It is well established that this potential is associated with porphyrin-centered oxidation and π-cation-radical formation.[13] The lower oxidation potential of $(TPP)FeF_2^-$ and the high reactivity of the oxidized product suggest an electronic structure different from that of oxidized five-coordinate complexes. Metal-centered oxidation of $(TPP)FeF_2^-$ to give an iron(IV) species is a viable possibility. The short lifetime of this species could be explained by subsequent oxidation of solvent and/or supporting electrolyte mediated by trace amounts of water.

The high reactivity of oxidized $(TPP)FeF_2^-$ suggested that the transient, electrochemically generated species could be utilized to effect the functionalization of organic substrates. Accordingly, methylene chloride solutions containing 10% cyclohexene, $(TPP)FeF_2^-$ (1 mM, generated from (TPP)FeF and excess $Bu_4NF{\cdot}3H_2O$), and Bu_4NClO_4 (0.1 M) were electrolyzed at potentials slightly anodic of the observed oxidation wave by using a platinum basket working electrode.[14] Volatile components were then separated from supporting electrolyte, excess fluoride salt, and iron porphyrin by flash vacuum distillation. The volatile mixture was analyzed by gas chromatography and gas chromatography–mass spectrometry. The principal oxidation products were found to be cyclohexenone, 2-cyclohexenol, and cyclohexene oxide. No oxidized hydrocarbons were detected if either the monofluoro iron(III) porphyrin or the fluoride salt was excluded from the solution. The small quantity of water introduced from the hydrated salt apparently provides a source of oxygen. Experiments designed to optimize yields, control product ratios, and discern mechanisms are in progress.

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Registry No. (TPP)FeF, 55428-47-2; $(TPP)FeF_2^-$, 76402-68-1; $(OEP)FeF_2^-$, 86668-09-9; $(TPP(p\text{-}OMe))FeF_2^-$, 86646-34-6; Bu_4NF, 429-41-4; cyclohexene, 110-83-8.

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(14) Addition of cyclohexene had no apparent effect on the variable-rate cyclic voltammetry profiles. This is likely due to the fact that cyclohexene (at the 10% level) is relatively no more reactive toward the oxidized iron porphyrin species than the solvent and/or supporting electrolyte.

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Interstitial and Intercalation Chemistry of the Double-Metal-Layered Yttrium Monochloride

Sir:

The particular monohalides ZrCl,[1] ZrBr,[2] ScCl,[3] and YCl[4] as well as those of many lanthanide elements[5] all provide a novel metal-like array within tightly bound slabs composed of four cubic-close-packed layers sequenced X–M–M–X. Two (Sc, Y etc.) or three (Zr) electrons per metal provide strong bonding of the double-metal layers, and the compounds appear to be metallic. We report that an extensive chemistry exists for YCl and presumably for other related phases; this involves compounds in which there has been interstitial insertion of small non-metals within the tetrahedral or trigonal-antiprismatic (TAP) interstices between the double-metal layers as well as simultaneous or separte intercalation of alkali-metal cations in the van der Waals gap between the chlorine layers with concomitant reduction of the metal layers. Compounds of the latter type are well-known for layered chalcogenides and other phases[6] but not heretofore for binary halides.[7] The insertion of hydrogen or oxygen in the tetrahedral metal interstices in ZrCl and ZrBr is already known, giving either $ZrXH_{0.5}$ and ZrXH where the four-layer slabs are restructured but retained[8] or $ZrXO_y$ with continuous variation of the amount of oxygen up to $y \sim 0.4$.[9] On the other hand, the synthesis of intercalation compounds of the ZrX phases has to date not succeeded.[2,9]

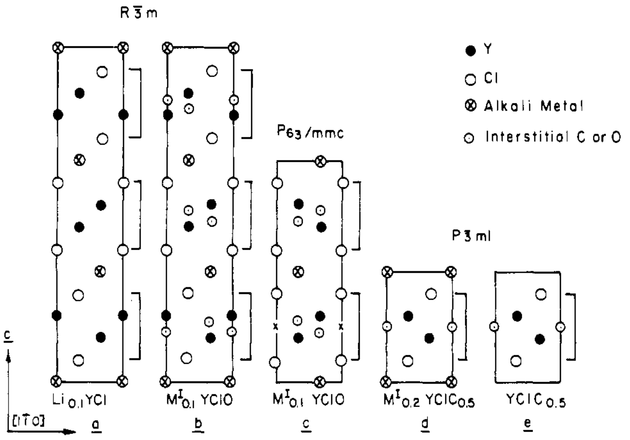

Figure 1. The (110) sections of (a) $3R\text{-}Li_{0.09}YCl$, (b) $3R\text{-}M^{I}_{0.1}YClO$, (c) $2H\text{-}M^{I}_{0.1}YClO$, (d) $1T\text{-}M^{I}_{0.2}YClC_{0.5}$, and (e) $1T\text{-}YClC_{0.5}$. (The small × in part c marks the correct origin.)

The new phases $Li_{0.09}YCl$, $ScClC_{0.5}$, $YClC_{0.5}$, $M^{I}_{0.1}YClO$ (two types), and $M^{I}_{0.2}YClC_{0.5}$ (M = Li–Cs) are all synthesized as black plates by stoichiometric reaction of metal powder or strips with the trichloride and, as appropriate, $M^{I}Cl$, Y_2O_3, YOCl, or C within sealed tantalum tubing at 950 °C for 1–3 weeks. The yields for all but $Li_{0.09}YCl$ are above 90%. The products are necessarily thermodynamically stable at high temperatures and well crystallized, in contrast to many reported intercalation compounds. The structures of six phases have been solved by single-crystal methods: $Li_{0.09}YCl$ (3R[10]), $Na_{0.08}YClO_{1.0}$ (3R), $K_{0.08}YClO_{0.8}$ (2H), $ScClC_{0.56}$ (1T), $K_{0.26}YClC_{0.4}$ (1T), and the parent YCl (3R). The alkali-metal, oxygen, and carbon coefficients are the refined values (neutral atoms). Those for oxygen and carbon do not differ significantly from full occupancy, 1.0 and 0.5, respectively, which will be assumed for brevity. The alkali-metal coefficients (x), which have in several cases been verified by microprobe analyis, would be 0.5 for full occupancy in all structures. Other phases isostructural with these have been identified with the aid of high-resolution (Guinier) X-ray powder diffraction and lattice constants refined therefrom by least-squares methods.

The crystal structures of the five new classes of compounds are shown schematically in Figure 1 as conventional (110)

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(10) This prefix indicates the number of slabs perpendicular to the c axis in the cell repeat and, by R, H or T, whether the symmetry is rhombohedral, hexagonal, or trigonal.

sections. (These contain all independent atoms in structures composed of close-packed planes perpendicular to the *c* axis.) Figure 1a shows that $Li_{0.09}YCl$ is derived directly from YCl (also $R\bar{3}m$) by random substitution of lithium in about 20% of the TAP interstices between double-chlorine layers. A clear decrease of 0.023 (3) Å in the interlayer Y–Y distance accompanies reduction of the slabs, though increasing Y–Cl and Cl–Cl separations caused an overall increase in *c*. Isostructural Li_xGdCl has also been found recently.[11]

A carbide $M'ClC_{0.5}$, M' = Sc, Y, analogous to $ZrClO_{0.4}$ is also stable, but in this case, the phase appears stoichiometric and the size of the non-metal requires substitution in TAP, not tetrahedral positions between the double-metal layers. Second-nearest-neighbor interactions appear responsible for the reordering of the layers into a one-slab repeat structure, Figure 1e. The isostructural compound $ZrXC_{0.5}$ also forms with ZrCl and ZrBr.[12]

Alkali-metal intercalates are also formed with interstitial (tetrahedral) oxygen in both 3R- and 2H-$M^I_{0.1}YClO$ and with TAP carbon in 1T-$M^I_{0.2}YCl_{0.5}$. These are depicted in Figure 1b,c,d, respectively. The two oxide structures may be formed with all the alkali metals (except 2H-$Li_{0.1}YClO$) and correspond to the placement of the alkali metal in either TAP or trigonal-prismatic (TP) interstices, respectively.[13] In contrast, intercalates of layered transition-metal disulfides generally occur with either TAP and TP coordination only for a single alkali metal.[14] The 3R structure type again represents the direct derivatization of the parent YCl. Depending on conditions, either the 3R or 2H type (and occasionally both) can be obtained with Y_2O_3 and YCl_3 as reactants but only the 3R type when YOCl is used. High concentrations of M^ICl produce only the 3R type, with a clear nonstoichiometry in 3R-K_xYClO, $\sim 0.11 < x < 0.25$, judging from the *c* axis dependence on KCl concentration; this probably occurs with other alkali metals as well. Oxidation of either M_xYClO type structure with I_2 in CH_3CN generates YOCl, the 3R phase yielding a well-crystallized sample in the new YOF type structure (YOCl is normally PbFCl type). The 3R phase reversibly picks up water from moist air to form a probable monohydrate (1T) for at least K and Rb but not Li. Liquid water gives slow oxidation to YOCl together with a striking exfoliation.

The new 1T-$ScClC_{0.5}$ and $YClC_{0.5}$ are isostructural with 1T-$TaSC_{0.5}$ and also occur as intercalates with alkali metals with retention of the 1T form, Figure 1d. ($TaSC_{0.5}$ intercalates evidently occur in other structures.[15]) Both the introduction of carbon into all TAP sites in M'Cl and the intercalation step provide striking reductions in the metal–metal distances within the slabs, i.e., by 0.0793 (5) and 0.131 (8) Å in the intra- and interlayer distances between YCl and $K_{0.26}YClC_{0.5}$. The intercalated carbides are readily decomposed by water. More details will be published in full articles.[16]

Interstitial non-metals have also been found within some extended-chain structures that exhibit strong metal–metal bonding[17] and may be quite common. Nonetheless, a good number of other cluster and chain compounds show no X-ray evidence whatsoever for incorporation of any guest impurity atoms.

Supplementary Material Available: A listing of atom and cell parameters for the six indicated compounds (2 pages). Ordering information is given on any current masthead page.

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Articles

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Electrochemical and Spectroscopic Studies of 3,5-Di-*tert*-butylcatecholato and 3,5-Di-*tert*-butyl-*o*-semiquinonato Complexes of Copper(II)

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Reduction of mixtures of copper(II) and 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) at mole ratios of 1:2 in acetonitrile or dimethyl sulfoxide yields a copper(II)–catecholato (DTBC)–semiquinonato (DTBSQ) complex [$Cu^{II}(DTBC)(DTBSQ)^-$] and a $Cu^{II}(DTBC)_2^{2-}$ complex. These complexes, their oxidation products, and three mixed-ligand complexes [$Cu^{II}(DTBC)(bpy)$, $Cu^{II}(DTBC)(phen)$, and $Cu^{II}(DTBC)(en)$] have been characterized by cyclic voltammetry, optical spectroscopy, and ESR. The formation constants, K_f, for the $Cu^{II}(DTBC)(DTBSQ)^-$ and $Cu^{II}(DTBC)_2^{2-}$ complexes have approximate values of 4×10^{14} and 1.6×10^{33} M^{-2}, respectively. Formation of a stable copper(II)–semiquinonato complex as a redox intermediate provides another versatile 1-electron pathway for the copper–catechol–quinone system, which may be pertinent to the redox chemistry of related systems in biology and to catalytic oxygen activation.

Copper, which is an essential component of many oxidase and oxygenase enzymes,[1-8] appears to be required for lignin formation in plants,[9] and its complexes catalyse oxidative delignification processes.[10] Electrochemical studies indicate

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