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Vibrational spectra study of Mo(V) phosphates as examples of different geometries of dimolybdenyl species†

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Three different phosphate structures, α-$K_2Mo_2P_2O_{11}$, β-$K_2Mo_2P_2O_{11}$ and $CdMoPO_6$, in which molybdenum(V) octahedra are assembled in different ways, have been studied by vibrational spectroscopy techniques. A correlation is given between crystal structure and infrared and Raman band behaviour which allows identification of vibrational modes sensitive to a particular configuration of molybdenum species. This represents a powerful tool for structure characterisation when amorphous or single layer supported phases are under study.

Introduction

Powders based on molybdenum oxides are the object of great interest because of their excellent behaviour as catalysts for selective oxidation.[1] Mixing of transition metal oxides with other oxides is frequently helpful to improve activity/selectivity as well as to obtain optimal acid–basic behaviour. Phosphoric anhydride is frequently used as a promoter component for selective oxidation catalysts, so that Mo–phosphates, either supported or as bulk materials, are reported to be interesting catalytic materials.[2–5] Mo(V) phosphates can be considered as analogues of V(IV) phosphates which represent the active phases for n-butane selective oxidation catalysts.[6,7] These catalysts are also expected to display quite strong acidic properties,[5,8,9] that can be moderated by doping with alkali metal ions such as potassium. For these reasons, the structure and spectroscopic properties of well characterised K–Mo–P mixed oxides are of interest as reference materials for the characterisation of supported heterogeneous catalysts with similar compositions.

Recently, several new phases of phosphates of molybdenum(VI) and molybdenum(V) have been prepared and characterised.[10–17] In particular, two different allotropic forms of potassium–molybdenum(V) phosphates, *i.e.* α-$K_2Mo_2P_2O_{11}$ and β-$K_2Mo_2P_2O_{11}$, have been synthesized and characterized.[11,15,16] They present different structural units of MoO_6 octahedra and PO_4 tetrahedra: corner-shared pairs of MoO_6 octahedra occur in the monophosphate α-$K_2Mo_2P_2O_{11}$, while edge-shared pairs of MoO_6 octahedra occur in the diphosphate β-$K_2Mo_2P_2O_{11}$. For further comparison, we have also investigated another Mo(V) monophosphate, $CdMoPO_6$,[17] which also contains edge-shared pairs of MoO_6 octahedra. The features of this phase will be compared with those of the $CdMo^{VI}O_4$ phase, previously investigated.[14] We report here an IR and Raman study of these three pentavalent molybdenum phosphates, the study being presented taking into account the increasing complexity of molybdo–phosphate units: first the phase constituted by octahedra sharing one edge is investigated, then that containing octahedra sharing one corner and connected by two phosphates, and finally $CdMoPO_6$ where two bioctahedral units are linked by two phosphates.

Experimental

α-$K_2Mo_2P_2O_{11}$, β-$K_2Mo_2P_2O_{11}$ and $CdMoPO_6$ powders were obtained *via* solid state reaction of precursors in an evacuated sealed silica tube at 973, 923 and 1173 K, respectively. Details relating to synthesis and phase recognition are reported in the literature.[11,15–17]

The IR and FIR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument. The FT-Raman spectra were recorded using a Brucker FTS100 (Nd-YAG laser). The skeletal spectra in the region above 400 cm^{-1} were recorded with KBr pressed disks and with a KBr beam splitter, while those in the far infrared region (400–50 cm^{-1}) were recorded using powder deposited on polyethylene disks, and with a "solid substrate" beam splitter.

Results and discussion

1. The vibrational spectra of β-$K_2Mo_2P_2O_{11}$

For the phase β-$K_2Mo_2P_2O_{11}$ we could record high quality FT-IR/FT-FIR and FT-Raman spectra, which are shown in Fig. 1a and 2a, respectively.

As determined previously by Guesdon *et al.* in their XRD study on single crystals and powders,[11,16] β-$K_2Mo_2P_2O_{11}$ crystallises in the *Pbcn* space group (D_{2h}^{14}, no. 60) with $Z=4$. It is a diphosphate, containing a complex Mo(V) oxocation, with formula $[Mo_2O_4]^{2+}$, so that this compound is better described by the formula $K_2[Mo_2O_4][P_2O_7]$. Consequently, it can be considered as an allotropic form with respect to the corresponding high-temperature form α-$K_2Mo_2P_2O_{11}$,[11,15] which is a monophosphate and can be expressed by the formula $K_2Mo_2O_3[PO_4]_2$.

The coordination around molybdenum in β-$K_2Mo_2P_2O_{11}$ is shown schematically in Fig. 3a. It presents Mo_2O_{10} bioctahedral units, formed by two edge-sharing octahedra. The Mo–O–Mo angle is 83.10°. Each of the octahedra around Mo has three

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†Electronic supplementary information (ESI) available: determination of the irreducible representation. and separation into internal and external modes for β-$K_2Mo_2P_2O_{11}$. See http://www.rsc.org/suppdata/jm/b0/b007416k/

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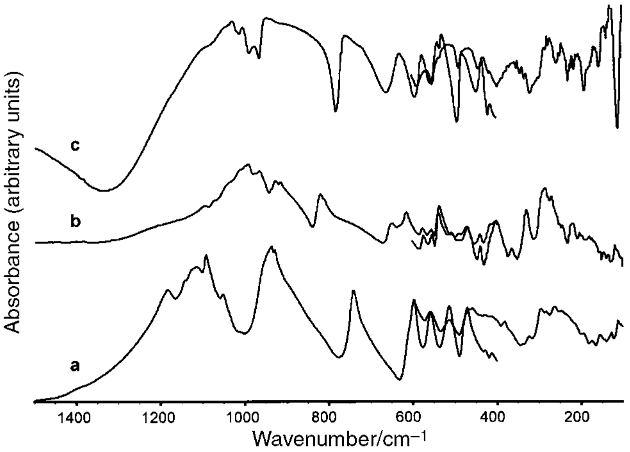

Fig. 1 FT-IR/FT-FIR spectra of β-$K_2Mo_2P_2O_{11}$ (a), α-$K_2Mo_2P_2O_{11}$ (b) and $CdMoPO_6$ (c). The spectrum in the FIR region was recorded by deposition of the pure powder on a polyethylene substrate.

coordinated diphosphate groups, two bridging oxygen atoms with the nearer Mo octahedron and one free corner or, more precisely, one short Mo=O "molybdenyl" bond (1.697 Å). This abnormally short bond is a characteristic feature of Mo(v)O_6 octahedra. The corresponding terminal oxygen atom interacts in this structure with two K atoms. The two molybdenyl bonds of the Mo_2O_{10} bioctahedral unit can be considered as essentially parallel to each other and to the ***b*** axis, although they are slightly divergent. The "cyclic" Mo_2O_2 units, nearly parallel to the ***ac*** plane, are not exactly square planar, the oxygen atoms lying at a lower level with respect to the molybdenum atoms. The diphosphate group has a bent P–O–P bridge (P–O–P 138.2°) and a "random" conformation of the PO_3 units.

On the basis of the site symmetries of the positions occupied in this structure[11,16] and according to the correlation method,[18] factor group analysis allowed us to obtain the following irreducible representation:

$$\Gamma_{\text{opt}} = 28A_g + 29B_{1g} + 28B_{2g} + 29B_{3g} + 28A_u + 29B_{1u} + 28B_{2u} + 29B_{3u}$$

According to the structure described above, we can separate the total modes of the structure into those associated to the diphosphate groups, to the Mo_2O_4 complex ion and to potassium, and we can also separate the vibrational and the acoustic modes. This is shown in Table 1, where the internal modes forecasted for the diphosphate ions and for the Mo_2O_4 complex cations are also identified. In Table 2 the observed maxima in the IR and Raman spectra of Figs. 1 and 2 are listed and assignment for the higher frequency features attempted.

In the fundamental IR spectrum ($\bar{\nu} < 1300$ cm^{-1}) we note the presence of 44 features among maxima and shoulders, while in the Raman spectra 13 maxima and several shoulders can be found. Thus many less features with respect to the number of expected IR-active and Raman active modes (77 and 102, respectively, see Table 1) are actually found.

In the region 1300–1000 cm^{-1} of the IR spectrum we distinguish eight features, between maxima and pronounced shoulders. This region is typical for the asymmetric and symmetric stretches of terminal PO bonds, in this case $\nu_{as}(PO_3)$ and $\nu_s(PO_3)$. According to the structure we forecast 9 IR-active modes, which means that only one of these eludes detection, probably because it is superimposed on another. In the Raman spectrum, in the same region we only find three well-resolved maxima, in contrast with the 12 Raman-active expected modes. However, we can remark that among these modes, three have A_g symmetry, *i.e.* are totally symmetric. The A_g symmetry modes are expected to be the most intense in the Raman spectrum. Consequently, we can assign the three Raman peaks to the three A_g symmetry modes, one of which is a symmetric stretch and two are asymmetric stretches.

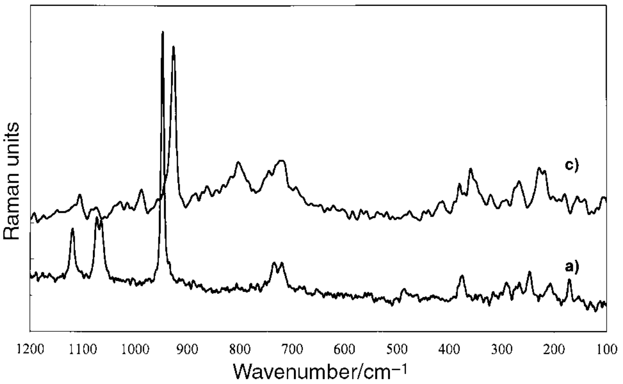

Fig. 2 Raman spectra of β-$K_2Mo_2P_2O_{11}$ (a) and $CdMoPO_6$ (c) in the range of the vibrational modes.

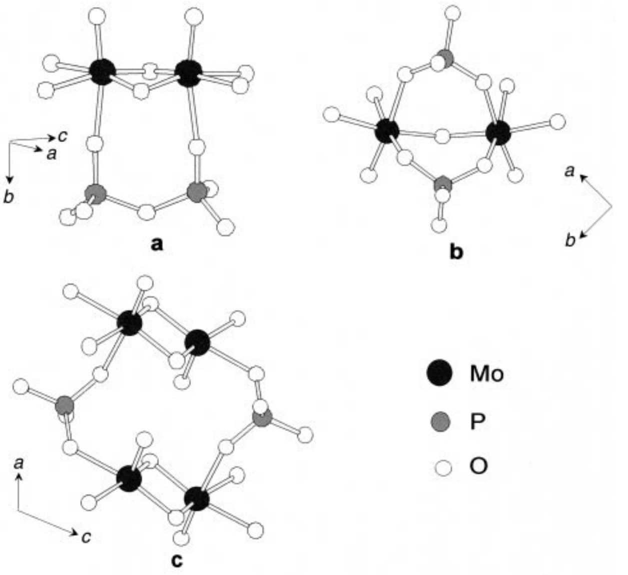

Fig. 3 The oxygen coordination around molybdenum and phosphorus seen from different directions for: β-$K_2Mo_2P_2O_{11}$ (a), α-$K_2Mo_2P_2O_{11}$ (b) and $CdMoPO_6$ (c).

In the region 1000–800 cm^{-1} of the IR spectrum we find a complex band whose maximum is definitely split but contains at least one shoulder at the higher frequency side. In the Raman spectrum a strong sharp maximum is found, with at least two additional weak components, one for each side. In this region, the asymmetric stretching modes of the P–O–P bridge of diphosphate groups and the stretches of terminal Mo=O bonds can be expected. According to Table 1 we expect here 5 IR active modes and 6 Raman active modes, one only of which belongs to the A_g symmetry. The IR and Raman spectra of different metal diphosphates[19,23] show that the $\nu_{as}(POP)$ modes on pyro- and poly-phosphates are responsible for strong and rather broad IR bands centred in the range 970–940 cm^{-1}, while the corresponding Raman-active modes are weak and become even inactive when the P–O–P bridges are linear. By contrast, the Mo=O stretching modes are generally strong and sharp both in IR and in Raman. These considerations allow us to confidently assign the strong Raman peak at 948 cm^{-1} to the totally symmetric stretching mode of molybdenyl groups. This position agrees with that of the Mo=O stretch in the Raman spectrum of α-$KMoO(P_2O_7)$, *i.e.* 947 cm^{-1}.[24] In the IR spectrum we can suppose that the overall absorption in this region (centred near 950 cm^{-1}) is due to the IR active $\nu_{as}(POP)$ modes, while the

Table 1 Assignments of the modes associated to P_2O_7 and Mo_2O_4 moieties (4 per unit cell) and to K atoms (8 per unit cell) in β-$K_2Mo_2P_2O_{11}$

Symmetry of modes →			A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}	
notation ↓	*N*	Act.:	R	R	R	R	=	IR	IR	IR	Total
$\nu_{as}(PO_3)$	4		2	2	2	2	2	2	2	2	16
$\nu_s(PO_3)$	2		1	1	1	1	1	1	1	1	8
$\delta_{as}(PO_3)$	4		2	2	2	2	2	2	2	2	16
$\delta_s(PO_3)$	2		1	1	1	1	1	1	1	1	8
Rock PO_3	4		2	2	2	2	2	2	2	2	16
Twist PO_3	2		1	1	1	1	1	1	1	1	8
ν_{as}(P–O–P)	1		0	1	0	1	0	1	0	1	4
ν_s(P–O–P)	1		1	0	1	0	1	0	1	0	4
δ(P–O–P)	1		1	0	1	0	1	0	1	0	4
Internal	21		11	10	11	10	11	10	11	10	84
Translations	3		1	2	1	2	1	2	1	2	12
Rotations	3		1	2	1	2	1	2	1	2	12
Total	27		13	14	13	14	13	14	13	14	108
ν_{as}(Mo=O)	1		0	1	0	1	0	1	0	1	4
ν_s(Mo=O)	1		1	0	1	0	1	0	1	0	4
δ(Mo=O)	4		2	2	2	2	2	2	2	2	16
ν_s/δ(Mo–O–Mo)	2		1	1	1	1	1	1	1	1	8
ν_{as}(Mo–O–Mo)	2		1	1	1	1	1	1	1	1	8
ν_s(O–Mo–O)	1		1	0	1	0	1	0	1	0	4
Rock Mo–O–Mo	1		1	0	1	0	1	0	1	0	4
Internal	12		7	5	7	5	7	5	7	5	48
Translations	3		1	2	1	2	1	2	1	2	12
Rotations	3		1	2	1	2	1	2	1	2	12
Total	18		9	9	9	9	9	9	9	9	72
K atoms	3		3	3	3	3	3	3	3	3	24
Total			25	26	25	26	25	27	26	27	204
Vibrational			25	26	25	26	25	26	25	26	201
Acoustic			0	0	0	0	0	1	1	1	3

N = number of modes per diphosphate ion or Mo_2O_4 molecular unit; Act. = activity.

two sharp maxima at 936 cm^{-1} and 928 cm^{-1} are associated to the IR active ν_s(Mo=O) (B_{2u}) and ν_{as}(Mo=O) (B_{1u}, B_{3u}) modes.

According to these data, we can assign the weak shoulders in the Raman patterns near 960 cm^{-1} and at 930 cm^{-1} to the Raman active components of the ν_{as}(POP) and ν_{as}(Mo=O) modes. The relative intensities of the observed maxima agree with these assignments.

Strong support for these assignments for the absorptions in the 1000–800 cm^{-1} region can be obtained by the analysis of the IR spectra in the corresponding first harmonic region, 2000–1600 cm^{-1} (Fig. 4). Here we found a quite broad band with some components, whose maximum is found at 1896 cm^{-1}. Consisting of first overtones and all self-combinations of either the IR-active or Raman-active modes IR-forbidden in the D_{2h} factor group, this band can be assigned to the mixed combinations of the IR- and Raman-active components of the asymmetric stretch of the P–O–P bridge ($\sim$960 + $\sim$950 = $\sim$1910). At lower frequency we found a sharp band with a split maximum (1872, 1862 cm^{-1}) but also a pronounced shoulder at 1855 cm^{-1}. This triplet can be assigned to the IR-active combinations of the three IR-active ($B_{1u}+B_{2u}+B_{3u}$), the four Raman-active ($A_g+B_{1g}+B_{2g}+B_{3g}$) and the inactive (A_u) Mo=O stretching modes of terminal molybdenyl groups. By using the experimentally observed maxima in the IR and Raman spectra, we can expect four maxima centred near 948 + 936 = 1884; 948 + 928 = 1876; 930 + 936 = 1866; 930 + 928 = 1858 cm^{-1}.

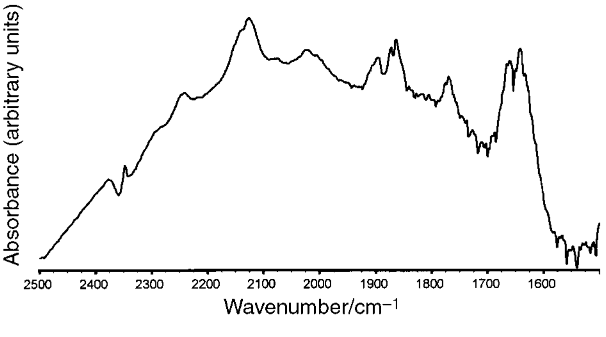

Fig. 4 FT-IR spectrum of β-$K_2Mo_2P_2O_{11}$ in the region containing overtones. The spectrum has been amplified and corrected by baseline subtraction.

In the region 800–700 cm^{-1} we find a strong band, centred at 741 cm^{-1}, with several unresolved components in the IR spectrum and a well resolved doublet at 735 and 720 cm^{-1} in the Raman spectrum. In this region we expect the vibrations associated to the symmetric stretch of the P–O–P diphosphate bridge ν_s(POP), which is known to give rise to a quite strong IR band at 740 cm^{-1} for bent-bridged diphosphates. This mode is expected to be IR-inactive for linearly-bridged diphosphate ions.[20] The corresponding Raman-active modes are generally of medium intensity or weak. According to the spectra, we expect one IR-active and two Raman-active components for ν_s(POP), (see Table 1). The assignment of the quite strong IR band at 741 cm^{-1} to the IR-active component ν_s(POP) mode (B_{2u}) is in accord with the experimental P–O–P angle of 138.2°.

The assignments of the features observed at lower frequencies are far less straightforward, due to the complexity of the vibrational pattern.

In the region 720–500 cm^{-1} we can observe three strong IR bands, at 597, 557 and 513 cm^{-1} with a prominent shoulder at 613 cm^{-1}, while in the Raman pattern we cannot distinguish with certainty any peak whose intensity is definitely higher than the noise level. We can expect here the asymmetric Mo–O–Mo single bond stretches of the nearly square planar Mo_2O_2 units, and the asymmetric bending modes of the PO_3 groups. These modes should in fact give rise to weak peaks in the Raman patterns. According to Table 1 we expect 3 IR-active components for the ν_{as}MoOMo modes, and six IR active modes for $\delta_{as}(PO_3)$, three of which belong to modes where the two PO_3 groups of each diphosphate unit bend "in phase" and three where they bend "out of phase". We can consequently tentatively assign, according to the spectra of

Table 2 Tentative assignment of IR and Raman vibrations for the β-$K_2Mo_2P_2O_{11}$ phase

IR bands/cm^{-1}	Symmetry	Mode	Symmetry	Raman peaks/cm^{-1}
1182				
1141	2 B_{1u}			
1130	+2 B_{2u}	$\nu_{as}(PO_3)$		
1113	+2 B_{3u}		A_g	1119
1092			A_g	1073
1066	B_{1u}			
1052	$+B_{2u}$	$\nu_{sym}(PO_3)$	A_g	1065
1020	$+B_{3u}$			
~950	$B_{1u}+B_{3u}$	ν_{as}(P–O–P)	$B_{1g}+B_{3g}$	960
936	B_{2u}	ν_{sym}(Mo=O)	A_g	948
928	$B_{1u}+B_{3u}$	ν_{as}(Mo=O)	$B_{1g}+B_{3g}$	930
741	B_{2u}		A_g+	735
		ν_{sym}(P–O–P)	B_{2g}	720
612	$B_{1u}+B_{2u}$			
597	$+B_{3u}$	ν_{as}(Mo–O–Mo)		
558	$B_{1u}+B_{2u}$			
	$+B_{3u}$			
513	$B_{1u}+B_{2u}$	$\delta_{as}(PO_3)$		
	$+B_{3u}$			
470	$B_{1u}+B_{2u}$	ν_s/δ(Mo–O–Mo)	A_g	486
	$+B_{3u}$			
427	$B_{1u}+B_{2u}$	$\delta_s(PO_3)$		
412	$+B_{3u}$			
382	$B_{1u}+B_{2u}$	δ(Mo=O)	A_g	375
	$+B_{3u}$			
371	$B_{1u}+B_{2u}$			
	$+B_{3u}$			
337	B_{1u}			
323	$+B_{2u}$	ν_s(O–Mo–O)		
295	$+B_{3u}$		A_g	291
282	$B_{1u}+B_{2u}$			
	$+B_{3u}$			
262	$B_{1u}+B_{2u}$	rock PO_3	A_g	267
	$+B_{3u}$			
245		twist PO_3	A_g	247
237		rock Mo–O–Mo		
217	B_{2u}	δ(POP)	A_g	207
194				
173			A_g	171
153				
127		KO_9 modes and lattice modes		
111				
102				
81				
69				

other diphosphates and of similar compounds, the complex band near 600 cm^{-1} to ν_{as}(MoOMo) modes and the bands at 558 and 513 cm^{-1} to $\delta_{as}(PO_3)$ modes.

In the region 500–450 cm^{-1} we found a quite strong IR band at 471 cm^{-1} and a weak Raman peak at 486 cm^{-1}. These features can be assigned to the symmetric stretches of the Mo–O–Mo bridges (this mode is expected to give rise to quite intense features in Raman as well as in IR).

The IR spectrum shows a complex absorption in the range 450–350 cm^{-1}. In this region a medium–strong Raman peak is found at 375 cm^{-1}, that can correspond to a sharp IR component at 382 cm^{-1}, which also shows a shoulder at 371 cm^{-1}. Possible assignments are to the bending modes of terminal Mo=O bonds, that is expected to give in IR three modes when the two molybdenyls of every unit Mo_2O_4 bend in their average plane and three when they bend out-of-plane. The two IR components at 427 and 412 cm^{-1}, that do not have detectable counterparts in the Raman pattern, can be assigned to the symmetric deformations of the diphosphate groups $\delta_s(PO_3)$.

In the range 350–200 cm^{-1} another very complex absorption is found in the IR spectrum, where also several Raman peaks fall. The main peak maxima are in IR at 295 and 262 cm^{-1} and in Raman at 291 and 267 cm^{-1}. These components can be assigned, in both techniques, to different deformations of the PO_3 groups of diphosphates, *i.e.* the twisting and the rocking modes. A further sharp peak in Raman is found at 207 cm^{-1} that can correspond to a quite sharp IR band at 194 cm^{-1} and can be tentatively assigned to the deformation of the P–O–P diphosphate bridges.

The modes arising from the vibrations of the KO_9 polyhedra are expected to lie below 190 cm^{-1}, together with modes that have the predominant character of lattice modes (translational and rotational modes of the P_2O_7 and M_2O_4 molecular units).

2. The vibrational spectra of α-$K_2Mo_2P_2O_{11}$

The IR spectrum of α-$K_2Mo_2P_2O_{11}$ is shown in Fig. 1b. We could not obtain a high-quality FT-Raman spectrum for this phase, due to thermoluminescence effects. The Raman spectrum we recorded (not shown here because of the high noise level) only shows definite peaks at 940 and 813 cm^{-1}. The tentative assignment of the vibrational modes is given in Table 3.

This phase crystallises into the space group $P2_1/c = C_{2h}^5 =$ no. 14, with $Z = 4$. As mentioned above, it is a monophosphate and its formula can thus be written as $K_2Mo_2O_3(PO_4)_2$.[11,15] The molybdenum atom is in octahedral coordination characteristic of Mo(V), *i.e.* with one free apex corresponding to one short Mo=O molybdenum bond (1.683 Å). Four of the five other apices are linked to four PO_4 tetrahedra and the fifth is shared with a similar MoO_6 octahedron, forming Mo_2O_{11} bioctahedral units in which the two molybdenyl bonds are directed along the same direction. The Mo–O–Mo angle in the Mo_2O_{11} unit is 149.79°.[11,15]

As already discussed in the case of the β phase, the complex IR region above 800 cm^{-1} (Fig. 1, curve b) contains symmetric and asymmetric P=O and Mo=O stretches. In particular, the 950–1100 cm^{-1} spectral range shows PO_x terminal stretches of phosphate groups. In the α phase the average P–O bond length is about 1.55 Å, while in the β structure it ranges between 1.50 and 1.52 Å, so being definitively shorter. This causes a decrease in the wavenumbers of the ν_{as} (1094, 1073, ~1035, ~1011 and 991 cm^{-1}) and $\nu_s(PO_3)$ (975 and 965 cm^{-1}) modes. As we can argue from Fig. 3b, the ν(POP) vibration cannot be taken into account in this compound, since the framework contains only monophosphate units. The Raman band at 940 cm^{-1} can be assigned to the terminal molybdenyl groups Mo=O symmetric stretching mode, while two of the 4 IR-active corresponding asymmetric modes give rise to the bands at 927 and 915 cm^{-1} (spectrum 1b); the shift towards lower frequencies of such peaks in comparison with the above discussed structure, can be ascribed to the Mo=O bond length, which is slightly shorter in the latter case.

The two bands at 819 in IR and 813 cm^{-1} in Raman (absent in the β structure) could likely be due to IR- and Raman-active components of the asymmetric stretches Mo–O–Mo (angle = 149.79°), which are definitely shorter here with respect to the β phase.[25]

Between 700 and 500 cm^{-1} we can expect the asymmetric Mo–O–Mo single bond stretches (650 and 615 cm^{-1}) and the asymmetric bending modes of the PO_3 groups (576, 556 and 538 cm^{-1}). The corresponding symmetric stretch of the Mo–O–Mo bridges should be represented by the peak at 471 cm^{-1}. A possible assignment of the peak at 440 cm^{-1} is to the symmetric $\delta_s(PO_3)$ bending of the phosphate groups, while the bands

Table 3 Tentative assignment of IR and Raman vibrations for the α-$K_2Mo_2P_2O_{11}$ phase

IR bands/cm^{-1}	Tentative assignment	Raman peaks/cm^{-1}
1094		
1073		
1035	$\nu_{as}(PO_3)$	
1011		
991		
975		
965	$\nu_s(PO_3)$	
	$\nu_s(Mo{=}O)$	940
927		
915	$\nu_{as}(Mo{=}O)$	
819		813
650	ν_{as} Mo–O–Mo	
615		
576		
556	$\delta_{as}(PO_3)$	
538		
514		
490		
471	ν_s(Mo–O–Mo)	
440	$\delta_s(PO_3)$	
414		
404	$\delta(Mo{=}O)$	
364		
355		
328		
287		
284		
278		
269		
250		
244		
221		
217		
203		
198		
191		
179		
173		
168		
154		
134		
119		

around 400 cm^{-1} are assignable to the bending modes of terminal Mo=O bonds. Other deformations of PO_3 units are responsible for the bands between 350 and 200 cm^{-1}, while the features below 200 cm^{-1} could be taken into account to explain vibrations of KO_9 polyhedra and lattice modes.

3. The vibrational spectra of $CdMoPO_6$

The monophosphate containing Mo(v) $CdMoPO_6$[11,17] crystallises in the $P2_1/c$ space group (C^5_{2h}, no. 14), with $Z=4$. As in the two previous structures, the molybdenum atom presents the characteristic octahedral coordination of Mo(v) with one short Mo=O bond (1.693 Å), corresponding to a molybdenyl group. Each octahedron thus presents one free corner and shares three apices with three PO_4 tetrahedra and one edge with another MoO_6 octahedron, leading to Mo_2O_{10} bioctahedral units (Mo–O–Mo angle = 84.05°, similar to that encountered in the β-$K_2Mo_2P_2O_{11}$ compound). These Mo_2O_{10} units are similar to those described for β-$K_2Mo_2P_2O_{11}$, except that in $CdMoO_2(PO_4)$ the two molybdenyl bonds of the units are antiparallel (whereas they are parallel in β-$K_2Mo_2P_2O_{11}$), *i.e.* they are in a *trans* symmetry.

Table 4 Tentative assignment of IR and Raman vibrations for the $CdMoPO_6$ phase

IR bands/cm^{-1}	Tentative assignment	Raman peaks/cm^{-1}
~1093		1106
~1047		1074
1029	$\nu_{as}(PO_3)$	
~1021		
1005		
977	$\nu_s(PO_3)$	988
946	$\nu_{as}(Mo{=}O)$	
936	$\nu_s(Mo{=}O)$	927
~920–790		803
761		
~750	ν(P–O–Mo)	
~725		722
631		
~622	ν_{as}(Mo–O–Mo)	
577		
541	$\delta_{as})PO_3)$	
530		
482		~480
~477	ν_s(Mo–O–Mo)	
435		
416	$\delta_s(PO_3)$	412
373		
359	$\delta(Mo{=}O)$	380
350		
339		~359
330	ν_s(O–Mo–O)	
~301		
~287		
~280	rock PO_3	267
272		
252		
245	twist PO_3	228
224		
212		
206	rock Mo–O–Mo	
~201		
169		
~164		155
144	CdO_6 and lattice modes	
129		
100		
77		

As shown in Fig. 3c, $CdMoPO_6$ can be regarded as constituted by an intermediate surrounding between that of α- and β-$K_2Mo_2P_2O_{11}$, *i.e.* two units of two edge-sharing molybdenum octahedra (like for β-$K_2Mo_2P_2O_{11}$) linked by monophosphate groups (as in the case of α-$K_2Mo_2P_2O_{11}$). For this reason we try here to assign IR and Raman modes by correlation with the two previous structures.

The FT-IR and Raman spectra of $CdMoPO_6$ are respectively shown in Figs. 1c and 2c. The tentative assignment of the vibrational modes is given in Table 4. As already discussed for the parent compounds, the complex feature between 1100 and 1000 cm^{-1} in the IR spectrum should be assigned to the asymmetric stretches of PO_3 monophosphate groups, with the corresponding Raman peaks situated at 1106 and 1074 cm^{-1}. The symmetric modes arising from the same units could be found at 977 (IR) and 988 (Raman) cm^{-1}. The rather intense peak at 946 cm^{-1} in the IR spectrum can be likely attributed to the asymmetric stretch of the molybdenyl bonds, the corresponding symmetric vibration giving rise to the main features at 936 (IR) and 927 (Raman) cm^{-1}.

The broad bump characterising the IR spectrum between ~920 and 790 cm^{-1} is rather difficult to interpret. Being at too low wavenumbers (and too intense) for an electronic effect, it could be assigned to the P–O–Mo stretches, together with the 761, ~750 and ~725 cm^{-1} IR bands and the 803 and 722 cm^{-1} Raman peaks. These features are in fact in a similar vibrational region to P–O–P bands for diphosphates, but at higher wavenumbers (Raman) and less resolved (IR) due to the average longer Mo–O bonds (from 1.944 to 2.130 Å) with respect to P–O bonds (1.518–1.559 Å). The IR band at 631 cm^{-1} and the shoulder at 622 cm^{-1} can be assigned to the asymmetric stretching mode ν_{as}(Mo–O–Mo), while the corresponding symmetric features are suggested at 482 and ~477 cm^{-1} (IR) and ~480 cm^{-1} (Raman). The triplet at 577, 541 and 530 cm^{-1} in the IR spectrum can be due to the $\delta_{as}(PO_3)$. The symmetric bending $\delta_s(PO_3)$ can be attributed to the vibrations at 435 and 416 cm^{-1} (IR) and at 412 cm^{-1} (Raman). The deformation δ(Mo=O) of the molybdenyl bond could give rise to the bands at 373, 359 and 350 cm^{-1} in the IR spectrum and to the Raman peak at 380 cm^{-1}. The doublet at 339 and 330 cm^{-1} in IR and the band at 359 cm^{-1} in Raman have been assigned to the ν_s(O–Mo–O). The features between 300 and 260 cm^{-1} can be due to the rocking mode of PO_3 units, whereas the corresponding twisting should give rise to bands at 252 and 245 cm^{-1} in IR and 228 cm^{-1} in Raman. Between 225 and 200 cm^{-1} in the IR spectrum may occur the rocking mode for the Mo–O–Mo bonds. Features below this are assignable to CdO_6 and lattice modes.

Conclusion

The analysis of the vibrational modes reported above with details for α and β phases and the corresponding interpretation of the experimental IR and Raman spectra allow us to confirm the usefulness of vibrational spectroscopy for structural characterisation of oxides and salts.

This is well known and indeed has been already discussed many times for simple metal phosphates. In the present case the spectral analysis of more complex mixed K–Mo phosphates allow us to obtain criteria for the spectra–structure relation of complex mixed Mo–O species.

In the case of the β-phase, the pairs of edge-sharing octahedra present nearly parallel short molybdenyl bonds in a *cis* configuration. They are characterised by three IR active modes and by three Raman active modes, giving rise to doublets in both spectra. The splitting of the absorption is between 10 and 20 cm^{-1} and the symmetric stretching modes are detected at higher frequencies than the asymmetric ones. By contrast the α polymorph presents bioctahedral units shared by corners; again two short molybdenyl bonds are present, being nearly parallel in the *cis* configuration. In this case we can observe a strong Raman peak at 940 cm^{-1}, which is confidently assigned to the asymmetric stretching mode, while the split IR mode is at lower frequencies. Again the splitting between symmetric and asymmetric stretching modes is in the range between 10 and 25 cm^{-1}. This confirms that molybdenyl(v) species in *cis* configuration, either edge- or corner-sharing, give rise to a couple of bonds in the region 950–910 cm^{-1}, the higher frequency being assigned to the symmetric stretching mode, and stronger in the Raman spectrum.

For $CdMoPO_6$, edge-sharing pairs of Mo octahedra exist with molybdenyl bonds in *trans*-configuration. Also in this case the splitting between symmetric and asymmetric modes is 10 cm^{-1} or higher, but now the symmetric stretch (the most intense in Raman spectroscopy) is at lower frequencies. Raman spectroscopy has been largely used to investigate the structures of amorphous materials such as glasses and of otherwise undetectable species such as supported species on catalysts. In particular[14,26–29] Raman and infrared spectroscopies are useful to characterise monomeric molybdenum species (where only one IR and Raman bands are expected) from dimeric species (where at least two bands are expected in the spectra). This suggests that vibrational spectroscopies and, in particular, the Raman technique are suitable to distinguish different molybdenum coordinate structures inserted in a matrix or coated on a support.

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