JOURNAL OF
Materials
CHEMISTRY

A new three-dimensional sodium molybdenum(V) hydroxymonophosphate: $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25H_2O$

A. Leclaire,*[a] C. Biot,[a] H. Rebbah,*[b] M. M. Borel[a] and B. Raveau[a]

[a]*Laboratoire CRISMAT, URA 1318 associée au CNRS, ISMRA et Université de Caen—Bd du Maréchal Juin 14050- Caen cedex- France*

[b]*Laboratoire de cristallographie et cristallogenèse-Institut de Chimie U.S.T.H.B. B.P. 32 El-Alia Bab-Ezzouar Alger—Algérie*

A new sodium molybdenum(V) hydroxymonophosphate, $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25\ H_2O$ has been synthesized. It crystallizes in the monoclinic space group $P2_1/c$ with $a=13.024(4)$, $b=25.936(4)$, $c=13.276(3)$ Å, $\beta=111.72(2)°$. Its structure involves $Na[Mo_6P_4O_{27}(OH)_4]_2$ clusters similar to those encountered in several other molybdenum(V) hydroxyphosphates. Such clusters built up of two rings of six edge-sharing Mo octahedra interconnected through one NaO_6 octahedron differ from those previously described by the fact that hydrogen is mainly connected to the Mo—O bond forming twelve $Mo(O_5OH)$ octahedra, whereas among the eight tetrahedra one observes two $P(O_3OH)$ tetrahedra and six PO_4 tetrahedra. The originality of this structure deals with the fact that such clusters form with several sodium octahedra, $Na(H_2O)_4O_2$ and $Na(H_2O)_2O_4$, a three-dimensional framework that delimits intersecting tunnels running along ***a***, ***b*** and ***c***. The coordination of other sodium cations and H_2O molecules that can be considered as intercalated species is also discussed.

The studies of reduced molybdenum phosphates and hydroxyphosphates performed in the last ten years, have shown that these compounds exhibit a large structural diversity. Numerous layer and tunnel structures have been generated which are of relevance to applications in catalysis owing to their microporous character and also their redox properties (for reviews see ref. 1–4).

The structural chemistry of the anhydrous molybdenum phosphates is generally different from that of the hydroxyphosphates. In the anhydrous phosphates, a large number of infinite three-dimensional frameworks built up from MoO_6 octahedra and PO_4 tetrahedra only can be generated. This is not the case for hydroxyphosphates, where most of the time molybdenum and phosphorus form isolated polyanionic groups with oxygen and hydroxy groups, that are held together in a three-dimensional framework by introducing foreign cations such as transition or post transition cations (*e.g.* iron, zinc) or univalent cations (*e.g.* alkali). Thus, the molybdenum hydroxyphosphates are less stable, involve stabilization by hydrogen bonding only and are generally prepared by hydrothermal techniques. For this reason, the number of molybdenum(V) hydroxyphosphates of alkali cations that do not involve any other transition or post transition elements is small compared to anhydrous molybdenum(V) phosphates. The sodium hydroxyphosphates $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$,[5] $Na_3[Mo_2O_4(HPO_4)(PO_4)]\cdot 2H_2O$,[6] and $(Et_4N)_6Na_2[Na_{12}(H_3PO_4)\{Mo_6O_{15}(HPO_4)(H_2PO_4)_3\}_4]\cdot xH_2O$[7] and the caesium hydroxyphosphate $Cs(H_3O)[Mo_2O_2(PO_4)_2(HPO_4)]$[8] are representative of the unusual molybdenum(V) alkali hydroxymonophosphates that do not involve any other transition element than molybdenum. Among these hydroxyphosphates, only one, $Na_3[Mo_2O_4(HPO_4)(PO_4)]$,[6] does not contain other univalent cations such as phosphonium, ammonium or oxonium. We report on the synthesis and crystal stucture of a new molybdenum(V) hydroxymonophosphate $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25H_2O$, with an original structure.

Synthesis procedure

Single crystals of the title compound were grown from a hydrothermal reaction of H_3PO_4 (Prolabo, 75%), NaOH (Prolabo, 98%) $Na_2MoO_4\cdot 2H_2O$ (Merck, 99.5%) and finely divided metallic molybdenum (Goodfellow, 99.9%). The best results for such a synthesis were obtained from a mixture of 1.442 g of $Na_2MoO_4\cdot 2H_2O$, 0.634 g of NaOH, 0.230 g of Mo, 1 cm^3 of H_3PO_4 and 7 cm^3 H_2O highly homogenized in a 25 cm^3 Teflon lined autoclave. The reaction vessel was maintained at 220 °C and autogenous pressure for 36 h before slow cooling at $1.6°\ h^{-1}$ to room temperature.

By this method, well formed orange crystals could be easily separated from a roseate powder, whose crystallographic nature was not identified. The orange crystals were washed with water, rinsed with ethanol and finally dried in a desiccator.

Microprobe analysis of these crystals evidenced a cationic ratio Na : Mo : P of 8 : 6 : 4 in accord with the formula $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25\ H_2O$ deduced later from the crystal structure determination.

Thermogravimetry, performed under argon between 25 and 600 °C, shows a continuous loss of water in good agreement with the presence of 28.5 hydrogen atoms per formula unit ($\Delta m_{obs}=17\%$; $\Delta m_{calc}=18\%$). No intermediate phase could be detected during the dehydration owing to the poor crystallization of the products.

Structure determination

An orange plate like crystal with dimensions 0.097×0.168 x 0.036 mm was selected for the structure determination. The cell parameters reported in Table 1 were determined and refined by diffractometric technique at 294 K with a least square refinement based upon 25 reflections with $18\leqslant\theta\leqslant 22°$. The systematic absences $l=2n+1$ for $h0l$ and $k=2n+1$ for $0k0$ are consistent with the space group $P2_1/c$. The data were collected with an Enraf Nonius CAD4 diffractometer, and parameters are reported in Table 1. Among the 9460 unique measured reflections, 3896 with $I\geqslant 3\sigma(I)$ corrected for Lorentz and polarization and absorption and secondary extinction effects were used to solve and refine the structure. The atoms were located by the heavy atom method, *i.e.* the molybdenum atoms were located by the deconvolution of the Patterson function and the other atoms by subsequent Fourier synthesis.

Table 1 Summary of crystal data, intensity measurements and structure refinement parameters for $Na_8Mo_6P_4O_{27}(OH)_4 \cdot 12.25H_2O$

crystal data:	
space group	$P2_1/c$
cell dimensions	$a = 13.024(4)$ Å
	$b = 25.936(4)$ Å $\beta = 111.72(2)°$
	$c = 13.276(3)$ Å
volume/Å^3	4116.1(7)
Z	4
D_c/g cm^{-3}	2.51
intensity measurements:	
λ(Mo-Kα)	0.71073
scan mode	ω–$2/3\theta$
scan width/°	$1.5 + 0.35 \tan\theta$
slit aperture/mm	$1.3 + \tan\theta$
max θ/°	27
standard reflections	three measured every 3600 s
measured reflections	9460
reflections with $I > 3\sigma$	3896
h min., max.	−16, 16
k min., max.	0, 33
l min., max.	0, 16
μ/mm^{-1}	2.11
structure solution and refinement:	
parameters refined	507
agreement factors	$R = 0.055$ $R_w = 0.066$
weighting scheme	$w = 1/\sigma^2$
Δ/σ max.	< 0.005

Table 2 Positional parameters and their estimated standard deviations[a]

atom	x	y	z	B/Å^2
Mo(1)	0.6111(1)	0.39072(7)	0.7077(1)	1.00(6)
Mo(2)	0.3980(2)	0.39170(7)	0.6374(1)	1.02(6)
Mo(3)	0.2416(1)	0.41456(7)	0.3596(1)	1.15(6)
Mo(4)	0.3438(2)	0.43037(7)	0.2277(1)	1.18(6)
Mo(5)	0.6362(2)	0.42959(7)	0.3236(1)	1.18(6)
Mo(6)	0.7485(2)	0.41246(7)	0.5275(1)	1.14(6)
P(1)	0.4947(5)	0.3531(2)	0.4404(5)	0.96(2)
P(2)	0.1888(5)	0.3142(2)	0.4946(5)	1.36(2)
P(3)	0.4798(5)	0.3882(2)	0.0782(5)	1.84(2)
P(4)	0.8126(5)	0.3127(2)	0.7029(5)	1.68(2)
Na(1)	1/2	1/2	1/2	1.20(3)
Na(2)	0.4936(8)	0.2330(3)	0.2970(7)	2.48(3)
Na(3)	0.483(1)	0.2512(4)	0.067(1)	6.40(6)
Na(4)	0.1152(8)	0.1993(4)	0.3428(8)	3.60(4)
Na(5)	0.7212(8)	0.2807(4)	0.4589(8)	3.28(4)
Na(6)	0.2774(8)	0.2855(4)	0.3108(8)	2.72(3)
Na(7)	0.569(1)	0.0232(4)	0.430(1)	6.32(6)
Na(8)	0.956(1)	0.4686(5)	0.378(1)	5.60(5)
Na(9)[b]	0.827(5)	0.141(2)	0.486(4)	6.40(2)
Na(10)[b]	0.109(4)	0.037(2)	0.440(4)	6.40(2)
O(1)	0.638(1)	0.4122(6)	0.835(1)	1.84(5)
O(2)	0.503(1)	0.3346(5)	0.683(1)	1.68(5)
O(3)	0.505(1)	0.4419(5)	0.625(1)	1.12(4)
O(4)	0.732(1)	0.3363(5)	0.751(1)	1.68(5)
O(5)	0.726(1)	0.4341(6)	0.669(1)	1.68(5)
O(6)	0.602(1)	0.3689(6)	0.538(1)	0.88(4)
O(7)	0.377(1)	0.4114(6)	0.747(1)	2.32(6)
O(8)	0.278(1)	0.4392(5)	0.522(1)	0.80(4)
O(9)	0.276(1)	0.3384(5)	0.599(1)	1.28(5)
O(10)	0.396(1)	0.3687(5)	0.470(1)	1.20(4)
O(11)	0.124(1)	0.4485(6)	0.302(1)	2.00(5)
O(12)	0.260(1)	0.3719(5)	0.247(1)	1.44(5)
O(13)	0.354(1)	0.4639(5)	0.363(1)	1.12(4)
O(14)	0.169(1)	0.3522(5)	0.400(1)	1.68(5)
O(15)	0.257(1)	0.4687(5)	0.133(1)	1.92(5)
O(16)	0.381(1)	0.3836(5)	0.119(1)	1.60(5)
O(17)	0.491(1)	0.4727(5)	0.247(1)	1.44(5)
O(18)	0.491(1)	0.3852(5)	0.342(1)	1.20(4)
O(19)	0.725(1)	0.4648(6)	0.291(1)	2.32(6)
O(20)	0.589(1)	0.3858(5)	0.184(1)	1.68(5)
O(21)	0.636(1)	0.4640(5)	0.456(1)	1.36(5)
O(22)	0.722(1)	0.3701(5)	0.399(1)	1.60(5)
O(23)	0.866(1)	0.4451(5)	0.543(1)	1.68(5)
O(24)	0.826(1)	0.3494(5)	0.614(1)	1.44(5)
O(25)	0.492(1)	0.2962(5)	0.420(1)	1.28(5)
O(26)	0.229(1)	0.2645(5)	0.468(1)	2.24(6)
O(27)	0.079(1)	0.3099(6)	0.515(1)	2.32(6)
O(28)	0.476(1)	0.3402(6)	0.013(1)	2.56(6)
O(29)	0.469(1)	0.4377(6)	0.019(1)	2.72(6)
O(30)	0.766(1)	0.2612(6)	0.649(1)	2.96(6)
O(31)	0.925(1)	0.3070(8)	0.799(1)	4.08(6)
$H_2O(32)$	0.065(1)	0.1346(6)	0.183(1)	2.40(3)
$H_2O(33)$	0.321(1)	0.1949(6)	0.324(1)	2.64(3)
$H_2O(34)$	0.357(1)	0.2788(6)	0.160(1)	2.96(4)
$H_2O(35)$	0.925(1)	0.3772(6)	0.354(1)	3.2(4)
$H_2O(36)$	0.086(1)	0.0470(6)	0.057(1)	3.12(4)
$H_2O(37)$	0.625(1)	0.2780(6)	0.243(1)	3.04(4)
$H_2O(38)$	0.890(1)	0.2550(7)	0.447(1)	3.92(4)
$H_2O(39)$	0.102(1)	0.2594(7)	0.190(1)	3.44(4)
$H_2O(40)$	0.642(1)	0.1943(7)	0.445(1)	3.76(4)
$H_2O(41)$	0.901(2)	0.319(1)	0.158(2)	8.32(7)
$H_2O(42)$[c]	0.151(2)	0.137(1)	0.478(2)	2.32(6)
$H_2O(43)$[c]	0.738(3)	0.433(2)	0.076(3)	4.80(8)
$H_2O(44)$[c]	0.266(3)	0.047(2)	0.378(3)	5.60(8)
$H_2O(45)$[c]	0.936(3)	0.069(2)	0.338(3)	4.80(8)
$H_2O(46)$[b]	0.091(4)	0.995(2)	0.308(4)	1.60(8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3\Sigma_i\Sigma_j a_i a_j \beta_{ij}$. Water molecules refined isotropically.

[b] Occupancy = 0.25.

[c] Occupancy = 0.5.

All the calculations were done on a Spark station with the XTAL package.[9] Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/71.

The molybdenum, phosphorus, oxygen atoms O(1)–O(31) and Na(1) were identified without any ambiguity. The distinction between the sodium atoms [Na(2)–Na(10)] and the water molecules [O(32)–O(46)] was difficult, owing to the same number of electrons of the two species. The identification of the different species was performed on the basis of the interatomic distances and the coordination of each atom. The refinement of the isotropic thermal factors and the occupancy factors, coupled with the ratios between the height of the Fourier peaks allowed first to distribute 0.25 Na^+ in the Na(9) and Na(10) sites, 0.5 H_2O in the O(42), O(43), O(44) and O(45) sites and one 0.25 H_2O in the O(46) site. Then in the following refinement the occupancy factors were fixed. The refinement of the atomic coordinates, the isotropic thermal factors of the water molecules and incompletely occupied sodium sites, and the anisotropic thermal factors of the remaining atoms led to $R = 0.055$ and $R_w = 0.066$ and to the atomic parameters listed in Table 2. As the compound was synthesized by hydrothermal reaction with an excess of sodium hydroxide, hydroxy groups were susceptible to be present in the structure. Thus, a calculation of the electrostatic bond strength balance was performed, using the Brese and O'Keeffe formulation[10] for Mo^V, Na and P^V species ($r_{ij} = 1.879$, 1.80, 1.604, respectively) and the Brown curves[11] for the hydrogen bonds. A lack of *ca.* 0.7 in the electrostatic valence of an oxygen atom is characteristic of an hydroxy group and a lack of *ca.* 1.4 indicates a water molecule. The O(32)–O(46) sites identified as water molecules during the resolution of the structure receive about 0.262 electrostatic valence from the Mo, P or Na atoms. Five oxygen sites O(5), O(8), O(17), O(31) and O(27) receive, respectively, 1.150, 1.033, 1.159, 1.380 and 1.180 electrostatic valence from the Mo, P or Na atoms. However, O(27) receives only 0.673 more electrostatic valence from the four water molecules O(32), O(35), O(38) and O(39). Thus it can be concluded that O(5), O(8), O(17) and O(31) are hydroxy groups so that three OH groups belong to the MoO_6 octahedra and one OH group to the PO_4 tetrahedra. The water loss deduced from thermogravimetry is consistent with 28.5 H atoms per formula. From these observations this compound can be formulated $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25\ H_2O$. The theoretical valency of five for molybdenum is confirmed by the bond strength calculations which lead to valencies of 4.85, 5.03, 4.81, 4.75, 4.95 and 4.93 respectively for the six molybdenum atoms.

Description of the structure and Discussion

The projection of the structure of this new molybdenum(v) hydroxymonophosphate along ***a*** (Fig. 1) shows that it consists of centrosymmetric clusters $Na[Mo_6P_4O_{27}(OH)_4]_2$ interconnected through sodium cations and water molecules.

Each $Na[Mo_6P_4O_{27}(OH)_4]_2$ cluster (Fig. 2) is very similar to the $Na[Mo_{12}P_4O_{24}(OH)_7]$ clusters observed for the phosphate polymer $(H_3O)_2NaMo_6P_4O_{24}(OH)_7(PPh_4)_2\cdot 5H_2O$, whose structure has been described by Haushalter and Lai.[5] Nevertheless the clusters of the two structures differ from each other by the distribution and the number of protons. Haushalter and Lai[5] observe fourteen OH groups per cluster, instead of eight in the present compound. Moreover in the Haushalter phase all OH groups are assumed to be linked to the phosphorus forming seven $PO_3(OH)$ tetrahedra per cluster, in contrast with the present structure where six OH groups per cluster are linked to molybdenum, forming $MoO_5(OH)$ octahedra, and only two OH groups are linked to phosphorus [P(4)] forming $PO_3(OH)$ tetrahedra. Then in our hydroxyphosphate the structure of each cluster consists of two rings of six $Mo(O_5OH)$ edge-sharing octahedra; each Mo_6 ring shares its apices with three PO_4 tetrahedra [two tetrahedra P(2) and P(3) at the periphery of the cluster and one central phosphate group P(1)] and one $P(O_3OH)$, P(4). The two Mo_6 rings are connected through one NaO_6 octahedron Na(1) that

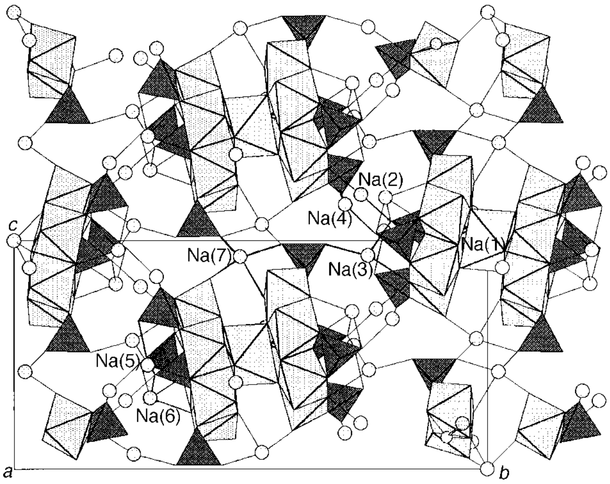

Fig. 1 Projection of the structure of $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)$ along ***a***

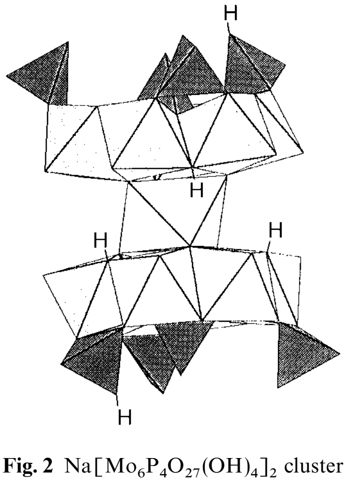

Fig. 2 $Na[Mo_6P_4O_{27}(OH)_4]_2$ cluster

Table 3 Distances (Å) and angles (°) in the polyhedra

Mo(1)	**O(1)**	**O(2)**	**O(3)**	**O(4)**	**O(5)**	**O(6)**
O(1)	1.69(2)	2.93(2)	2.79(2)	2.76(2)	2.89(2)	3.96(2)
O(2)	106.6(7)	1.96(1)	2.89(2)	2.77(2)	3.93(2)	2.82(2)
O(3)	100.5(6)	95.6(6)	1.94(1)	3.91(2)	2.72(2)	2.76(2)
O(4)	95.3(6)	87.8(6)	162.1(7)	2.03(1)	2.75(2)	2.83(2)
O(5)	99.6(7)	153.1(7)	85.1(6)	84.0(6)	2.08(2)	2.53(2)
O(6)	170.0(6)	82.9(6)	81.1(5)	81.9(5)	70.7(5)	2.29(1)
Mo(2)	**O(2)**	**O(3)**	**O(7)**	**O(8)**	**O(9)**	**O(10)**
O(2)	1.96(1)	2.89(2)	2.90(2)	3.99(2)	2.76(2)	2.79(2)
O(3)	95.0(6)	1.96(1)	2.83(2)	2.76(2)	3.93(2)	2.78(2)
O(7)	106.7(7)	102.8(7)	1.65(2)	2.87(2)	2.69(2)	3.94(2)
O(8)	154.5(6)	84.9(5)	98.1(6)	2.13(1)	2.81(2)	2.64(2)
O(9)	87.6(6)	161.8(6)	93.7(7)	85.1(5)	2.03(1)	2.83(2)
O(10)	81.7(6)	81.0(5)	170.1(6)	73.1(5)	81.5(6)	2.30(1)
Mo(3)	**O(8)**	**O(10)**	**O(11)**	**O(12)**	**O(13)**	**O(14)**
O(8)	2.12(1)	2.64(2)	2.88(2)	3.97(2)	2.72(2)	2.83(2)
O(10)	72.6(5)	2.33(1)	3.99(2)	2.83(2)	2.79(2)	2.78(2)
O(11)	97.4(6)	168.8(7)	1.69(1)	2.93(2)	2.84(2)	2.78(2)
O(12)	154.9(5)	82.4(5)	107.3(6)	1.94(2)	2.86(2)	2.75(2)
O(13)	84.0(6)	81.5(5)	102.8(6)	94.8(6)	1.94(1)	3.92(2)
O(14)	85.5(6)	78.7(5)	95.9(7)	87.3(6)	159.6(5)	2.04(2)
Mo(4)	**O(12)**	**O(13)**	**O(15)**	**O(16)**	**O(17)**	**O(18)**
O(12)	1.94(2)	2.86(2)	2.93(2)	2.74(2)	3.98(2)	2.82(2)
O(13)	94.5(6)	1.95(1)	2.84(2)	3.98(2)	2.76(2)	2.78(2)
O(15)	108.1(6)	103.2(6)	1.67(1)	2.78(2)	2.86(2)	3.92(2)
O(16)	85.7(6)	160.8(5)	95.0(7)	2.08(2)	2.91(2)	2.77(2)
O(17)	155.2(5)	84.6(6)	96.2(6)	87.3(6)	2.14(2)	2.60(2)
O(18)	83.4(5)	82.1(5)	166.7(7)	78.9(5)	71.9(5)	2.28(1)
Mo(5)	**O(17)**	**O(18)**	**O(19)**	**O(20)**	**O(21)**	**O(22)**
O(17)	2.11(1)	2.60(2)	2.88(2)	2.86(2)	2.73(2)	3.96(2)
O(18)	71.9(5)	2.31(2)	3.94(2)	2.83(3)	2.82(2)	2.85(2)
O(19)	99.7(7)	170.3(6)	1.65(2)	2.74(2)	2.82(3)	2.85(2)
O(20)	86.7(5)	80.5(6)	94.3(7)	2.07(1)	3.99(2)	2.77(2)
O(21)	84(1) 0	82.2(6)	102.2(7)	162.2(6)	1.97(1)	2.89(2)
O(22)	155.4(6)	83.6(6)	104.5(7)	87.2(6)	95.0(6)	1.95(1)
Mo(6)	**O(5)**	**O(6)**	**O(21)**	**O(22)**	**O(23)**	**O(24)**
O(5)	2.08(2)	2.53(2)	2.74(2)	3.93(2)	2.90(2)	2.78(2)
O(6)	71.1(5)	2.26(1)	2.80(2)	2.82(2)	3.93(2)	2.75(2)
O(21)	85.6(6)	82.9(6)	1.95(1)	2.89(2)	2.82(2)	3.93(2)
O(22)	154.4(6)	83.8(6)	95.9(6)	1.95(1)	2.88(2)	2.72(2)
O(23)	100.1(7)	170.0(6)	101.3(6)	104.6(7)	1.69(1)	2.77(2)
O(24)	85.0(6)	79.3(5)	161.8(7)	86.1(6)	95.7(6)	2.04(1)
P(1)	**O(6)**	**O(10)**	**O(18)**	**O(25)**		
O(6)	1.57(1)	2.50(2)	2.51(2)	2.53(2)		
O(10)	107.5(8)	1.53(2)	2.48(2)	2.48(2)		
O(18)	107.5(8)	107.8(8)	1.54(2)	2.53(2)		
O(25)	111.2(7)	109.9(9)	112.8(9)	1.50(1)		
P(2)	**O(9)**	**O(14)**	**O(26)**	**O(27)**		
O(9)	1.56(1)	2.51(2)	2.51(2)	2.50(2)		
O(14)	108.1(8)	1.54(2)	2.46(2)	2.49(2)		
O(26)	110.7(8)	109(1)	1.48(2)	2.55(2)		
O(27)	106.7(9)	107.7(9)	114(1)	1.55(2)		
P(3)	**O(16)**	**O(20)**	**O(28)**	**O(29)**		
O(16)	1.57(2)	2.52(2)	2.46(3)	2.48(2)		
O(20)	105.9(9)	1.58(1)	2.50(2)	2.55(2)		
O(28)	106.2(9)	107.7(8)	1.51(2)	2.53(2)		
O(29)	109(1)	112.4(9)	116(1)	1.48(2)		
P(4)	**O(4)**	**O(24)**	**O(30)**	**O(31)**		
O(4)	1.55(2)	2.56(2)	2.51(2)	2.48(2)		
O(24)	110.4(9)	1.57(2)	2.51(2)	2.56(2)		
O(30)	109(1)	108.2(9)	1.53(2)	2.57(2)		
O(31)	106(1)	110(1)	113(1)	1.55(2)		

Mo(1)···Mo(2) 2.581(3). Mo(2)···Mo(3) 3.541(3).
Mo(3)···Mo(4) 2.594(3). Mo(4)···Mo(5) 3.541(3).
Mo(5)···Mo(6) 2.595(3). Mo(6)···Mo(1) 3.524(3).

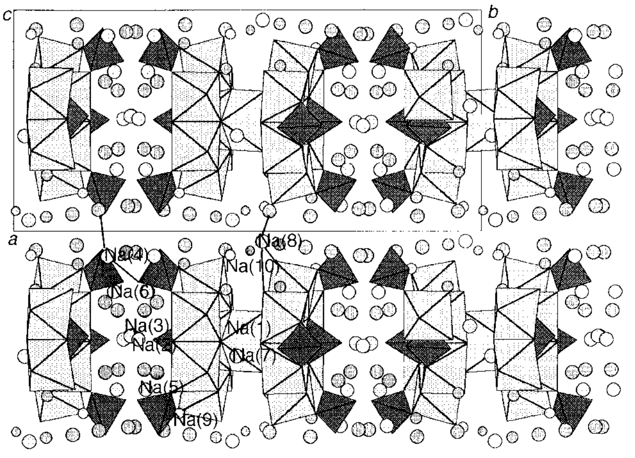

Fig. 3 Projection of the structure of $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)·12.25H_2O$ along ***c***

shares three apices with each of them. Thus these clusters can be formulated $Na[(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)]_2$. Similarly to $(H_3O)_2NaMo_6P_4O_{24}(OH)_7(PPh_4)_2·5H_2O$, each Mo octahedron has one free apex characteristic of Mo^V. Note also that in our phase the OH groups of the $MO_5(OH)$ octahedra are always shared by two octahedra. The presence of OH groups linked to molybdenum in the $Na[Mo_6P_4O_{27}(OH)_4]_2$ cluster is unusual so making direct comparison with the structures of Haushalter *et al.* may be of limited value since the hydrogen atoms were not localised but only assumed to be linked to the phosphate groups. Recent work on $Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4·10H_2O$ and $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8·15H_2O$[12] show also the presence of six OH linked to molybdenum in the clusters.

In these condensed polyanions, the geometry of the $MoO_5(OH)$ octahedra is characteristic of that encountered for Mo^V. As observed in Table 3, abnormally short Mo—O bonds ranging from 1.65 to 1.69 Å are observed corresponding to the free apex, opposite very long Mo—O bonds, ranging from 2.26 to 2.33 Å, and four intermediate equatorial Mo—O bonds, ranging from 1.94 to 2.14 Å. Nevertheless a distinction can be

Table 4 Na—O distances < 3.2 Å[a]

Na(1)—O(3)	2.23(1)	Na(6)—O(12)	2.38(2)
Na(1)—O(3)^{i}	2.23(1)	Na(6)—H_2O(33)	2.41(2)
Na(1)—O(13)	2.29(1)	Na(6)—O(26)	2.46(2)
Na(1)—O(13)^{i}	2.29(1)	Na(6)—H_2O(34)	2.58(2)
Na(1)—O(21)	2.27(1)	Na(6)—O(25)	2.64(2)
Na(1)—O(21)^{i}	2.27(1)	Na(6)—O(14)	2.76(2)
Na(2)—O(25)	2.32(2)	Na(6)—O(10)	3.01(2)
Na(2)—O(2)^{ii}	2.35(2)	Na(7)—O(29)^{v}	2.29(2)
Na(2)—H_2O(34)	2.34(2)	Na(7)—O(29)^{iv}	2.42(2)
Na(2)—H_2O(37)	2.39(2)	Na(7)—O(1)^{ii}	2.46(2)
Na(2)—H_2O(40)	2.41(2)	Na(7)—O(17)^{iv}	2.55(2)
Na(2)—H_2O(33)	2.60(2)	Na(7)—H_2O(43)^{v}	2.59(2)
Na(3)—O(25)^{ii}	2.34(2)	Na(7)—O(15)^{iv}	3.03(2)
Na(3)—O(28)	2.41(2)	Na(7)—H_2O(44)^{vi}	3.22(2)
Na(3)—H_2O(34)	2.49(3)	Na(7)—O(7)^{ii}	3.25(2)
Na(3)—H_2O(37)	2.49(2)	Na(8)—H_2O(36)^{iv}	2.35(2)
Na(3)—O(2)^{ii}	2.66(2)	Na(8)—H_2O(36)^{x}	2.38(2)
Na(3)—O(26)^{ii}	3.09(2)	Na(8)—H_2O(35)	2.40(2)
Na(4)—O(31)^{iii}	2.33(2)	Na(8)—H_2O(46)^{iv}	2.41(2)
Na(4)—H_2O(42)	2.34(2)	Na(8)—O(11)^{vii}	2.78(2)
Na(4)—O(26)	2.45(2)	Na(8)—O(19)	2.80(2)
Na(4)—H_2O(39)	2.51(2)	Na(8)—O(23)	2.91(2)
Na(4)—H_2O(32)	2.59(2)	Na(8)—O(23)^{viii}	3.12(2)
Na(4)—H_2O(33)	2.78(2)	Na(9)—H_2O(41)^{v}	2.36(2)
Na(5)—H_2O(38)	2.36(2)	Na(9)—H_2O(40)	2.64(2)
Na(5)—O(30)	2.42(2)	Na(9)—H_2O(43)^{v}	2.75(2)
Na(5)—O(22)	2.45(2)	Na(9)—O(1)^{ii}	2.89(2)
Na(5)—H_2O(40)	2.45(2)	Na(9)—O(4)^{ii}	2.96(2)
Na(5)—O(6)	3.15(2)	Na(9)—H_2O(38)	3.15(2)
Na(5)—H_2O(37)	2.67(2)	Na(10)—H_2O(45)^{xi}	2.31(2)
Na(5)—O(24)	2.68(2)	Na(10)—H_2O(44)	2.48(2)
Na(5)—O(25)	2.86(2)	Na(10)—O(15)^{v}	2.58(2)
Na(6)—H_2O(39)	2.35(2)	Na(10)—H_2O(42)	2.65(2)

[a] Symmetry codes: i: $1-x$, $1-y$, $1-z$; ii: x, $1/2-y$, $z-1/2$; iii: $x-1$, $1/2-y$, $z-1/2$; iv: $1-x$, $y-1/2$. $1/2-z$; v: x, $1/2-y$, $z+1/2$; vi: $1-x$, $-y$, $1-z$; vii: $1+x$, y, z; viii: $2-x$, $1-y$, $1-z$; ix: $1+x$, $3/2-y$, $3/2+z$; x: $1+x$, $1/2-y$, $1/2+z$; xi: $x-1$, y, z.

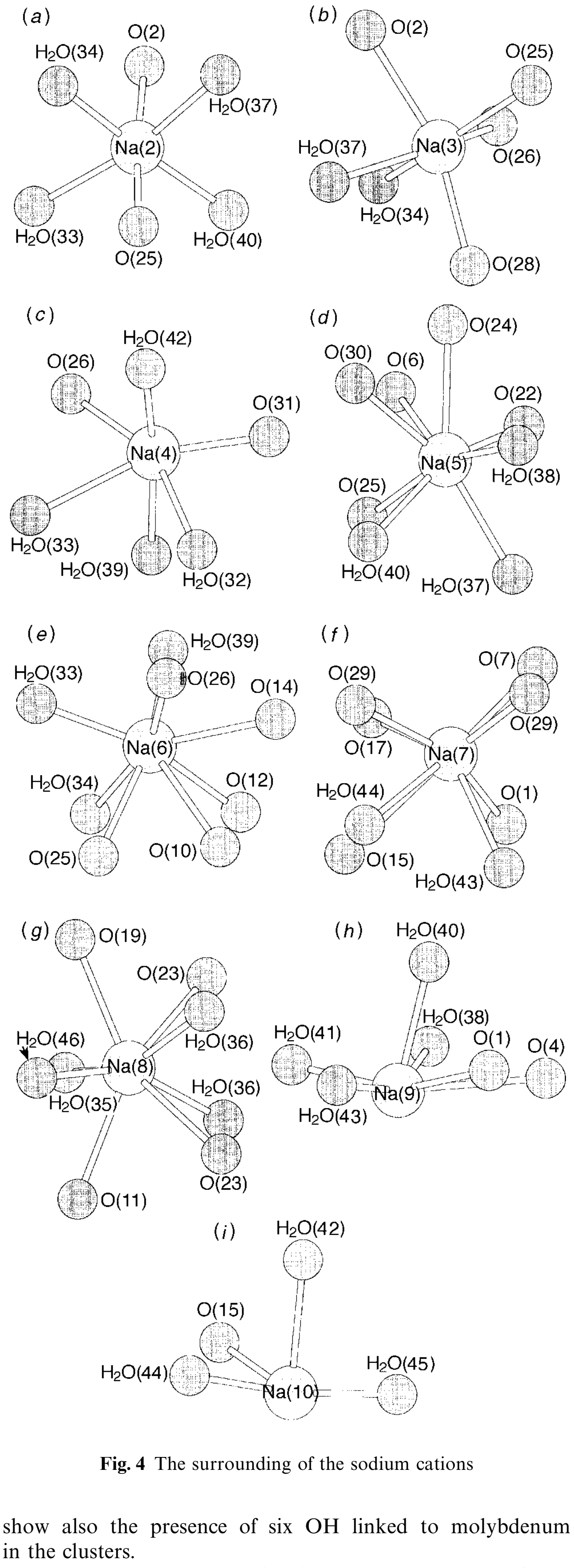

Fig. 4 The surrounding of the sodium cations

made for the equatorial Mo—O distances: smaller distances (1.94–1.97 Å) correspond to oxygen atoms bridging two octahedra, intermediate distances (2.03–2.08 Å) characterize the Mo—O—P bonds, whereas larger Mo—O bonds (2.08–2.14 Å) characterize the hydroxy groups bridging two Mo octahedra, *i.e.* Mo—OH—Mo.

With P—O distances ranging from 1.48–1.58 Å (Table 3) the monophosphate groups are less regular than observed in many monophosphates. The shortest P—O distances (1.48–1.53 Å) are due to the fact that the corresponding oxygen atom is free, whereas the longer ones correspond either to P—O—H or to P—O—Mo bonds.

The Na(1) octahedron that ensures the junction between two Mo_6 rings exhibits a remarkable regular octahedral coordination with six Na—O distances ranging from 2.23–2.29 Å (Table 4).

The Mo—Mo distances in the Mo_6 clusters (Table 3), ranging from 2.581–2.595 Å and from 3.524–3.541 Å are very similar to those observed for $(H_3O)_2NaMo_6P_4O_{24}(OH)_7$-$(PPh_4)_2$·$5H_2O$, suggesting the existence of some strong Mo—Mo interactions.

The great difference between this phase and that described by Haushalter and Lai[5] deals with the relative position of the molybdenum clusters and with their connection through Na^+ cations. In $(H_3O)_2NaMo_6P_4O_{24}(OH)_7$, the molybdenum clusters are linked through Na^+ cations, along one direction only forming one dimensional chains,[5] whereas in $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH)$·$12.25H_2O$ the Na^+ cations form a three-dimensional network with the $Na[Mo_6P_4O_{27}(OH)_4]_2$ clusters. Fig. 1 shows that Na(2) forms indeed one Na—O—P bond with one cluster and one Na—O—Mo bond with another cluster, that Na(3) shares two bonds, Na—O—P bond with the same cluster and forms one Na—O—P bond with another cluster, whereas Na(4) forms one Na—O—P bond with one cluster and a second one with another cluster, and Na(7) is connected to two different clusters through two Na—O—Mo and two Na—O—P bonds, respectively. In the same way, the projection of the structure along ***c*** (Fig. 3) shows that Na(8) ensures the connection between two clusters, forming one Na—O—Mo bond with one unit and two Na—O—Mo bonds with a second unit. By contrast, atoms Na(5), Na(6), Na(9) and Na(10) form Na—O bonds within the same cluster only so that such ions do not participate to the cohesion of the framework, at least from the viewpoint of strong Na—O—P or Na—O—Mo bonds.

We can consider this structure as a mixed framework 'Mo–P–Na–O' built up only of octahedra and tetrahedra. In such a description, the Na(2), Na(3) and Na(4) cations that, like Na(1), exhibit an octahedral coordination, are sufficient to construct a tridimensional framework with the $Na[Mo_6P_4O_{27}(OH)_4]_2$ clusters. In the latter, the Na^+ cations Na(5), Na(6), Na(7), Na(8), Na(9) and Na(10) which exhibit a different coordination can then be considered as interpolated cations.

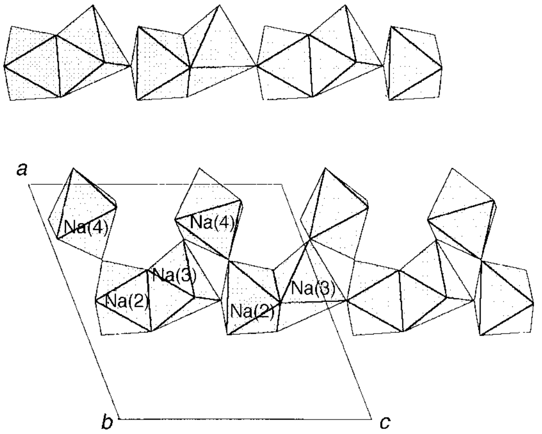

Fig. 5 Chains of NaO_6 octahedra running along ***c*** at $y=1/4$

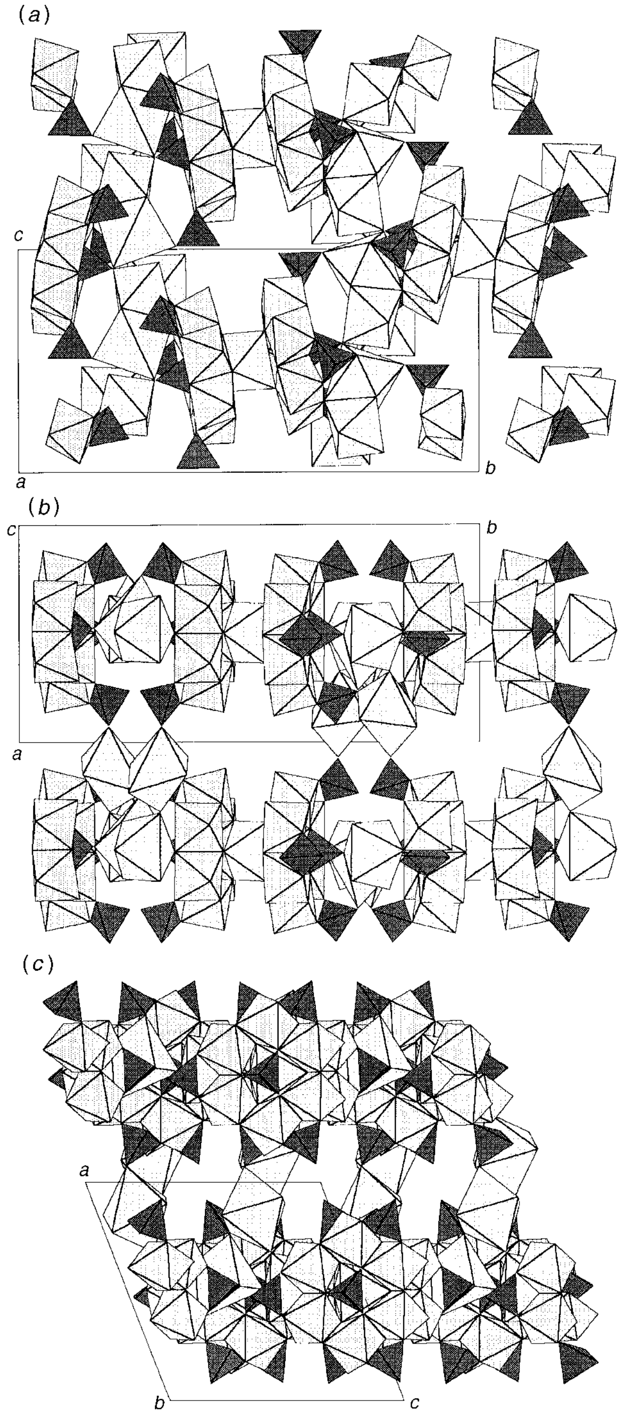

Fig. 6 Tunnels running along ***a*** (*a*), ***b*** (*b*), ***c*** (*c*)

The Na(2) and Na(4) atoms form $Na(H_2O)_4O_2$ octahedra [Fig. 4(*a,c*)] with Na—O distances ranging from 2.32–2.78 Å (Table 4) whereas more distorted $Na(H_2O)_2O_4$ octahedra [Fig. 4(*b*)] are observed for Na(3) with Na—O distances ranging from 2.34–3.09 Å (Table 4). Such $Na(H_2O)_4O_2$ and $Na(H_2O)_2O_4$ octahedra share their apices and edges to form disconnected chains running along ***c***, at $y \approx 0.25$ (Fig. 5); the association of the $Na(H_2O)_4O_2$ and $Na(H_2O)_2O_4$ octahedra with the $Na[Mo_6P_4O_{27}(OH)_4]_2$ clusters, by sharing corners and edges, leads to the formation of large tunnels running along ***a*** [Fig. 6(*a*)], ***b*** [Fig. 6(*b*)] and ***c*** [Fig. 6(*c*)] so that this hydroxymonophosphate can also be described as an intersecting tunnel structure.

In such an intersecting tunnel structure the Na(5), Na(6) and Na(8) cations form bicapped triangular prisms, $Na(H_2O)_3O_5$ [Fig. 4(*d,e*)] and $Na(H_2O)_4O_4$ [Fig. 4(*g*)] respectively, with seven Na—O distances ranging from 2.35 to 2.91 Å, the eight Na—O bonds being > 3 Å (3.01–3.15 Å); it is noted that two adjacent Na(8) polyhedra share one face. The Na(7) cations exhibit a strongly distorted cubic coordination [Fig. 4(*f*)] with two adjacent $Na(H_2O)_2O_6$ cubes sharing one edge. The Na(9) and Na(10) sites are only partially occupied (Table 2). These cations that form bonds with only one $Na[Mo_6P_4O_{27}(OH)_4]_2$ cluster have their ligands displayed on the same side with respect to Na^+; in the polyhedra $Na(H_2O)_4O_2$ [Fig. 4(*h*)] and $Na(H_2O)_3O$ [Fig. 4(*i*)], the interatomic Na—O distances range from 2.31–3.15 Å.

In conclusion, a new sodium molybdenum hydroxymonophosphate has been synthesized. It is to our knowledge an unusual molybdenum(v) hydroxyphosphate that contains only sodium as a univalent interpolated cation, the only other example being $Na_3[Mo_2O_4(HPO_4)(PO_4)]\cdot 2H_2O$[6] which exhibits a layer structure. The presence of clusters $A[Mo_6P_4O_{31}H_n]_2$ seems to be a characteristic of molybdenum(v) hydroxyphosphates, since it has previously been observed in several compounds with Na or Fe or Zn, *viz.* $(Et_4N)_6Na_2[Na_{12}(H_3PO_4)\{Mo_6O_{15}(HPO_4)(H_2PO_4)_3\}]\cdot xH_2O$,[7] $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$,[5] $[(CH_3)_4N]_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot 11.5H_2O$,[13] $[(CH_3)_4N]_2(NH_4)_2[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]\cdot nH_2O$,[14] and $[(CH_3)_4N]_2Na_4[Fe_3Mo_{12}O_{30}(H_xPO_4)_8]\cdot nH_2O$.[14]

Two important features characterize this original structure: its three-dimensional mixed framework built up of Mo and Na octahedra and P tetrahedra that forms intersecting tunnels and the presence of OH groups not only on the P tetrahedra but also on the Mo octahedra.

Based on these observations, it should be possible to synthesize many other molybdenum(v) hydroxymonophosphates with microporous properties by associating Na^+ with larger univalent cations, such as rubidium, caesium or alkyl/arylammonium ions.

References

1 R. C. Haushalter and L. A. Mundi, *Chem. Mater.* 1992, **4**, 31.
2 G. Costentin, A. Leclaire, M-M. Borel, A. Grandin and B. Raveau, *Rev. Inorg. Chem.*, 1993, **13**, 77.
3 R. Peascoe and A. Clearfield, *J. Solid State Chem.*, 1991, **95**, 289.
4 K. Kasthuri Rangan and J. Gopalakrishnan, *Inorg. Chem.*, 1996, **35**, 6080.
5 R. C. Haushalter and F. W. Lai, *Inorg. Chem.*, 1989, **28**, 2904.
6 L. A. Mundi and R. C. Haushalter, *Inorg. Chem.*, 1990, **29**, 2879.
7 R. C. Haushalter and F. W. Lai, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 743.
8 L. A. Mundi, L. Yacullo and R. C. Haushalter, *J. Solid State Chem.*, 1991, **95**, 283.
9 *Xtal3.2 Reference Manual*, ed. S. R. Hall, H. D. Flack, J. M. Stewart, Universities of Western Australia, Australia, Geneva, Switzerland and Maryland.
10 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B.* 1991, **47**, 192.
11 I. D. Brown, *Acta Crystallogr., Sect. A.* 1976, **32**, 24.
12 A. Guesdon, M. M. Borel, A. Leclaire and B. Raveau, *Chem. Eur. J.*, 1997, **3**, 1797.
13 L. A. Mundi and R. C. Haushalter, *Inorg. Chem.*, 1992, **31**, 3050.
14 L. A. Meyer and R. C. Haushalter, *Inorg. Chem.*, 1993, **32**, 1579.

Paper 7/07568E; *Received* 20*th October*, 1997