process at these temperatures is given by eq 1, where τ is the

$$\eta_{ic} = 1 - (\tau_T/\tau_{77}) \qquad (1)$$

luminescence lifetime at temperature T and τ_{77} is the lifetime at 77 K ($\tau_{77} = (k_r + k_{nr})^{-1}$). At 77 K, the thermally activated population of the ^{3}LF state does not contribute to the relaxation of the ^{3}MLCT state. At 150 K the efficiency for populating the ^{3}LF state is 0.09, while at room temperature (298 K) the efficiency is essentially 1.0 (there is no luminescence). This explanation of nonradiative relaxation is consistent with the observed photochemistry. At low temperatures, photoreactivity is dominated by redox reactions of the ^{3}MLCT state while room-temperature photochemistry results in photosubstitution via the ^{3}LF state.

We are currently examining other complexes that exhibit the crossover between photoredox reactivity and photosubstitution at temperatures closer to room temperature.

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(18) The prefactor of the fit, 1×10^{16} s^{-1} is larger than any reasonable value (upper limit 10^{11}–10^{13}s^{-1}). The simple fitting algorithm used does not include effects on the luminescence lifetime due to changes in the solvent in the 100–125 K region (glass to fluid transition region).[19] The parameters obtained may still be used to determine the magnitude of the thermally activated decay relative to the radiative and nonradiative decay paths of the ^{3}MLCT state.

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Synthesis and Structural Characterization of $[(MoO)_4O_4(PO_4)_2]^{2-}$: A New Layered Oxide Produced by Hydrothermal Synthesis

In an effort to identify new materials with interesting properties, we have recently employed hydrothermal synthesis techniques to produce oxide lattices containing both octahedral and tetrahedral sites. This has resulted[1,2] in a new group of microporous materials, the stannosilicates, containing octahedral tin(IV) in an oxide lattice with tetrahedrally coordinated silicon. We have now extended this work to include another class of mixed framework oxides consisting of octahedral molybdenum(V) with phosphate tetrahedra. We report herein the first example of a hydrothermal synthesis product from this ternary group, a new layered compound, $[N(C_3H_7)_4(NH_4)][(MoO)_4O_4(PO_4)_2]$, which is made up of extended sheets of Mo_4O_8 cubes linked through corner-sharing phosphate tetrahedra.

When 12.70 g of commercial "molybdic acid" (ammonium dimolybdate, Aldrich, 85% MoO_3 by weight) was dissolved in a phosphoric acid solution (8.14 g of 85% phosphoric acid diluted with 19.76 g of distilled water), a yellowish solution resulted. Addition of tetrapropylammonium bromide (9.40 g, Alfa) produced a smooth gel that was sealed in a 23-mL Teflon-lined autoclave (Parr) and reacted hydrothermally for 2 weeks at 200 °C and autogenous pressure. The resulting red/brown solid (16.25 g, 96% yield based on Mo) was removed and washed repeatedly with water.

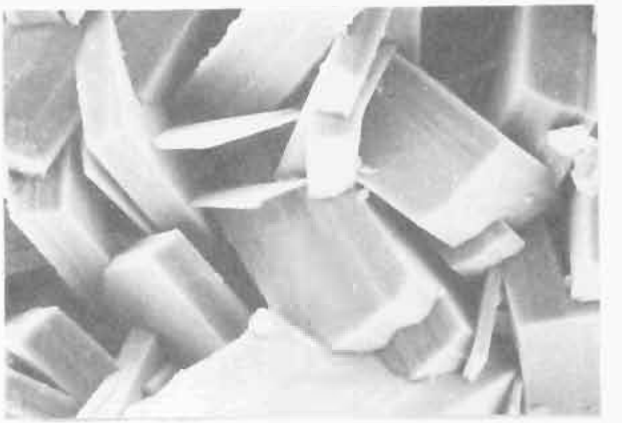

Figure 1. Scanning electron micrograph of the layered compound $[N(C_3H_7)_4(NH_4)][(MoO)_4O_4(PO_4)_2]$, 1575×, showing single crystals of stacked sheets.

Powder X-ray diffraction analysis of the material indicated a single-phase sample had been produced that was indexed by using a tegragonal unit cell having lattice constants of $a = 7.5$ Å and $c = 11.5$ Å. Multiple orders of 00l were apparent in the pattern, suggesting a layered topology for the compound. Scanning electron micrographs (Figure 1) supported this argument, showing single crystals approximately 0.2 mm on each edge comprised of stacked rectangular sheets. A suitable crystal was selected for structural characterization[3] by X-ray crystallography, which provided a structural solution (shown in Figure 2) consistent with thermogravimetric and chemical analysis.[4]

The structure of $[(MoO)_4O_4(PO_4)_2]^{2-}$ consists of infinite two-dimensional sheets of Mo_4O_8 cubes, with each cube separated from the next by a corner-sharing phosphate tetrahedron. This results in a regular arrangement of alternating cubes and tetrahedra, in each direction within the (00l) plane, with every cube connected to four others by four phosphate tetrahedra and with each phosphate group linking two cubes. Tetrapropylammonium cations are located within the interlayer space (beneath phosphate tetrahedra) with the nitrogen atoms distributed over two equivalent Wyckoff f sites at 50% occupancy. The ammonium groups, which sit in d positions, are within the layer plane centered in cavities created by four adjacent cubes. The overall lattice structure resembles that of $Cs_3Mo_4P_3O_{16}$,[5] which exhibits the same arrangement of molybdenum cubes as $[(MoO)_4O_4(PO_4)_2]^{2-}$, but, in addition, has two corner-sharing phosphate tetrahedra per cube that join adjacent layers to generate a three-dimensional framework.

The Mo_4O_8 cubes in $[(MoO)_4O_4(PO_4)_2]^{2-}$ (Figure 3) are comprised of four, triply edge-sharing Mo^VO_6 octahedra each having a molybdenyl group (Mo═O, 1.669 (7) Å) in a position

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(3) The structure of $[N(C_3H_7)_4(NH_4)][(MoO)_4O_4(PO_4)_2]$ was initially solved and refined in three different space groups ($P2$, $P222$, and $P\bar{4}2m$) with little effect on the molybdenum phosphate network; the cation was disordered in all three space groups. Refinement in $P\bar{4}2m$ resulted in the lowest residuals. Crystal data: tetragonal, $P\bar{4}2m$ (No. 111), a = 7.512 (3) Å, c = 11.384 (3) Å, V = 642.4 (6) Å^3, Z = 1, D(calcd) = 2.342 g/cm^3, λ(Mo Kα) = 0.71069 Å, T = −115 °C. A Rigaku AFC6R diffractometer, with a graphite monochrometer and a 12-kW rotating anode generator, was used to collect 1316 reflections ($2\theta < 50°$) on a red pyramidal crystal 0.2 × 0.1 × 0.1 mm. Of these, 385 were unique, R_{int} = 0.021, and 311 were observed ($I > 3\sigma(I)$). An empirical absorption coefficient, using the program DIFABS (Walker, Stuart, *Acta Crystallogr.* **1983**, *A39*, 158), was applied to the data, which resulted in transmission factors between 0.87 and 1.18. The structure was solved by using direct methods and refined by full-matrix least-squares refinement. The Mo, O, P, and N atoms were refined anisotropically and the remaining atoms refined isotropically. R = 0.024, R_w = 0.031, GOF = 1.42. Highest peak on the final difference Fourier map was 1.26 e/Å^3. All computations were performed by using TEXSAN (TEXRAY structure analysis package, Molecular Structure Corp., 1985).

(4) Weight loss by thermogravimetric analysis: 22.5% calcd; 22.2% obsd. Bulk element anal. calcd: Mo, 42.35; P, 6.84; C, 15.91; H, 3.56; N, 3.09. Found: Mo, 41.99; P, 5.78; C, 16.42; H, 3.82; N, 3.20.

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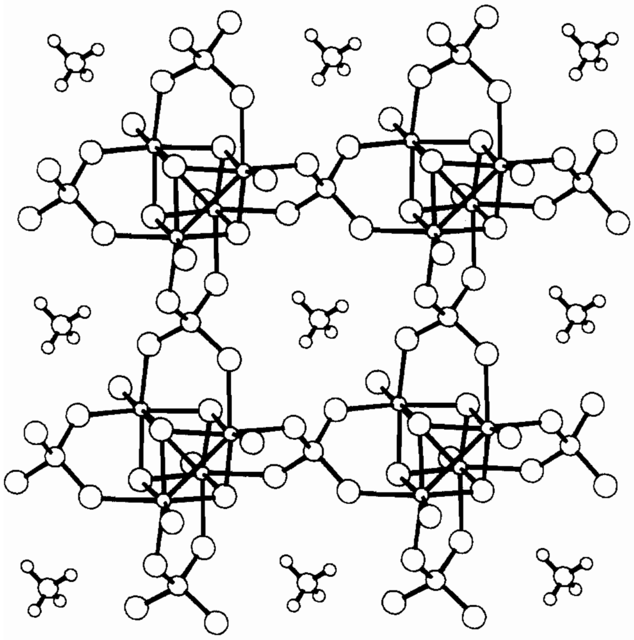

Figure 2. CHEMX (copyright, Molecular Design, Ltd.) generated view of $[N(C_3H_7)_4(NH_4)][(MoO)_4O_4(PO_4)_2]$ showing a layer of Mo_4O_8 groups joined through phosphate tetrahedra with ammonium groups centered in cavities within the layer (interlayer tetrapropylammonium groups omitted for clarity).

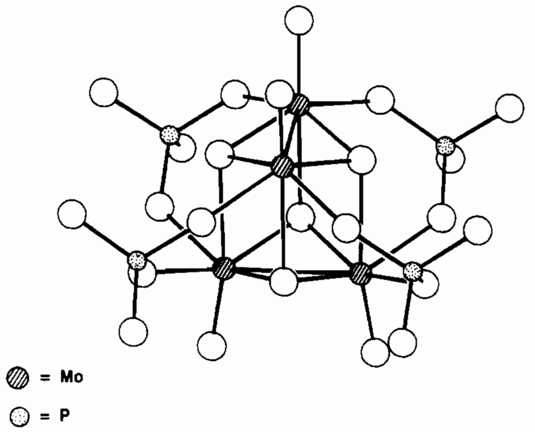

Figure 3. Illustration of the bonding in the Mo_4O_8 cube showing the four, triply edge-sharing Mo(V) octahedra. The octahedron is distorted because of a long Mo—O bond trans to a shorter Mo═O. There are two Mo–Mo single bonds per cube between edge-sharing Mo atoms; adjacent pairs of Mo atoms are connected to a common phosphate group through corner-shared oxygens. Overall, each Mo has two Mo–O–P linkages and a single Mo–Mo unit within its coordination sphere.

trans to a long (2.388 (6) Å) Mo—O bond; the four equatorial Mo—O bonds are similar in length (1.95–2.05 Å). This distortion of the octahedron is typical of other structurally characterized Mo(V) phosphates[6] and can be thought of in pronounced cases[6a] as a square-pyramidal arrangement of oxygen atoms around molybdenum. It is interesting to note that this bonding trend is also observed[7] for the cubane molybdenum(V) molecule $Mo_4O_8[(CH_3)_2POS]_4$. Pouchard[8] has proposed that the partial-double-bond character of the terminal oxo group is necessary for the stabilization of the d^1 state of Mo(V).

Estimation of the oxidation state of molybdenum in $[(MoO)_4O_4(PO_4)_2]^{2-}$ by summing the calculated[9] Mo–O bond strengths gives a value of +5.08, which is in good agreement with that based on stoichiometry. The four Mo(V) d^1 electrons in each cube pair to produce two metal–metal bonds (2.634 (2) Å) which form between edge-shared pairs of molybdenum atoms and are aligned parallel to the layers. This distance is similar to those reported for Mo–Mo bonds in $Cs_3Mo_4P_3O_{16}$,[5] $Cs_3Mo_5P_6O_{25}$,[10] and $Cs_3Mo_5P_7O_{24}$,[11] the only other examples of molybdenum phosphate structures containing metal–metal-bonded Mo_4O_4 cubes. It is also almost identical with that reported[7] for the molecular Mo(V)–oxygen cube $Mo_4O_8[(CH_3)_2POS]_4$, which has two Mo–Mo bonds of 2.635 Å and a geometry that is remarkably similar to that of the Mo_4O_8 subunit in $[(MoO)_4O_4(PO_4)_2]^{2-}$.

The reaction of molybdenum(VI) oxide with phosphoric acid normally leads to the formation of heteropoly anions, such as $[PMo_{12}O_{40}]^{3-}$, known as Keggin structures.[12] These molecules are avoided in the hydrothermal preparation of $[(MoO)_4O_4(PO_4)_2]^{2-}$ since the Mo(VI) common to these polyoxometalates is reduced (possibly by ammonium) to Mo(V) during the course of the reaction. Another, related molybdenum (V) phosphate has also been prepared in this manner by Haushalter et al.[13] Further synthetic investigations are in progress.

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Supplementary Material Available: Tables of experimental details for the structure solution, atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles and an observed powder X-ray diffraction pattern (25 pages); a table of structure factors (3 pages). Ordering information is given on any current masthead page.

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Molecular Structure of $[nido\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_{10}H_{11}]^-$: The Kinetic Product Formed by Protonation of $[nido\text{-}(CH_3)_2C_2B_{10}H_{10}]^{2-}$

The $[nido\text{-}C_2B_{10}H_{12}]^{2-}$ anion, produced by the reduction of $closo\text{-}1,2\text{-}C_2B_{10}H_{12}$, provides a valuable synthon for many interesting and useful metallacarboranes.[1-5] The protonation of

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