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Sodium Tetramolybdenum Hexoxide ($NaMo_4O_6$). A Metallic Infinite-Chain Polymer Derived by Condensation of Octahedral Clusters

Sir:

Recently there has been intense activity in the study of metal-metal bonded compounds of molybdenum, which cover the range from discrete dimers with $Mo\overset{n}{-}Mo$ bonds of order 1 to 4,[1] to the larger cluster units containing three,[2] four,[3-5] five,[6] and six metal atoms. A particularly important family of compounds, known generally as Chevrel phases,[7] incorporate the discrete Mo_6X_8 cluster unit with X = S, Se, and Te. Representative of this family are Mo_6Se_8, $PbMo_6S_8$, and $Mo_6S_6I_2$, all having the same basic solid-state structure and interesting properties as superconductors with high critical temperature and magnetic field values.[7] We report here the synthesis and structure of the compound $NaMo_4O_6$ which contains octahedral cluster units welded on opposite edges to form linear chains.

This new compound represents the result of condensation of cluster units, a consequence of progressive lowering of nonmetal/metal ratio. One way to achieve lower nonmetal/metal ratios is by substitution of divalent nonmetal atoms for monovalent atoms in the structure. For example, by substitution of chalcide atoms for halogens in the molybdenum(II) halides $(Mo_6X_8)X_2X_{4/2}$, the ligand/metal ratio is decreased and the Mo_6X_8 cluster units become more closely coupled together through filling the "exo" coordination sites of one cluster unit by the nonmetal atoms of neighboring cluster units, as represented by the formulation[8] $(Mo_6S_2{}^{i}S_{6/2}{}^{i-o})S_{6/2}{}^{o-i}$ for the compound Mo_6S_8. This close coupling of the Mo_6S_8 cluster units combined with electron delocalization leads to the interesting solid-state properties observed (vide supra). Continued lowering of the nonmetal/metal ratio for Mo_6X_8 clusters can be viewed conceptually as causing condensation of the cluster units via sharing of both nonmetal and metal atoms, thereby resulting in fusion of adjacent clusters to form chain and sheet structures. In halide compounds, examples of such condensed cluster systems have been reported recently by Corbett and Simon, e.g., in the structures of Gd_2Cl_3,[9] ZrCl,[10] GdCl,[11] TbCl,[11] Sc_5Cl_8,[12] and Sc_7Cl_{10}.[13] The structure of Gd_2Cl_3 contains extended chains of condensed octahedral clusters derived from the M_6X_8 unit,[14] as represented by the formulation $Gd_2Gd_{4/2}Cl_4Cl_{4/2}$, whereas in the structure of Sc_5Cl_8 the extended chains are formed by condensation of M_6X_{12} units,[12] as represented in the anion of the formula $[ScCl_2{}^+][Sc_2Sc_{4/2}Cl_2Cl_{8/2}{}^-]$, the first example of this mode of condensation. The structure of $NaMo_4O_6$, described below as a second example of M_6X_{12} cluster condensation, provides evidence that the range of compounds with such structures may extend over numerous metal-nonmetal combinations.

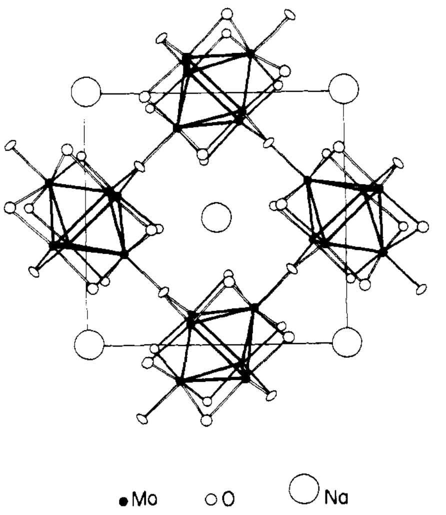

Figure 1. The structure of $NaMo_4O_6$ as viewed down the *c* axis of the tetragonal crystal. All atoms occupy positions in mirror planes at $z = 0$ or $z = 1/2$.

This new ternary oxide was first detected as one product resulting from reaction of Na_2MoO_4, MoO_2, and ZnO (in 1:5:2 mole ratio, respectively) in a sealed molybdenum tube at 1100 °C; the other identified product was the well-known compound $Zn_2Mo_3O_8$.[15] The new compound grew from the surface of the pressed reaction mixture and container walls as thin whiskers with metallic luster. Electron microprobe analysis of the whiskers established that Na and Mo were the only metallic elements present. By viewing crystals on a hot-stage microscope, it was determined that the compound is stable in air up to at least 300 °C. A rough two-probe measurement showed that the crystals were moderately good electrical conductors.

A single crystal selected from this reaction provided excellent X-ray diffraction data from which both the composition and structure were established.[16,17] Once again nature has provided a structure remarkable in its complexity, yet beautiful in its ultimate simplicity and symmetry. The 22 atoms in the tetragonal unit cell all are located in mirror planes at $z = 0$ or $z = 1/2$ with the repeat distance along the *c* axis of only 2.860 (1) Å. A view of the structure along the *c* axis is given in Figure 1, from which it can be discerned that the Na^+ ions occupy sites in channels formed by four metal oxide cluster chains cross-linked by metal-oxygen bonds. A view of one of the chains which are extended parallel to the *c* axis is provided in Figure 2. The architecture of the chains is comprised of clusters of the type Mo_6O_{12} fused at opposite edges by removal of two edge-bridging O atoms and sharing of the metal atoms on those edges between cluster units, as indicated by the formulation $Na^+[Mo_2Mo_{4/2}O_2O_{8/2}{}^-]$. Thus the structure of these chains is exactly the same as that in the anion component of $[ScCl_2{}^+][Sc_4Cl_6{}^-]$. However, because of the greater number of valence electrons available per repeat unit for metal-metal bonding in the Mo chains, viz., 13 in $[Mo_4O_6{}^-]$ vs. 7 in $[Sc_4Cl_6{}^-]$, the metal-metal bonds are stronger and closer to being equivalent over the various edges of the octahedral units. The individual Mo-Mo bond distances, 2.751 (3) (1x), 2.860 (1) (4x), and 2.778 (2) (8x)Å within the repeat unit, result in an average distance of 2.801 Å, which is only 0.076 Å longer than the distance between nearest neighbors in bcc molybdenum metal. Each O atom is strongly bonded to three Mo atoms at distances of 2.014 (8) to 2.067 (8) Å, with the shortest of these involving the O atoms bridging between chains.

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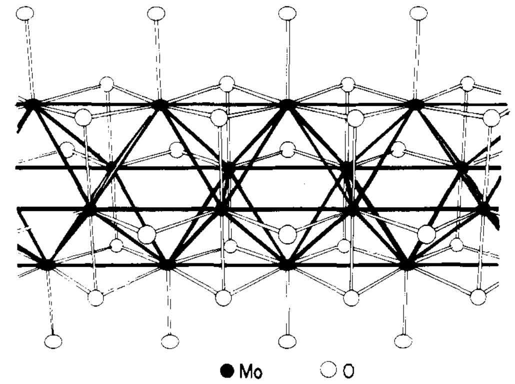

Figure 2. A view of one cluster chain, $[Mo_2Mo_{4/2}O_2O_{8/2}^-]$, extended parallel to the *c* axis. The repeat distance along the chain is 2.860 (1) Å.

Another interesting feature of this structure is the site occupied by Na^+ ions within the channels. Each Na^+ ion is surrounded by eight oxygen atoms at a distance of 2.740 (8) Å in tetragonal symmetry.[18] The Na–O distance is ~0.39 Å longer than the sum of ionic radii (2.35 Å) and accordingly the Na^+ ions exhibit unusually large isotropic thermal parameters, 7.2 (9) $Å^2$. This feature suggests that still larger cations can be accommodated in this structure and that the Na^+ ions indeed may be exchangeable as in the zeolites or Molecular Sieves. It also may be possible to remove the Na^+ ions altogether in an oxidative process leaving intact the Mo_4O_6 structure, or to prepare compounds $M^{n+}[Mo_4O_6{}^{n-}]$ with n = 2, 3, or 4 such that the electron/metal ratio is varied over the range 3.0–4.0. These aspects and intensive examination of properties are currently being studied in this laboratory.

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(16) The crystals of $NaMo_4O_6$ are tetragonal, a = 9.559 (3), c = 2.860 (1) Å; $Z = 2$; V = 261.3 $Å^3$. A total of 216 reflections with $I > 3\sigma(I)$ averaged from data taken over four octants was used to solve and refine the structure. The structure was solved in the space group *P4/mbm* and all atoms were refined to convergence using anisotropic thermal parameters. Since the transmission factor varied only from 0.85 to 0.87 over all orientations, no absorption correction was applied to the data. The occupancy of the Na positions was included as a variable in the refinement and converged to the value 1.02. The final cycle of least-squares refinement provided $R_1 = 0.046$ and $R_2 = 0.054$.
(17) Subsequent work has shown that essentially pure $NaMo_4O_6$ can be prepared in the reaction $Na_2MoO_4 + 4MoO_2 + 3Mo = 2NaMo_4O_6$ when the stoichiometric quantities of Na_2MoO_4 and MoO_2 are heated in a sealed Mo tube at 1100 °C for 7 days. The X-ray diffraction powder pattern of this preparation was identical with that of the single crystals.
(18) The eight O atoms in the coordination sphere of Na^+ form a cube compressed along the c axis with O–O distances of 2.860 and 3.304 Å.

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An Unexpected Hydride Transfer Reaction of Hydridoborates. A Convenient New Route to Highly Hindered Potassium Trialkylhydridoborates[1a]

Sir:

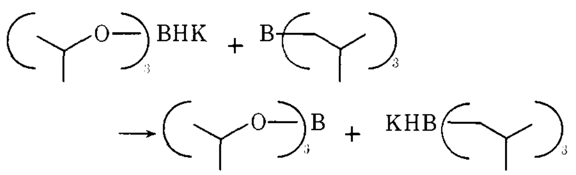
Potassium triisopropoxyhydridoborate [KHB(O-*i*-Pr)$_3$],[1b] a "mild" reducing agent,[1c] transfers hydride rapidly and quantitatively to both simple and highly hindered trialkylboranes to form potassium trialkylhydridoborates ($KHBR_3$), reducing agents of exceptional activity and nucleophilicity. KHB(O-*i*-Pr)$_3$ is readily formed from potassium hydride (KH) and triisopropoxyborane [B(O-*i*-Pr)$_3$, "isopropylborate"]. Thus the observed hydride transfer provides a convenient new route to highly hindered potassium trialkylhydridoborates from trialkylboranes which fail to react with KH.[1d] In addition, it provides an unprecedented example of nonsteric kinetic factors inhibiting the apparent reducing power of a hydridoborate.

Hydridoborates have achieved widespread use as reducing agents. Virtually no systematic comparisons exist among the various hydridoborates to delineate relative reactivities. However, certain trends may be deduced.

Some years ago it was reported that replacement of hydride by alkoxide in sodium tetrahydroborate ($NaBH_4$) appeared to facilitate transfer of the remaining hydride(s).[2,3] Thus NaHB(O-*i*-Pr)$_3$ was found to be more reactive toward organic carbonyl compounds in ether solvents. Similarly, KHB(O-*i*-Pr)$_3$ is far more reactive toward reduction of methyl iodide in ether solvents than is $NaBH_4$,[4] and it reduces metal carbonyl complexes with greater facility than does $NaBH_4$.[5]

Recently, a variety of trialkylhydridoborates[6] have been shown to be highly reactive as reducing agents in organic[6,7] and organometallic[8] chemistry. These reagents appear far more reactive than KHB(O-*i*-Pr)$_3$. For example, trialkylhydridoborates reduce cyclic ketones readily at −78 °C or below,[7b,9] while KHB(O-*i*-Pr)$_3$ is very sluggish below −23 °C.[1c,4] Similarly, *n*-octyl chloride is reduced in 30–60 min at 25 °C by $MHBR_3$ (M = Li, R = Et;[10a] M = K, R = *i*-Bu[10b]), but KHB(O-*i*-Pr)$_3$ is inert toward *n*-octyl chloride at room temperature.

These observations clearly indicate an order of reactivity $HBH_3^- < HB(OR)_3^- < HBR_3^-$. Thus it was highly surprising to observe that trialkylhydridoborates failed to convert trialkoxyboranes to trialkoxyhydridoborates. In fact, the opposite reaction occurred with great ease. Addition of $(i\text{-}Bu)_3B$ [isostructural with $(i\text{-}PrO)_3B$] to 1.0 equiv of KHB(O-*i*-Pr)$_3$ in THF solution at 25 °C resulted in rapid, quantitative hydride transfer to yield an equimolar mixture of KHB(*i*-Bu)$_3$ and $(i\text{-}PrO)_3B$ (eq 1), as may be seen from the ^{11}B NMR



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