BRIEF COMMUNICATION

A Nickel Molybdenum Phosphate with Tunnel: Hydrothermal Synthesis and Structure of $(NH_3CH_2CH_2NH_3)_4 \cdot (NH_3CH_2CH_2NH_2) \cdot Na \cdot [Ni_2Mo_{12}O_{30}(PO_4)(HPO_4)_4(H_2PO_4)_3] \cdot 6H_2O$

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A nickel molybdenum phosphate, $(NH_3CH_2CH_2NH_3)_4 \cdot (NH_3CH_2CH_2NH_2) \cdot Na \cdot [Ni_2Mo_{12}O_{30}(PO_4)(HPO_4)_4(H_2PO_4)_3] \cdot 6H_2O$, involving molybdenum present in V oxidation, has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. Deep brown-red crystals are formed in the triclinic system, space group $P\bar{1}$, $a = 12.011(2)$, $b = 14.612(3)$, $c = 21.252(4)$ Å, $\alpha = 80.54(2)°$, $\beta = 83.10(2)°$, $\gamma = 76.29(2)°$, $V = 3561.4(12)$ Å^3, $Z = 2$, $\lambda(MoK\alpha) = 0.71073$ Å $(R(F) = 0.0529$ for 9880 reflections). Data were collected on a Siemens P4 diffractometer at 20°C in the range of $1.75° < \theta < 23.02°$ using the ω-scan technique. The structure was solved by direct methods using the program SHELXTL-93 and refined with the method of full-matrix least-squares on F^2. The structure of the title compound may be considered to be two $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ units bonded together with a nickel atom, although several P–O groups are not protonated on account of coordination with a Na$^+$ cation. The one-dimensional tunnels were formed in the solid of the title compound. A probe reaction of the oxidation of acetaldehyde with H$_2$O$_2$ using the title compound as catalyst was carried out in a liquid– solid system, showing that the title compound had high catalytic activity in the reaction. © 1999 Academic Press

Key Words: nickel molybdenum phosphate; tunnel structure; hydrothermal synthesis; catalytic activity.

INTRODUCTION

The synthesis of organic/inorganic solid state materials with pore or tunnel structure are receiving increasing interest in materials science owing to their applications to catalysis, sorption, and electrical conductivity (1–3). A number of structurally complex solid state inorganic materials have recently been prepared by the methods of hydrothermal syntheses and high temperature solid state syntheses (4, 5). In particular, a new class of solid state materials of metal oxide cluster based on anionic molybdenum phosphate frameworks has received much attention as a consequence of their potential applications in catalysis and materials science (6–11). The molybdenum phosphates are structurally very diverse and include examples of one-dimensional (1-D) polymers (12), two-dimensional layered materials (13), and three-dimensional solids prepared both at high temperatures (14) and under hydrothermal conditions (5). Previously, we synthesized several mixed valence polyoxometalates (15, 16), but they were prepared in solution and without the incorporation of other transition elements. To our knowledge, the preparation of first-row transition metal-molybdenum-phosphates by hydrothermal syntheses has been infrequently reported (17, 18). In this communication, we report the hydrothermal synthesis and structural characterization of a novel nickel molybdenum phosphate, $(NH_3CH_2CH_2NH_3)_4(NH_3CH_2CH_2NH_2)Na[Ni_2Mo_{12}O_{30}(PO_4)(HPO_4)_4(H_2PO_4)_3] \cdot 6H_2O$ (**1**). Its catalytic activity has been explored by means of a probe reaction of the oxidation of acetaldehyde with H$_2$O$_2$.

EXPERIMENTAL

Hydrothermal Preparation and Characterization

The compound **1** was prepared by hydrothermal reaction. A mixture of NiCl$_2$, Na$_2$MoO$_4$, Mo, H$_3$PO$_4$, H$_2$N(CH$_2$)$_2$

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NH_2, and H_2O in the mole ratio of $1.0:5.0:1.0:10:8.0:250$ was sealed in a 18 cm^3 Teflon-lined reactor which was kept at 200°C for 48 h. Deep brown-red crystals of **1** were isolated (yield of 79.1% based on Mo) by filtering and washing with water. The water and ethylenediamine content were determined from TGA and DSC analysis of the sample on a Perkin-Elmer TGA 7. The FT-IR spectrum was recorded on a PHA Centauri FT/IR spectrometer (KBr pellet). Elemental analysis (ICP) showed that the mole ratio of Ni:P:Mo was 1:4:6.

Single Crystal X-Ray Diffraction

The structure of **1** was determined by single-crystal X-ray diffraction. The portion of the structure of **1** and the simplified scheme are shown in Figs. 1 and 2, respectively. Crystallographic data are as follows: $C_{10}H_{71}Ni_2Mo_{12}N_{10}NaO_{68}P_8$, triclinic, space group $P\bar{1}$; $a = 12.011(2)$ Å, $b = 14.612(3)$ Å, $c = 21.252(4)$ Å, $\alpha = 80.54(2)°$, $\beta = 83.10(2)°$, $\gamma = 76.29(2)°$, $V = 3561.4(12)$ Å^3, $Z = 2$, $D_{calc} = 2.760$ gcm^{-3}, $\lambda(MoK\alpha) = 0.71073$ Å. A deep brown-red crystal with dimensions of $0.50 \times 0.42 \times 0.24$ mm was mounted on a glass fibre. Data were collected on a Siemens P4 diffractometer at 20°C in the range of $1.75° < \theta < 23.02°$ using an ω-scan technique. A total of 11905 (9880 independent, $R_{int} = 0.0166$) reflections was measured. A semi-empirical absorption correction from ψ-scans was applied. The structure was solved by the direct method (SHELXTL-93) and refined by the full-matrix least-squares method on F^2. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. Structure solution and refinement were based on 9880 reflections with $I > 2\sigma(I)$ and on 994 parameters gave $R1(wR2) = 0.0529$ (0.1442) $\{R1 = \sum \|F_o| - |F_c\| / \sum |F_o|;$ $wR2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}\}$. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are deposited in supplementary crystallographic data.

Catalytic Reaction

Catalytic reaction was carried out in a 50 mL three-neck flask with reflux condenser. The three-neck flask was charged with 5.70 mL (0.05 mole) of 40% acetaldehyde solution, then 10 mL of 30% H_2O_2 (0.10 mole) were pipetted into the solution. When the solution was heated to 333 K, the powder of compound **1** (0.1 gram) was added to the solution. After lasting for 3 h at the same temperature, the reaction was stopped and the catalyst was separated off. The standard NaOH solution was used to titrate the reactant solution. The formation rate of the produced acetic acid (mmol · (g-cat)$^{-1}$ h^{-1}) was taken to assess the activity of the catalyst.

RESULTS AND DISCUSSION

The single crystal X-ray analysis revealed the anionic dimers (**1**a), sodium cations, ethylenediamines, and lattice water molecules. The structure of **1**a may be considered to be two $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ ($\equiv [Mo_6P_4]$) units linked with an octahedral Ni^{2+} (see Fig. 1a), although several P–O groups are not protonated on account of coordination with a Na$^+$ cation. This $[Mo_6P_4]$ unit has been observed in some molybdenum phosphate derivatives (17, 18). Each $[Mo_6P_4]$ cluster consists of a ring of six edge-sharing MoO_6 octahedra with alternating long (~ 3.60 Å) and short (~ 2.58 Å) Mo–Mo contacts, the latter suggesting direct Mo–Mo single bonds. A central phosphate group bridges the ring internally, and three phosphate groups bridge each long Mo–Mo contact externally, as shown in Fig. 1. Structurally, all phosphate tetrahedra are corner-sharing with the correspondent molybdenum octahedra. The assignment of the oxidation states for the molybdenum (5 +) and nickel atom (2 +) is consistent with the valance sum calculation^2 (19). The bond valence sums (BVS) for some oxygen atoms whose BVS values are in the range of 1.1–1.4 indicate that they are hydroxyl oxygen atoms in view of the bond valence contribution of ~ 0.80 for the O–H bond. In addition, the appearance of brown-red crystals of compound **1** is the typical color of an oxide cluster containing Mo^{5+} cation, as described in Refs. (17, 18). Each Mo^{5+} cation in compound **1** has a distorted octahedral configuration with an apical Mo–O bond at a length of ~ 1.68 Å and five other Mo–O bonds at lengths ranging from ~ 1.92 to ~ 2.28 Å. These bond lengths are comparable with those found in $[(CH_3)_4N]_2(NH_4)_2$ $[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]nH_2O$ (18) and (TMA) $(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]11.5H_2O$ (17). Interestingly, two kinds of Ni[MoP$_4$]$_2$ clusters are not crystallographically identical, indicated as Ni(1)[Mo$_6$P$_4$]$_2$ (**2**) and Ni(2)[Mo$_6$P$_4$]$_2$ (**3**), respectively. The main difference between the two clusters is that in **2** only one oxygen atom from the P–O group in each $[Mo_6P_4]$ coordinates with a Na$^+$ ion while in **3** two oxygen atoms from different P–O groups in each $[Mo_6P_4]$ coordinate with two Na$^+$ cations (see Fig. 1b). In addition, two anions of **2** and two anions of **3** are associated together by bonding with two Na$^+$ cations, as shown in Fig. 1b. Substantially, the two Na$^+$ cations are crystallographically identical. Another difference between **2** and **3** is their arrangement in crystal lattice in two different directions which are almost perpendicular to each other. As shown in Fig. 1b, each Na$^+$ cation is coordinated with six O atoms from four P–O groups, a water molecule, and an

^{2} The bond valence sums of the principal atoms in compound **1** are as follows:

Mo 5.21; Ni 1.43; P 4.93; O (M=O) 1.91; O (μ_3) 1.91; O (Mo–O–Mo) 1.88; O (Mo'--O--Mo') 1.15; O (P–Ot) 1.40; O (P–O–Mo) 1.22.
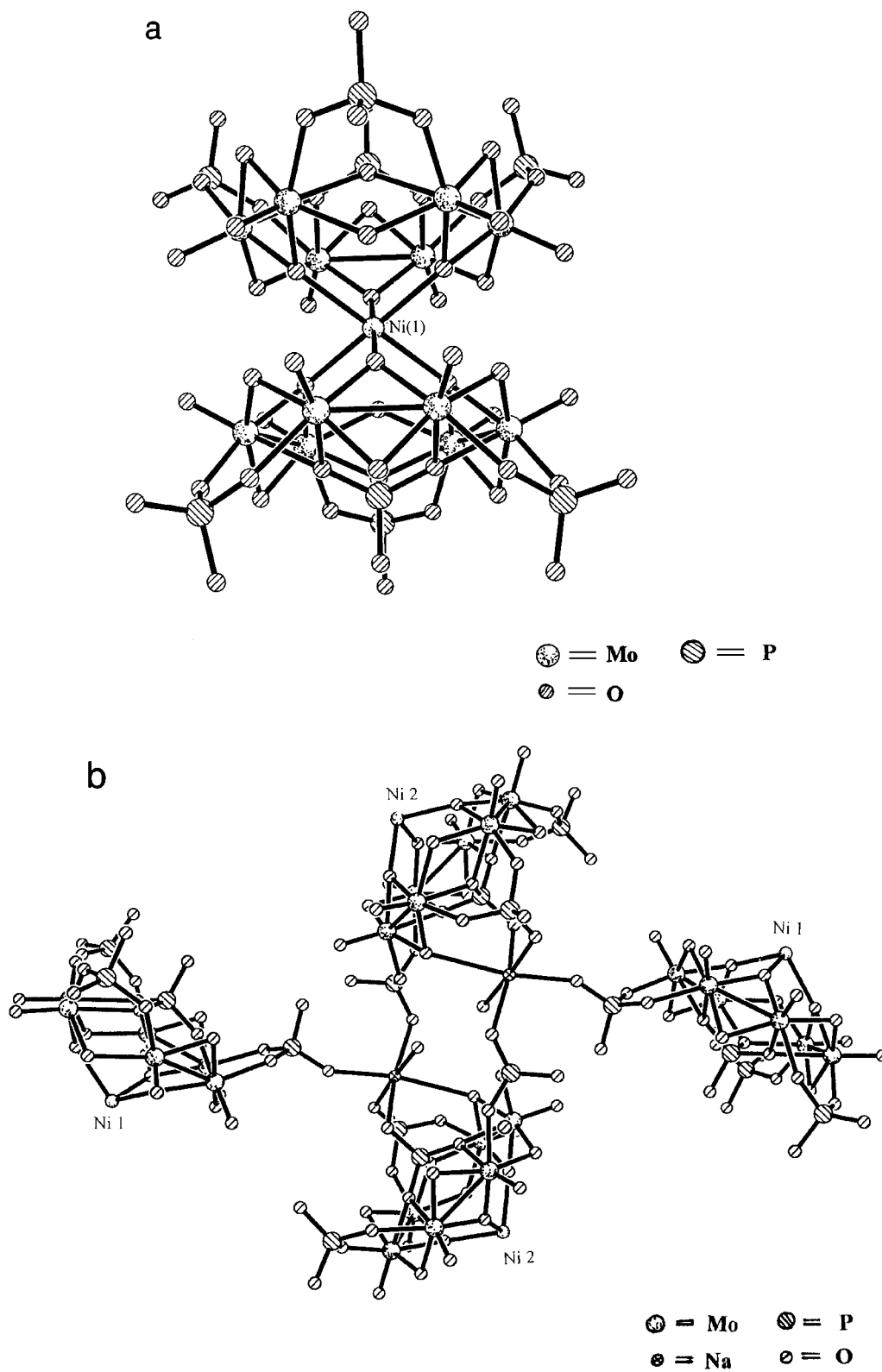
FIG. 1. (a) Ni[Mo$_6$O$_{15}$(HPO$_4$)(H$_2$PO$_4$)$_3$]$_2$ dimers in **1** showing the octahedral coordination of Ni^{2+}. Two [Mo$_6$P$_4$] clusters are linked by Ni(1) at the (1/2, 1/2, 1/2) inversion centre. (b) Portion of the structure of **1** showing how the two Ni(1) [Mo$_6$P$_4$]$_2$ and the two Ni(2) [Mo$_6$P$_4$]$_2$ are linked together by bonding with two Na$^+$ cations. They are approximately situated on the (100) plane layer. A [Mo$_6$P$_4$] part of Ni(1) [Mo$_6$P$_4$]$_2$ or of Ni(2) [Mo$_6$P$_4$]$_2$ is not drawn. It is shown in the view that Ni(1) [Mo$_6$P$_4$]$_2$ and Ni(2) [Mo$_6$P$_4$]$_2$ are crystallographically independent.
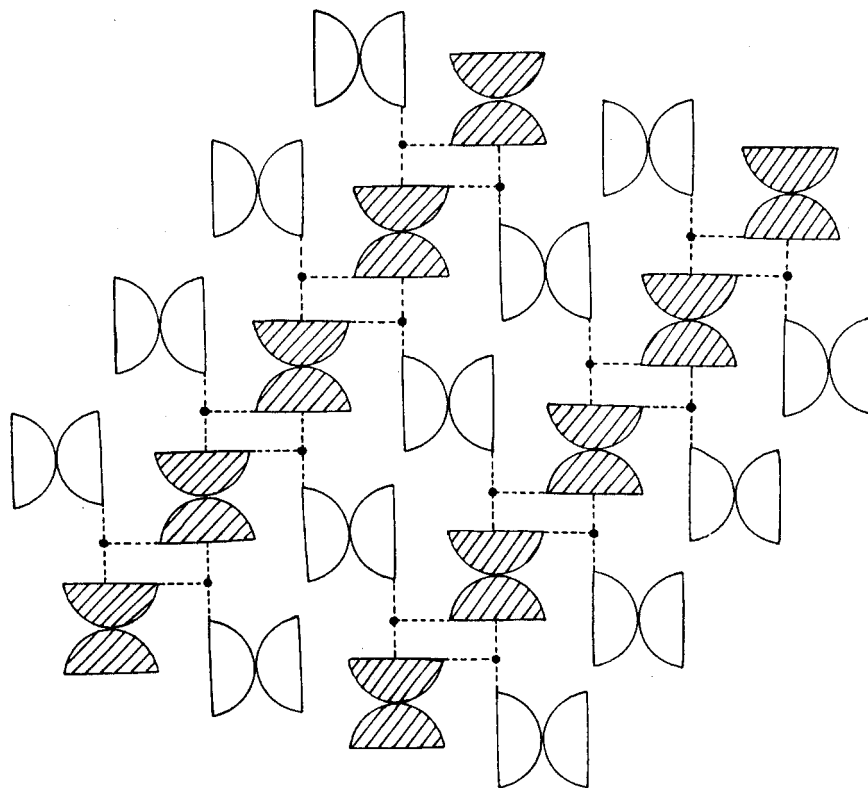
FIG. 2. Simplified schematic representation of the structure of **1**, in which the two-dimensional linkages of Na^+ cations, $Ni(1)[Mo_6P_4]_2$ and $Ni(2)[Mo_6P_4]_2$, are situated on the (100) plane layer. The $Ni(1)[Mo_6P_4]_2$ clusters are represented as blank double-half-circles, the $Ni(2)[Mo_6P_4]_2$ as striped double-half-circles, and the Na^+ cation as black circles.

oxo-bridge shared by Mo atoms with a Mo–Mo single bond. The most unusual feature of **1** is that the one-dimensional tunnel along the *a*-axis is formed in the solid of **1**. As the linkages of two Na^+ cations with four $Ni[Mo_6P_4]_2$ are situated on the (100) plane layer, the infinite plane layers are stacked parallell along the *a*-axis to constitute a three-dimensional crystal structure, resulting in the formation of two kinds of one-dimensional tunnels along the *a*-axis. A small tunnel is surrounded by two Na^+ cations and two $Ni(2) [Mo_6P_4]_2$ anions (see Fig. 1b), with a tunnel bore diameter of ca. 6.26 Å based on the Na–Na distance. The other tunnel in the aperture shape of "⌐" is surrounded by four Na^+ cations, two **2** anions, and two **3** anions. This ⌐ shaped tunnel is filled with ethylenediamine molecules and water molecules, which may be removed by heating. Moreover, these plane layers are interconnected in-sheet (axial) through multipoint hydrogen bonding between the ethylenediamine nitrogen atoms and the cluster oxygen atoms. This feature is supported by both the distances between the nitrogen and oxygen atoms ranging from 2.69 to 3.02 Å and the result of DSC thermal analysis that a large endothermic effect occurs in the release of the ethylenediamine molecules. An investigation on the microporous

property is in progress. Since it is difficult to determine the positions of the nine protons in **1**, these nine protons are assumed to associate with ethylenediamine molecules (20). The assumption is based on the charge balance requirement and on the chemical reasonableness.

The IR spectrum of compound **1** exhibited a strong band at 952 cm^{-1}, characteristic of $\nu(Mo=O)$, and features at 733 and 1038 cm^{-1} associated with $\nu(Mo-O-M)$ and $\nu(P-O)$, respectively. The feature at 3493, 3026, and 1522 cm^{-1} are characteristic for the protonated ethylenediamine, while other strong features at 3368 and 1577 cm^{-1} are assigned to the water molecules. In comparison with the IR spectra of other compounds containing analogous groups, it is evident that the bonds in the 900–950 cm^{-1} region were attributed to $\nu(Mo=O)$ and the features in the 700–750 cm^{-1} range were assigned to $\nu(Mo-O-M)$ (21). Generally, the bands observed around 1500–1600 cm^{-1} are characteristic of $-NH_3^+$ (22).

Thermogravimetric analysis (TGA) of compound **1**, carried out under N_2 with a heating rate of $10°C \cdot min^{-1}$, showed a first weight loss of 3.2% in the temperature range 104–256°C and a second weight loss of 10.5% in the temperature range 280–470°C. These two weight losses correspond

to the release of water molecules (calculated value of 3.6%) and the ethylenediamine molecules (calculated value of 10.4%), respectively. Compound **1** continued to lose weight gradually up to 600°C, the highest temperature measured. The result of DSC thermal analysis showed two endothermic events in which the temperature of the first peak ($\Delta H_1 = 91.3 \text{ kJ} \cdot \text{mol}^{-1}$) was 189°C and that of the second peak ($\Delta H_2 = 3002.1 \text{ kJ} \cdot \text{mol}^{-1}$) 365°C. The two endothermic events respectively correspond to the two release processes of the water molecules and the ethylenediamine molecules. Noteworthily, the large endothermic effect in the second release process implies the occurrence of a hydrogen bond between the nitrogen atom from the ethylenediamine and the oxygen atom from the anion. This is in agreement with the N–O average distance (2.83 Å) determined from the data of single crystal X-ray diffraction. However, it is very difficult to localize the accurate orientations of these hydrogen bonds in the crystal structure, because they formed in various directions and in large numbers. An XRD pattern of the dehydrated compound **1** (after compound **1** was heated at 250°C for 2 h) was still similar to that of the original sample. This indicates that compound **1** is still crystalline after the removal of water molecules and without obvious structural changes accompanying the water loss. Evidently, most of the water molecules in compound **1** have not participated in coordinate bonds.

To investigate the oxidative catalytic activity of compound **1**, we performed a probe reaction of the oxidation of acetaldehyde with H_2O_2 using compound **1** as the catalyst. Under the above-mentioned experimental condition, the formation rate of acetic acid was 43.9 $(\text{mmol} \cdot (\text{g-cat.})^{-1} \cdot \text{h}^{-1})$, which was 5.5 times that of the clay catalyst of $Ni_2Al–CO_3[8.0(\text{mmol} \cdot (\text{g-cat.})^{-1} \cdot \text{h}^{-1})]$. The selectivity to acetic acid was nearly 100%. This suggests that compound **1** may become an oxidative catalyst of high activity in some organic syntheses.

The incorporation of the nickel cation into the molybdenum phosphate framework suggests that analogous compounds can be derived from other first-row transition elements. Compound **1** represents the first structurally char-acterized example of a nickel molybdenum phosphate with both a tunnel structure and crystallographically different $Ni[Mo_6P_4]_2$ clusters. A probe reaction of the oxidation of acetaldehyde with H_2O_2 shows that compound **1** has high catalytic activity in the reaction.

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