Magnetochemistry of copper(II)

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Abstract. A selective review of some recent studies of the magnetic properties of
compounds containing the spin $S = \frac{1}{2}$ copper(II) ion is presented. The emphasis lies with
those compounds in which indirect exchange interactions are important. There is much
variety, for there are dimers and clusters with either antiferromagnetic or ferromagnetic
interactions, both uniform and alternating linear chains, two-dimensional or planar
systems, and finally, some substances which exhibit predominantly three-dimensional
interactions. In addition, recent *ab initio* and model calculations of indirect (super-)
exchange interactions, responsible for the observed magnetic behavior, are discussed.

1. Introduction

The paramagnetic properties of monomeric compounds of copper(II) are straight-
forward. This is due in large part to the fact that copper has but one unpaired
electron irrespective of the local geometry and therefore always has spin $S = \frac{1}{2}$.
The ground state in an octahedral complex is ^2E_g; the orbital degeneracy of the
ground state is usually resolved by the Jahn-Teller effect. The g-values are often
anisotropic, but are always of the order of 2·1 to 2·2; the effective magnetic
moments are in the range 1·75–2·20 μ_B, where μ_B is the Bohr magneton. The
moments are independent of temperature in the absence of cooperative effects.
The epr spectra of more copper compounds than those of any other metal ion have
been reported. Spin-orbit coupling is strong with copper, which is the source of the
increase in the g-values above 2, yet the result of this effect is not nearly as dramatic
as that with several other iron series ions. These properties stand in striking
contrast to those of nickel(II), for example, whose planar compounds are
diamagnetic and whose octahedral compounds are affected, at low temperatures,
by zero-field splitting effects (Carlin and van Duyneveldt 1977; McGarvey 1966;
O'Connor 1982; Bencini and Gatteschi 1982; Carlin 1986). Similarly, octahedral
cobalt generally has g-values which are quite anisotropic, while the magneto-
chemistry of tetrahedral cobalt(II) is determined by the zero-field splitting of the
$^4A_2$ state (Carlin 1985).

Perhaps the most notable feature of copper(II) chemistry and physics is the fact
that this ion, with a doubly-degenerate electronic ground state, is susceptible to the
Jahn-Teller effect. The coordination sphere is therefore generally distorted. In

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some cases, the coordination sphere is close to octahedral at room temperature, and the distortion becomes important only as the temperature is lowered. This is often accompanied by a structural or lattice dynamical phase transition (Reinen and Friebel 1979).

Although many copper compounds exhibit such structural distortions, they nevertheless display relatively little magnetic anisotropy. In general, such anisotropy is due only to g-value anisotropy, which is typically about 5 or 10%. This leads copper, then, to be second only to manganese(II) in providing magnetically ordered compounds with only weak anisotropy (de Jongh and Miedema 1974). Such systems are found to follow what is called the Heisenberg magnetic model, which is defined below.

Another feature of copper magnetochemistry is the high tendency the ion exhibits for ferromagnetic interactions. The series of compounds $A_2CuX_4.2H_2O$. where A is an alkali metal ion or ammonium ion, and X is chloride or bromide, is one of the best-known series of ferromagnetic insulators (de Jongh and Miedema 1974). Ferromagnetic interactions predominate in such diverse materials as $[(CH_3)_3NH]CuCl_3.2H_2O$ (Algra *et al* 1977), $CuCl_2.DMSO$ (Swank *et al* 1979), and $(C_2H_5NH_3)_2CuCl_4$ (Steijger *et al* 1984).

Copper also has a tendency to form compounds in which there are two or more metal ions near one another. These polynuclear compounds often exhibit strong magnetic interactions between the copper ions, and the study of these has contributed greatly to our understanding of such magnetic exchange interactions. Furthermore, another important feature of the structural chemistry of copper is that compounds of different lattice dimensionalities are so readily available. The different behaviors, depending on this dimensionality, is one of the major themes of this article. This brief paper will review some of the recent theoretical and experimental work that is of interest in this area of magnetochemistry. The compounds discussed· here are recently studied examples which are chosen to illustrate the varied physical phenomena.

Paramagnetic behavior is described by the Curie law, which is the magnetic analog of the ideal gas law. The magnetic susceptibility χ, which is a measure of the response of a material to an applied magnetic field, varies inversely with temperature according to the Curie law. This may be written as $\chi = C/T$, where C is called the Curie constant; in the common case of spin-only magnetism. $C = Ng^2\mu_B^2S(S+1)/3k_B$, where N is Avogardro's number, S is the spin quantum number and k_B is the Boltzmann constant. Deviations from the Curie law are found as the temperature is decreased sufficiently for the magnetic ions to begin to interact with one another. This is described in a high-temperature approximation by the Curie-Weiss law, $\chi = C/(T{-}^\prime\theta)$ where the non-zero θ indicates that such interactions are present. This is a molecular field approximation; as we shall see, more detailed models at the molecular level are available.

2. Dimers and clusters

The properties of hydrated copper acetate, $[Cu(OAc)_2(H_2O)]_2$, are well-known (O'Connor 1982; Carlin 1986) and illustrate many of the important concepts about magnetic interactions in copper compounds. The basic ideas concerning this

substance were worked out by Bleaney and Bowers (1952), and the model that they developed now goes by their names. The facts are that the susceptibility of copper acetate increases as the temperature is decreased from room temperature, goes through a maximum at about 255 K, and then decreases towards zero as the temperature is lowered further. This can be explained if $[Cu(OAc)_2(H_2O)]_2$ is actually a dimer and the metal ions are close enough together to interact with one another via the superexchange path provided by the bridging acetate ions. This exchange interaction between the two spin-½ ions results in a ground state with total spin $S = 0$ and an excited state with total spin $S = 1$. The interaction operator used to describe formally this type of interaction is the Heisenberg-Dirac-Van Vleck hamiltonian

$$H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \qquad (1)$$

in which $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin operators of the interacting ions and J is called the exchange constant. The energy separation $E(S = 1) - E(S = 0)$ is $-2J/k_B$, in energy units, and corresponds in $[Cu(OAc)_2 \cdot (H_2O)]_2$ to some 429 K. The negative value of the exchange constant indicates that the spin-singlet is the lower state (antiferromagnetic exchange coupling). If the exchange constant J has a positive sign, $S = 1$ level is lower, and this situation is called ferromagnetic exchange interaction. The susceptibility which arises from (1) is found as

$$\chi = \frac{2Ng^2\mu_B^2}{3k_BT} \cdot \frac{1}{1 + \frac{1}{3}\exp(-2J/k_BT)}. \qquad (2)$$

This relationship fits the experimental data excellently.

After the success of this analysis by Bleaney and Bowers, dozens, if not hundreds, of other copper dimers have been found which are well-described by (2). The vast majority have been shown to exhibit a negative exchange constant. A number of examples and literature references are provided by O'Connor (1982) and Carlin (1986).

The question arises then whether compounds can be found with a positive exchange constant, that is, with ferromagnetic intrapair interaction. The problem, as sample calculations with the Bleaney-Bowers equation quickly show, is that the susceptibility curve is then featureless and simply rises rapidly in Curie-Weiss fashion with decreasing temperature. Very accurate data and careful data analysis are required in order to prove that one has a half-mol of $S = 1$ dimers rather than a mol of $S = $ ½ ions (Carlin 1986). Two compounds which were thought to have $S = 1$ ground states are $[Cu(S_2CNEt_2)_2]$ and $[Cu(C_5H_5NO)_2(NO_3)_2]$. Both materials contain dimers in the crystal structure, but a comparison with the susceptibility of that of simpler salts, such as the Tutton salts, showed indeed that neither such compound exhibited strong pairwise ferromagnetic interactions (van Duyneveldt *et al* 1976; van Santen *et al* 1980; Carlin *et al* 1983).

In the case of $[Cu(S_2CNEt_2)_2]$, the data suggest the existence of an intra-pair ferromagnetic interaction of 0·9 K, and a weak antiferromagnetic interaction of $-0\cdot007$ K between the pairs. This is in contrast to the pairwise ferromagnetic interaction of 34·5 K reported earlier (McGregor *et al* 1973a,b). Similarly, in the case of $[Cu(C_5H_5NO)_2(NO_3)_2]$, the Curie-Weiss law was found to be obeyed at temperatures above 2 K and the data could be analysed in terms of non-interacting $S = $ ½ copper ions (Carlin *et al* 1983). Any exchange interaction begins to manifest

itself only at temperatures of about $1 \cdot 2$ K. These data cannot be analysed in terms of the previously-reported ferromagnetic intra-pair interaction of about 14 K (McGregor *et al* 1973a,b).

A weak ($0 \cdot 22$ K) ferromagnetic interaction has been found (Benelli *et al* 1985a) between the pairs of metal ions in *bis*-[(adenosine 5'-triphosphato) (2,2'-bipyridine) copper(II)] tetrahydrate. The metal atoms are held together by two O–P–O bridges from the α-phosphates of two ATP moieties. A determined effort to synthesize a variety of ferromagnetically ordered dimers has been carried out by Kahn and co-workers (Kahn *et al* 1983; Kahn 1985a,b).

Numerous efforts are still in progress to prepare and characterize copper dimers with spin $S = 1$ ground states. A curious situation arises when azide, N_3^-, is the bridging ligand, for it can bind in two ways (Kahn *et al* 1983; Sikorav *et al* 1984; Kahn 1985a,b). When the binuclear unit is of the form (chart 1)
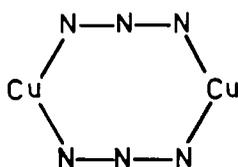
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        N — N — N
       /          \
     Cu            Cu
       \          /
        N — N — N
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Chart 1

antiferromagnetic interaction is found. However, a compound with the different kind of binding (chart 2),

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         OH
        /    \
     Cu        Cu
        \    /
          N
          |
          N
          |
          N
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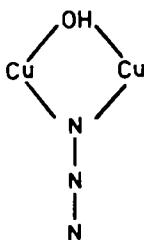
Chart 2.

has been suggested to exhibit a strong, intradimer ferromagnetic interaction. Cairns and Busch (1986) have recently reviewed ferromagnetic interactions in polynuclear complexes.

The range of possibilities offered by inorganic chemistry is emphasized by the recent studies on several bimetallic compounds of another kind (Bencini *et al* 1985; Bencini *et al* 1986; Vaziri and Carlin 1986). The lanthanides form few covalent bonds and there are few lanthanide compounds in which superexchange interactions are important. The unusual bimetallic materials contain a central gadolinium ion coordinated to two tetradentate Schiff bases of copper. The synthesis of such materials is straightforward, and the interesting point was the demonstration of the fact that the Gd-Cu exchange interaction is as large as 7 cm^{-1} (10 K) in strength and ferromagnetic in sign.

3. Magnetic linear chains

The magnetochemistry of copper(II) is an active field of research, with much of the attention centered on linear chain systems. By this, we mean substances whose magnetic interactions occur primarily in one dimension. These systems display extensive short-range order in the paramagnetic region. Before describing some of these materials, it will be useful to summarize several of the results due to Bonner and Fisher (1964).

The calculations of Bonner and Fisher are used frequently. Their model is the Heisenberg or isotropic antiferromagnetic linear chain; the Hamiltonian, a generalization of (1) is

$$H = -2J \sum_{i<j} \mathbf{S}_i \cdot \mathbf{S}_j \tag{3}$$

where the summation extends over all nearest-neighbor ions i and j in the chain. The authors calculated the behavior of both the zerofield susceptibility and the magnetic specific heat. A broad maximum is found in both; the susceptibility (in reduced units) is displayed in figure 1, over the range of validity of the calculation. Bonner and Fisher find that

$$k_B T_{max}/|J| \approx 1.282, \tag{4}$$

and

$$\chi_{max}|J|/Ng^2\mu_B^2 = 0.07346, \tag{5}$$

for the pure Heisenberg (isotropic) model, where χ_{max} is the maximum value of the susceptibility, at temperature T_{max}.

Copper forms many-chained compounds, some of them antiferromagnetic such as Cs_2CuCl_4, and some of them ferromagnetic, as in $[(CH_3)_3NH]CuCl_3.2H_2O$ (Losee et al 1972). Ferromagnetic linear-chain systems have recently been reviewed (Willett et al 1983).
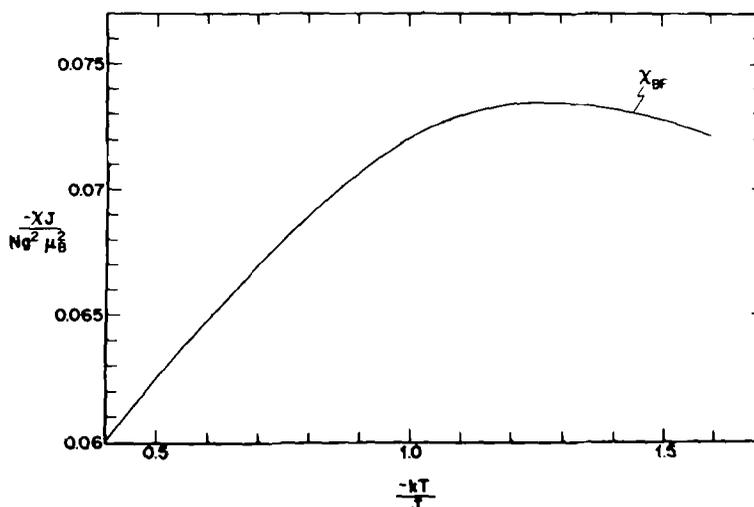

Figure 1. The calculated Bonner-Fisher susceptibility behavior, in reduced units.

The first example of a ferromagnetic spin $S = \frac{1}{2}$, Heisenberg linear chain was provided by $[(CH_3)_3NH]CuCl_3.2H_2O$ (Algra *et al* 1977). The material contains planar $CuCl_2(H_2O)_2$ ions which stack as an asymmetrical bibridged linear chain (Losee *et al* 1972). The water molecules lie above and below the plane defined by the $(CuCl_2)_n$ repeating units. Adjacent chains are hydrogen-bonded into sheets by an uncoordinated chloride ion, and then these sheets are separated by the bulky trimethylammonium ions.

The specific heat, figure 2, displays a broad maximum, characteristic of a system with extensive short-range order, and then a sharp peak at $T_c = 0.165$ K. This is the temperature of a phase transition from short-range order to long-range order. Only 28% of the magnetic entropy change occurs below T_c. The data cannot be analyzed simply in terms of a one-dimensional system; curve a) in the figure represents the specific heat of a ferromagnetic linear chain and does not fit the data below 1 K. The two-dimensional Heisenberg prediction, curve b), does not fit either. The observed values do lie between the two curves, however, indicating substantial interchain coupling. A 10% Ising-like anisotropy, curve c), causes the specific heat to rise again at lower temperatures. The data furthermore show the effects of lattice-dimensionality crossover: for $T > 1$ K, one-dimensional behavior is observed; two-dimensional behavior is found between 0.2 and 1 K. Finally, three-dimensional ordering behavior is seen below 0.2 K. The reanalysis of the susceptibility data (Algra *et al* 1977) is consistent with this analysis.

There are several linear chain systems which do not contain ligands bridging the metal ions in the usual fashion. One of these is CTN, $[Cu(NH_3)_4](NO_3)_2$, which contains discrete, planar $[Cu(NH_3)_4]^{2+}$ units (Bhatia *et al* 1977) and another is Cs_2CuCl_4 (Carlin *et al* 1985). In the case of CTN, susceptibility maxima are found near 5 K, figure 3. Note the lack of anisotropy (except for that due to the different g-values) among the three data sets. The specific heat yields a maximum in the same temperature region, and then a small anomaly, due to long range ordering, which occurs at $T_c = 0.15$ K. Both sets of data may be fit by the model of Bonner and Fisher, and yield an antiferromagnetic exchange constant of $J/k_B = -3.9$ K. The values of T_c and J/k_B are compared in table 1 with those reported for several other copper chain compounds. One sees that $[Cu(NH_3)_4](NO_3)_2$ is one of the

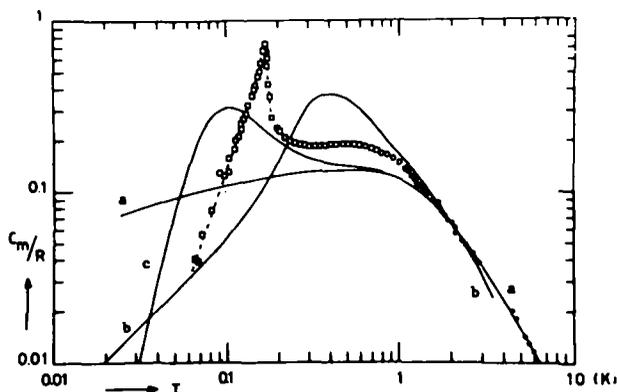**Figure 2.** The magnetic specific heat of $[(CH_3)_3NH]CuCl_3.2H_2O$ vs temperature, on a double logarithmic scale. The several curves are described in the text. From Algra *et al* (1977).
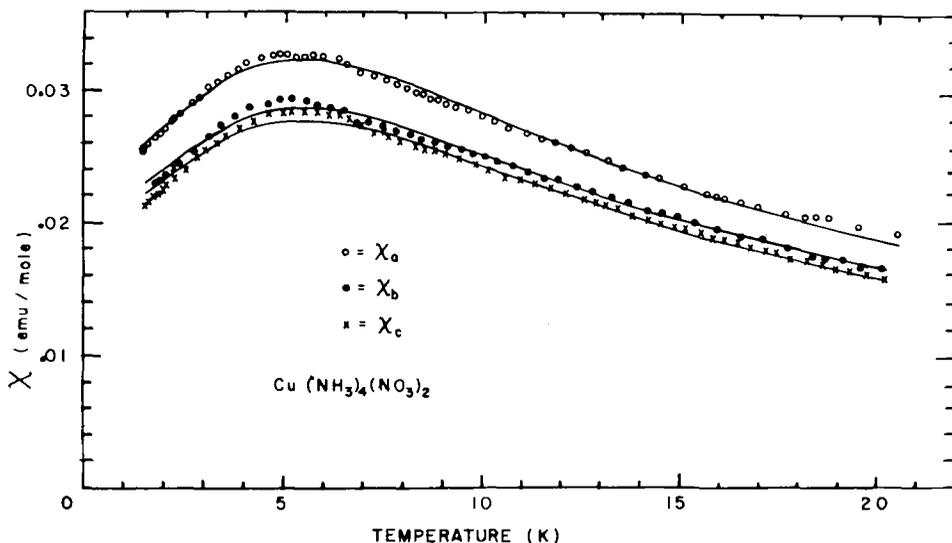
Figure 3. The three orthogonal susceptibilities of $[Cu(NH_3)_4](NO_3)_2$, along with the best fits to the theory of Bonner and Fisher. From Bhatia *et al* (1977).

Table 1. Exchange parameters for some linear chain magnets.*

	$T_c(K)$	$-J/k_B(K)$	$k_B T_c/|J|$
$Cu(NH_3)_4SO_4 \cdot H_2O$	0.43	3.15	0.137
$CuCl_2 \cdot 2C_5H_5N$	1.13	13.4	0.084
$[Cu(NH_3)_4](NO_3)_2$	0.15	3.9	0.038
$[Cu(pyrazine)(NO_3)_2]$	<0.05	5.20	<0.01
$[Cu(C_5H_5NO)_6](ClO_4)_2$	0.142	1.02	0.193
TMMC	0.85	6.5	0.130

* All compounds are spin $S = \frac{1}{2}$ except for TMMC, which has $S = \frac{5}{2}$. Data are from Bhatia *et al* (1977) and Mennenga *et al* (1984).

more ideal one-dimensional antiferromagnets with spin value $S = \frac{1}{2}$. To compare with examples of other S, for example with the well-known TMMC, $[(CH_3)_4]MnCl_3$, we look at the quantity $t_c \equiv k_B T_c/|J|S(S+1)$, finding $t_c = 0.026$ for $[Cu(NH_3)_4](NO_3)_2$ and $t_c = 0.015$ for TMMC ($S = \frac{5}{2}$). Thus the copper compound is only slightly inferior in approximating the ideal one-dimensional structure.

There has recently been a study (Carlin *et al* 1985) of Cs_2CuCl_4, in which antiferromagnetic interactions occur over a relatively long superexchange path. The crystal structure is built up by the packing of discrete $CuCl_4^{2-}$ anions and cesium ions; the anion is distorted, in that coordination around the metal is intermediate between square planar and tetrahedral. The compound is isomorphous with Cs_2CoCl_4, a substance whose magnetic properties have been extensively investigated (McElearney *et al* 1977; Algra *et al* 1976; Duxbury *et al* 1981). Linear chain antiferromagnetic interactions have been found to predominate in Cs_2CoCl_4, and they also dominate the magnetic ordering behavior of Cs_2CuCl_4. An extensive

discussion of the exchange paths in Cs_2CoCl_4 and a rationalization of the linear chain character has been presented (McElearney *et al* 1977). The copper analog is found to behave somewhat similarly. The low-temperature susceptibility data on polycrystalline samples exhibit the broad maximum diagnostic of lower-dimensional antiferromagnetism.

The data above 10 K may be fit by the Curie-Weiss law for spin $S = \frac{1}{2}$, with $\langle g \rangle = 2\cdot20$ and $\theta = -5$ K. The data then go through a broad maximum, with $\chi_{max} \simeq 0\cdot0665$ emu/mol at $T_{max} \simeq 2\cdot6-2\cdot7$ K. The data were fitted to the calculations of Bonner and Fisher and gave a good fit with but one parameter, $-J/k_B = 2$ K.

The straightforward Bonner-Fisher procedure for the analysis of these data was also modified in terms of a molecular-field correction to this theory (McElearney *et al* 1973). That is,

$$\chi' = \frac{\chi_{BF}}{1-(2zJ'/Ng^2\mu_B^2)\chi_{BF}} \tag{6}$$

Where χ_{BF} is the Bonner-Fisher calculation and χ' is the measured susceptibility. An adequate fit could be obtained with $J/k_B = -2\cdot0$ K, and a molecular field correction of $zJ'/k_B = -0\cdot10$ K. The molecular field correction is barely statistically significant. One of the major questions that remains in magnetochemistry research is the discovery of the empirical factors which determine whether the magnetic interactions will be antiferromagnetic or ferromagnetic in sign. The theoretical treatments of copper systems usually deal with metal ions which are μ-bridged by ligands, such as in a
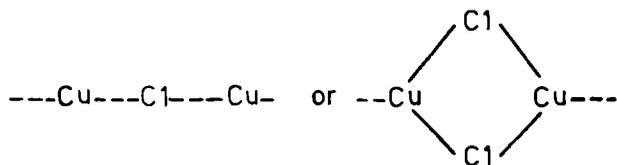
$$---Cu---Cl---Cu- \quad \text{or} \quad --Cu \underset{\displaystyle \diagdown Cl \diagup}{\overset{\displaystyle \diagup Cl \diagdown}{}} Cu---$$

moiety. The apparent interaction in Cs_2CuCl_4 is of the form Cu–Cl---Cl–Cu, of which there seem to be no previous examples in linear chain systems. There are however some two-dimensional systems with this configuration; they will be discussed below. The exchange interaction is remarkably strong for this lengthy superexchange path, as it also is for the two-dimensional systems.

There is an extensive series of compounds formed between the divalent iron series ions and pyridine N-oxide. A comprehensive review is available elsewhere (Carlin and de Jongh 1986). At room temperature all the compounds, including both $[Cu(C_5H_5NO)_6](ClO_4)_2$ and $[Cu(C_5H_5NO)_6](BF_4)_2$, are rhombohedral with one molecule in the unit cell. The coordination spheres are strictly octahedral but the magnetic behavior of the $[Cu(C_5H_5NO)_6]X_2$ compounds is controlled, at low temperatures, by the cooperative Jahn-Teller effect. The ligand C_5H_5NO is pyridine N-oxide, and X is either perchlorate, fluoborate or nitrate.

The magnetic specific heat of $[Cu(C_5H_5NO)_6](ClO_4)_2$, shown in figure 4, is found to be excellently described by the Bonner-Fisher prediction for a $S = \frac{1}{2}$
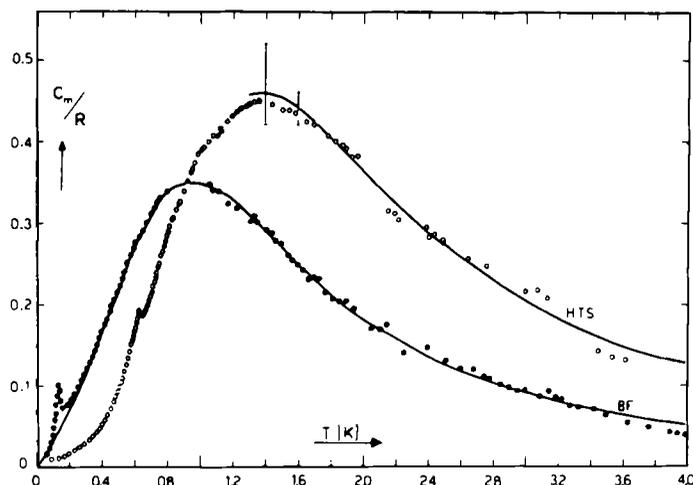
Figure 4. The magnetic specific heats for $[Cu(C_5H_5NO)_6](ClO_4)_2$ and $[Cu(C_5H_5NO)_6](BF_4)_2$ (● and ○, respectively). Curve B-F is the Bonner-Fisher (1964) prediction for a linear chain antiferromagnet with $J/k_B = -1.02$ K; curve H.T.S. is the prediction from the high-temperature series for the quadratic-layer antiferromagnet with $J/k_B = -1.10$ K. From Algra *et al* (1978a,b).

antiferromagnetic Heisenberg chain (Algra *et al* 1978a,b). The fit yields the intrachain exchange constant $J/k_B = -1.02$ K. Below $T \simeq 0.3$ K deviations from the chain prediction are seen, which are ascribed to the weaker interchain interactions, leading to the onset of long-range order at $T_c = 0.142$ K. Below T_c, the experimental specific heat is found to be well represented by the sum of a T^3 dependence and the T^{-2} dependence arising from the hyperfine interactions. As regards the T^3 term, such a steep fall of the specific heat below T_c is usually observed in quasilinear chain compounds (de Jongh and Miedema 1974). Measurements (Reinen and Krause 1979) of the epr spectrum of the material confirmed this analysis. The epr spectra of these systems have yielded a great deal of information regarding the Jahn-Teller phenomena.

The substances Cs_2CuCl_4, $[Cu(NH_3)_4](NO_3)_2$, $[Cu(C_5H_5NO)_6](ClO_4)_2$ and $K_2Pb[Cu(NO_2)_6]$ (Blöte 1979) all exhibit (quasi-) linear chain antiferromagnetism and the copper atom is found in a discrete (non-bridging) polyhedron. Indeed, of the four substances listed, the first contains distorted tetrahedra, the second planar coordination units, and distorted octahedra are found with the last two. None of the crystal structures are related nor are any of the structural details, such as the superexchange paths. The crystal lattices of both the pyridine N-oxide and nitro complexes have high symmetry at room temperature, but both undergo cooperative Jahn-Teller distortions as they cool. The one constant feature exhibited by this varied group of copper compounds is the existence of antiferromagnetic linear chain interactions.

The systems described above may be considered as uniform linear chains, in that the exchange constant between each metal ion in the chain has the same value. The subject of alternating linear chains has recently (de Groot *et al* 1982) become of interest, where the system is described by the Hamiltonian

$$H = -2J \sum_i (S_i \cdot S_{i-1} + \alpha S_i \cdot S_{i+1})$$

(7)

The parameter α has the limiting values of 1 for a uniform chain and zero for a dimer, and $0 < \alpha < 1$ for an alternating chain. Thus the value of the exchange interaction between two metal ions depends on their location in the chain. The susceptibility behavior for an alternating chain is found to lie between that of the two extremes.

An example of such a material is provided (Benelli *et al* 1985b) by the adduct between the hexafluoroacetylacetonate of copper and the nitroxide, 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-N-oxy. The compound is called $Cu(hfac)_2.TEMPOL$. A sketch of the repeating unit in the structure is shown in figure 5. There is a strong (19 K) ferromagnetic interaction between the copper ion and the nitroxide, evident in the data taken above 4·2 K, and the susceptibility rises rapidly as the temperature is lowered below 1 K. Then a broad maximum, characteristic of an antiferromagnetic linear chain, is found at about 80 mK, figure 6. These data have been analysed in terms of a spin $S = 1$ linear chain, with a weak $(2J/k_B = -78$ mK) antiferromagnetic interaction between the spin-1 units. That is, the alternating character is obtained by repeating strong ferromagnetic and weak antiferromagnetic interaction. Similar results were also obtained from magnetization data on (4-benzylpiperidinium)$CuCl_3$ (de Groot *et al* 1982).
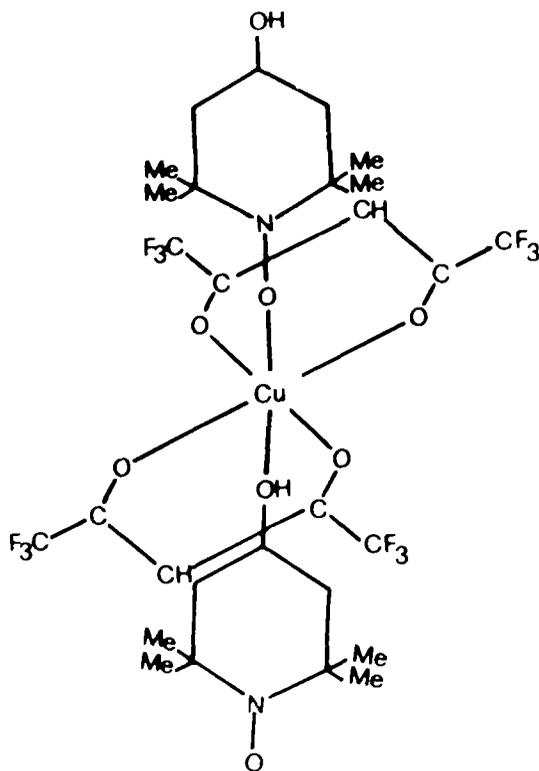
Figure 5. The repeating structural unit (schematic) of the Cu(hfac)2. TEMPOL chain. From Benelli *et al* (1985b).

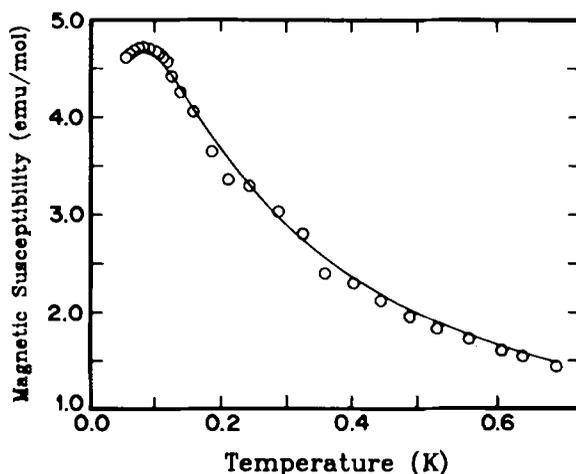**Figure 6.** The low-temperature susceptibility data of Cu(hfac)₂. TEMPOL, along with the fit described in the text. Note that the origin is off-set. From Benelli *et al* (1985b).

Another linear chain compound that has recently been studied (Mennenga *et al* 1984) is [Cu(pyrazine)(NO₃)₂], which contains copper ions bridged by the pyrazine rings. The aromatic ring appears to provide a substantial superexchange path. Broad maxima are evident near 5 K in both the susceptibility and the specific heat; the data may be fit by the Bonner-Fisher model with $J/k_B = -5\cdot20$ K. Long range order is not observed above 50 mK, so that this material provides one of the best examples of a magnetic linear chain. The quantity t_c is less than $0\cdot013$ for [Cu(pyrazine)(NO₃)₂], which means that this compound is comparable to or even superior in approximating the ideal one-dimensional structure than the archetypal 1-*d* compound, TMMC.

Another feature of this material is that it exhibits evidence of random exchange effects. These are superimposed upon the behavior of the uniform Heisenberg linear chain and appear in the form of a strong increase in the susceptibility at low temperatures which is characteristic neither of the linear chain nor of a Curie-like impurity. The random exchange behavior is attributed to lattice defects, such as chain segments of finite size. Among these will be chain segments with an odd number of spins; in the present case, it was argued that the data could be explained if the chains consisted of about 200 copper spins on the average. The model is only applicable to the low temperature data.

The related series of compounds [CuCl₂(pyridine)₂], [CuCl₂(3-methylpyridine)₂], and [CuCl₂(4-methylpyridine)₂] have also been investigated (Wolthuis *et al* 1985). The room temperature structure in each case consists of chains of copper ions bridged by halide. The parent material, [CuCl₂(pyridine)₂], behaves as a uniform antiferromagnetic Bonner-Fisher chain with exchange constant $J/k_B = -13\cdot4$ K, while the 4-picoline adduct behaves as an alternating chain with $J/k_B = -13\cdot6$ K and an alternation parameter, α, of $0\cdot6$. The difference between the two compounds appears to arise from a freezing of methyl-group rotations in [CuCl₂(4-methylpyridine)₂] near 75 K which causes a dimerizing transition; this is evidenced by a sharp increase in dielectric permittivity at that

temperature. No such transition occurs with the 3-picoline adduct either, which is also a uniform Heisenberg magnetic chain with $J/k_B = -12.4$ K.

The material [CuCl$_2$(3-methylpyridine)$_2$] was studied in an attempt to prepare samples with irregular methyl group orientation; indeed, by changing the rate of crystallization, the number of stacking faults was found to be variable. As with [Cu(pyrazine)(NO$_3$)$_2$], there is an extra, divergent contribution to the susceptibility at low temperatures that is superimposed on the uniform magnetic chain behavior. The contribution becomes more predominant the faster the rate of crystallization of the sample, but the effect has a much weaker temperature dependence in the present case than that found with the pyrazine compound.

4. Planar systems

There are many planar or two-dimensional magnets of copper(II). The best-known are probably the (RNH$_3$)$_2$CuCl$_4$ series, which consist of planar (CuCl$_4$)$_n$ sheets, separated by the alkylammonium groups. Another example of planar antiferro-magnets is provided by [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$, which is octahedral at room temperature. As it cools, it undergoes a cooperative Jahn-Teller transition, in this case to a two-dimensional magnetic system. It is fascinating that the fluoborate is isostructural with the perchlorate analog at room temperature, but that the perchlorate is a one-dimensional magnet at low temperatures. The packing of the distorted octahedra should be different in the two salts, since they must lead to a lack of overlapping unpaired electron densities in one and in two spatial directions for [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$ and [Cu(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$, respectively. The perchlo-rate undergoes an antiferrodistortive transition upon cooling below 60 K, while the fluoborate undergoes a ferrodistortive transition (Reinen and Krause 1979). That is, the axes of elongation of the nearest neighbor ions in the distorted perchlorate are mutually orthogonal, while the axes of elongation are parallel in the low temperature phase of the fluoborate.

The magnetic specific heat of [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$ is also shown in figure 4 and is found to be in good agreement with predictions obtained for the quadratic $S = \frac{1}{2}$ Heisenberg antiferromagnet (Navarro *et al* 1977). The fit of the high temperature series prediction to the experiment yields $J/k_B = -1.10$ K. The single crystal susceptibilities of [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$ have also been measured (A Lambrecht, R Burriel and R L Carlin, unpublished.) parallel and perpendicular to the three-fold axis as well as along one of the rhombohedral axes. The presence of three domains, confirmed by neutron diffraction measurements on this compound (Wood *et al* 1980), prevents the establishment of a macroscopic easy axis and thus a weighted average of $\chi_\parallel$ and $\chi_\perp$ is obtained. Only broad maxima are observed, with little anisotropy.

In the above the magnetic contributions to the specific heat of [Cu(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$ and [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$ have been compared. Although the magnetic behavior points to a lower-dimensional magnetic structure in both cases, very pronounced differences are found. Since the magnetic ordering phenomena occur at low temperatures, the magnetic specific heat is easily separated from the lattice contributions. The results for [Cu(C$_5$H$_5$NO)$_6$](BF$_4$)$_2$ show very clearly that the specific heat of the quadratic Heisenberg antiferromag-

net will have the form of a non-singular curve, with a broad maximum of height $c/R \simeq 0.45$ at $k_B T/|J| \simeq 1.3$.

A remarkable feature which emerges from the analyses is the fact that the *intrachain* exchange $(J/k_B = -1.02 \text{ K})$ for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ is so nearly equal to the *intralayer* exchange $(J/k_B = -1.10\text{K})$ found for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$. This implies that the Cu–O---O–Cu superexchange paths corresponding to these interactions should also be very nearly equivalent. This condition should in fact be very stringent in view of the extreme sensitivity of the interaction strengths to the interatomic distances. As mentioned earlier, we ascribe the lower-dimensional properties of both compounds to the occurrence of (static) Jahn-Teller distortion of the oxygen octahedra surrounding the Cu^{2+} ions.

There have been recently some experimental (Snively *et al* 1981; Rubenacker *et al* 1984, 1985) and theoretical (Block and Jansen 1982; Straatman *et al* 1984) studies of a new series of copper compounds, the alkanediammonium copper halides. A representative example is provided by the derivative of 1,2-ethanediamine, $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]\text{CuCl}_4$. The structure consists of planar layers of CuCl_4^{2-} ions separated by organic chains which can be used to vary the interplanar separation. The copper ions in adjacent layers lie nearly directly above one another, so there can be a significant superexchange path between them via the two intervening halides. This exchange interaction along the linear Cu–Cl---Cl–Cu path has a significantly stronger dependence upon the Cu–Cu distance than expected normally, and is much larger than anticipated. Recall that a large exchange interaction for this path was also observed with Cs_2CuCl_4. Block and co-workers have been able to reproduce this behavior theoretically.

5. Long range order

There are relatively few copper compounds which order three-dimensionally. The compounds described above which exhibit substantial short-range order generally undergo long-range order at some low temperature, but we refer here to materials which are primarily three-dimensional substances. The previously mentioned $A_2CuCl_4.2H_2O$ series of compounds falls in this class, as does $CuCl_2.2H_2O$ (de Jongh and Miedema 1974). Another such substance is $[\text{Cu}(\text{en})_3]\text{SO}_4$, where the ligand is ethylenediamine, which orders at 109 mK (Carlin and Chirico 1981). This substance is trigonal at room temperature, but undergoes a cooperative Jahn-Teller distortion as it is cooled and is only triclinic in symmetry at 120 K and below. Nevertheless, the room-temperature unique (trigonal) axis is found to be the easy axis of antiferromagnetic alignment.

Another example of three-dimensional ordering is provided by CuL.HCl, where H_2L = 2,3-pyrazinedicarboxylic acid. The crystal structure of this material consists of polymeric chains which lie in a criss-cross fashion. This structure- led to the suggestion (O'Connor *et al* 1982) that the material was a magnetic linear chain, with a small ferromagnetic interaction. Susceptibility measurements extended from 300 K down to 6 K, and a positive Weiss constant was observed. Measurements down to 1.1 K (Burriel *et al* 1985) could not, however, be fit by the calculations for a ferromagnetic Heisenberg linear chain, $S = \frac{1}{2}$, nor could the fit be improved by introducing either spin or lattice anisotropy. An excellent fit of the data was

obtained on the other hand with the three-dimensional, (simple cubic), $S = \frac{1}{2}$, ferromagnetic Heisenberg model; the parameters are $\langle g \rangle = 2 \cdot 18$ and $zJ/k_B = 2 \cdot 610$ K.

This unexpected result suggested that measurements should be carried out to lower temperatures, and when this was done (Burriel *et al* 1985), the data shown in figure 7 were observed. Two sharp peaks, characteristic of long-range ferromagnetic ordering, were found, at $0 \cdot 770$ and $0 \cdot 470$ K. The behavior is typical of that of a powdered sample of a ferromagnetic material in which demagnetization effects become important (Carlin 1986). The existence of two peaks suggests that perhaps a spin-reorientation occurs at the temperature of the lower one. Perhaps dipolar interactions between copper ions in neighboring chains contribute to the ordering;
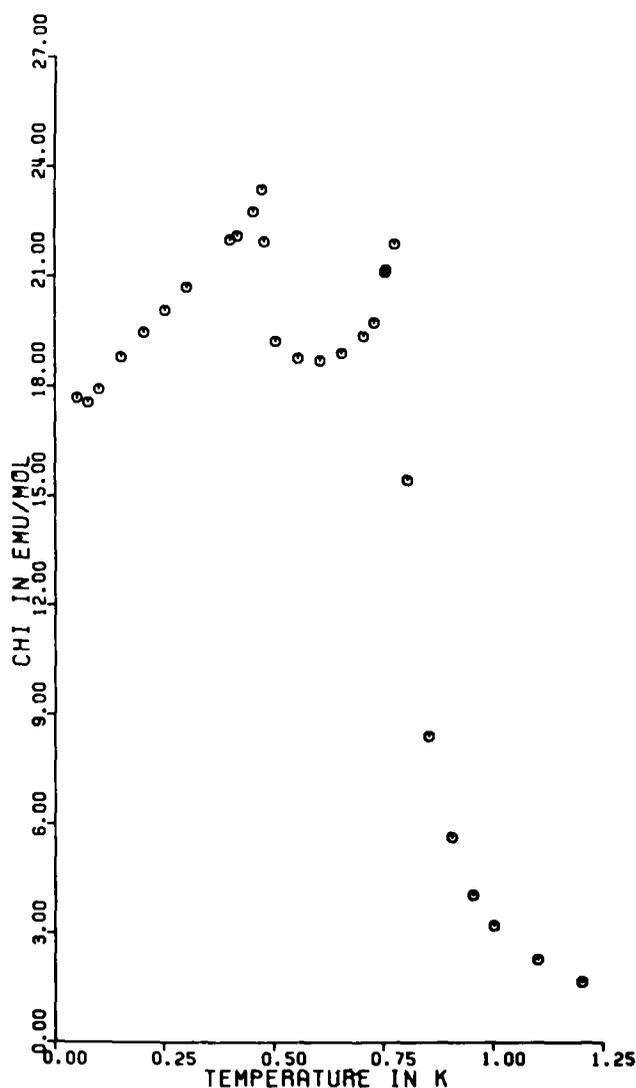

Figure 7. The susceptibility of CuL.HCl at low temperatures. From Burriel *et al* (1985).

whatever the cause, the data and the analysis require a three-dimensional magnetic interaction while only a one-dimensional superexchange path is apparent in the crystal structure. These results are a reminder that magnetic susceptibility measurements should be made in a temperature region where magnetic exchange makes a significant contribution to the measured quantity if inferences regarding the character of the magnetic exchange are to be made.

Another odd material is $[Cu(NH_3)_2(CH_3COO)Br]$, which has a polymeric structure. The acetate ion bridges two copper ions such that the structure consists of zig-zag chains of coordination polyhedra running parallel to [100]. The Cu–O bond distances of the acetate which bridges the metal ions are the same (about 2 Å) but the Cu–O–C–O–Cu superexchange path is not a symmetric one, as in $[Cu(OAc)_2(H_2O)]_2$. From the predominant linear chain structure one would expect magnetic linear chain behavior, but this is in fact not found (Carlin *et al* 1986).

Specific heat measurements show that the material undergoes long-range order at 4·146 K, and there is no broad maximum, typical of lower-dimensional materials, noticeable in the data above T_c. Furthermore, the critical entropy, the amount of entropy acquired below T_c, is estimated as 42%, and is so large as to argue against substantial linear chain character. Nevertheless, the material appears not to obey the Curie-Weiss law at temperatures below 30 K, which is consistent with the presence of substantial short-range order. There is some indication that the material may best be viewed as an alternating linear chain, but the substance as yet is not well understood.

The materials discussed here should have interesting phase diagrams in an applied field (Carlin and van Duyneveldt 1980). These must be studied on large single crystals below the long-range ordering temperature, T_c. Since these substances order at such low temperatures, no such phase diagrams have yet been reported.

6. Theoretical aspects of superexchange

The accurate experimental results on the weak ferromagnetic and antiferromagnetic interactions, available on a variety of solids and molecular complexes, have stimulated a number of theoretical efforts to formulate a quantitative description of this phenomenon. Analysis on this subject, ranging from a crude semi-empirical level to large scale *ab initio* methods, can be found in the literature (de Loth *et al* 1981). It appears, however, that the weakness of the interactions (usually several hundred Kelvin or less) generally puts too excessive a demand on the accuracy of the first-principles calculations. Moreover, in evaluating final expressions obtained in *ab initio* treatments, empirical parameters such as ionization potentials and covalency parameters deduced from hyperfine splitting data are often used, thus rendering these methods semi-empirical (Wachters and Nieuwpoort 1972; Fuchikami 1970). Even present-day calculations have not eliminated the intrinsic problems (e.g., persistent basis-set deficiencies, superposition errors and slow convergence of electron-correlation contributions) arising in the milliHartree energy range and below. In this context we mention the recent calculations by de Loth *et al* (1981, 1985), Daudey *et al* (1985), and Astheimer (1986) in exchange-coupled copper(II)

dimers. The singlet-triplet splitting energy is obtained by a perturbative treatment of configuration interaction (up to and including 4th order), which is closely related to Anderson's (1963) formalism. Although fair agreement with the experimental data is claimed, it is of interest to observe the successive contributions in the perturbation expansion. As an example we have listed in table 2 the numerical values of the different contributions to the singlet-triplet splitting energy as calculated   by   de   Loth   *et   al*   (1985)   for   the   dimeric   complex $\{CuBr[OCH_2CH_2N(C_2H_5)_2]\}$. Apart from the lack of convergence in the expansion, it should be noted that the method itself is open for discussion: the first-order interaction term, the potential exchange, is always of ferromagnetic sign whereas the required antiferromagnetic contributions to the exchange constant only arise in second- and higher-order of perturbation which make the CI expansion rather poor (Noodleman 1981).

Instead of adopting such extended calculational schemes, one also defines a priori simple theoretical models, affording an accurate quantitative evaluation of the exchange constant, in which it is assumed that relevant quantum-mechanical characteristics for the interactions are retained. Such model approaches show the advantage of covering exchange coupling in a series of chemically and structurally related compounds, and have been proposed by, e.g., Hay *et al* (1975), Kahn and Briat (1976), Harcourt (1976) and Jansen and Block (1977). A discussion and numerical comparison of these methods is given by van Kalkeren *et al* (1979). Irrespective of their differences in the pre-suppositions of the relevant quantum-mechanical basis, the methods show, for example, the same qualitative behavior with respect to geometrical variation of the superexchange unit M-L-M. For values of the bridging angle around 90°, the angular dependence of the exchange constant is found to be large and a ferromagnetic coupling becomes quite possible in a small range of the angle. The same trend was obtained in a model analysis of the exchange coupling between two paramagnetic cations *doubly* bridged by two diamagnetic ligands (Bominaar and Block 1983). The model used was a four-center, six-electron description of the superexchange unit (symmetry D_{2h}) with $1s$ Slater-type orbitals corresponding to a
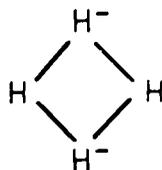
system In this study it is also shown that the ligand potentials, often at best roughly accounted for in the various models, are essential in the evaluation of the exchange constant.

Recently, the exchange-channel model (Eremin and Rakitin 1978) has been compared numerically with the effective-electron model of Jansen and Block (1977) for the prediction of exchange constants in linear M-L-M units (for M = Sc to Cu; L = F, Cl and Br) (Bominaar and Block 1986). Although completely different in their basic assumptions, a striking mutual consistency in the results was found.

Table 2. Numerical values of the different contributions to the singlet-triplet energy (in cm^{-1}) according to de Loth *et al* (1985).

Potential exchange	710
Kinetic exchange	−972
Double spin polarization	46
Charge-transfer, ligand → copper	−292
Charge-transfer, copper → ligand	−24
Second order exchange + polarization	−134
Fourth order exchange + polarization	−430
Total	−1095
Experimental value	−817

Following previous effective-electron model calculations of exchange constants in superexchange units with one (de Jongh and Block 1975), two (van Kalkeren *et al* 1978), and even three (ter Maten and Jansen 1978) bridging ligands, the inter-layer antiferromagnetic interaction in the alkane-diammonium copper halides (cf. above) was studied (Block and Jansen 1982; Straatman *et al* 1984). In this model the number of electrons is drastically reduced to *one* per cation and *two* spin-paired electrons for each intervening anion. These electrons occupy "effective" orbitals of spherical symmetry with consistently determined extensions. The numerical results obtained for the exchange constants in the lengthy, linear Cu–X---X–Cu paths, with X = Cl or Br, are found to agree with experiment, provided that the observed non-linearity in a few units was taken seriously. The latter effect of non-linearity in the two-halogen bridge on the calculated value of *J* is quite substantial.

7. Conclusions

Copper forms many compounds with important lower dimensional character; we include dimers and clusters in this phrase. One interesting fact is the existence of relatively few materials which order as three-dimensional materials; perhaps the reason for this is that the metal ions have to be well-separated and thus ordering of 3-*D* systems will be found at temperatures below 1 K. In any case, it seems to be worthwhile to search for more copper compounds which order three-dimensionally.

The field-dependent behavior of the compounds described would also be useful to explore; the observation of spin-flop would yield several interesting parameters.

As far as the theoretical calculation of exchange constants is concerned, the state of *ab initio* theory still implies an evident need of model calculations which describe satisfactorily the observed trends and systematics.

Research of the National Science Foundation. Ramon Burriel provided several important comments on the manuscript.

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