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Structural Correlations in Pseudo-Planar Bibridged $Cu_nCl_{2n}L_2$ Oligomers

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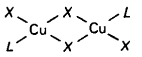
Abstract

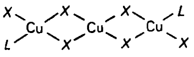
The structures and magnetic behavior of a large number of quasi-planar bibridged $Cu_nCl_{2n}L_2$ oligomers have been reported in recent years. Systematic variations in bond distances and angles are analyzed, both within oligomers of a given value of n, and between oligomers of different lengths. In particular, an alternation of Cu—Cl bond distance occurs within the oligomers. The magnitude of this alternation increases as n increases. The magnetically important bridging Cu—Cl—Cu angles vary in an irregular fashion for various values of n. It is shown that, by considering the effects of both the Cu—Cl distances and the Cu—Cl—Cu angles, the major magnetic characteristics can be rationalized.

Introduction

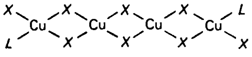
A major research effort in this laboratory has focused on the design, synthesis and characterization of low-dimensional magnetic materials, with particular emphasis on systems involving organoammonium salts of copper(II) halides (Landee & Willett, 1981; Willett, 1985). With the low symmetry imposed upon the copper(II) coordination sphere by the Jahn–Teller effect and the bridging capability of the halide ion, a myriad of structural types are attainable. Since the comprehensive review of copper(II) chlorides in 1976 (Smith, 1976), a substantial number of new systems have been characterized. The structural chemistry of $ACuCl_3$ (where A is an alkali metal or organic cation) salts has recently been summarized (Willett & Geiser, 1984). The corresponding bromide salts appear to share similar characteristics (Place, 1986). Particular species of interest in this laboratory, both structurally and magnetically, have been the quasi-planar bibridged $Cu_nX_{2n}L_2$ oligomers, shown in (I) for $n = 2$, 3 and 4, where X is a halide ion and L is either a neutral ligand or a halide ion, and the Cu^{II} ion assumes coordination geometry close to square planar. These oligomers can be viewed as segments of the anhydrous CuX_2 structures ($n = \infty$) (Wells, 1947) in which Cu^{II} ions occupy octahedral holes between hexagonal close-packed layers of anions. These quasi-planar oligomers aggregate to form stacks through the formation of longer semi-coordinate bonds between adjacent oligomers. The stacking patterns so formed, illustrated by 'envelope' diagrams in (II) for $n = 2$, have been recently reviewed (Geiser, Willett, Lindbeck, Emerson, 1986). In (IIa) and (IIb), each Cu^{II} ion attains a 4 + 2 coordination geometry (four normal, two semi-coordinate bonds) while for (IIc) and (IId) a 4 + 1 geometry is usually found, although occasionally the sixth site is occupied by another ligand. With stacking patterns like (IIa) or (IIb), the oligomers are constrained to a nearly planar configuration. However, with (IIc) and (IId) stacking, the oligomers often distort significantly towards a trigonal bipyramidal geometry for the Cu^{II} ions. For $n = 3$ and 4, additional permutations of these patterns are observed, although the oligomers invariably retain a pseudo-planar configuration. The magnetic properties of these oligomers, and the influence of these stacking patterns and associated distortions have been reviewed (Willett, Grigereit, Halvorson & Scott, 1987). For a given n, the magnetic behavior correlates well with the observed structural parameters, primarily the bridging Cu—Cl—Cu angles and the deviations from planarity. However, intercorrelation of the magnetic properties of the $n = 2$, 3, 4 and ∞ systems cannot be explained on this basis (Halvorson, Grigereit & Willett, 1987). For this reason, a systematic analysis of the structural characteristics of the nearly planar members of these $Cu_nX_{2n}L_2$ oligomers was undertaken, the results of which are reported in this paper.



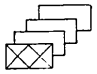
(Ia)



(Ib)

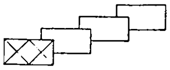


(Ic)

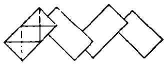


(IIa)

(IIb)



(IIc)



(IId)

Structural characterization

The copper(II) chloride compounds analyzed in this paper are listed in Table 1. The list contains 12 dimeric, six trimeric, and three tetrameric systems, as well as four compounds containing infinite $(CuCl_2)_n$ chains. In addition to dimers which stack like (IIa) and (IIb), two isolated planar dimers and four type (IIc) stacks are

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Table 1. *Summary of structural parameters for* $Cu_nCl_{2n}L_2$ *oligomers*

See Fig. 2 for definition of distance and angle labels.

Acronym *	Compound	Stacking pattern †	t(Å) (ave)	b_1(Å) (ave)	b_2(Å) (ave)	b_3(Å) (ave)	α_1(°) (ave)	α_2(°) (ave)	θ_1(°)		θ_2(°)		φ_1(°) (ave)	φ_2(°) (ave)	J_1/k(°)	Ref.
Dimers																
Li	$LiCuCl_3.2H_2O$	*c,L'*	2·271	2·303			91·7		174·1	175·1			95·0		3D‡	22
K	$KCuCl_3$	*a*	2·257	2·314			91·2		172·8	176·2			96·0		−27	11
NH_4	NH_4CuCl_3	*a*	2·270	2·311			91·7		172·6	175·8			96·2		3D‡	11, 19
MEL	$(C_3N_6H_8)Cu_2Cl_6$	*b*	2·262	2·334			90·8		171·3	175·5			95·8		−28	25, 31
PUR	$(C_5H_5N_4)Cu_2Cl_6$	*c,L'*	2·260	2·314			90·9		171·7	174·8			95·0		—	*a*
									165·8	170·7						
BENZ	$(C_7H_7N_2)CuCl_3$	*c*	2·269	2·312			91·6		163·8	172·5			97·2		—	*b*
									167·9	173·7						
EOA	$(C_2H_8NO)CuCl_3$	*c,L'*	2·263	2·312			90·8		165·2	174·1			95·8		−6	*c*
ACET	$Cu_2Cl_4(CH_3CN)_2$	*a*	2·27	2·305			91		172·5	173·4			94		—	*d*
NMP	$(C_6H_8N)Cu_2Cl_5(H_2O)$	*a*	2·265	2·316			91·6		171·6	174·1			94·7		—	*e*
									168·7	175·7						
4AP	$(C_5H_7N_2.H_2O)Cu_2Cl_5(H_2O)$	*a*	2·286	2·300			90·5		170·5	170·6			94·9		—	*e*
DBTTF	$(C_{14}H_8S_4)CuCl_3$		2·224	2·287			91·1		173·2	173·2			96·2		−55	*f*
MOR	$(C_4H_{10}NO)CuCl_3$		2·240	2·284			91·6		175·6	175·9			95·8		−43	
Average §			2·265 (5)	2·314 (9)			91·3 (4)						85·7 (8)			
Trimers																
NMPZ	$(C_5H_{14}N_2)Cu_3Cl_8$	*b*	2·223	2·323	2·246		90·5	93·0	163·1	173·1	178·0	178·4	94·2		−29	*g*
									163·2	172·7						
3MAP	$(C_6H_9N_2)_2Cu_3Cl_8$	*b*	2·244	2·354	2·289		90·0	92·4	167·0	175·5	177·4	177·4	93·6		−30	*g*
4MP	$(C_6H_8N)_2Cu_3Cl_8$		2·248	2·339	2·276		91·4	93·4	166·8	175·6	179·0	179·0	94·1		−30	*h*
NMPH	$(C_9H_{14}N)Cu_3Cl_7(C_2H_5OH)$	*c*	2·265	2·329	2·273		90·8	92·9	165·9	174·2	177·3	178·3	94·0		−19	*g*
									169·1	171·6						
ACET	$Cu_3Cl_6(CH_3CN)_2$	*a*	2·256	2·302	2·274		92	93	174·0	176·3	180	180	94		−33	*d*
$TMSO_2$	$Cu_3Cl_6(H_2O)_2.2C_4H_8SO_2$	*c,L'*	2·243	2·289	2·286		89	92	173·5	176·7	180	180	93·5		−20	33
Average §		*c,L'*	2·246 (14)	2·323 (24)	2·274 (15)		90·6 (11)	92·8 (5)					93·9 (3)			
Tetramers																
TrMA	$[(CH_3)_3NH]_2Cu_4Cl_{10}$	*c*	2·244	2·306	2·266	2·310	90·8	93·2	165·4	175·0	171·4	173·4	94·6	93·2	—	34
TeMA	$[(CH_3)_4N]_2Cu_4Cl_{10}$	*a*	2·234	2·318	2·269	2·310	91·0	93·0	162·2	173·1	168·3	174·9	94·6	93·5	−62	*i*
4MAP	$(C_6H_9N_2)_2Cu_4Cl_{10}$	*a*	2·227	2·360	2·256	2·296	90·4	93·0	166·6	171·2	177·5	178·6	94·5	93·7	−64	*i*
Average §			2·235 (9)	2·328 (28)	2·264 (7)	2·305 (8)	90·7 (3)	93·0 (2)					94·6 (1)	93·5 (3)		
Infinite chains						b_∞		α_∞			θ_∞			φ_∞		
	$CuCl_2$					2·3		93			180			93	−55	*j*
SN	$CuCl_2.S_4N_4$					2·294		92·8			180			91·8		*k*
DMNA	$CuCl_2.(CH_3)_2N_2O$					2·289		93·1			171·3			88·7		*l*
DX	$Cu_3Cl_6.2C_4H_8O_2$					2·302		93·2			180			93·7		*m*
Average §						2·295 (5)		93·0 (2)								

References: numbers refer to references cited in Geiser *et al.* (1986). (*a*) Sheldrick (1981), (*b*) Bukowska-Strzyzewska *et al.* (1985), (*c*) Scott & Willett (1988), (*d*) Willett & Rundle (1964), (*e*) Bond & Willett (1987), (*f*) Honda *et al.* (1985), (*g*) Grigereit *et al.* (1987), (*h*) Bond (1988), (*i*) Chang *et al.* (1973), (*j*) Wells (1947), (*k*) Thewalt (1980), (*l*) Klement (1969), (*m*) Barnes & Weakley (1977).

* Acronyms designate the counterion or coordinated ligand: MEL = melaminium, PUR = purinium, BENZ = benzylimidazole, EOA = ethanolammonium, ACET = acetonitrile, NMP = *N*-methylpyridinium, 4AP = 4-aminopyridinium, DBTTF = dibenzotetrathiafulvalene, MOR = morpholinium, NMPZ = *N*-methylpiperazinium, 3MAP = 3-methyl-2-aminopyridinium, NMPH = *N*-methylphenethylammonium, $TMSO_2$ = tetramethylenesulfone, TrMA, TeMA = tri-, tetramethylammonium, 4MAP = 4-methyl-2-aminopyridinium, SN = tetrasulfur tetranitride, DMNA = dimethylnitrosamine, DX = dioxane.

† Stacking patterns *a*, *b* and *c* refer to patterns analogous to diagrams (II*a*), (II*b*), and (II*c*), respectively. *L'* indicates the sixth coordination site of the Cu ion in the (II*c*)-type stacks is occupied by a ligand atom.

‡ Denotes three-dimensional ordering.

§ Errors account only for variations between values reported for each compound, and do not include errors associated with individual entries in the table.

included. These are stabilized in a planar conformation by semi-coordinate bonds to atoms on the counter ions or by steric effects (Scott *et al.,* 1988; Scott & Willett, 1988; Bukowska-Strzyzewska, Tosik, Głowiak & Wnek, 1985; Honda, Katayama, Tanaka & Tanaka, 1985; Sheldrick, 1981). Along with compounds containing simple $Cu_2Cl_6^{2-}$ species, one neutral $Cu_2Cl_4L_2$ ($L = CH_3CN$) species and two hydrated $Cu_2Cl_5(H_2O)^-$ species are included. A similar variation in structure type is seen in the trimeric systems, for which three $Cu_3Cl_8^{2-}$, one $Cu_3Cl_7L^-$ (L = EtOH) and two $Cu_3Cl_6L_2$ ($L = CH_3CN$, H_2O) species are known. Again, semi-coordinate bonds to other atoms stabilize the planarity of the two compounds which stack analogously to the type (II*c*) pattern. The tetramers are all of stoichiometry $Cu_4Cl_{10}^{2-}$. Since the structure of $CuCl_2$ has not been redetermined, its structural parameters are not accurately known. Hence, three compounds of the type $CuCl_2.L_n$ ($n = 1$ or $\frac{2}{3}$) have been included which contain symmetrically bibridged chains. For $L = S_4N_4$ (Thewalt, 1980) and $(CH_3)_2N_2O$ (Klement, 1969), the Cu ions retain a nearly square-planar primary coordination geometry. However, for $L = C_4H_8O_2$ (Barnes & Weakley, 1977), only one-third of the Cu ions remain free from a major distortion from a square-planar configuration. Finally, it is to be noted that an $n = 5$ system, $Cu_5Cl_{10}(C_3H_7OH)_2$, is known (Willett & Rundle, 1964). Since it is the only pentameric oligomer known, and the structural determination is of marginal quality by today's standards, it is not included in this analysis.

The analysis will concentrate on three aspects of the geometry. The first of these is the variation in the semi-coordinate bond lengths. The distorted octahedral geometry exhibited by copper(II) complexes is often described as a 4 + 2 geometry, where the second number denotes the number of semi-coordinate bonds. However, a 4 + 1 + 1 designation is frequently more appropriate, since considerable difference in the two semi-coordinate bond lengths is often observed. Next, the changes in the in-plane bond lengths as the length of the oligomer increases will be examined. Finally, the variations in the angular distortions within the individual $Cu_nCl_{2n}L_2$ oligomers will be examined, both with respect to the in-plane angles characterizing the coordination geometry, and to the bridging geometries. These structural parameters are summarized as part of Table 1.

Semi-coordinate bond lengths

Copper(II) complexes exhibit four, five and six coordination. The six-coordinate complexes are frequently characterized as having a 4 + 2 coordination geometry, while the five-coordinate species typically show an ill-defined 4 + 1 geometry which is neither square pyramidal nor trigonal bipyramidal. It is not surprising then, that the two semi-coordinate bond distances in many six-coordinate species have substantially different lengths, with a resulting 4 + 1 + 1 geometry. The minimum bond length normally observed for a semi-coordinate bond is conveniently estimated as the distance for which the semi-coordinate atom just makes van der Waals contact with the in-plane atoms. For chloride salts, this distance is approximately 2·8 Å when the Cl—Cu···Cl angle is 90°. In the planar $A_2Cu_nCl_{2n}L_2$ salts, the interoligomer spacing is largely determined by these Cl—Cl interactions between adjacent oligomers and is typically 2·90–3·05 Å. If the 4 + 2 geometry represents the minimum in potential energy for the distorted octahedral copper(II) chloride species, the oligomers should retain their planarity and the observed geometries should have two nearly equal semi-coordinate bonds of approximately 3·0 Å. On the other hand, if the potential energy surface is skewed towards the 4 + 1 geometry, or if the axial ligands are in substantially different environments, the oligomers should distort from planarity so as to shorten one semi-coordinate bond, yielding a predominance of the 4 + 1 + 1 geometries. Fig. 1 shows a plot of $\Delta = d' - d$, the difference in semi-coordinate bond lengths, *versus* d, the shorter of the two semi-coordinate lengths for those instances where two semi-coordinate Cu···Cl bonds exist to a given Cu^{II} ion. For the trimeric system, the central Cu atom frequently occupies a site of $\bar{1}$ symmetry, so that the value of Δ is required to be zero. A general trend is seen where Δ increases as the one semi-coordinate bond length decreases. Details of this relationship are different for dimers than for trimers and tetramers. Specifically, the magnitude of the slope of the correlation line is approximately unity for the trimeric and tetrameric systems, indicating that the interplanar spacing stays relatively constant in these, independent of the extent of the 4 + 1 + 1 distortion. For the dimeric

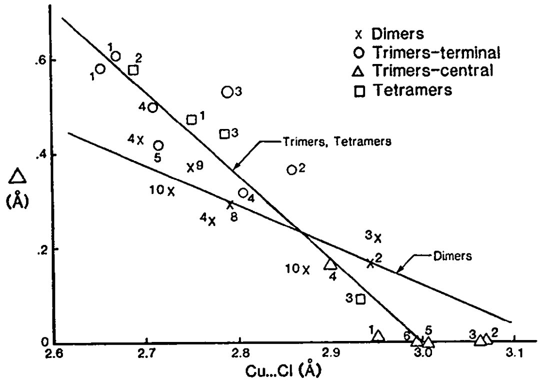

Fig. 1. Plot of the difference, Δ, between the two semi-coordinate Cu···Cl distances *versus* the shorter Cu···Cl distance for $Cu_nCl_{2n}L_2$ oligomers. The number by each data point corresponds to the place in which the oligomer occurs in its category in Table 1.

systems, on the other hand, the magnitude of the slope is less than unity, so that the dimers move closer together as the 4 + 1 + 1 distortion increases.

Variations in in-plane bond lengths

The in-plane Cu—Cl bond lengths depend strongly upon n and upon position within the oligomer, as shown by Fig. 2(*a*). The terminal non-bridging bonds (denoted by t) are short, and become shorter as the length of the oligomer increases. The bridging bonds (where the ith bridging bond, starting from the terminal Cu atom, is denoted by b_i) show remarkable variation with their position in the oligomer with a short–long–short··· alternation for the t—b_1—b_2··· sequence. This behavior can be rationalized from simple electrostatic arguments. In the hexagonal close-packed arrangement, the halide ions will tend to stay equidistant from each other, so that as the Cu ion moves closer to one pair of Cl ions, the distance to the other pair increases. Likewise, for the bridging halide ions, simple electrostatics again predict that as one Cu—Cl bond to one Cu ion shortens (strengthens), the bond to the other Cu ion should lengthen (weaken). Thus, the alternation propagates to the middle of the oligomer, but with decreasing amplitude. The average Cu—Cl distance for each type of oligomer agrees well with that observed in the infinite chain systems. It is also observed that the magnitude of the alternation increases as n increases, presumably because the two ends of the oligomers are further apart.

Angular distortions

The distortion of the primary coordination sphere from planarity is rather small in the systems included in this study. The smallest *trans* L—Cu—L angle (θ) is 162° and in a majority of the cases the distortion is square-pyramidal (*e.g.*, the Cu atom lies further 'above' the least-squares plane through the four basal ligands than any of the ligands) rather than tetrahedral. It is known both theoretically and experimentally (Hay, Thiebault & Hoffmann, 1975; Willett, Grigereit, Halvorson & Scott, 1987) that distortion of the θ angles from 180° causes a decrease in the antiferromagnetic coupling. However, it has been shown experimentally that the magnetic coupling is little affected by distortion in which the θ angles are greater than 165–170°. Since the observed variations in these angles do not correlate with the variations in magnetic coupling in the series of compounds under consideration, they will not be discussed further.

The variation in the angular distortion for the bridging geometry is quite small. However, there are systematic variations as n varies and it is known that the exchange coupling is extremely sensitive to the bridging Cu—L—Cu angle (Hatfield, 1985). In Fig. 2(*b*), the average value of φ_i, the ith Cu—Cl—Cu bridging angle, as well as α_i, where α_i is the lateral Cl—Cu—Cl bond angle, is plotted versus $1/n$. For the planar $n = \infty$ structure (anhydrous $CuCl_2$), $\varphi = \alpha$. Examining Fig. 2(*b*), it is observed that α_1 (the lateral angle for the terminal Cu atom in the oligomer) stays roughly constant at 91°. In contrast, the α_2 values are just under 93°. The φ_1 values show unusual behavior, with the value observed for the trimers being significantly smaller than the values observed for either the dimers or tetramers. However, as seen by the dashed line in Fig. 2(*a*), the sequence φ_1 ($n = 2$), φ_1 ($n = 3$), φ_2 ($n = 4$) of the innermost bridging angles extrapolates smoothly to the φ_∞ values of 93°. The reason for this behavior is readily understood. Since the terminal Cl ions are not restricted by intraoligomer bridging interactions, electrostatic repulsion forces the terminal Cl—Cu—Cl angles to be particularly large (~93–95°). The opposite (interior) Cl—Cu—Cl angles are consequently abnormally small, yielding the large φ_1 values.

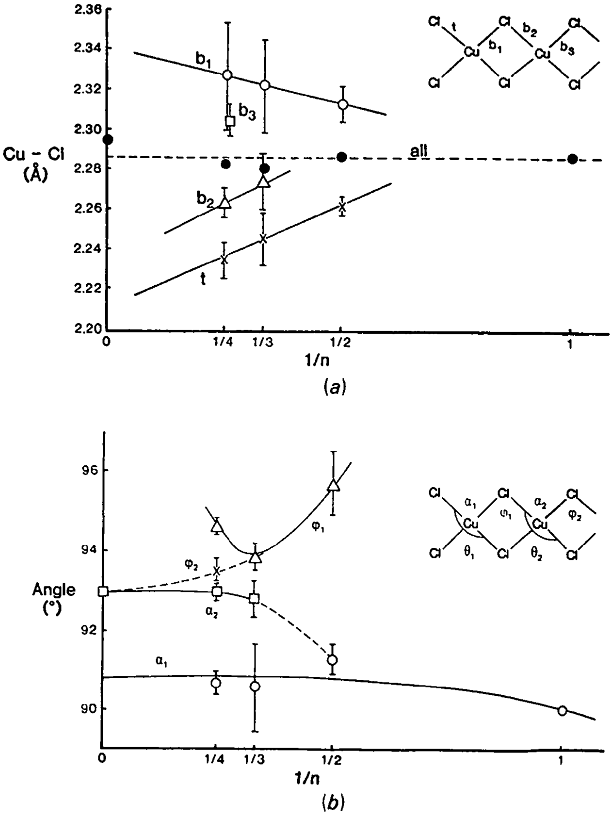

Fig. 2. (*a*) Plot of the average values for various types of Cu—Cl bond length *versus* $1/n$ for $Cu_nCl_{2n}L_2$ oligomers. t denotes terminal Cu—Cl distance; b_1 denotes first bridging Cu—Cl distance, b_2 denotes second bridging Cu—Cl distance, *etc.* The dotted line represents the average value for all Cu—Cl bonds in the oligomer. (*b*) Plot of average lateral Cl—Cu—Cl angles, α_i, and bridging Cu—Cl—Cu angles, φ_i, *versus* $1/n$ for $Cu_nCl_{2n}L_2$ oligomers. Solid lines represent the behavior of the outermost angles; the dashed lines represent the behavior of the innermost sets of angles.

Relation to magnetic properties

In Fig. 3, the plot of the average values of J/k *vs* n is given for the pseudo-planar stacked oligomers, where J_D and J_{Tr} are the coupling parameters for the dimers and trimers, J_{T_1} is the exchange coupling between Cu_1 and Cu_2, J_{T_2} between Cu_2 and Cu_3 in the tetramers, and J_∞ is the coupling observed in anhydrous $CuCl_2$. Here the J values are determined by the isotropic nearest-neighbor spin Hamiltonian with $J < 0$

$$\mathscr{H} = -2 \sum_{i=1}^{n-1} J_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$$

corresponding to antiferromagnetic coupling. For the dimer system, this leads to a singlet–triplet separation of $2J$ which is found to be antiferromagnetic for the pseudo-planar dimers. Unfortunately, the J_{T_2} value for $n=4$ cannot be determined accurately from susceptibility measurements since the large value for J_{T_1} effectively couples the end pairs of Cu^{II} ions into ground-state singlets. The values of J_D and J_{Tr} have been found experimentally to be approximately equal, but both $|J_{T_1}|$ and $|J_\infty|$ are approximately twice as large as $|J_D|$ and $|J_{Tr}|$. Within the dimeric subsystem, deviations from planarity cause J to become less negative and eventually change sign (Willett, 1985). The isolated planar dimers, on the other hand, have stronger antiferromagnetic coupling. The bromide salts show a very similar sequence of values for the oligomers with $J_D/k \simeq -90$ K, $J_{Tr}/k \simeq -100$ K, $J_{T_1}/k \simeq -180$ K, J_{T_2}/k ($n=4$) $\simeq -140$ K and $J_\infty/k \approx -165$ K (Rubenacker, Drumheller, Emerson & Willett, 1986), and similar distortions from planarity within the dimeric system (Scott & Willett, 1988).

In order to understand these trends, it is pertinent to examine the effect which specific structural parameters will have upon the value of the exchange interaction. In the usual semi-empirical treatments, J is broken down into two terms, J_F and J_{AF}, which represent the ferromagnetic and antiferromagnetic contributions respectively (Hay *et al.*, 1975; Kahn & Briat, 1976). Crudely, J_F is given by the normal quantum mechanical exchange integral and is usually assumed to be independent of small perturbations in geometry (such as are being discussed in this context). In the Hoffmann formalism, J_{AF} is proportional to $(\varepsilon_s - \varepsilon_a)^2$ where ε_s and ε_a are the energies of the symmetric and antisymmetric combination of magnetic orbitals, while in the Kahn approach, J_{AF} is proportional to the overlap integral between those orbitals. In this latter approach, which is a simple extension of Hund's rules, orthogonality will lead to ferromagnetic behavior and increased overlap will cause an increase in the magnitude of J_{AF}. These arguments, supported by experimental observations, allow the following conclusions to be drawn.

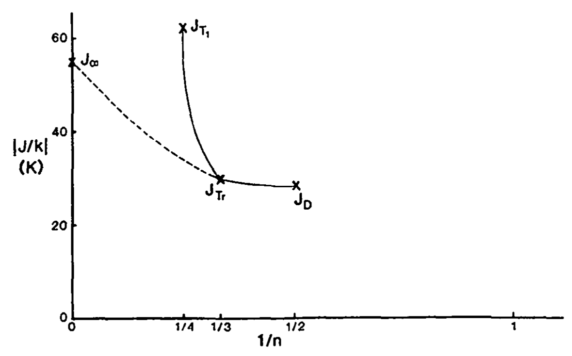

Fig. 3. Plot of average $|J/k|$ values *versus* $1/n$ for $Cu_nCl_{2n}L_2$ oligomers. The solid line represents the trends for the outermost pairs of copper ions; the dashed line for the innermost pairs.

(i) J_{AF} increases as the bridging Cu—Cl—Cu angle increases in the range 90–100° (Hatfield, 1985; Broer & Maaskant, 1986). This follows directly from the overlap arguments, since the primary exchange pathway is through the p_σ orbitals on the chloride ions.

(ii) J_{AF} increases as the bridging Cu—Cl distance decreases. This follows because a shorter distance will lead to greater delocalization of the magnetic electron onto the chloride ions, and thus to a greater overlap. This effect is clearly seen in the magnetic data for $KCuCl_3$ (planar, stacked) *versus* (DBTTF)$CuCl_3$ (planar, isolated). Both have long semicoordinate bonds (Cu···Cl = 2·941 and 3·113 Å for K, Cu···S = 3·276 Å for DBTTF) and nearly identical bridging angles (96·0° for K, 96·2° for DBTTF). The shortening of the bridging Cu—Cl distance (2·314 Å for K, 2·297 Å for DBTTF) leads to an increase of $-J_1/k$ from 27 to 55 K.

(iii) J_{AF} increases as the semi-coordinate distances increase. An increase in the semi-coordinate distance is associated with a decrease in the EPR g values, which implies an increased delocalization of the unpaired electron into the in-plane chloride orbitals (Chang, Wong & Willett, 1973); yielding increased overlap and a larger contribution to J_{AF}. This is not wholly independent of (ii), since it will also cause a change in the average Cu—Cl bond length.

(iv) J_{AF} decreases as the coordination geometry distorts from square planar. These distortions cause the ligands to move away from the ideal orientation for interaction with the unpaired electron in the $d_{x^2-y^2}$-type orbital. Delocalization, and hence overlap, decreases. This effect has been observed for several types of distortions (Willett, 1985) and helps explain the weaker exchange coupling in the ethanolammonium dimer as compared to $KCuCl_3$.

(v) J_{AF} decreases as the bond lengths opposite the bridging atoms shorten. This causes more of the electron density to be localized onto the nonbridging chloride ions thereby lowering electron density on the bridging chloride ions. Again, this effect is not independent of (ii), since shortening of one type of bond will induce a lengthening of the bond *trans* to it.

It is now possible to look qualitatively at the effect that changes in these various parameters will have on the values of J. Items (i) and (ii) will have the most pronounced effect; (iii) and (v) will have a lesser influence, while the influences related to (iv) show no systematic variations between oligomer types. In Fig. 4, a plot of the average value of the various parameters involved in (i), (ii), (iii) and (v) is shown, with the vertical direction representing (on an arbitrary scale) increasing antiferromagnetic contribution to the exchange. It can be seen from this that for the dimers, the bridging angles give the strongest contribution to J_{AF}, while the bridging bond distances give the weakest contribution. Conversely, the situation is just reversed for the infinite chain. From the order of these two dominant contributions, (i) and (ii), shown in Fig. 4, the following order of exchange coupling is predicted: $|J_{T_1}| > |J_{Tr}| \sim |J_\infty| > |J_D| > |J_{T_2}|$. This corresponds relatively well with the experimental observations (Fig. 3), except for the interchange of positions of J_{Tr} and J_∞. When the other two contributions, the axial Cu···Cl distances and the non-bridging Cu—Cl distances, are examined, it is seen that both favor an increased antiferromagnetic contribution to J_∞. It also gives some slight enhancement of J_D relative to J_{Tr}. Thus, a final ordering of $|J_{T_1}| > |J_\infty| > |J_{Tr}| \sim |J_D| > |J_{T_2}|$ seems reasonable on the basis of this qualitative analysis.

Concluding remarks

Systematic trends in interatomic distances and angles are observed within and between various $Cu_nCl_{2n}L_2$ oligomers. These variations can be correlated with the unusual behavior of exchange parameters in this series of compounds. The most noticeable variation in the structural parameters is the alternation in the length of the Cu—Cl distances in the oligomers. This is caused by a *trans* effect induced by the short terminal Cu—Cl distances. The magnitude of alternation observed at the ends of the oligomers increases as n increases, but decreases towards the middle of the oligomers. Associated with these changes in distances are non-regular variations in bridging Cu—Cl—Cu angles. A comparison with the magnetic exchange coupling in these systems shows that the major variations can be accounted for by changes in bridging angles and bridging bond distances. Lesser influences of the semi-coordinate and non-bridging bond lengths must be included to obtain the best correlation with the observed magnetic behavior.

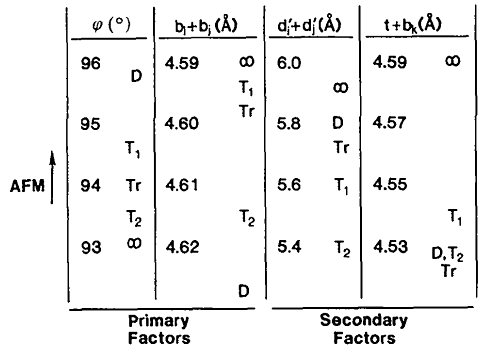

Fig. 4. Schematic plot of J_{AF} for various structural parameters for $Cu_nCl_{2n}L_2$ oligomers. Exchange pathways are defined in Fig. 3.

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