be consistent with a decrease of tetragonal distortion in going from the crystal to the glass.

In contrast with the observation of a half-field transition in the powder ESR spectrum, which implies the presence of an exchange interaction, the magnetic susceptibility data down to 10 K show only an extremely small interaction. The data obey the Curie–Weiss law, $\chi_A = C/(T - \Theta)$ with $C = 0.419$ and $\Theta = -1.46$ K.[27] From the very small negative value of Θ, it can be estimated that the compound is slightly antiferromagnetic. Least-squares fitting to the Bleany–Bowers equation yields $g = 2.10$ and $J = -0.50$ cm^{-1} (assuming the TIP = 60×10^{-6} cgsu).

As previously mentioned, four complexes are structurally related to our compound in that they have the copper atoms bridged through two coordinated oxygen atoms of the carboxylate anions. Their relevant structural features are quoted in Table V. To our knowledge, the magnetic properties of the 1-methylimidazole derivative have not yet been reported. $[Cu(L')CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$ (L′ being the anion of *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine), which has two inequivalent Cu–O–Cu bridges, is characterized by a J value of +0.63 cm^{-1}.[4] In $Cu_2(L'')(CH_3COO)_2 \cdot 2CH_3OH$ (L″ being the dianion of *N*,*N*′-bis(2-((*o*-hydroxybenzhydrilene)amino)ethyl)-1,2-ethanediamine) the occurrence of 1,2-ethanediamine bridges together with acetate bridges prevents an unambiguous assignment of the coupling constants to the respective type of bridging ligands. However, the authors suggest that the value −1.50 cm^{-1} may be associated with the Cu_2O_2 unit.[6] Examination of these three sets of data provides no obvious correlation between the coupling constant and any of the structural features. This is likely due to the restricted range of values exhibited by the structural parameters and coupling constants. Tentatively, we would suggest that, for most of the complexes reported in Table V, the structural parameters would lie in the vicinity of the crossover values from antiferromagnetic to ferromagnetic coupling. In this respect, it may be recalled that the hydroxide-bridged dimers show an angular dependence of J with a crossover at a Cu–O–Cu bridging angle of 97.6°.[28] Obviously, more examples are aimed at relating magnetic properties and structural features for this type of bridging.

Finally, the proper conclusions here is that $[Cu(AE)CH_3COO]_2$ is characterized by a small value of $|J|$. This results is not unexpected on the basis of the rationale proposed by Kahn and co-workers[29] and the actual geometry of the dimer. The two magnetic orbitals are essentially localized in parallel planes separated by 3.305 Å, and the resulting overlap density should be small. A co-square-planar geometry for the dimeric unit would result in a much more significant interaction. Systems of this type involving the AEH ligand are being studied.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, hydrogen parameters, and least-squares plane equations and a plot of the inverse of the atomic susceptibility χ_A^{-1} against temperature (18 pages). Ordering information is given on any current masthead page.

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Exchange Coupling in the Alternatingly Spaced Linear-Chain Compounds Lithium Copper(II) Trichloride Dihydrate, $LiCuCl_3 \cdot 2H_2O$, and Isopropylammonium Copper(II) Trichloride, $(C_3H_{10}N)CuCl_3$

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New magnetic susceptibility data on lithium copper(II) trichloride dihydrate, $LiCuCl_3 \cdot H_2O$, and isopropylammonium copper(II) trichloride, $(C_3H_{10}N)CuCl_3$, exhibit maxima at 6.6 and 23 K, respectively. These maxima are indicative of antiferromagnetic exchange interactions. Interpretation of the magnetic susceptibility data by alternating Heisenberg linear-chain theory for $S = {}^1/_2$ ions yields $J = -3.7$ cm^{-1} and $\alpha = 0.89$ for $LiCuCl_3 \cdot 2H_2O$ using the EPR g value of 2.14 and $J = -13.7$ cm^{-1} and $\alpha = 0.35$ for (IPA) $CuCl_3$ using the EPR g value of 2.17.

Introduction

The theoretical problem of alternatingly spaced linear spin chains has been studied extensively[1-5] and reviewed recently.[5,6] Organic compounds with alternatingly spaced linear-chain structures have been known and studied for quite some time.[7] Exchange-coupled transition-metal compounds that are composed of alternatingly spaced linear chains have only recently received attention. The most thoroughly studied transition-metal compound that exhibits alternating-chain magnetism is $Cu(NO_3)_2 \cdot 2.5H_2O$.[6] However, the room-temperature X-ray crystal structure of $Cu(NO_3)_2 \cdot 2.5H_2O$ is ladderlike.[8]

Other transition-metal compounds[9-21] that exhibit alternat-

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Table I. Antiferromagnetically Exchange-Coupled Transition Metal Ion Alternating-Chain Compounds

compd	α	J, cm^{-1}	g	structure	ref
$Cu_2(OAc)_4pyr$[a]	3×10^{-4}	−160	2.18	alternatingly bridged	9
$Cu_2L(CH_3COO)_2\cdot 2CH_3OH$[b]	0.19	−7.9	2.11	alternatingly bridged	10
$Cu(NO_3)\cdot 2.5H_2O$	0.27	−1.8	2.18	ladderlike at room temp	6, 8
$(IPA)CuCl_3$[c]	0.35	−13.7	2.17	alternatingly spaced	11, this work
$Fe^{IV}(\mu\text{-}O)(hpz)$[d]	0.40	−133	2.30	disordered bridges	12
$Cu(N\text{-}MeIm)_2Br_2$[e]	0.40	−7.2	2.14	uniformly spaced at room temp	13, 14
$Cu(4\text{-}Mepy)_2Cl_2$[f]	0.67	−9.6	2.17	uniformly spaced at room temp	4, 15, 16, 17
$Cu(3,6\text{-}DTO)Cl_2$[g]	0.69	−2.7	2.08	alternatingly bridged	18
$LiCuCl_3\cdot 2H_2O$	0.89	−3.7	2.14	alternatingly spaced	19, this work
Cu-OTS[h]	0.90	−12.9	2.11	no X-ray structure	4
Cu-HTS[i]	0.91	−10.1	2.06	no X-ray structure	4
Cu-KTS[j]	0.98	−4.5	2.08	alternatingly spaced	20, 21

[a] OAc = acetate; pyr = pyrazine. [b] L^{2-} = dianion of *N,N'*-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine. [c] IPA = isopropylammonium. [d] hpz^{2-} = dianion of hemiporphyrazine. [e] *N*-MeIm = *N*-methylimidazole. [f] 4-Mepy = 4-methylpyridine. [g] 3,6-DTO = 3,6-dithiaoctane. [h] OTS^{2-} = 2,3-octanedione bis(thiosemicarbazonate). [i] HTS^{2-} = 2,3-hexanedione bis(thiosemicarbazonate). [j] KTS^{2-} = 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonate).

ing-chain magnetism are listed in Table I. The compounds $Cu(3,6\text{-}DTO)Cl_2$[18] (where 3,6-DTO = 3,6-dithiaoctane), $Cu_2L(CH_3COO)_2\cdot 2CH_3OH$[10] (where L^{2-} = dianion of *N,N'*-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine) and $Cu_2(OAc)_4pyr$[9] (where pyr = pyrazine) are the only alternatingly bridged (and hence alternatingly exchange-coupled) linear-chain structures for which magnetic data have been obtained. The remaining alternating-chain compounds in Table I are alternatingly spaced chain structures that have only one chemical type of bridge. However, there are two sets of structural features associated with the bridging units, and these alternate along the chain axis, leading to the alternating-chain magnetism. This alternatingly spaced feature is not apparent in the room-temperature crystal structures of some of the compounds in Table I, and this feature must, therefore, result from a lattice-driven structural transition from the uniform chain to a static, alternatingly spaced chain. This transition is different from the magnetoelastic spin–Peierls[22] transition, which leads to progressively dimerizing chains and is energetically driven by the interaction of the spin lattice with the crystal lattice.

The Hamiltonian that describes the static alternating linear chain may be written as

$$\mathcal{H} = -2J \sum_{i=1}^{(N/2)-1} [\hat{S}_{2i}\cdot\hat{S}_{2i-1} + \alpha\hat{S}_{2i}\cdot\hat{S}_{2i+1}] \qquad (1)$$

where J is the exchange integral between a spin and its right neighbor and αJ is the exchange integral between a spin and its left neighbor. The alternation parameter, α, is temperature independent.

The model of interest here is the static alternating chain with antiferromagnetic ($J < 0$) exchange and $0 \leq \alpha \leq 1$, where the limit $\alpha = 1$ corresponds to the uniform chain and the limit $\alpha = 0$ corresponds to the magnetically isolated dimer.

The problem associated with magnetostructural correlations in transition-metal alternating-chain compounds is that one can not usually assign either one of the exchange-coupling constants, (J or αJ), obtained from the analysis of experimental data, to the respective chemical bridges from which they arise. As part of our program dedicated toward alternating chains and magnetostructural correlations, we report here new determinations of the magnetic properties of $LiCuCl_3\cdot 2H_2O$ and $(IPA)CuCl_3$ (IPA = isopropylammonium) with an analysis of the data in terms of their alternatingly spaced structures. The structures of these compounds afford the unique opportunity of correlating the exchange-coupling constants, determined from the analysis of the magnetic properties, to the respective ligand bridges from which they arise.

Experimental Section

Preparation and Characterization. $LiCuCl_3\cdot 2H_2O$ was prepared[19] by dissolving an excess of LiCl with an appropriate amount of $CuCl_2\cdot 2H_2O$ in a minimum amount of water. Good-quality crystalline material was obtained by the slow evaporation of the solution over anhydrous $CaSO_4$. The product was filtered from the solution, and due to its hygroscopic nature, it was kept in a desiccator at all times. $(IPA)CuCl_3$ was prepared according to the method previously described.[11] Microanalytical data (Galbraith Laboratories, Inc., Knoxville, TN) confirmed the identity and purity of the compounds.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of $LiCuCl_3\cdot 2H_2O$ and $(IPA)CuCl_3$ by using a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM), which was operating from zero field to 10 kOe with procedures that have been described previously.[23] The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li).

The VSM was calibrated with $HgCo(NCS)_4$.[24] Powdered samples of the compounds and calibrant used in this study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each was used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[25-27] Magnetic susceptibility data were analyzed in terms of the theoretical models described below with use of a nonlinear Simplex[28-30] fitting routine. The function that was minimized in all curve-fitting procedures was

$$F = \sum(\chi_i^{obsd} - \chi_i^{calcd})^2/(\chi_i^{obsd})^2$$

Electron Paramagnetic Resonance. EPR spectra were recorded with a Varian E-109 spectrometer operating at X-band (ca. 9.5 GHz) frequencies. The magnetic field of the E-109 spectrometer was calibrated by using an NMR gaussmeter (Magnion Model G-502) and a Hew-

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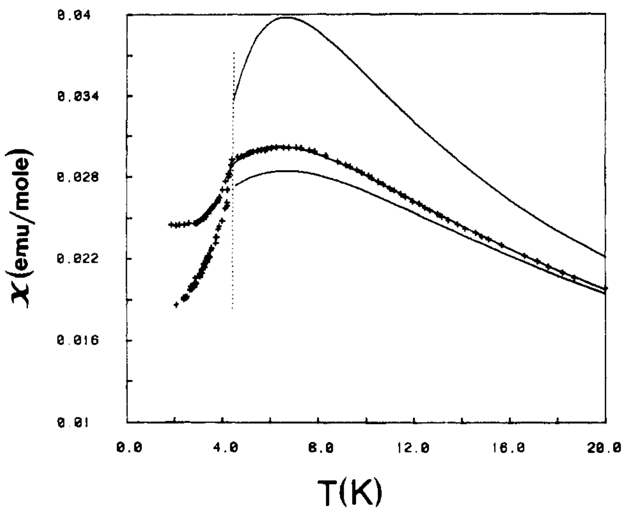

Figure 1. Magnetic susceptibility data for $LiCuCl_3 \cdot 2H_2O$. The solid line through the data was generated by the expression given in the text for the alternating Heisenberg chain model with $J = -3.7$ cm^{-1} and $\alpha = 0.89$. The upper and lower solid curves correspond to the predictions of magnetic susceptibility for the dimer ($\alpha = 0.0$) and the uniformly spaced chain ($\alpha = 1.0$) models, respectively, using the best-fit parameters for the alternating-chain model. The vertical dotted line marks the critical temperature of 4.4 K, below which the susceptibility is field dependent.

lett-Packard precision frequency counter (Model 5340A). In addition, the klystron frequency was measured directly with the frequency counter at all times, and the free radical DPPH ($g = 2.0036$) was used as a field marker. Spectra were recorded on finely ground powders enclosed in commercially available quartz tubes.

Results

Magnetic Properties. Magnetic susceptibility data for $LiCuCl_3 \cdot 2H_2O$ and $(IPA)CuCl_3$ are given in Figures 1 and 2. The maxima in the susceptibility curves occur at 6.6 and 23 K, respectively. These maxima provide strong evidence for antiferromagnetic exchange interactions. In view of the structures of the compounds, these interactions occur along the chains of alternatingly spaced, chloro-bridged, copper(II) ions. At $T = 4.4$ K, the data for $LiCuCl_3 \cdot 2H_2O$ exhibit a phase transition. The data below 4.4 K, which corresponds to the larger magnetic susceptibility values shown in Figure 1, were taken with an external applied field strength of 10 kOe. The data below 4.4 K in Figure 1, with the smaller susceptibility values, were taken with an external applied field strength of 100 Oe. These results clearly indicate the magnetic field dependence below 4.4 K of the susceptibility in $LiCuCl_3 \cdot 2H_2O$. Above 4.4 K, the data were field independent in the range studied (0.1–10 kOe). Only the data in the paramagnetic ($T > 4.4$ K) temperature regime were considered in the data analysis given below. $(IPA)CuCl_3$ does not exhibit a magnetic phase transition in the magnetic susceptibility data down to 1.8 K. The magnetic susceptibility data for $(IPA)CuCl_3$ are in substantial agreement with those published earlier, although no attempt was made there to analyze the data in terms of an alternating chain of Heisenberg spins.

Exchange interactions between copper(II) ions are essentially isotropic and are, therefore, described by Heisenberg theory. Attempts to describe the susceptibility data of $LiCuCl_3 \cdot 2H_2O$ and $(IPA)CuCl_3$ using the Van Vleck[31] equation for an exchange-coupled pair of $S = {}^1/_2$ (eq 2) failed for any reasonable set of

$$\chi_M = [Ng^2\beta^2/3k(T-\Theta)][1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1} \tag{2}$$

parameters. Likewise, the Bonner–Fisher results[32] adapted by

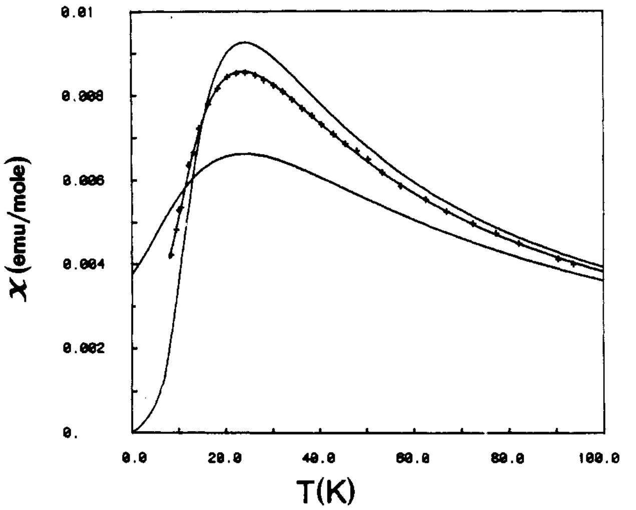

Figure 2. Magnetic susceptibility data for $(IPA)CuCl_3$. The solid line through the data was generated by the expression given in the text for the alternating Heisenberg chain model with $J = -13.7$ cm^{-1} and $\alpha = 0.35$. The upper and lower solid curves correspond to the predictions of magnetic susceptibility for the dimer ($\alpha = 0.0$) and the uniformly spaced chain ($\alpha = 1.0$) models, respectively, using the best-fit parameters for the alternating-chain model.

Hall[33] for the uniformly spaced, antiferromagnetically exchange-coupled chain of $S = {}^1/_2$ ions (eq 3) could not explain the

$$\chi_M = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3}\right) \tag{3}$$

$$x = |J|/kT$$

temperature dependence of the magnetic susceptibilities. The Θ term in eq 2 was included to allow for magnetic interactions beyond the isolated dimer limit. Allowance for magnetic interchain interactions was made through the use of the molecular field correction given in eq 4. In this case, the corrected susceptibility,

$$\chi_{cor} = \chi_{iso}/[1 - (2zJ'\chi_{iso}/Ng^2\beta^2)] \tag{4}$$

χ_{cor}, is a function of the isolated-chain (eq 3) susceptibility, χ_{iso}, and the parameters z (number of nearest neighbors in adjacent chains) and J' (the interchain exchange interaction parameter). The EPR g values of 2.14 for $LiCuCl_3 \cdot 2H_2O$ and 2.17 for $(IPA)CuCl_3$ were used in attempts to analyze the data with these theoretical expressions. The "best-fit" parameters for $LiCuCl_3 \cdot 2H_2O$ were $J = -2.4$ cm^{-1} and $\Theta = -11.8$ K from eq 2, while eq 4 yielded $J = -3.96$ cm^{-1} and $zJ' = -0.7$ cm^{-1}. Likewise for $(IPA)CuCl_3$, eq 2 yielded $J = -14.8$ cm^{-1} and $\Theta = -8.3$ K and eq 4 yielded $J = -12.6$ cm^{-1} and $zJ' = -9.4$ cm^{-1}. In view of the structures, it is not surprising that neither the dimer theory nor the uniform-chain theory is able to describe the experimental data. As suggested by the structures themselves, the experimental results can be explained through the use of alternating Heisenberg chain theory described below.

Alternating Heisenberg Chain. The results for the model Hamiltonian (eq 1) describing the alternating Heisenberg chain have been recalculated[4] by using the cluster approach for short alternating rings of $S = {}^1/_2$ spins for $\alpha = 0.1, 0.2, 0.3, 0.4, 0.6, 0.8$, and 1.0. The calculated susceptibilities were used to generate the following expression for the magnetic susceptibility in terms of the exchange integral, J, the alternation parameter, α, and the temperature ($x = |J|/kT$):

$$\chi_M(\alpha) = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{A(\alpha) + B(\alpha)x + C(\alpha)x^2}{1 + D(\alpha)x + E(\alpha)x^2 + F(\alpha)x^3}\right) \tag{5}$$

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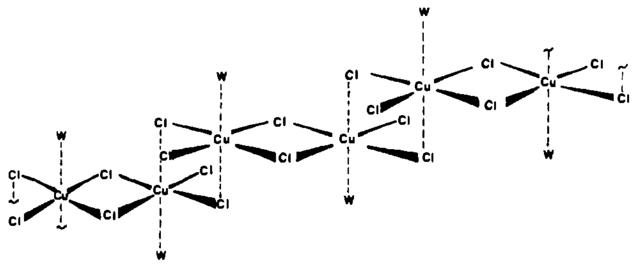

Figure 3. Structure of the alternating chain in $LiCuCl_3{\cdot}2H_2O$. The chain structure in $(IPA)CuCl_3$ is identical, except that the copper(II) ions are only five-coordinate since there are no coordinated water molecules in the sixth position.

The constants A–F are power series in α. The exchange-coupling constants and the alternation parameters for the alternating-chain compounds $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$ were determined by fitting eq 5 to the experimental data in the region where $kT/|J| \geq 0.5$. The best fit obtained from the Simplex fitting procedure and criteria given above yielded $J = -3.7$ cm^{-1} and $\alpha = 0.89$ for $LiCuCl_3{\cdot}2H_2O$ and $J = -13.7$ cm^{-1} and $\alpha = 0.35$ for $(IPA)CuCl_3$. The EPR g values of 2.14 and 2.17, respectively, were held constant during all fitting procedures. The solid curves drawn through the experimental data points in both Figures 1 and 2 are the theoretical susceptibilities calculated with the best-fit parameters by using eq 5. As expected, and as is indicated in Figures 1 and 2, the corresponding $\alpha = 0.0$ (dimer) and $\alpha = 1.0$ (uniform chain) curves for both compounds, calculated with the best-fit parameters from the alternating-chain model, fall above the below the alternating-chain curves (and the experimental data), respectively.

Discussion

Structural Descriptions. The crystal structures of $LiCuCl_3{\cdot}2H_2O$[19] and $(IPA)CuCl_3$[11] have been determined previously. In both compounds, the nearly planar $Cu_2Cl_6^{2-}$ dimeric anion is the fundamental structural unit used to form the alternatingly spaced linear chains (Figure 3). Long Cu–Cl bonds between these dimeric units link the dimers into the alternatingly spaced, bibridged chain structures. In the case of $LiCuCl_3{\cdot}2H_2O$, the sixth position of the copper(II) ion coordination sphere is filled by a coordinated water molecule. In $(IPA)CuCl_3$, each copper(II) ion is surrounded by five chlorides in a nearly perfect, square-pyramidal coordination site. The sixth position is not occupied in $(IPA)CuCl_3$.

The important structural parameters required for this study are listed in Table II. In both compounds, the *symmetrically* bibridged $Cu_2Cl_6^{2-}$ dimer will be referred to in this paper as the "structural" dimer with which the *intradimer* structural features are associated. The *interdimer* structural features are associated with the *unsymmetrical* Cu_2Cl_2 bridging unit, which links the structural $Cu_2Cl_6^{2-}$ dimers into the alternatingly spaced linear chains.

Magnetic Properties. There are no structurally and magnetically characterized precedents of alternating-chain compounds composed of paramagnetic transition-metal ions linked by identical ligand bridges to guide the analysis of the magnetic studies. However, the failure of both the exchange-coupled $S = {}^1/_2$ pair model and the Bonner–Fisher results for the uniformly spaced Heisenberg chain to account for the magnetic susceptibility data of $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$ can be understood in terms of the structural features of the compounds that are outlined in Table II. The theoretical susceptibility curves generated by the alternating Heisenberg chain theory are drawn in Figures 1 and 2 and represent precise fits to the experimental data.

Exchange Coupling. There is now a considerable body of data for exchange-coupled, ligand-bridged copper(II) systems which reveals that the experimentally observed exchange-coupling energy is a function of the angle at the ligand bridge, ϕ, and the length of the long copper–ligand bond, R_0.[34] A relatively smooth correlation of $2J$ with the quotient ϕ/R_0 exists for chloro-bridged copper(II) complexes. In effect, subtle changes in the structural parameters of the ligand bridges that transmit the superexchange can often lead to substantial changes in the magnitude of the exchange-coupling constant because of the alterations that occur in the intersite orbital interactions.

Table II. Structural Parameters for $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$

struct param	$LiCuCl_3{\cdot}2H_2O$	(IPA)-$CuCl_3$
intradimer Cu–Cu, Å	3.40	3.42
interdimer Cu–Cu, Å	3.82	3.51
terminal Cu–Cl, Å	2.28	2.27
intradimer Cu–Cl, Å	2.30 2.31	2.30 2.315
interdimer Cu–Cl, Å	2.26 2.92	2.27 2.70
intradimer Cu–Cl–Cu, deg	95.08	95.51
interdimer Cu–Cl–Cu, deg	94.25	89.35
intra ϕ/R_{av}, deg/Å	41.3	41.4
inter ϕ/R_{long}, deg/Å	32.25	33.1

The chloro bridges that occur in $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$ are of two major types. Type I is the intradimer symmetrical bridging unit composed only of the short Cu–Cl bonds (ca. 2.3 Å) and occurs in the structural $Cu_2Cl_6^{2-}$ dimeric units. Type II is the unsymmetrical Cu_2Cl_2 bridging unit that links the structural $Cu_2Cl_6^{2-}$ dimeric units into alternatingly spaced chains. Both long and short Cu–Cl bonds are involved in this bridge, and it is this type of bridge for which a substantial body of magnetostructural correlation data exist.

The data in Table II show that the intradimer structural features are essentially the same for both $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$. The difference between the ϕ/R values, for example, is negligible when one attempts to correlate magnetic properties. Hence, it is expected that the exchange-coupling constants corresponding to the type I bridges will be substantially the same in the two compounds. The data analysis confirms this conclusion since each of the compounds exhibit at least one exchange-coupling constant that is on the order of 4 cm^{-1}.

The structural features that correspond to the interdimer bridging pathways are distinctly different in the two compounds. The ϕ/R_0 values of 32.2°/Å for $LiCuCl_3{\cdot}2H_2O$ and 33.1°/Å for $(IPA)CuCl_3$ suggest that the exchange-coupling constants corresponding to these type II bridges should be different and that both should be antiferromagnetic. Indeed, the alternating Heisenberg chain analysis of the $(IPA)CuCl_3$ data indicates that one of the two exchange-coupling constants is -13.7 cm^{-1} and hence larger than either of the two exchange-coupling constants in $LiCuCl_3{\cdot}2H_2O$. The larger magnitude of this exchange constant is also in qualitative agreement with the 0.3-Å decrease in interdimer Cu–Cu separation on going from $LiCuCl_3{\cdot}2H_2O$ to $(IPA)CuCl_3$.

Although the two exchange-coupling constants that have been determined for $LiCuCl_3{\cdot}2H_2O$ cannot be conclusively assigned to their respective exchange-coupled units within the chain, they indirectly aid the assignment of the exchange-coupling constants in the case of $(IPA)CuCl_3$. The unsymmetrical bridging unit in $(IPA)CuCl_3$ clearly corresponds to the larger of the two exchange-coupling constants, whereas the αJ value corresponds to the symmetrical bridging unit.

An additional structural feature in both of these alternating-chain compounds is that the neighboring Cu_2Cl_2 exchange-coupled units are nearly perpendicular to one another. Current models for superexchange focus attention on relative orientations of exchange-coupled units. For example, the Cu_2Cl_2 units in typical chains such as $Cu(py)Cl_2$[34] are coplanar. When only the relative orientation of neighboring exchange-coupled units in $LiCuCl_3{\cdot}2H_2O$ and $(IPA)CuCl_3$ is considered, a similar perpendicular

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(34) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105.

orientation of exchange-coupled units can be identified in Cu(3,6-DTO)Cl_2[18] and in Cu–KTS.[20,21] However a major distinction between the compounds in this study and Cu(3,6-DTO)Cl_2 and Cu–KTS should be mentioned. The orientations of the copper(II) ions with respect to the planar, bibridged exchange-coupled units are different. In both Cu(3,6-DTO)Cl_2 and Cu–KTS, the "tetragonal" symmetry axis of the copper(II) ion lies in the plane of both the exchange-coupled units that form the alternating chain. But in $LiCuCl_3{\cdot}2H_2O$ and (IPA)$CuCl_3$ this is not the case. The "tetragonal" symmetry axis of the copper(II) ion in the title compounds lies perpendicular to the planar $Cu_2Cl_6^{2-}$ units, but it lies in the plane of the type II Cu_2Cl_2 bridges. It is interesting to note that in the present study, and in the cases of Cu(3,6-DTO)Cl_2 and Cu–KTS, the exchange-coupling constants determined from magnetic susceptibility studies are more positive than the predicted values obtained from the magnetostructural correlations that exist for similar systems. This result seems to indicate that neighboring exchange-coupled units in a 1-D system that are perpendicular to one another either increase the ferromagnetic contributions, or decrease the antiferromagnetic contributions, to the effective exchange energy, which is measured experimentally.

Phase Transition in $LiCuCl_3{\cdot}2H_2O$. The phase transition that appears at 4.4 K in $LiCuCl_3{\cdot}2H_2O$ is of interest.[35]

Unlike uniformly spaced Heisenberg chains, alternating Heisenberg chains have a singlet ground state that is separated from the band of excited triplet states by an energy gap, ΔE. To a first approximation, $\Delta E/2J$ is proportional to the quantity $1 - \alpha$.[5] The consequence is that alternating chains are theoretically not expected to exhibit a T_N in zero field when interchain exchange interactions are present, whereas uniform chains may do so. And, likewise, alternating chains are not expected to exhibit a spin–Peierls transition to a progressively dimerizing chain if the energetics are based solely on the quantum mechanical energy arguments of the degenerate → singlet-ground-state phase transition. However, alternating chains can show complex LRO regions in their phase diagrams between specific critical fields, and these LRO regions are a function of the alternation parameter and interchain magnetic coupling.[5] This has been found true in the studies on $Cu(NO_3)_2{\cdot}2.5H_2O$.[6]

The magnetic phase diagram[35] of $LiCuCl_3{\cdot}2H_2O$ exhibits similar anomalous high-field behavior. The phase diagram displays a high-field phase that corresponds well with the results from the alternating-chain analysis presented above. The upper critical field of the complex phase in an alternating chain can be estimated[5] from the values of $2J$ and the alternation parameter, α. From the values obtained above, the upper critical field for $LiCuCl_3{\cdot}2H_2O$ is estimated to be 151 kOe, in good agreement with the experimental result[35] of 155 kOe. The lower critical field in $LiCuCl_3{\cdot}2H_2O$ can be estimated to be 21 kOe, an estimate that is in good agreement with the experimental results in the low-field region.

An important point, however, is that an additional phase boundary was found[35] to extend from the expected complex phase region down to $T = 4.4$ K in zero field.

The problems of slow convergence associated with the theoretical results for finite chain systems of large alternation parameters (i.e., $0.8 < \alpha < 1.0$) have limited the understanding of the thermodynamic properties for these systems, especially under the conditions of magnetic interchain interactions. If the alternation parameter is large (ΔE is small) and magnetic interchain interactions are also appreciable, the effective magnetic ground state of the system at low temperatures is no longer accurately described by simple alternating-chain theory. In effect, the ratio $J'/\Delta E$ is no longer sufficiently small and hence a T_N could be realized. In such a case the high-temperature data ($T \ll \alpha J$) should be interpretable in terms of alternating-chain theory, but the low-temperature data will require a more detailed understanding of the ground state of an alternating chain in the presence of interchain interactions. Since the chains in $LiCuCl_3{\cdot}2H_2O$ are only separated from one another by Li ions and water molecules, and since the alternation parameter is large, a significant $J'/\Delta E$ is likely the cause of the additional phase boundary in $LiCuCl_3{\cdot}2H_2O$. In the same light, it is interesting to speculate that if the energetics of interchain spin–phonon interactions are favorable, and the spin system can lower its net energy due to the effects of structural changes on the nonlinear $2J(r_{ij})$ behavior of copper(II) exchange-coupled systems, one could visualize the possibility of a static alternating chain entering a phase in which it is progressively dimerizing.

Note that in (IPA)$CuCl_3$ there is a larger interchain separation distance (because of the larger IPA cations) and that the alternation parameter is smaller than in $LiCuCl_3{\cdot}2H_2O$. As a consequence, the data for (IPA)$CuCl_3$ do not show a phase transition down to 1.8 K.

In conclusion, the theoretical results for alternating chains work well for systems with significant alternation. This is evidenced by the thoroughly studied compound $Cu(NO_3)_2{\cdot}2.5H_2O$ and the (IPA)$CuCl_3$ system studied here. However, the results of this work emphasize the fact that alternating chains with large (0.8–1.0) alternation parameters present an area in which a large amount of new theoretical and experimental research must be done. In particular, the results presented here demonstrate that more complex forms of the phase transitions found in uniform chains are likely to be found in slight alternating-chain structures, i.e. chains on the borderline of being uniform chains.

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Note Added in Proof. Solomon and Wilcox[36] have spectroscopic evidence which suggests that pairs of copper(II) ions in the $Cu_2Cl_6^{2-}$ unit in $LiCuCl_3{\cdot}2H_2O$ are ferromagnetically coupled. Resolution of this problem must await additional experimental and theoretical work.

Registry No. $LiCuCl_3{\cdot}2H_2O$, 15890-89-8; $(C_3H_{10}N)CuCl_3$, 18285-04-6.

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