

Formation, Structure, and Topotactic Exchange Reactions of the Layered Hydrogen Bronze $H_xV_3O_8$

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Summary On reaction of the non-stoichiometric vanadium bronze $Li_{1+x}V_3O_8$ with aqueous acids a novel type of layered hydrogen bronze $H_{1+x}V_3O_8 \cdot nH_2O$ (**1**; monoclinic lattice parameters: $a = 10.27$, $b = 3.61$, $c = 12.42$ Å, $\beta = 112.5^\circ$), which exhibits Brønsted acid and polyelectrolyte character, is obtained in a topotactic process; reaction of (**1**) with organic Lewis bases L results in the formation of a new class of layered intercalation complexes $L_nH_{1+x}V_3O_8$.

SOLID state redox reactions at ambient temperature of layered oxide bronzes $A_xM_yO_z$ (A = alkali metal, M = transition metal) proceeding with retention of the two-dimensional M_yO_z lattice elements are of interest with respect to the potential application of these phases as electrode materials for reversible high energy density batteries.¹⁻³ In the course of a study on the electrochemistry of the non-stoichiometric semiconducting lithium vanadate $Li_{1+x}V_3O_8$ system in aqueous electrolytes we observed the topotactic formation of hydrogen bronzes $H_{1+x}V_3O_8 \cdot nH_2O$ in the reaction of single crystals or polycrystalline samples of lithium vanadate with aqueous mineral acids. The structure of $Li_{1+x}V_3O_8$ (monoclinic, $a = 6.68$, $b = 3.60$, $c = 12.03$ Å, $\beta = 107^\circ 50'$) may be described as puckered $[V_3O_8]$ layers formed by VO_6 octahedra and VO_5 distorted trigonal bipyramids sharing edges and corners (Figure).⁴

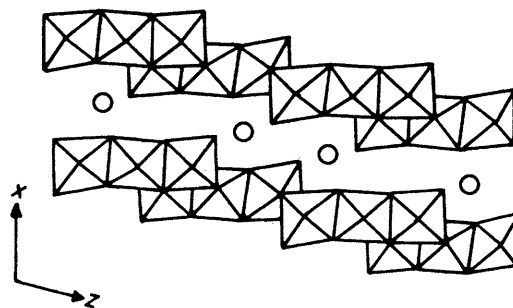
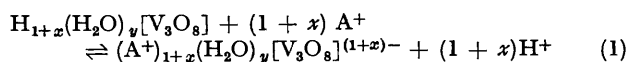


FIGURE. Schematic representation of the $Li_{1+x}V_3O_8$ structure.
○ = Li.

The layers are held together by Li^+ ions in octahedral sites between the V_3O_8 sheets. On treatment of $Li_{1.15}V_3O_8$ with 1 N acids the black colour of single crystals changed to dark red with a metallic lustre. Weissenberg photographs showed that the single crystal nature was preserved in the reaction product. Analytical data and evaluation of the oxidation state of vanadium revealed that Li quantitatively leaves the lattice and is replaced by protons with a concurrent uptake of H_2O into the interlayer space. Indexing of the X-ray powder pattern of the resulting hydrated

hydrogen bronze $H_{1.08}V_3O_8 \cdot 2.5 H_2O$ leads to the monoclinic lattice parameters $a = 10.27$, $b = 3.61$, $c = 12.42$ Å, $\beta = 112.45^\circ$. As a consequence of the uptake of H_2O the interlayer spacing d between neighbouring V_3O_8 sheets increases from 6.36 Å for $Li_xV_3O_8$ to 9.49 Å in the hydrated bronze, whereas retention of the V_3O_8 layer units is reflected in relatively small changes only for the b and c parameters. Exposure of $H_{1.08}V_3O_8 \cdot 2.5 H_2O$ to a vacuum of 10^{-3} Torr at 25 °C results in a partial dehydration to $H_{1.07}V_3O_8 \cdot 0.5 H_2O$ with a large decrease in interlayer spacing from 9.49 to 6.11 Å. Both hydrogen bronzes behave as strong Brønsted acids: on reaction with aqueous solutions of *e.g.*, neutral alkali salts, the pH of the suspension rapidly falls to below 7. Repeated treatment with solutions of alkali or alkaline earth salts or hydroxides results in rapid quantitative ion exchange according to equation (1). The products are hydrated alkali and alkaline earth bronzes $A^{n+}_{(1+x)/n}(H_2O)_y[V_3O_8]^{(1+x)-}$ with negatively charged $[V_3O_8]$ layers and hydrated mobile cations in the interlayer space. As expected, the b and c parameters of these compounds, all of



which can be indexed in the monoclinic system, vary only by a few tenths of an angstrom as compared to those of the parent phase $H_{1.08}(H_2O)_y[V_3O_8]$. The interlayer distance d , which is correlated with the a -axis *via* the monoclinic angle, was found to be strongly dependent upon the charge/radius ratio e/r (*i.e.* upon hydration energy) of the cations taken up into the interlayer space. Three distinct ranges could be observed for alkali and alkaline earth ions: (i) small bivalent cations with $e/r > 1.7$ corresponding to d values of *ca.* 11 Å, (ii) large monovalent cations with $e/r < 1.1$ and d values of *ca.* 8.5 Å, and (iii) an intermediate range corresponding to d values of *ca.* 10 Å (Table). Transition metal

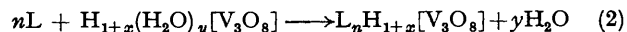
TABLE. Interlayer spacings d of hydrated layered vanadium bronzes obtained by ion exchange according to equation (1); A^{n+} = interlayer cation

A^{n+}	$d/\text{Å}$	A^{n+}	$d/\text{Å}$	A^{n+}	$d/\text{Å}$
Li ⁺	9.82	Cs ⁺	8.69	Ba ²⁺	9.59
Na ⁺	8.19	Mg ²⁺	11.19	Cr ³⁺	11.92
K ⁺	8.53	Ca ²⁺	11.18	Cd ²⁺	11.05
Rb ⁺	8.31	Sr ²⁺	11.42	Co ²⁺	10.94

cation derivatives show interlayer spacings of 11–12 Å. This rather complex hydration behaviour is different from

the simple pattern found for hydrated layered chalcogenide bronzes $A^{n+}_x(H_2O)_y[MX_2]^{n-}$ ($X = S, Se$) which exhibit only two clearly different hydration stages with mono- and bi-layers of water.⁵ As in the case of the hydrated molybdenum oxide bronzes this difference may be interpreted in terms of a competitive influence between cation–water interaction and hydrogen bond formation between H_2O and the negatively charged oxide layer surfaces;² similar arguments may apply to the related vanadium mineral hewettite $Ca[V_6O_{16}] \cdot nH_2O$, for which hydration and cation exchange has been reported.⁶

The hydrogen bronzes $H_{1+x}(H_2O)_y[V_3O_8]$ were also found to provide a novel versatile host lattice for the intercalation of organic Lewis bases L which react according to equation (2). Treatment of the hydrogen bronzes with



pyridine (pyr) or solutions of pyridine in H_2O or organic solvents leads, within 24 h, to the formation of $(C_5H_5N)_{0.98}H_{1+x}[V_3O_8]$ with the monoclinic lattice parameters $a = 11.700$, $b = 3.605$, $c = 11.971$ Å, $\beta = 107.49^\circ$ and an interlayer spacing of 11.16 Å. The compound is stable under vacuum (10^{-4} Torr) up to 150 °C; above this temperature line broadening in X-ray powder diagrams indicates increasing lattice disorder. The relatively high stability of this phase is supposedly due to the formation of cations in the interlayer space by partial transfer of lattice protons to the nitrogen lone pair of electrons at the pyridine; a more pertinent description of the structure would therefore be $pyr_{1-n}(pyrH)_n^+[H_{(1+x)-n}V_3O_8]^{n-}$. A systematic study on the intercalation of nitrogen heterocycles, aliphatic and aromatic amines, acid amides, *etc.* gave evidence for a strong dependence of stability and reaction kinetics on the pK_B values of the Lewis base molecules. This observation, in turn, supports the idea of a partial protonation of the guest molecules.

The close similarity between the layered vanadate hydrogen bronzes described and the layered molybdate hydrogen bronzes H_xMoO_3 ² with respect to Brønsted acid character, ion exchange processes, and Lewis base intercalation extends also to topotactic redox reactions. Preliminary studies on galvanostatic reduction and oxidation of $H_{1.07}(H_2O)_y[V_3O_8]$ in acids revealed the reversible formation of hydrogen bronzes $H_{1.8}(H_2O)_y[V_3O_8]$.

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