detailed reaction mechanisms are not clear. The CCl_4–potassium superoxide reaction should yield an active intermediate, the $Cl_3COO\cdot$ radical, which oxidizes electron-rich olefins to afford the corresponding epoxides and which is a markedly more potent oxidizing agent than superoxide alone.

Layered Double Hydroxides as Supported Anionic Reagents. Halide Ion Reactivity in $[Zn_2Cr(OH)_6]X\cdot nH_2O$

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Several new families of heterogeneous catalysts recently have been synthesized by intercalating metal ions and cationic metal complexes between the negatively charged layers of smectite clay minerals.[1,2] A complementary class of layered compounds exist in which the charge on the layers and gallery ions is the reverse of that found for smectite clays. These are the layered double hydroxides (LDH's) of the type $[M_x^{II}M_y^{III}(OH)_{2(x+y)}]A_{y/n}\cdot zH_2O$.[3-5] The positively charged layers are brucitelike ($Mg(OH)_2$) with trivalent cations substituting for divalent cations in octahedral sites of the hydroxide sheet. Typically, the ratio y/x is in the range 0.20–0.50. In naturally occurring LDH minerals the interlayer anion A^{n-} is most commonly carbonate as in hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, and pyroaurite, $Mg_6Fe_2(OH)_{16}(CO_3)\cdot 4H_2O$. However, a wide range of derivatives containing various combinations of M^{II}, M^{III}, and A^{n-} ions can be synthesized either by direct crystallization[6-9] from aqueous solution or by anion exchange[10] for A^{n-} in a precrystallized host.

LDH's have been investigated as solid ionic conductors[11] and as catalyst precursors,[12,13] but the properties of the pristine compounds as supported anionic reagents or as catalysts for chemical synthesis have not been addressed. Unlike the galleries of smectites, which can be swelled by multiple layers of solvent to mimic a solution-like environment,[1] the galleries of LDH's accommodate only one or two layers of water and other polar molecules. This limitation in gallery swelling, along with the relatively high layer charge density, means that typical organic reagents are unable to penetrate the intracrystal space occupied by the anions. Here we demonstrate that although the gallery anions in a typical LDH are not accessible for direct intracrystalline reaction, they are readily transferred to external edge surfaces for reaction with substrates adsorbed at those sites.

The reactions investigated were simple halide-exchange processes between the halide ions in $Zn_2Cr(OH)_6X\cdot H_2O$ and alkyl halides in the condensed state (toluene) or in the vapor phase. The chloride form of the LDH was prepared by reaction of aqueous $CrCl_3$ with ZnO according to previously described procedures.[14,15] The product was identified by X-ray diffraction analysis (d_{003} = 7.7 Å). Exchange of the chloride form with excess 1.0 M NaI solutions afforded the iodide form with d_{003} = 8.3 Å.[15] N_2 BET surface areas were 7.7 and 9.4 m^2/g, respectively, for LDH samples dried under Argon at 25 and 150 °C.

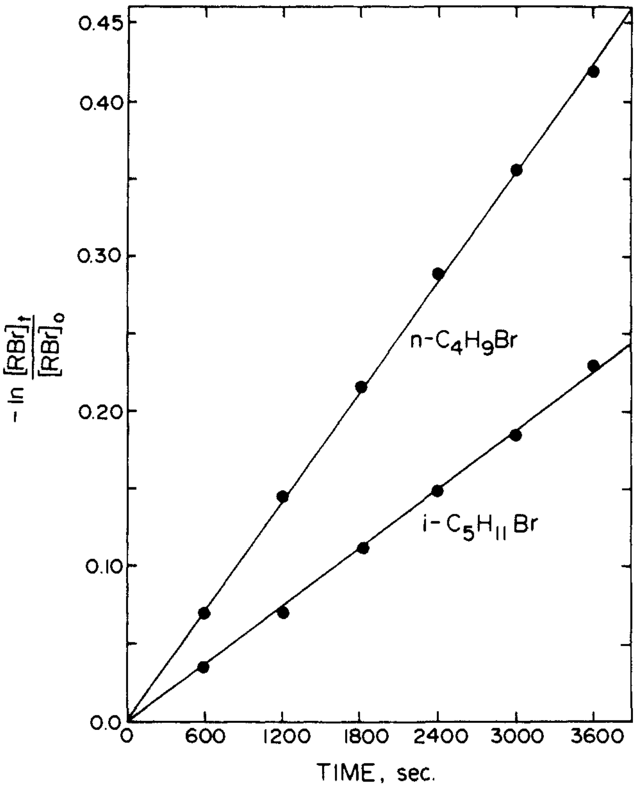

Figure 1. Pseudo-first-order kinetic plots for the reaction of (A) *n*-butyl bromide and (B) 3-methylbutyl bromide with $Zn_2Cr(OH)_6I\cdot 2H_2O$ in toluene suspension at 90 °C. The LDH was predried at 150 °C under argon prior to reaction. The initial reaction mixtures contained 1.0 mmol of alkyl bromide and LDH in 3.0 mL of toluene. $[RBr]_t/[RBr]_0$ is the fraction of substrate unreacted at time *t*.

Table I. Pseudo-First-Order Rate Constants[a] (90 °C) for Halide Exchange between Alkyl Bromides in Toluene and $Zn_2Cr(OH)_6I\cdot 2H_2O$

	10^5k_{obsd}, s^{-1} m^{-2}	
alkyl bromide	LDH dried at 25 °C	LDH dried at 150 °C
$n-C_4H_9Br$	1.1	3.0
$n-C_5H_{11}Br$	1.1	3.6
$i-C_5H_{11}Br$	0.60	1.6
$n-C_6H_{13}Br$	0.83	3.1
$n-C_8H_{17}Br$	0.87	2.4

[a] Rate constants have been normalized per unit surface area of LDH.

Condensed-phase reactions were carried out in culture tubes containing 3.0 mL of toluene and 1.0 mmol each of LDH and alkyl halide. The reaction mixture was stirred vigorously while being maintained at 90 °C in an oil bath, and samples were withdrawn periodically for analysis by gas chromatography. Reactions of alkyl halides in the vapor phase with LDH were carried out in a microreactor in the temperature range 90–150 °C. The reactor was loaded with 1.0 mmol of LDH and 1.0 mmol of alkyl halide was passed through the LDH under a flow of helium to allow for a contact time of 0.19 s. The products were condensed and analyzed by gas chromatography.

As is illustrated in Figure 1 for *n*-butyl bromide and 3-methylbutyl bromide, halide exchange between alkyl bromides in toluene and intercalated iodide ions in the LDH followed

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Table II. Reaction of Gaseous *n*-Butyl Bromide with Intercalated Halide Ions in $Zn_2Cr(OH)_6X{\cdot}2H_2O$[a]

intercalated halide	temp, °C	C_4H_9X yield, %
I	150	80
Cl	150	80
Cl	140	71
Cl	130	60
Cl	90	33

[a] One millimole of butyl bromide was passed over 1 mmol of LDH at a contact time of 0.19 s and the net yields were determined. The LDH was predried at 150 °C for 2 h under argon.

pseudo-first-order kinetics over the initial stages of the reaction. As the extent of reaction proceeded beyond ~30%, the rate decreased and eventually became very low above 80% reaction. It is noteworthy, however, that the reaction could be forced essentially to completion by using an excess of LDH.

Initial pseudo-first-order rate constants, normalized per unit surface area of LDH, are provided in Table I for several alkyl bromides. Reaction was more facile when the LDH was predried at 150 °C than at 25 °C, even though the mobility of the intercalated halide ion should decrease with decreasing hydration. Also, the size of the alkyl group had little or no effect on reactivity.

The possibility that halide exchange for alkyl bromides in the condensed state involves dissolution of the LDH was precluded by the observation that exchange also occurred for alkyl halides in the vapor state. Table II summarizes the yields of butyl halide obtained by reaction of gaseous *n*-butyl bromide with the iodide and chloride exchange form of the LDH. Significant yields were obtained even at 90 °C. Although LDH's are potentially basic, we observed no evidence for olefin formation through hydrodehalogenation of the alkyl halide.

The layer charge density of $Zn_2Cr(OH)_6{\cdot}X{\cdot}2H_2O$ requires the presence of one gallery halide ion per ~16.5 Å^2 of basal surface. Since the ionic radii of I^- and Cl^- are 2.16 and 1.81 Å, respectively, there is insufficient free volume between gallery ions to allow intracrystalline adsorption of alkyl halide. Therefore, the halide exchange reactions are confined to occurring at external basal and edge surfaces. Because the morphology of our LDH crystals is platelike with a platelet thickness of about 500 Å,[15] a negligible fraction (<2%) of the halide ions are exposed at external basal surfaces.

The high reaction yields observed under stoichiometric reaction conditions demonstrate that most (>80%) of the intercalated halide ions are capable of migrating to external *edge* surfaces for reaction with substrate. In addition, the pseudo-first-order kinetics observed up to 30% reaction suggest that the halide ions near edge sites are readily transported to external surfaces for reaction. The ability of the substrate to adsorb at edge surfaces is another important aspect of the observed reactivity. We tentatively propose that the approximately 2-fold increase in reactivity which occurs upon increasing the drying temperature of the LDH from 25 to 150 °C arises from the removal of more water from the edge surfaces and the enhancement of alkyl halide adsorption. Further evidence for water competing for adsorption sites is provided by the observation that reaction essentially ceases when liquid water is added to the reaction mixture under condensed-phase conditions.

Our results suggest that layered double hydroxides are potentially useful compounds for supporting anionic reagents and for designing new classes of crystalline solid-state catalysts. Although the galleries of LDH's are effectively "stuffed" and do not permit intracrystal adsorption of simple organic substrates, the intercalated anions are accessible for reaction of substrate at edge sites. Larger, more complex anions with charge densities lower than those of the halide ions studied here should be even more reactive. Future studies will focus on intercalated metal complex anions as catalysts and photocatalysts.

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Observation of a Spin-Peierls Transition in the Linear Chain Compound Aqua[*N*-(salicylaldiminato)glycinato]copper(II) Hemihydrate

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The Peierls distortion[1] of a quasi-one-dimensional system containing paramagnetic transition-metal ions has not been realized experimentally prior to this report. Some low-dimensional conductors[2] undergo a regular electronic Peierls (RP) transition to an insulating ground state. The spin analogue of the RP transition, the spin-Peierls (SP) transition, may arise in electrically insulating, antiferromagnetically coupled, uniformly spaced spin chains. Two types of compounds {TTF-$MX_4C_4(CF_3)_4$, M = Cu or Au, X = S or Se,[3a–c] and MEM-$(TCNQ)_2$ [MEM is methylethylmorpholinium][3a]} exhibit the SP transition, and it has been suggested, but not confirmed, for others.[3a,d] SP behavior has been observed in chain compounds in which the spins are located on large, flat organic molecules, but not in antiferromagnetically coupled chains[4] in which the spins are localized on transition-metal centers. We have identified a linear chain complex with metal-ion-based spins which exhibits magnetic properties characteristic of an SP transition. The compound is aqua[*N*-(salicylaldiminato)glycinato]copper(II) hemihydrate, CuNSG.

The criteria for selection of a candidate for the distortion are as follows: the chain should have ligand bridged paramagnetic metal ions to permit antiferromagnetic interactions, the structural features of the chain should allow strong 3-D interchain phonon interactions, and the chains should be magnetically isolated from one another to minimize interchain magnetic interactions which may lead to long-range 3-D magnetic ordering.

Coordination of copper(II) in CuNSG is square pyramidal. The basal plane is formed by the donor atoms of the tridentate Schiff base and coordination of one water molecule,[5] and the apical position is filled by the second carboxylate oxygen from a neighboring molecule to form the chain link for superexchange. Neighboring chains pack antiparallel (Figure 1) with a resultant interweaving of molecular units. This interweaving allows for good interchain phonon interaction, yet interchain magnetic superexchange paths are not present.

Magnetic susceptibility measurements were made in the range 1.8–60 K by using a vibrating sample magnetometer and an applied field of 0.1 T.[6] Magnetization was measured as a function of applied magnetic field at a number of temperatures from 1.3 to 4.2 K.[7] The g_{av}(EPR) = 2.14 was used in the data analysis. Magnetic susceptibility data shown in Figure 2 for a powdered sample exhibit a maximum near 4 K. At approximately 2.2 K the susceptibility falls off rapidly, too rapidly to be a 3-D magnetic ordering.

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