O_{24} octahedra share their edges.



1

2

Fig. 2 Figures showing the connectivity between the cyclic cluster and the phosphate tetrahedrons in the $[P_4Mo_6O_{31}]$ moieties of **1** and **2**. P atoms are represented by shaded circles, O atoms by small striped circles, Mo atoms by large striped circles.

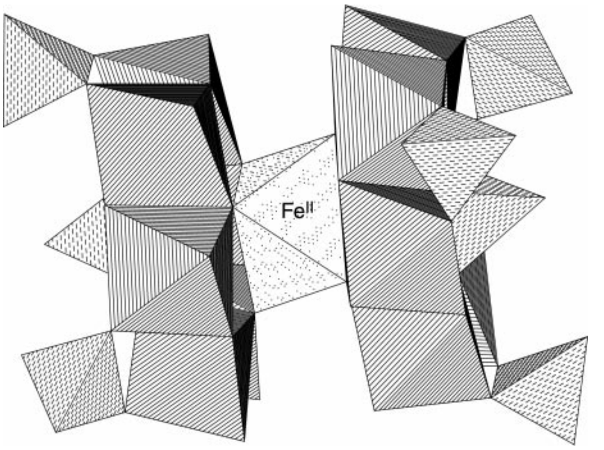


Fig. 3 The connectivity between the two [$P_4Mo_6O_{31}$] moieties through a $Fe^{II}O_6$ octahedron, forming a $Fe^{II}(P_4Mo_6O_{31})_2$ unit.

respectively, which are due to the formation of strong hydrogen bonds with O44(x, $1+y$, z) and O31 (x, $-1+y$, z) respectively, of its neighboring chain [O31···O44 = 2.472(2) Å]; that is, O31 in one chain shares one proton with O44 in the neighboring chain and *vice versa*, as described below.

Also, according to the bond valence calculations[24,25] and the geometry configuration, it is known that the Fe atoms coordinating to six nitrogen atoms of three 2,2′-bipyridine molecules in both **1** and **2** have a $+2$ oxidation state.

In both **1** and **2**, each of the distinct Mo atoms is coordinated to six oxygen atoms with Mo–O distances in the range 1.651(9)–2.330(8) Å for **1** and 1.667(4)–2.343(4) Å for **2**, and O–Mo–O bond angles in the range 71.6(3)–171.5(4) for **1**, and 71.57(14)–171.24(18)° for **2**. Of the six oxygen atoms connected to Mo, three have a normal twofold coordination, one is a terminal linkage and the remaining two have threefold coordination. Thus, the oxygen bond lengths show a "one short-four intermediate-one long" geometry, which is unusual for molybdenum(VI) oxides. The molybdenums are connected to each other, forming a cyclic cluster of the formula [Mo_6O_{24}] (Fig. 1) with an Mo···Mo distance near 2.6 Å, which is reminiscent of the Anderson structure with the central atom removed.[26] This type of linkage appears to be recurrent in the rich structural chemistry of reduced oxo-molybdenum clusters and has been observed in a number of one-, two- and three-dimensional reduced organic/MoPO and MMoPO solids.[8,9,14–19]

The phosphate groups decorate these clusters: three groups are around the periphery of the ring and one group in the center of the structure, forming a [$P_4Mo_6O_{31}$] moiety (Fig. 2). The phosphorous atoms have P–O bond lengths in the range 1.472(9)–1.617(11) Å for **1** and 1.296(9)–1.614(8) Å for **2**, while the O–P–O bond angles are in the range 100.3(7)–116.6(6)° for **1** and 81.3(9)–127.0(6)° for **2**. It is worth noting that one of the four PO_4 group in the [$P_4Mo_6O_{31}$] moiety of **2** is disordered (Fig. 2).

The [$P_4Mo_6O_{31}$] moieties are connected to each other *via* an $Fe^{II}O_6$ octahedron bonded to six O atoms from each hexamer ring unit that bridge the molybdenum atoms, with Fe–O bond lengths in the range 2.208(8)–2.239(8) Å for **1** and 2.203(4)–2.234(4) Å for **2**, and with O–Fe–O bond angles in the range 82.7(3)–180.0(4)° for **1** and 82.45(14)–180.00(19)° for **2**, resulting in an $Fe^{II}(P_4Mo_6O_{31})_2$ unit (Fig. 3).

The most important aspect of **1** and **2** are that these $Fe^{II}(P_4Mo_6O_{31})_2$ units are connected to each other *via* an Fe^{III} atom, which coordinates to two water molecules and four oxygen atoms with Fe–O bond lengths in the range 1.887(9)–2.159(10) Å for **1** and 1.910(6)–2.162(4) Å for **2**, and with O–Fe–O bond angles in the range 82.5(4)–175.0(4)° for **1** and 83.79(19)–174.1(2)° for **2**, giving rise to infinite one-dimensional chains (Fig. 4 and 5). Though layer architectures of FeMoPO systems are known from the literature,[14–19] to our knowledge these are the first mixed-valence uni-

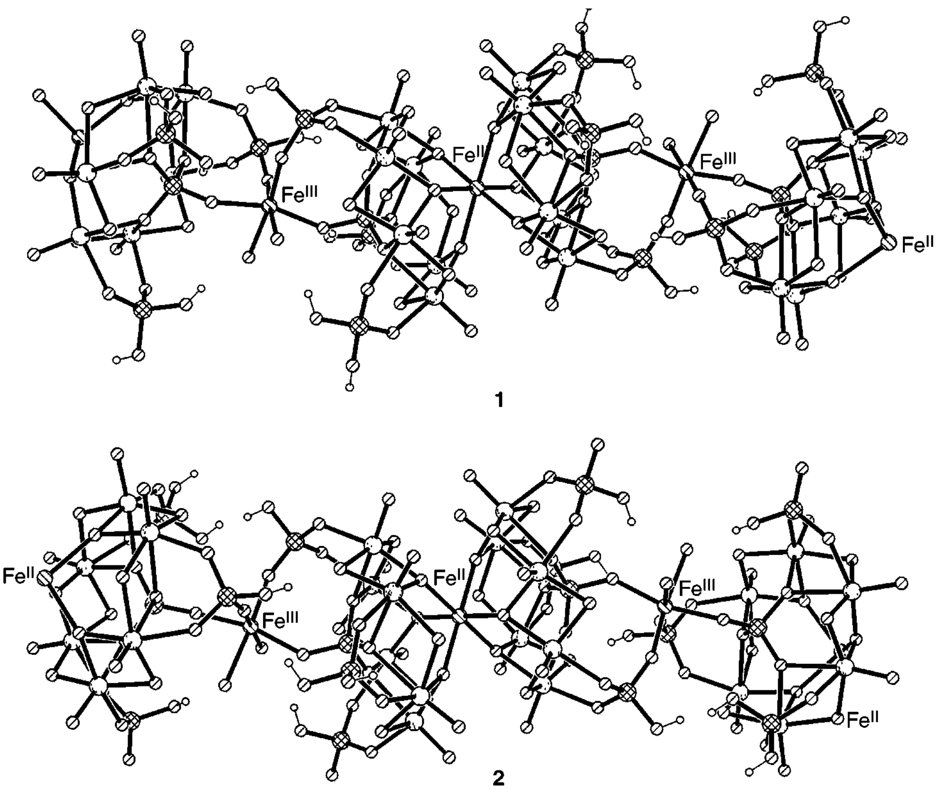


Fig. 4 Chains consisting of alternating $Fe^{II}(P_4Mo_6O_{31})_2$ and $Fe^{III}O_6$ units in **1** and **2**. Note that for **1** all terminal O atoms of the PO_4 groups are protonated, while for **2** in each $P_4Mo_6O_{31}$ moiety, only one of the two PO_4 groups having two terminal O atoms is fully protonated, while the two terminal O atoms of the other are partially protonated to share protons with the neighboring chain (only hydrogen atoms attached to PO_4 groups are shown for clarity).

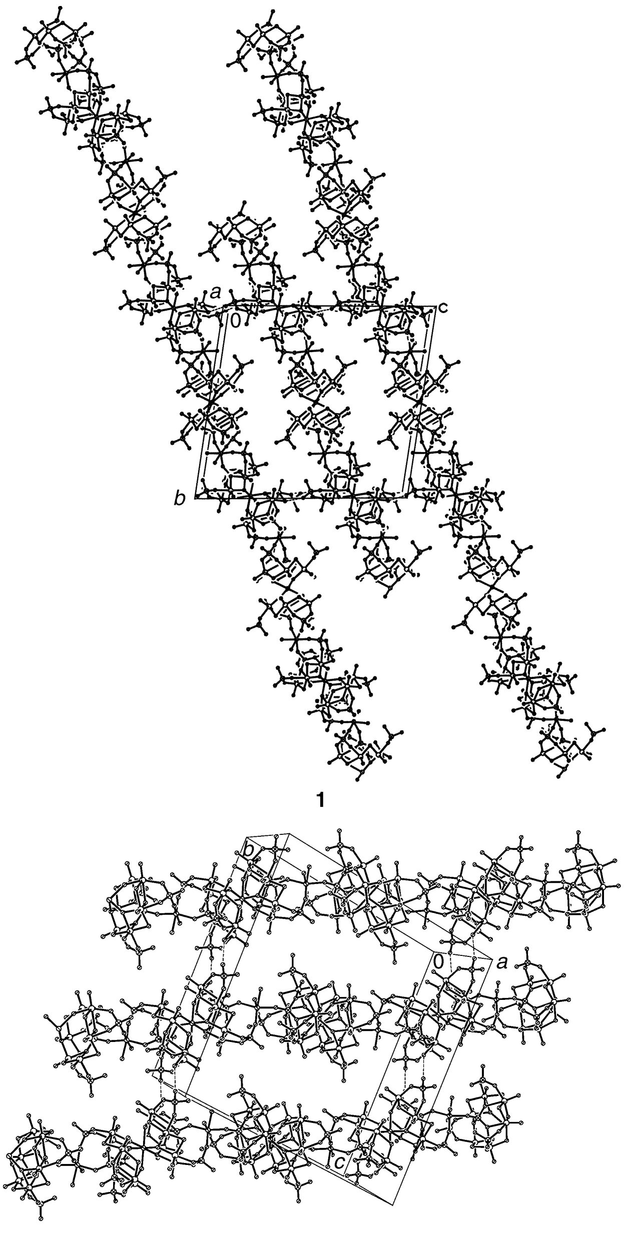


Fig. 5 Packing of the anionic chains of **1** and **2** down the *a* axis, showing the inter-chain hydrogen bonds (hydrogen atoms, water molecules and 2,2′-bipyridinium cations are omitted for clarity).

dimensional solids that incorporate two octahedrally coordinated transition elements.

The one-dimensional chains are stabilized by hydrogen bond interactions among the terminal –OH groups of the HPO_4, H_2PO_4 units, water $-OH_2$ and –OH groups of the bridging Fe^{III} atoms, forming infinite layer-like arrangements as shown in Fig. 5. The important hydrogen bond distances within the layers are O9···O10 = 2.607 Å and O34···O47 = 2.603 Å for **1** and O31···O44 = 2.472(2) Å for **2**. The Fe(2,2′-bipyridine)$_3$ complexes are situated between the layers in both **1** and **2**.

What is especially noteworthy is that the non-hydrogen atomic ratio of Mo, Fe, P, O in the anionic chains of **1** and **2** are the same, but the protonation of the PO_4 groups are different between **1** and **2**. In **1**, all of the four terminal oxygen atoms of two of the PO_4 groups in the $[P_4Mo_6O_{31}]$ moiety are protonated; in **2**, of the two PO_4 groups that have two terminal oxygen atoms each, only one PO_4 group is fully protonated as H_2PO_4, the other PO_4 group is only partially protonated: one terminal O is protonated, while the other terminal oxygen atom O31 (or O44) shares a proton with O44 (or O31) of the neighboring chain (Fig. 5). This results in each $\{Fe^{III}_2\,[Fe^{II}_2(P_{16}Mo^{V}_{24})]\}$ unit in **1** having two more protons than that in **2**, and subsequently causes each $\{Fe^{III}_2\,[Fe^{II}_2(P_{16}Mo^{V}_{24})]\}$ unit in **1** to carry one less Fe^{II}(2,2′-bipyridine)$_3$ than in **2**.

It is expected that the two compounds will possess different physical and chemical properties and this matter is being investigated in our laboratory.

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