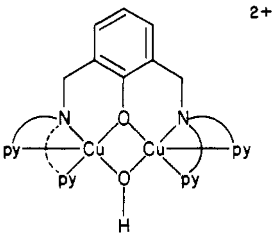

III

is shorter than the 3.6–3.7-Å Cu(I)···Cu(I) distance observed in the precursor complex I. The C1–C6 (1.38 (2) Å) and the C–O (C1–O1 = 1.33 (2) Å, C6–O2 = 1.31 (2) Å) bond lengths of the coordinated $Cl_4C_6O_2$ ligand indicate that the complete reduction of tetrachloro-*o*-benzoquinone to the coordinated tetrachlorocatecholate (TCC) dianion has occurred, since these bond lengths are diagnostic of the ligand oxidation state (i.e. whether it is coordinated as catecholate, a semiquinone, or a quinone).[1,5,18]

The UV–vis absorption spectrum of II in CH_2Cl_2 shows broad peaks with λ_{max} (nm) (ϵ M^{-1} cm^{-1}) 640 (1900), 570 (2000), 410 (sh, 3100), and 315 (sh, 9100). The absorption at 410 nm is probably due to a phenoxide to Cu(II) CT transition,[17,19] and the 570-nm band may arise from a catecholate to Cu(II) CT transition by analogy to assignments made for other monomeric Cu(II)–catecholate complexes.[3,7,20] The IR spectrum of II exhibits two strong absorptions at 1260 and 1390 cm^{-1} where only weak absorptions are observed in the hydroxo-bridged complex, III;[17] thus these bands are assigned to catecholate C–O and ring-stretching vibrations, respectively.[20c]

By contrast to the method of synthesis of complex II, which is stable in the presence of O_2, 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) does not react with I. In fact, the "reverse" reaction takes place readily in which 3,5-di-*tert*-butylcatechol (DTBC) is oxidized catalytically to the quinone DTBQ by the binuclear phenoxo- and hydroxo-bridged complex III in the presence of dioxygen.[21] This is therefore a model reaction for the catecholase activity by tyrosinase. In such systems, it is presumed[6,8,9] that a Cu^{II}_2–catecholate complex is formed as an intermediate, which subsequently decomposes to the 1,2-benzoquinone product and a dicopper(I) species. The stability of II to such decomposition reactions is consistent with the higher reduction potential of TCBQ compared to DTBQ.[2] The catecholate complex II thus serves as a structural model for the probable intermediate in the catalytic oxidation of catechols by dicopper moieties and also possibly in copper-catalyzed catechol C–C ring cleavage reactions.[6,7]

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Supplementary Material Available: Listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (12 pages). Ordering information is given on any current masthead page.

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Interlayer Chemistry between Thick Transition-Metal Oxide Layers: Synthesis and Intercalation Reactions of K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$] ($3 \le n \le 7$)

Sir:

Layered oxides with structures related to perovskite or K_2NiF_4 can be generally formulated $M_m[A_{n-1}B_nO_{3n+1}]$, where $A_{n-1}B_nO_{3n+1}$ is the layer composition and M is an interlayer cation. Each layer has a cubic arrangement of corner-shared BO_6 octahedra with the large A cations occupying twelve coordinate sites in the center of each cube as found in the perovskite lattice. The layers are formed by limiting the extension of this lattice along one of the three cubic directions. The thickness of each perovskite layer is given then by the value of *n* that determines the number of BO_6 corner-shared octahedra that are connected along a direction perpendicular to the layers. For example, Ruddlesden and Popper described a series of layered alkaline-earth-metal titanates that can be formulated $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ where $1 \le n \le 3$.[1] Two of the Sr atoms in each compound occupy nine coordinate sites between the perovskite layers. Most of the phases of this general type that have been reported in the literature[2] contain two M cations ($m = 2$) per formula unit and show no interlayer reaction chemistry. Recently, however, the syntheses and structures of the perovskite layered oxides $MCa_2Nb_3O_{10}$ (M = K, Rb, Cs, Tl; $n = 3$; $m = 1$) have been reported[3] (Figure 1). These new phases, which have a lower layer charge density ($m = 1$), were observed to exchange the interlayer cations in molten lithium, sodium, and ammonium nitrates. The difference in reactivity for ion exchange between the compounds with $m = 1$ and with $m = 2$ has an analogy in the 2:1 clay minerals. The smectites have a low interlayer cation density and undergo facile interlayer ion-exchange reactions. In contrast, the micas and vermicultes have a higher interlayer cation density than the smectites and do not readily ion exchange.[4]

We anticipated, by analogy with other layered oxides of comparable layer charge density such as $KTiNbO_5$[5] and $K_2Ti_4O_9$,[6] that ion exchange of $KCa_2Nb_3O_{10}$ in aqueous acid would lead to the formation of $HCa_2Nb_3O_{10}$ and, further, that chemical substitution should allow for variation of the layer thickness while preserving the chemical reactivity. In this paper we report the synthesis of the series of layered compounds K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$] by high-temperature reactions of $KCa_2Nb_3O_{10}$ with $NaNbO_3$. All of the compounds are structurally related to $KCa_2Nb_3O_{10}$ but differ in the thickness of the perovskite layers. The phases K[$Ca_2Na_{n-3}Nb_nO_{3n+1}$] readily exchange potassium ions for protons to form H[$Ca_2Na_{n-3}Nb_nO_{3n+1}$] ($3 \le n \le 7$). The compounds formed by this procedure are solid acids and react with organic bases such as primary alkylamines to form intercalated alkylammonium compounds. The intercalation reactions are the first examples of such reactions in perovskite-related layered oxides and are unusual in that they lead to the formation of compounds with thick inorganic layers (up to 27 Å) separated by organic layers in a regular, crystalline manner.

The compound $KCa_2Nb_3O_{10}$ was prepared at 1200 °C by firing in air $CaCO_3$, K_2CO_3, and Nb_2O_5 mixed in stoichiometric amounts, a procedure similar to that used by Dion et al.[3] The next member of the series $KCa_2NaNb_4O_{13}$ was prepared similarly by using $KCa_2Nb_3O_{10}$ and $NaNbO_3$ as starting materials. Higher homologues were prepared by reaction of $KCa_2NaNb_4O_{13}$ with stoichiometric amounts of $NaNbO_3$. Higher reaction tempera-

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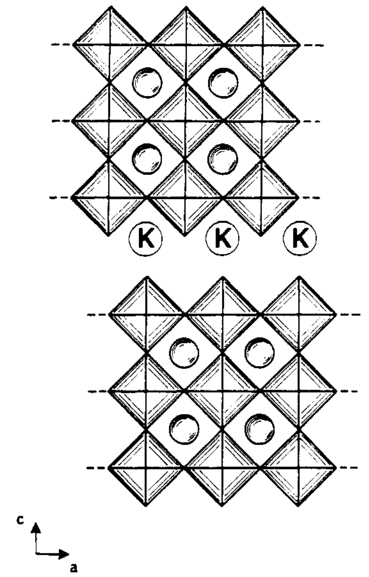

Figure 1. Schematic representation of the structure of $KCa_2Nb_3O_{10}$.[3] The shaded squares represent NbO_6 octahedra in projection, and the circles within the layers are the calcium atoms. The *c* axis is perpendicular to the layers.

Table I. Lattice Constants for $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$

n	a, Å	b, Å	c, Å
3	3.853	3.868	29.47
4	3.861	3.878	37.23
5	3.863	3.882	45.00
6	3.869	3.883	52.80
7	3.870	3.887	60.57

Table II. Lattice Constants for $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]\cdot xH_2O$

		c, Å	
n	a, Å	x = 1–1.5	x = 0
3	3.849	16.21	14.37
4	3.863	20.14	18.35
5	3.870	24.02	22.25
6	3.872	27.92	26.25
7	3.876	31.82	30.10

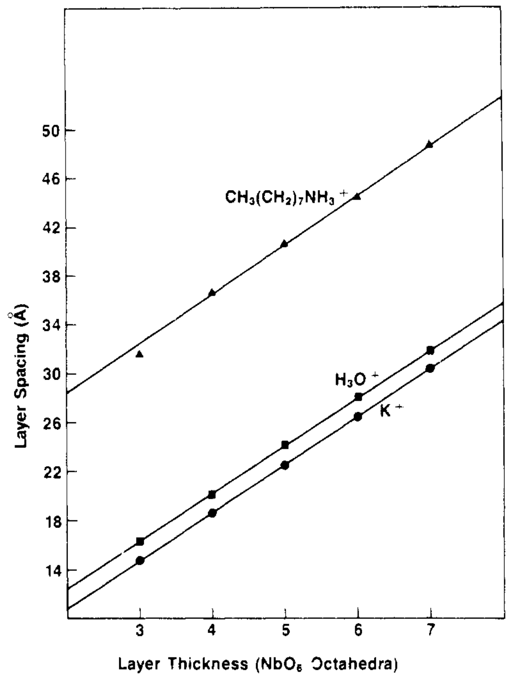

Figure 2. Layer spacings of $M[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ vs. *n* for M = K, H_3O, and $C_8H_{17}NH_3$.

Table III. Lattice Constants for n-$C_8H_{17}NH_3[Ca_2Na_{n-3}Nb_nO_{3n-1}]$

n	a, Å	c, Å	n	a, Å	c, Å
3	3.854	31.51	6	3.873	44.35
4	3.866	36.61	7	3.881	48.58
5	3.870	40.64			

tures, 1250–1350 °C, were needed to obtain the compounds with $n > 4$.[7] Lattice constants for the potassium compounds were obtained by least-squares fitting the powder X-ray diffraction data.[8] The results are summarized in Table I. The data were indexed by using an orthorhombic cell in which the *c* axis is perpendicular to the layers. This unit cell is similar to the tetragonal cell reported by Dion et al.[3] which contains two perovskite layers displaced relative to each other by $a/2$. The translation of adjacent layers results in trigonal-prismatic coordination for the interlayer potassium atoms. The *a*-axis dimension is slightly smaller than that of the *b* axis, and the mean value increases from 3.861 Å for $n = 3$ to 3.879 Å for $n = 7$. The increase is consistent with the addition of increasing amounts of $NaNbO_3$, which has a pseudocubic *a*-axis dimension of 3.903 Å.[9] The interlayer separation ($c/2$) increases linearly with increasing *n* (Table I and Figure 2). The slope of the line obtained by least-squares fitting the data of Table I is 3.887 Å for each NbO_6 octahedron added to the layer, consistent with the structural model.

The potassium phases were converted to the hydrogen compounds $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ for all values of *n* by ion exchange in 6 M aqueous HCl at 60 °C for 16 h.[10] Hydrated phases $H[Ca_2Na_{n-3}Nb_nO_{3n+1}]\cdot xH_2O$ with $x \sim 1$–1.5 are obtained when the solid products recovered from the exchange reaction are dried at ambient temperature. Anhydrous phases are obtained by further drying at 100 °C and were observed to rehydrate slowly under ambient conditions.[11] Lattice constants for the hydrated compounds are summarized in Table II and Figure 1. Similar results for the *c*-axis dimensions for the anhydrous materials are also given in Table II. In neither case do the X-ray data contain any evidence for a doubled *c* axis, indicating that ion exchange of potassium by protons produces a relative translation of adjacent layers. The unit cells, therefore, contain only one perovskite layer, no orthorhombic distortion from tetragonal symmetry is observed. Least-squares fits to the interlayer separation as a function of layer

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(7) It was necessary to carry out the higher temperature reactions in sealed platinum tubes to prevent volatilization of the alkali-metal oxide. No evidence was found for the compound with $n = 8$ even at reaction temperatures of 1400 °C. Higher temperatures were not used because above 1400 °C partial melting of the reactants occurs. At intermediate stages in the heat treatments multiple phases are observed. These phases were usually the starting phases and the desired product, but occasionally different members of the series were observed. For example, at one intermediate point in the synthesis of the compound with $n = 6$, phases with $n = 4$, 5, and 7 were detected. The X-ray powder patterns of such mixed-phase systems gave sharp diffraction lines for each phase present, suggesting little disorder or phase intergrowth. The final products contained only a single member of the series except for the $n = 7$ sample, which contained a small amount of the $n = 6$ compound. Small amounts of unreacted $NaNbO_3$ were observed in the higher homologues. High-resolution transmission electron microscopy for the $n = 6$ and 7 compounds confirmed the X-ray observations; the electron diffraction patterns were sharp, and very few defects were observed in lattice images. A more detailed description of the electron microscopy results will be given elsewhere.

(8) X-ray powder diffraction patterns were measured with the use of a Siemens D500 diffractometer and Cu Kα radiation. Lattice parameters were determined by least-squares fits to the diffraction maxima. Standard deviations were less than 0.001 Å for *a* and *b* and 0.01 Å for *c*.

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(10) These conditions represent convenient rather than the mildest conditions that can be used. For example, exchange of $KCa_2Nb_3O_{10}$ was observed to occur over a period of days in 1 M HCl at 25 °C. Potassium contents were analyzed by atomic absorption spectroscopy for some samples. Residual potassium contents in the range 0.03–0.05 per $Ca_2Nb_3O_{10}$ were observed.

(11) The water contents were determined by thermogravimetric analysis. The interlayer water is lost below 100 °C in a single step. Further heating to 350 °C results in a weight loss that corresponds to loss of the interlayer protons as water.

thickness (n) give increases of 3.904 and 3.936 Å for each NbO_6 octahedron added to the layer for the hydrated and anhydrous materials, respectively. The values are consistent with preservation of the connectivity of the perovskite layers, and the small differences observed in the slopes probably reflect differences in the relative tilting of NbO_6 octahedra. The intercept, 2.58 Å, obtained by extrapolating the data for the anhydrous phases to $n = 0$ is consistent with a structural model in which the proton is bonded to a terminal layer oxygen atom to form an –OH that is hydrogen bonded to a terminal oxygen atom from an adjacent layer. On hydration the lattices expand by 1.7–1.9 Å.

The proton-exchanged forms of these perovskite-layered compounds are solid acids and react with organic bases. For example, reaction of the solid phases with excess n-octylamine in heptane at 95 °C leads to the formation of the octylammonium compounds $n\text{-}C_8H_{17}NH_3[Ca_2Na_{n-3}Nb_nO_{3n+1}]$.[12] This acid–base reaction produces large increases in the layer separations as shown by the X-ray data summarized in Figure 2 and Table III. The results for the compounds with $n = 4$–7 give a linear increase in c-axis spacing with increase in the layer thickness (3.964 Å/NbO_6 octahedron); the data point for $n = 3$ is 1.1 Å too short relative to the other members of the series, which may indicate a slightly different orientation of the hydrocarbon chain in the interlayer. In all cases, the spacings are too large to be accounted for by a single layer of organoammonium cations and indicate a bilayer arrangement with inclined hydrocarbon chains.[13]

In summary, the perovskite-related layer structures $KCa_2Na_{n-3}Nb_nO_{3n+1}$ ($3 \leq n \leq 7$) have been synthesized and shown to have interlayer reactivity under mild conditions both in ion-exchange reactions and in intercalation of large organic bases. The chemical reactivity is largely independent of the layer thickness even when the oxide layers are very thick (27.2 Å for $n = 7$). Further studies of the reaction chemistry and properties of these new phases are in progress.

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(12) The stoichiometry of the reaction was determined by thermogravimetric oxidation in air up to 1000 °C. Observed and calculated weight changes for $n\text{-}C_8H_{17}NH_3[Ca_2Na_{n-3}Nb_nO_{3n+1}]$: $n = 3$, 21.9% obsd, 21.3% calcd; $n = 4$, 17.9% obsd, 17.0% calcd; $n = 5$, 14.2% obsd, 14.2% calcd.; $n = 6$, 11.4% obsd, 12.1% calcd; $n = 7$, 8.7% obsd, 10.6% calcd. The weight losses observed indicate nearly stoichiometric reaction except for the case of the $n = 7$ compound, where the analysis indicates intercalation of 0.8 mol of octylamine/mol of solid.

(13) From the unit cell dimensions the calculated area for each alkylammonium cation is 15 Å^2, assuming a single-layer arrangement. This area is too small to accommodate alkyl chains close-packed at van der Waals contacts, and consequently a bilayer structure is observed.

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Articles

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Kinetics of Oxidation of Simple Complexes of Molybdenum(IV) and -(V) by Iron(III)

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The kinetics of the oxidation of the dimer Mo(V) cation $Mo_2O_4^{2+}$ by $Fe(H_2O)_6^{3+}$ and $Fe(phen)_3^{3+}$ in aqueous solution have been studied at 25 °C, ionic strength $I = 2.0$ M ($NaClO_4$), by conventional spectrophotometry. In both systems the rate of reaction is first order in reductant and oxidant and thus indicates that the first electron-transfer step is rate determining for the overall process. With the Fe(III) aquo complex as oxidant, the predominant pathway involves a hydroxo species, probably $Fe(OH)^{2+}$, which reacts with a second-order rate constant $k_{FeOH} = 1.3 \times 10^3$ M^{-1} s^{-1}, presumably by an inner-sphere mechanism. Oxidation by $Fe(H_2O)_6^{3+}$ is much slower, $k_{Fe} \leq 0.2$ M^{-1} s^{-1}. The reaction of $Fe(phen)_3^{3+}$ with $Mo_2O_4^{2+}$ is expected to proceed by an outer-sphere path; the rate constant of this process is $k_{FePh} = 13$ M^{-1} s^{-1}. The mechanism of the (outer-sphere) oxidation of the $(\mu\text{-}S)_2Mo^V$ complex $Mo_2O_2S_2^{2+}$ by $Fe(phen)_3^{3+}$ is more complicated, involving either a change in the rate-determining step or the appearance of a non-steady-state intermediate. The initial slopes of the reaction curves yield for the rate of the first electron-transfer step $k = 0.4$ or 0.8 M^{-1} s^{-1}, respectively, depending on the interpretation (25 °C, 1 M $HClO_4$, $I = 1.0$ M). The results reveal that $Mo_2O_2S_2^{2+}$ is a less efficient reducing agent than $Mo_2O_4^{2+}$. The oxidation of the trimeric Mo(IV) species $Mo_3O_4^{4+}$ by $Fe(phen)_3^{3+}$ is characterized by a rate-determining first electron-transfer step (outer sphere) with $k = 51$ M^{-1} s^{-1} in 1 M HCl, $I = 2.0$ M (NaCl). Due to coordination of Cl^- to the Mo(IV) cation, the rate in the chloride solution is much higher than that in a noncomplexing medium.

Introduction

The chemistry of molybdenum has found much interest in recent years. New compounds have been prepared and characterized,[2] and mechanistic aspects of reactions involving molybdenum compounds are also studied to an increasing extent.[3]

The interest in molybdenum chemistry arises to a good deal from the occurrence of this element in biological systems. Molybdenum is an essential component of a series of enzymes that catalyze biological redox processes.[4] All of these enzymes contain also iron, and it is believed that at least in some of them direct electron transfer occurs between the Mo and Fe centers during the catalytic action.[4,5]

It is desirable, therefore, to learn more about the kinetics and mechanisms of redox reactions between Mo and Fe compounds, including simple complexes of these metal ions which cannot be considered as models of the biological systems. Until recently, very little has been done in this area. In this paper we report on the reactions $Mo_2O_4^{2+} + Fe(H_2O)_6^{3+}$, $Mo_2O_4^{2+} + Fe(phen)_3^{3+}$, $Mo_2O_2S_2^{2+} + Fe(phen)_3^{3+}$, and $Mo_3O_4^{4+} + Fe(phen)_3^{3+}$ in

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(2) See, e.g.: *J. Less-Common Met.* **1977**, *54*.

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