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 {$TTF\text{-}MX_4C_4(CF_3)_4$, 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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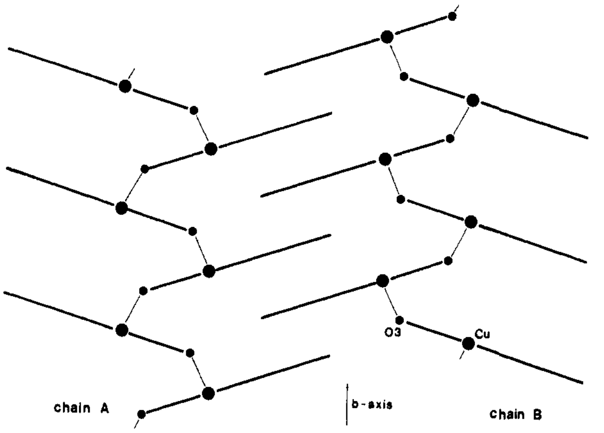

Figure 1. View normal to two chain axes which shows the antiparallel packing of the chains and the interleaving of the molecular units.

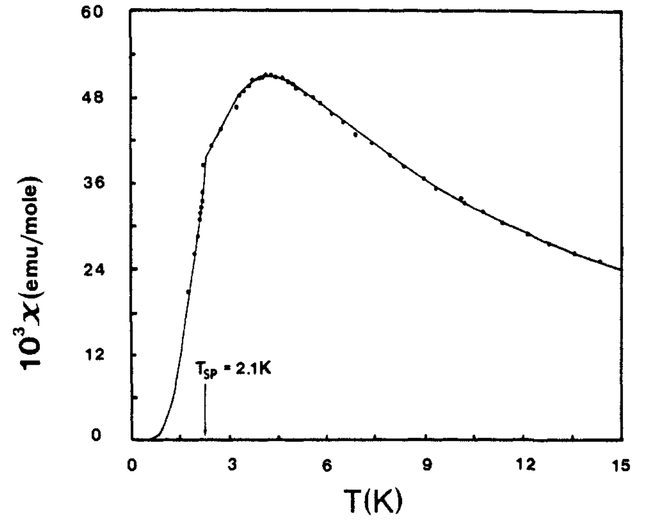

Figure 2. Magnetic susceptibility data which show the spin-Peierls transition. Solid lines were generated by the theoretical expressions and parameters described in the text.

Isothermal magnetization data show the expected behavior for an SP transition. Uniform chain magnetization behavior is observed at 4.2 and 2.4 K, but at 2.1 K and lower temperatures the magnetization behavior is characteristic of an alternating chain. Isofield magnetization data show an abrupt change in magnetization at T_{SP} which is dependent on the applied magnetic field, T_{SP} being 2.1 K at 1 T and ~1.8 K at 4 T. The magnetization behavior is complex above 4.4 T.

The magnetic susceptibility data for CuNSG may be fit by the $S = {}^1/_2$ 1-D Heisenberg theory[8] by using $J = -1.55$ cm^{-1}. The fit is improved if a slightly temperature-dependent exchange coupling constant is used below $T = 5.5$ K. Temperature-dependent exchange coupling was also found in TTF-Cu^{I}BDT.[3b]

Below T_{SP} the spin chain is an alternating chain, and the degree of alternation is temperature-dependent. If T_{SP} is taken as the temperature of maximum $d\chi/dT$,[3] the data in Figure 2 indicate that T_{SP} = 2.1 K. Below T_{SP} the magnetic susceptibility cannot be fit by either the static alternating chain model,[4] or the temperature-dependent alternating chain model of Bulaevskii.[9] This is probably due to large spin–phonon coupling in CuNSG. The magnetic susceptibility below T_{SP} may be fit by the expression

$$\chi_M = (Ng^2\beta^2/3kT)A \exp[-2J(1 - T/T_c)/kT]$$

where the parameter $A = 0.75$ is the $S(S + 1)$ value for $S = {}^1/_2$, and the temperature parameter T_c in the Boltzmann term qualitatively accounts for the progressive dimerization in CuNSG. The best fit of T_c = 5.8 K is nearly the temperature at which the correction to the Bonner–Fisher chain result becomes important. A quantitative description of the dimerization in CuNSG will require a more accurate description of the variation of the exchange energies with structural parameters.

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Enantioselective Deprotonation by Chiral Lithium Amide Bases: Asymmetric Synthesis of Trimethylsilyl Enol Ethers from 4-Alkylcyclohexanones

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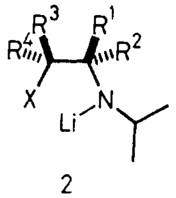
Highly selective transformations of enantiotopic groups in prochiral or meso compounds having a σ-plane are well-known in enzymatic processes.[1] Chemical approaches have also been made mainly by diastereoselective methods,[2] and a few enan-



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	R^1	R^2	R^3	R^4	X
a	H	Pr^i	H	H	OMe
b	H	Bzl	H	H	OMe
c	Bu^t	H	H	H	OMe
d	Ph	H	H	H	OMe
e	Ph	H	H	H	NMe_2
f	Ph	H	H	H	
g	Ph	H	H	H	
h	Ph	H	H	H	
i	Me	H	Ph	H	OMe
j	Me	H	H	Ph	OMe
k	H	Ph	H	H	H
l	1-Naph	H	H	H	H

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