Hydrothermal synthesis and characterisation of new methylenediphosphonates of molybdenum(VI), A[MoO₂(O₃PCH₂PO₃H)] (A = Rb, NH₄ and Tl)¶

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Abstract. Three new, isostructural methylenediphosphonates of molybdenum, $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**), NH_4 (**2**) and Tl (**3**)) have been synthesized by hydrothermal method and structurally characterised by X-ray diffraction and spectroscopic techniques. These compounds crystallize in monoclinic space group, $P2_1/c$ with $Z = 4$ and consist of $[MoO_2(O_3PCH_2PO_3H)]^-$ anionic layers interleaved with A^+ ions.

Keywords. Metal diphosphonate; hydrothermal synthesis; layered structure; X-ray diffraction.

1. Introduction

Hydrothermal synthesis, using organic cations as templating agents of metallo-phosphates with open framework structures has been a major research activity in the field of porous solids.[1,2] Realization of these types of several new, organic–inorganic hybrid phosphate materials, by hydrothermal method, has become possible because such low synthetic-temperatures of 150–250°C ensure the retention of structure and composition of organic moieties. However, the removal of organic cations from these hybrid materials can lead to the collapse of the inorganic framework. Therefore, there is definitely a need to develop new synthetic routes giving large pores and avoiding templates.

The pioneering work of Clearfield[3,4] on the use of phosphonates opened the way. The strategy in developing new routes for synthesizing microporous solids with accessible porosity was to use diphosphonic acids instead of phosphoric acid. The inorganic part of the acid chelates the cationic species while its organic part, acting as a pillar and spacer, links the inorganic parts together, frequently leading to pillared, two- or three-dimensional structures. This method does not need any templating agent, and therefore, the porosity becomes readily accessible.

It is noteworthy that the recent expansion of metal organophosphonate chemistry includes phosphonates and diphosphonates of *d*- and *p*-block metals. These organic–inorganic hybrid, metal organophosphonates exhibit a remarkable range of structural types,[4–15] including mononuclear species, complex molecular clusters, one-dimensional

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¶Dedicated to Professor C N R Rao on his 70th birthday
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structures, layered materials and open three-dimensional frameworks. The design of metal organophosphonates with desirable bulk properties continues to be pursued by many researchers due to their potential applications.[16–18] For example, the vanadyl organophosphonates, $[VO(O_3PPh)].H_2O$ and $[(VO)_2(O_3PCH_2PO_3)].4H_2O$ exhibit structurally well-defined void spaces, permitting the intercalation of alcohols by substrate coordination to the vanadium centres of the V/P/O layers of the solid.[18]

Our specific interest in the diphosphonates of ternary system, A/Mo/diphosphonic acid (A = alkali metal, NH_4 and Tl), stems from our earlier successful study of tellurites. We have reported[19] that two types of tellurites of molybdenum, two-dimensional $A_2Mo_3TeO_{12}$ (A = Cs and NH_4) and zero-dimensional $A_4Mo_6Te_2O_{24}.4H_2O$ (A = Rb and K), synthesized under hydrothermal conditions, possess the anions of the same empirical formula $[Mo_3TeO_{12}]^{2-}$, with pyramidal TeO_3^{2-} moieties. The phosphonate RPO_3^{2-} and pyramidal TeO_3^{2-} tellurite are similar, with the stereoactive lone pair of TeO_3^{2-} being equivalent to the P–R bond of RPO_3^{2-} as shown below schematically.
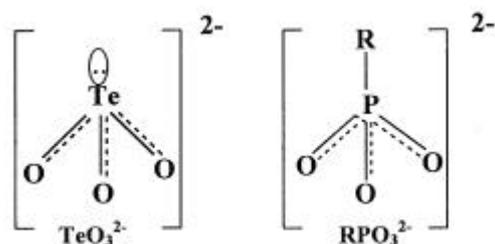
Thus organophosphonate analogoues of those tellurites of molybdenum could be formulated as $A_2[(MoO_3)_3(O_3PR)]$ and $A_4[(MoO_3)_6(O_3PR)_2]$. Layered methylphosphonates of the first type, $A_2[(MoO_3)_3(O_3PCH_3)]$ (A = Cs and Rb), have indeed been reported[20] to possess, as in tellurites, HTO-like layers of composition (Mo_3O_{12}), capped by methylphosphonate groups. These $[(MoO_3)_3(O_3PCH_3)]^{2-}$ anionic layers are interleaved with A^+ ions. Somewhat similar to zero-dimensional tellurites is a molybdenum methylarsonate,[21] $Na_4[(CH_3As)_2Mo_5O_{21}]$.

We have become interested in the synthetic and structural solid state chemistry of diphosphonates of the above mentioned two types, namely, layered- and zero-dimensional compounds with the empirical formula, $A_4[(MoO_3)_6(O_3P–R–PO_3)]$, to know whether or not HTO-like layers or zero-dimensional inorganic moieties are pillared. It is during these synthetic attempts for diphosphonates in the 'A/Mo/methylenediphosphonic acid' system that three new layered diphosphonates, $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**), NH_4 (**2**) and Tl (**3**)) have been isolated. These three compounds are isostructural with the reported[22] cesium analogue. They are, however, entirely different from known[23] methylenediphosphonate of molybdenum, $Cs_4[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4].7H_2O$. The hydrothermal synthesis, structural characterization by X-ray diffraction, thermal analysis and spectroscopic studies of these novel layered, diphosphonates are described in this paper.

2. Experimental

2.1 *Synthesis*

Teflon lined, acid digestion bombs of 23 ml capacity and the chemicals, MoO_3, A_2CO_3 (A = Rb, NH_4 and Tl), $(NH_4)_6Mo_7O_{24}.4H_2O$ and $H_2O_3PCH_2PO_3H_2$ of >99·5% purity were employed for the hydrothermal synthesis.

A mixture of Rb_2CO_3 (0.0548 g, 0·237 mmol), MoO_3 (0·1025 g, 0·712 mmol) and methylenediphosphonic acid (0·0418 g, 0·237 mmol) in the molar ratio of 1:3:1, taken along with 4 ml of distilled water in an acid digestion bomb, was heated at 225°C for four days and then cooled to 80°C over a period of one and half days. The final pH of the solution was around 6 and a homogeneous, single-phase of compound **1**, in the form of transparent block shaped crystals (0·078 g, 76% yield based on MoO_3), was obtained. It was washed with water, filtered and then air-dried. This compound was also obtained as polycrystalline powder (0·1728 g, 78% yield based on MoO_3) from 1:2:2 molar reactant mixture of Rb_2CO_3 (0·0660 g, 0·2876 mmol), MoO_3 (0·0823 g, 0·572 mmol) and methylenediphosphonic acid (0·1006 g, 0·572 mmol).

Compound **2** was similarly synthesized as a homogeneous powder (0·3189 g, 73% yield based on MoO_3), from a 1:3:1 molar reactant mixture of $(NH_4)_2CO_3$, (0·096 g, 1 mmol), MoO_3 (0·4318 g, 3 mmol) and methylenediphosphonic acid (0·1760 g, 1 mmol). The initial and final values of pH of the solution were 4 and 6 respectively. This compound was isolated as single crystals under similar hydrothermal conditions from $(NH_4)_6Mo_7O_{24}.4H_2O$ (0·0618 g, 0·005 mmol) and methylenediphosphonic acid (0·0616 g, 0·35 mmol).

A similar synthetic attempt at 200°C, involving a 1:2:2 molar reactant mixture of Tl_2CO_3 (0·0938 g, 0·2 mmol), MoO_3 (0·0576 g, 0·4 mmol) and methylenediphosphonic acid (0·0704 g, 0·4 mmol), yielded a homogeneous phase of thallium compound **3** (0·198 g, 98% yield based on MoO_3) in the form of block-shaped crystals.

2.2 *X-ray diffraction and crystal structure*

The powder X-ray diffraction (XRD) patterns of the three new compounds **1–3** were recorded on XD-D1 X-ray Diffractometer, Shimadzu, using $CuK\alpha$ (λ = 1·5405 Å) radiation. The powder XRD patterns of compounds **1–3** were simulated, using the LAZY-PULVERIX program[24] on the basis of single crystal X-ray structure, for the purpose of ascertaining their compositions and isostructural nature.

Single crystals of compounds **1** and **2**, suitable for X-ray diffraction, were selected and mounted on thin glass fibers with glue. The data sets were gathered at 25°C, using Mo-$K\alpha$ radiation (λ = 0·71073 Å), on an Enraf–Nonius CAD4 automated four-circle diffractometer, by standard procedures involving ω-2θ scan techniques. The data sets were reduced by routine computational procedures. The structure solution and refinements were carried out using the program,[25] SHELXL-97 and the graphic program[26] ATOMS was used to draw the structures.

$P2_1/c$ is the space group, determined unambiguously from the systematic absences of the measured data for both compounds. For compound **1**, the positions of rubidium, molybdenum and some of other nonhydrogen atoms were located by direct methods. Refinement of these positions and subsequent Fourier difference maps led to the location of remaining nonhydrogen atoms of the asymmetric unit. All the atoms were refined

anisotropically and the final Fourier difference map showed only one of the methylene protons and no attempts were made to include it in the final refinement. It is clear, from the nonhydrogen atom content of the asymmetric unit, that one of the four acidic protons of methylenediphosphonic acid must have been retained for charge neutrality and, therefore, the composition determined from single crystal X-ray diffraction is $Rb[MoO_2(O_3PCH_2PO_3H)]$ (**1**). The structure of compound **2** was refined successfully, using the model and the positional parameters of compound **1**. Pertinent crystallographic data, refined positional and thermal parameters and selected bond lengths of the compounds **1** and **2** are given in tables 1–3 respectively. The quality of single crystals of compound **3** was not good enough for X-ray diffraction.

2.3 *Spectroscopy*

The samples of the compounds **1–3** were ground with dry KBr and pressed into transparent discs. The infrared and Raman spectra, in the range 400–4000 cm^{-1}, were measured on these discs on a Bruker IFS 66V FT-IR spectrometer. Solid-state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 121·5 and 75·5 MHz for ^{31}P and ^{13}C respectively. Chemical shifts were referenced to an external standard of 85% H_3PO_4 for ^{31}P and glycine for ^{13}C. The recycle delay times were 5 and 2 s and the pulse lengths were 4·75 and 3·0 *μs* for ^{31}P and ^{13}C respectively whereas the spinning frequency was 7·0 kHz for both.

2.4 *Thermal analysis*

Thermogravimetric analytical data were collected on a Perkin–Elmer Delta series TG instrument. The samples were heated to 800°C at a rate of 20°C per minute under flowing nitrogen gas.

Table 1. Pertinent crystallographic data for $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**) and NH_4 (**2**) compounds.

Parameter	Compound	
	1	**2**
Formula	$RbMoP_2O_8CH_3$	$NMoP_2O_8CH_7$
Formula weight	386·38	318·96
Crystal system	Monoclinic	Monoclinic
a (Å)	8·038 (9)	8·0100 (6)
b (Å)	11·900 (10)	11·9720 (6)
c (Å)	9·089 (10)	9·0970 (4)
$\boldsymbol{b}$ (°)	114·78 (9)	115·352 (5)
V (Å^3)	789·4 (14)	788·35 (8)
Space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)
Z	4	4
$\boldsymbol{r}_{calcd}$ (g/cm^3)	3·251	2·687
$\boldsymbol{m}$(Mo K$\boldsymbol{a}$) mm^{-1}	8·206	2·088
Total reflections	1384	1365
Independent reflections	1032	1336
^aR	0·051	0·029
^bR_w	0·1245	0·089

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$: $^bR_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for A[MoO$_2$(O$_3$PCH$_2$PO$_3$H)] (A = Rb (**1**) and NH$_4$ (**2**)) compounds.

Compound	Atom	x	y	z	*$U_{(eq)}$
1	Mo	0·97389 (11)	0·12641 (7)	0·74452 (9)	0·0081 (3)
	Rb	0·69594 (15)	0·12496 (10)	0·98827 (12)	0·0245 (4)
	P (1)	0·2459 (3)	0·2467 (2)	0·0791 (3)	0·0089 (6)
	P (2)	0·7287 (3)	0·0031 (2)	0·3941 (3)	0·0081 (6)
	C	0·2715 (14)	0·1218 (9)	0·4911 (12)	0·014 (2)
	O (1)	0·9089 (10)	0·0174 (6)	0·8277 (8)	0·0165 (16)
	O (2)	0·8523 (9)	0·2343 (6)	0·7723 (8)	0·0149 (15)
	O (3)	0·0903 (9)	0·2444 (6)	0·6320 (7)	0·0115 (14)
	O (4)	0·2078 (9)	0·1564 (5)	0·9470 (7)	0·0098 (14)
	O (5)	0·1372 (9)	0·0127 (6)	0·6841 (7)	0·0119 (14)
	O (6)	0·7845 (8)	0·1015 (6)	0·5157 (8)	0·0113 (15)
	O (7)	0·4329 (10)	0·2204 (6)	0·2188 (8)	0·0164 (15)
	O (8)	0·5366 (10)	0·0248 (6)	0·2660 (9)	0·0203 (17)
2	Mo	0·96734 (5)	0·12564 (3)	0·74244 (4)	0·0103 (2)
	N	0·6950 (7)	0·1247 (3)	0·9882 (6)	0·0287 (11)
	P (1)	0·24015 (14)	0·24632 (9)	0·07996 (13)	0·0106 (3)
	P (2)	0·72714 (14)	0·00104 (9)	0·38943 (13)	0·0106 (3)
	C	0·2707 (7)	0·1229 (3)	0·4981 (6)	0·0158 (10)
	O (1)	0·9045 (4)	0·0168 (3)	0·8259 (4)	0·0181 (7)
	O (2)	0·8443 (4)	0·2331 (3)	0·7693 (4)	0·0168 (7)
	O (3)	0·0835 (4)	0·2437 (2)	0·6305 (4)	0·0148 (6)
	O (4)	0·2018 (4)	0·1577 (3)	0·9467 (4)	0·0140 (6)
	O (5)	0·1376 (4)	0·0129 (2)	0·6858 (4)	0·0160 (7)
	O (6)	0·7824 (4)	0·0986 (3)	0·5118 (4)	0·0134 (6)
	O (7)	0·4264 (4)	0·2179 (3)	0·2237 (4)	0·0192 (7)
	O (8)	0·5328 (4)	0·0231 (3)	0·2593 (4)	0·0230 (8)

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalised U_{ij} tensor

Table 3. Selected bond lengths ($\mathring{A}$) for A[MoO$_2$(O$_3$PCH$_2$PO$_3$H)] (A = Rb (**1**) and NH$_4$ (**2**)) compounds.

	1	**2**
Mo–O (1)	1·691 (7)	1·690 (3)
Mo–O (2)	1·695 (7)	1·700 (3)
Mo–O (6)	2·019 (7)	2·010 (3)
Mo–O (4)	2·037 (7)	2·034 (3)
Mo–O (5)	2·112 (7)	2·133 (3)
Mo–O (3)	2·167 (7)	2·171 (3)
P (1)–O (3)	1·521 (7)	1·515 (3)
P (1)–O (4)	1·543 (6)	1·540 (3)
P (1)–O (7)	1·539 (7)	1·543 (3)
P (1)–C	1·808 (10)	1·794 (4)
P (2)–O (5)	1·531 (7)	1·518 (3)
P (2)–O (8)	1·517 (8)	1·522 (3)
P (2)–O (6)	1·542 (7)	1·542 (3)
P (2)–C	1·816 (11)	1·799 (4)

3. Results and discussion

Our synthetic efforts did not yield the desired $A_4[(MoO_3)_6(O_3P-CH_2-PO_3)]$ compounds. The new $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**), NH_4 (**2**) and Tl (**3**)) compounds are obtained as single-phase products under the experimental conditions employed. These three compounds as well as the reported cesium analogue could also be synthesized from stoichiometric mixtures of A_2CO_3, MoO_3 and methylenediphosphonic acid. The XRD powder patterns (figure 1) of all three new diphosphonates, **1–3** compare well with those simulated on the basis of single crystal X-ray structure, confirming their single-phase nature. The monoclinic unit cell parameters of thallium compound **3** are $a = 7{\cdot}893$, $b = 11{\cdot}792$, $c = 9{\cdot}041$ Å and $b = 113{\cdot}5°$.

The structural features of these three isostructural compounds are described by taking rubidium compound as an example. $Rb[MoO_2(O_3PCH_2PO_3H)]$ (**1**) is a new two-dimensional compound having Rb^+ ions interleaved between $[MoO_2(O_3PCH_2PO_3H)]^-$ anionic layers which are stacked along a-axis. MoO_6 octahedra and diphosphonate $(O_3PCH_2PO_3H)$ moieties, corner-connected to one another, constitute these anionic layers. As shown in figure 2, MoO_6 octahedron has two, unshared, *cis* oxygen atoms and is connected, through the other four oxygen atoms, to two diphosphonate moieties in
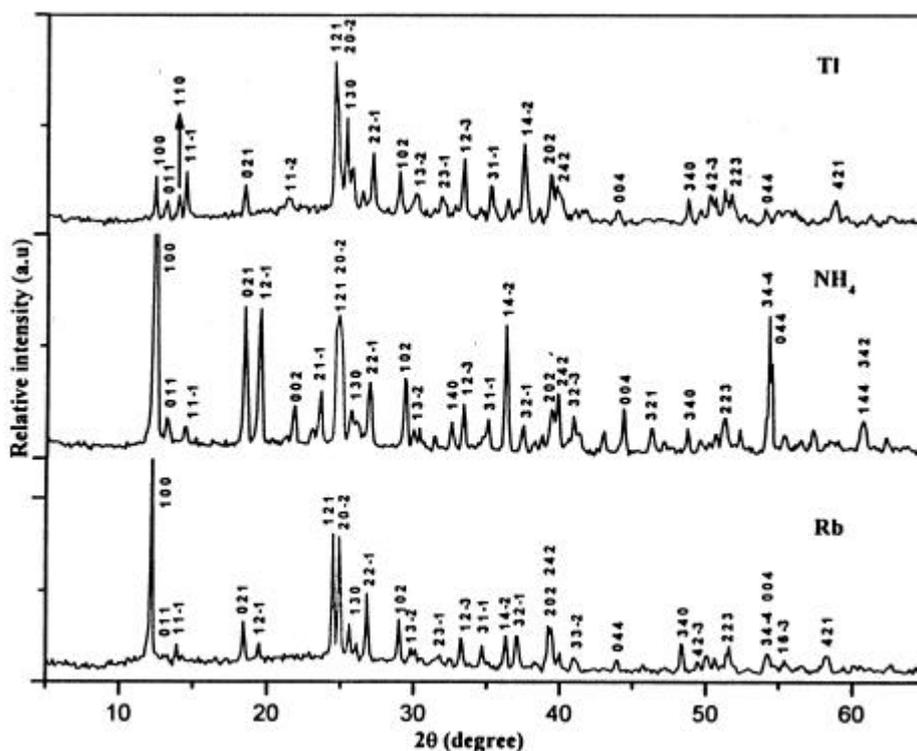

Figure 1. Powder X-ray diffraction patterns, recorded with CuK*a* ($l = 1{\cdot}5405$ Å) radiation, of $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**), NH_4 (**2**) and Tl (**3**)) compounds.
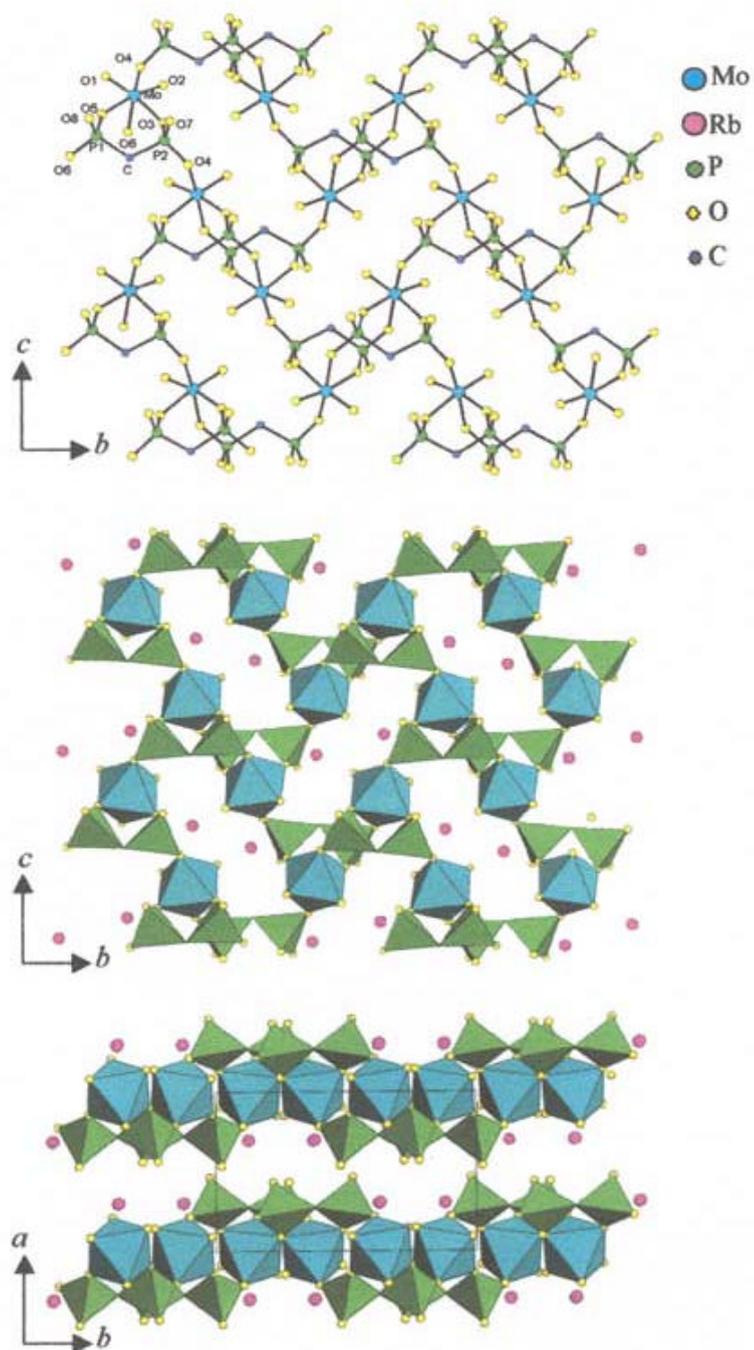
Figure 2. Ball-stick (top) and polyhedral (middle) representations of a segment of $[MoO_2(O_3PCH_2PO_3H)]^-$ anionic layer and polyhedral (bottom) representation unit cell of $Rb[MoO_2(O_3PCH_2PO_3H)]$, viewed along $c\sin b$.

monodentate fashion and to one diphosphonate moiety in bidentate fashion. Similarly, each diphosphonate moiety is connected, through four of its six oxygen atoms, to two octahedra in monodentate fashion and one octahedron in bidentate fashion. Thus both the phosphorous atoms of the diphosphonate moiety have each one unshared oxygen atom, which points towards the interlayer region. Rb^+ ions reside in the interlayer region, near the ring-like cavities of the anionic layers. They are bonded to oxygen atoms of both the layers.

The asymmetric unit contains one formula unit, $Rb[MoO_2(O_3PCH_2PO_3H)]$. Molybdenum and six oxygen atoms, O(1)–O(6) (table 2) represent the MoO_6 octahedra whereas P(1), P(2), C(1) and six oxygen atoms, O(3) to O(8), constitute the diphosphonate moiety. The two cis oxygen atoms, O(1) and O(2) of the octahedron are exclusively bonded to molybdenum with short molybdyl bonds of about 1·7 Å length (table 3). The values of other four Mo–O bond lengths vary from 2·018(7) to 2·168(6) Å. The values of O–Mo–O bond angles with the maximum deviation from the ideal values for an octahedron are 81·7(3)° and 165·4(3)°.

The values of P–C bond lengths are 1·806(10) and 1·813(11) Å and those of P–O bond lengths vary from 1·515(7) to 1·546(6) Å. O(7) and O(8) of the diphosphonate moiety are not involved in corner-connection to MoO_6 octahedra and do not significantly differ in P–O bond lengths, from the other four oxygen atoms, O(3)–O(6). The hydrogen atom of the diphosphonate moiety is believed to have bonded to either O(7) or O(8) and thus P(1) and P(2) are different. The eleven oxygen atoms found, at distances ranging from 2·886(7) to 3·485(8) Å, around rubidium include all the eight oxygen atoms, O(1) O(8) of the asymmetric unit. With the cut-off value of 3·4 Å for Rb–O bond length, rubidium is found to be bonded to only nine oxygen atoms which do not include O(4).
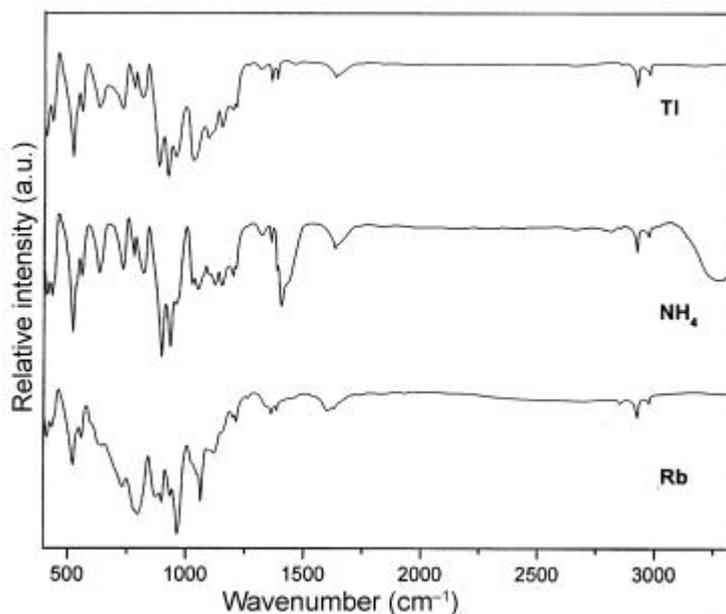

Figure 3. Infrared spectra of $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb (**1**), NH_4 (**2**) and Tl (**3**)) compounds.

The values of bond lengths and angles in the layered $[MoO_2(O_3PCH_2PO_3H]^-$ anion of compound **2** (table 3) are similar to those in **1**. However, only seven oxygen atoms are found within a sphere of radius 3·4 Å around nitrogen in compound **2**.

Infrared spectra of compounds **1–3** are presented in figure 3. The infrared spectrum of ammonium compound shows two peaks at 3263 and 1403 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of the ammonium ion.[27] The C–H stretching vibrations of the phosphonate group are observed around 2970 and 2920 cm^{-1} whereas their bending vibrations[11] are seen at 1380 cm^{-1}. The P–C stretching vibrations of the phosphonate group are observed[28] at 1305 cm^{-1}. The peaks in the region 1200–1000 cm^{-1} are due to P–O stretching vibrations[11]. The peaks in the region 540–413 cm^{-1} could be attributed to O–P–O bending vibrations. The peaks at 950–730 cm^{-1} could be due to one or more of the vibrations[20] of Mo–O or P–O bonds. Infrared spectra of compounds **1** and **3** similarly contain all the peaks except those due to ammonium ion. The C–H stretching frequencies at 2970 and 2920 cm^{-1}, Mo–O stretching frequency at 830 cm^{-1}, and those due to P–O stretching vibration in the region 1000–900 cm^{-1} are observed in the Raman spectra[20] of all three compounds.

The solid-state ^{13}C and ^{31}P NMR spectra of these three compounds are presented in figure 4. Solid-state ^{13}C NMR spectra have only one signal between 25·00 and 26·32 ppm, due to methylene carbon atom. Solid-state NMR ^{31}P spectra have two signals
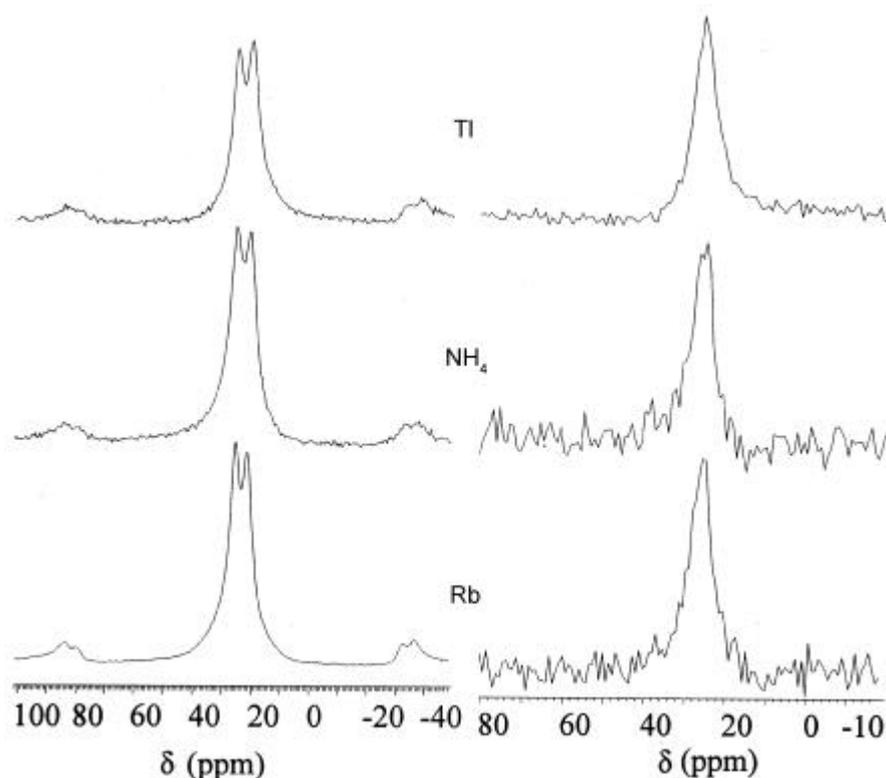

Figure 4. Solid-state ^{31}P (left) and ^{13}C (right) NMR spectra of $A[MoO_2(O_3PCH_2 PO_3H)]$ (A = Rb (**1**), NH$_4$ (**2**) and Tl (**3**)) compounds.

between 20·80 and 25·46 ppm, indicating the presence of two distinct phosphorus atoms, P(1) and P(2).

Compounds **1** and **3** are stable up to 500°C, after which they undergo a one-step weight loss of 8·3 and 4·3% respectively. Similarly the ammonium compound shows a one-step weight loss of 16% in the temperature range, 300–800°C.

The layered $[MoO_2(O_3PCH_2PO_3H)]^-$ anions of these three compounds could be regarded as Brönsted acids. Our preliminary investigations of ion-exchange reactions of rubidium compound with $Ba(OH)_2$ to yield $Ba[MoO_2(O_3PCH_2PO_3)]$ seem to be successful.

4. Conclusion

Three new methylenediphsphonates of molybdenum(VI), $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb, NH_4 and Tl) have been synthesised under hydrothermal conditions and characterised by X-ray diffraction and spectroscopy. They are isostructural, layered compounds.

Acknowledgements

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