Magnetic Exchange in Some Polynuclear Bis(azole)dihalogenocopper(II) Complexes

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Variable-temperature (4.2—80.0 K) magnetic-susceptibility data are reported for compounds CuX_2L_2 [X = Cl or Br; L = imidazole (imH), *N*-methylimidazole (mim), pyrazole (Hpz), and indazole (Hind)]. The magnetic data have been analysed with five different equations, *i.e.* the Heisenberg polynomial, the Ising expression, the parallel component of the Ising expression, the Monte-Carlo calculation of Jotham, and the dimeric Bleaney–Bowers expression. Ligand-field and e.s.r. spectra (*X*- and *Q*-band) are also presented. The magnetic properties of none of the compounds can be described with the Ising model of anisotropic coupling. For the compounds $CuBr_2L_2$ (L = Hpz or Hind) excellent fits are obtained with the Heisenberg model of isotropic coupling, yielding $J = -19.0$ cm^{-1} and g 2.06, and $J = -18.7$ cm^{-1} and g 2.06 respectively. For $CuCl_2L_2$ (L = imH or mim) and $CuBr_2(mim)_2$ the Jotham expression gives the best results, with $J = -5.36$ cm^{-1} and g 2.19, $J = -2.88$ cm^{-1} and g 2.36, and $J = -11.7$ cm^{-1} and g 2.15 respectively. The magnetism of $CuCl_2(Hpz)_2$ can best be described with the dimeric Bleaney–Bowers expression ($J = -1.3$ cm^{-1} and g 2.18). In $CuCl_2(Hind)_2$ the copper(II) ions appear to be coupled ferromagnetically. Unfortunately no unique fit has been obtained; both the parallel Ising and Bleaney–Bowers expressions fit the data ($J = 0.9$ cm^{-1} and g 2.21, and $J = 5.2$ cm^{-1} and g 2.10 respectively).

RECENTLY, the magnetism and spectroscopy of several one-dimensional linear-chain compounds CuX_2L_2 [X = Cl or Br; L = (substituted)pyridine] were investigated.[1] It was found that these compounds are good examples of infinite chains in which the magnitude of the exchange constant varies slightly with different ligands. In each case the exchange is antiferromagnetic in nature.

It is known that hydrogen bonding can contribute significantly to interactions within the crystal lattice and may influence magnetic exchange. Therefore, a class of ligands has been selected in which hydrogen bonding is expected to occur, *i.e.* substituted imidazoles and pyrazoles. Lundberg[2] published the *X*-ray crystal-structure analysis of the chain compound $CuCl_2(imH)_2$ (imH = imidazole) in which the copper(II) atom is five-co-ordinate in a tetragonal-pyramidal configuration. The four closest ligand atoms lying at the corners of an approximate square plane are two nitrogen and two chlorine atoms. The apex of the pyramid is a chlorine atom that lies in the co-ordination plane of another pyramid. Since only one chlorine atom forms a bridge between successive symmetry-related copper atoms, a polynuclear chain with alternating short and long Cu–Cl distances is formed. The co-ordination geometry around Cu^{II} is totally different from that in the compound $CuCl_2(py)_2$ (py = pyridine).[3] This is shown schematically in Figure 1. In the imidazole compound the chains are held together by hydrogen bonds; for comparison, the *N*-methylimidazole (mim) compound was prepared, in which no hydrogen bonds occur. The pyrazole (Hpz) compound was prepared and investigated in order to compare the magnetic properties of the imH and Hpz compounds. Witteveen *et al.*[4,5] suggested that the

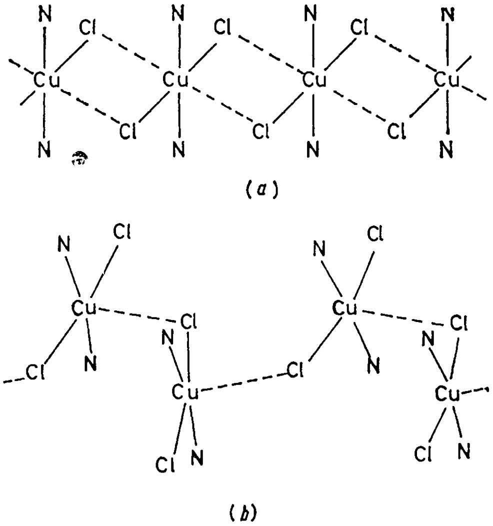

FIGURE 1 Basic structural units in the compounds $CuCl_2(py)_2$ (*a*) and $CuCl_2(imH)_2$ (*b*)

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[1] J. A. C. van Ooijen and J. Reedijk, *Inorg. Chim. Acta*, 1977, **25**, 131.

[2] B. K. S. Lundberg, *Acta Chem. Scand.*, 1972, **26**, 3977.

[3] J. D. Dunitz, *Acta Cryst.*, 1957, **10**, 307.

[4] H. T. Witteveen, B. Nieuwenhuyse, and J. Reedijk, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1535.

[5] H. T. Witteveen, W. L. C. Rutten, and J. Reedijk, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1.

Hpz compound has a $CuCl_2(py)_2$-like structure. The indazole (Hind) compound was also investigated in order to determine whether the exchange constant is influenced by the steric effects of this bulky ligand, as found in the case of some $CuCl_2(py)_2$-like chains.[1]

In interpreting powder magnetic-susceptibility data only the Heisenberg (isotropic coupling) and Ising (anisotropic coupling) models can be used, because for the XY model (anisotropic coupling) only the perpendicular susceptibility has been calculated.[6] Within the Ising model the theoretical parallel and perpendicular susceptibility have been published,[7] but within the Heisenberg model no exact expressions are known and only numerical approximations are available.[8] Very recently, Jotham [9] discussed the problems concerning the description of magnetic data for copper(II) chains and proposed an empirical susceptibility formula. In the present paper attempts have been made to fit the susceptibility data to these models, together with the Bleaney–Bowers equation [10] for dimeric copper(II) compounds. In addition, the possibility of the alternating antiferromagnetic Heisenberg linear chain [11] has been considered.

TABLE 1

Chemical analyses and colours of compounds CuX_2L_2

Compound	Analysis (%)				Colour
	Cu	C	H	N	
$CuCl_2(imH)_2$ [a]	23.5 (23.5)	27.1 (26.6)	3.00 (2.95)	20.4 (20.7)	Green
$CuCl_2(mim)_2$ [b]	21.3 (21.3)	32.6 (32.3)	4.10 (4.00)	18.5 (18.8)	Green
$CuCl_2(Hpz)_2$ [c]	23.6 (23.5)	27.2 (26.6)	3.00 (2.95)	20.5 (20.7)	Green
$CuCl_2(Hind)_2$	17.2 (17.2)	45.7 (45.4)	3.35 (3.25)	14.9 (15.1)	Yellow-green
$CuBr_2(mim)_2$ [b]	16.3 (16.4)	24.8 (24.8)	3.10 (3.10)	14.6 (14.5)	Green
$CuBr_2(Hpz)_2$ [c]	17.7 (17.7)	20.9 (20.0)	2.25 (2.25)	15.6 (15.6)	Green
$CuBr_2(Hind)_2$	13.8 (13.8)	37.2 (36.6)	2.75 (2.60)	12.2 (12.2)	Brown

[a] First prepared by Lundberg.[2] [b] First prepared by Goodgame *et al.*[15] [c] First prepared by Reedijk *et al.*[14]

EXPERIMENTAL

Preparations.—Compounds CuX_2L_2 (5 mmol) ($X = Cl$ or Br; L = imH, mim, Hpz, or Hind) were prepared by mixing alcoholic solutions of the hydrated copper(II) halides and ligand, in a ratio slightly less than 1 : 2 in order to prevent the formation of the tetra-adducts CuX_2L_4. For dehydration, an excess of triethyl orthoformate was added to the solution. The immediately formed crystals were filtered off, washed several times with ethanol and diethyl ether, and finally dried *in vacuo* at room temperature. All the samples were checked for purity by chemical analysis (Cu, C, H, and N) and i.r. spectra.

Physical Measurements.—Ligand-field spectra were obtained on a Beckman DK-2 ratio recording spectrometer, furnished with a reflectance attachment (4 000—35 000 cm^{-1}). Infrared spectra were recorded on a Beckman Acculab-6 spectrometer as Nujol mulls, sandwiched between potassium chloride windows (400—4 000 cm^{-1}). Far-i.r. spectra (20—500 cm^{-1}) were recorded on a Beckman IR-720 Fourier spectrophotometer, in pressed polyethylene plates. X-Ray powder diagrams were obtained with a Guinier camera using Cu-K_α radiation; the samples were mounted with vaseline. E.s.r. powder spectra were recorded on commercial Varian Instruments at X- and at Q-band frequencies at room temperature. Low-temperature magnetic-susceptibility measurements in the 4.2—80.0 K region were performed on a PAR-vibrating sample magnetometer, calibrated with a pure Ni sample. The temperatures were measured indirectly using chromium potassium alum.[12] All the susceptibility measurements were carried out at a field strength of 12 kG.*

RESULTS AND DISCUSSION

General.—The analytical results for the present compounds (Cu, C, H, and N) are listed in Table 1. The compound $CuBr_2(imH)_2$ could not be prepared pure (from an alcoholic solution), due to the formation of imidazolyl compounds for which three modifications are known,[13] and is excluded from the present study. Infrared spectra showed that no water, solvent, or free ligand molecules are present in the compounds. X-Ray powder-diffraction patterns and i.r. spectra show that none of the compounds is mutually isomorphous.

Far-i.r. Spectra.—Far-i.r. spectra were recorded (40—450 cm^{-1}) in order to characterise the compounds with the aid of published data, to see whether the compounds show similar absorptions, and to assign possible M–X and M–L vibrations. The absorptions and tentative assignments are listed in Table 2, together with the free-ligand data for Hind. Reedijk *et al.*[14] published some far-i.r. data for the Hpz compounds. The apparatus used at the moment has a much better resolution and goes down to very low frequencies. This allowed us to assign some bending vibrations by comparing the spectra of the chloro- with the bromo-complex.

Our data for the mim compounds agree with those published by Goodgame *et al.*[15] who only assigned the absorptions of $CuCl_2(mim)_2$. We had to reassign the band at *ca.* 310 cm^{-1} which occurs for both the chloride and bromide. Because the free ligand shows no absorptions in this region, this band can only be assigned to a

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* Throughout this paper: $1\ G = 10^{-4}\ T$.

[6] S. Katsura, *Phys. Rev.*, 1962, **127**, 1508.

[7] M. E. Fisher, *J. Math. Phys.*, 1963, **4**, 124.

[8] J. C. Bonner and M. E. Fisher, *Phys. Rev.*, 1964, **A135**, 640.

[9] R. W. Jotham, *J.C.S. Dalton*, 1977, 266.

[10] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, **A214**, 451.

[11] W. Duffy, jun., and K. P. Barr, *Phys. Rev.*, 1968, **165**, 647.

[12] G. van Veen, personal communication.

[13] M. Inoue and M. Kubo, *Co-ordination Chem. Rev.*, 1976, **21**, 1.

[14] J. Reedijk, J. C. A. Windhorst, N. H. M. Ham, and W. L. Groeneveld, *Rec. Trav. chim.*, 1971, **111**, 234.

[15] D. M. L. Goodgame, M. Goodgame, and G. W. Rayner Canham, *Inorg. Chim. Acta*, 1969, **3**, 339.

Cu–L vibration. For $CuCl_2(imH)_2$, for which an *X*-ray crystal-structure analysis has been published,[2] the far-i.r. spectrum is complicated, presumably due to the asymmetric co-ordination sphere around the copper ions. The only spectrum available for comparison is that of the free ligand, making an assignment rather doubtful. For the Hind compounds assignments were based on those of the Hpz compounds; the Cu–L vibrations are expected to occur at lower energies because of the smaller pK_a value of the Hind ligand[1] whereas the Cu–X vibrations are expected to occur at similar frequencies. The agreement between the chloride and bromide assignment is not very good, making the assignment at best tentative.

TABLE 2

Far-i.r. data (40—450 cm^{-1}) of the compounds CuX_2L_2 and of the ligand Hind

Compound	ν(M–X)	ν(M–L)	Ligand and unassigned bands
$CuCl_2(imH)_2$	278br, 206s	305m, 242s, 160m	100br, 75w, 53m
$CuCl_2(mim)_2$ [a]	284s, 188s	314s, 213m, 167s	383m, 265m, 236w, 105m, 72w, 62w
$CuCl_2(Hpz)_2$ [b]	282s, 189s	302m, 236s, 201s	217m, 122s, 90(sh), 82m, 70m
$CuCl_2(Hind)_2$	282br, 184s	282br, 248s, 200m	441s, 425s, 128s, 82s
Hind			432s, 401s, 273s, 238m, 224m, 104s, 62s
$CuBr_2(mim)_2$ [a]	200s, 128s	306s, 223s, 179s	376s, 87s, 69s, 40m
$CuBr_2(Hpz)_2$ [b]	206s, 131s	304s, 259s, 186s	95s, 65m, 52s
$CuBr_2(Hind)_2$	216s, 123s	271s, 216s, 171s	429s, 70s, 50s

[a] Data are in agreement with those published by Goodgame *et al.*[15] [b] Data are in agreement with those published by Reedijk *et al.*[14]

Ligand-field and E.S.R. spectra.—In order to obtain information about the geometry and co-ordination of the compounds the diffuse-reflectance and e.s.r. spectra (*X*- and *Q*-band) of the powdered solids were recorded (Table 3). Such spectra may give evidence about the tetrahedral or octahedral geometry[16] and about the nature and magnitude of distortions from these symmetries.

TABLE 3

E.s.r. and ligand-field maxima of the compounds CuX_2L_2. Uncertainties in the last digit are given in parentheses

	E.s.r. at *Q*-band frequencies				Ligand-field maxima
Compound	g_1	g_2	g_3	$\bar{g}, g_i$ [a]	(10^3 cm^{-1})
$CuCl_2(imH)_2$	2.24(1)	2.09(1)	2.03(1)	2.12(2)	14.0(3)
$CuCl_2(mim)_2$	2.27(1)	2,09(1)	2.04(1)	2.14(2)	12.4(3)
$CuCl_2(Hpz)_2$	2.27(1)	2.10(1)	2.03(1)	2.14(2)	14.2(3)
$CuCl_2(Hind)_2$	2.27(1)	2.09(1)	2.04(1)	2.14(2)	13.9(3)
$CuBr_2(mim)_2$				2.14(1) [b]	12.5(4)(sh), 14.7(2)
$CuBr_2(Hpz)_2$				2.09(2) [b,c]	14.3(2), 21(1)
$CuBr_2(Hind)_2$				2.13(2) [b]	14.5(2), 21.7(5)

[a] $\bar{g} = [(g_1^2 + g_2^2 + g_3^2)/3]^{\frac{1}{2}}$. [b] Isotropic g values; linewidths vary from 1 000 to 1 200. [c] A small anisotropy appeared in the g value.

From the results in Table 3 it is seen that each chloro-compound shows a three *g*-value e.s.r. spectrum, characteristic of rhombic geometry.[16] The *X*-band parameters for mim and Hpz are in agreement with those published by Goodgame *et al.*[15] and Reedijk *et al.*[14] respectively. The e.s.r. spectra of the bromo-compounds exhibit only a single absorption, presumably due to exchange coupling. This phenomenon was also observed in $CuBr_2(py)_2$-like compounds.[1]

It is well known that the position of the band maximum in ligand-field spectra is a function of both the spectrochemical position of the surrounding atoms and the distortion from octahedral geometry.[16] The observed band maxima are all [except for $CuCl_2(mim)_2$] at *ca.* 14 000 cm^{-1}; this is in agreement with a distorted octahedral geometry around the copper ions. Goodgame *et al.*[15] suggested that the compound $CuCl_2(mim)_2$ has a distorted tetrahedral configuration, since the band maximum occurred at 12 400 cm^{-1}; however, from the e.s.r. spectrum and the curve of magnetic susceptibility against temperature (see later) magnetic interaction must be present.

Magnetic Measurements.—Magnetic-susceptibility measurements down to 4.2 K have been carried out in order to determine whether the copper(II) ions are coupled and what kind of model is able to describe these measurements. The relevant data are in Table 4. The molar susceptibility values are corrected for diamagnetism of constituent atoms using Pascal's constants[17] and for temperature-independent paramagnetism (t.i.p.) of 60×10^{-6} e.m. units mol^{-1}.[18] In order to describe the experimental susceptibility data for infinite copper(II) chain compounds the Heisenberg model for isotropic coupling is usually chosen. According to Jotham,[9] this model, having an effective spin-exchange Hamiltonian (1) (where the symbols take their conventional meanings), best describes antiferromagnetically coupled linear-chain copper(II) compounds. Bonner and Fisher[8] published a curve of ' theoretical ' susceptibility against temperature for the infinite Heisenberg $S = \frac{1}{2}$ chain, whereas Jotham[9] published the polynomial expression (2) ($P = kT/|J|$). The latter has the advantage that a fitting program can be used. However, at the lowest temperatures this polynomial is not correct,

$$H = -J \sum_{i,j} S_i S_j \qquad (1)$$

$$\chi_m = (Ng^2\beta^2/|J|)\,(0.092\,281) + 0.186\,10P - 0.205\,56P^2 + 0.074\,679P^3 - 0.009\,180\,8P^4) \qquad (2)$$

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[16] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[17] E. König, ' Magnetic Properties of Coordination and Organometallic Transition Metal Complexes,' Springer Verlag, Berlin, 1966.

[18] E. Maarschall, A. Botterman, S. Veta, and A. Miedema, *Physica*, 1969, **41**, 473.

because it disobeys the third law of thermodynamics, *i.e.* $\partial\chi/\partial T \rightarrow 0$ as $T \rightarrow 0$. Anyway, for values of $\boldsymbol{k}T/|J| > ca.\ 0.1$ the polynomial can be used.

Anisotropic coupling is described by the Ising model (*i.e.* only coupling of the z component of spin angular momentum). Fisher[7] published the theoretical parallel and perpendicular susceptibilities for the infinite $S = \frac{1}{2}$ Ising chain [equations (3) and (4)]. The expression for the powder susceptibility is (5).

Following Jotham,[9] who published Monte-Carlo

$$\chi_{m\parallel} = (N\beta^2/4\boldsymbol{k}T)\cdot g_{\parallel}^2\cdot\exp(J/\boldsymbol{k}T) \qquad (3)$$

$$\chi_{m\perp} = (N\beta^2/J)\cdot g_{\perp}^2\,.\,\{\tanh(J/2\boldsymbol{k}T) + (J/2\boldsymbol{k}T)\mathrm{sech}^2(J/2\boldsymbol{k}T)\} \qquad (4)$$

$$\chi_{p} = (\chi_{\parallel} + 2\chi_{\perp})/3 \qquad (5)$$

calculations on 100 and 101 atoms in a chain, the present data were also fitted to an empirical equation derived from Monte-Carlo calculations, which were

$$\chi_m = \frac{Ng^2\beta^2}{|J|}\cdot\left[\frac{\exp(0.5P)}{4|P|} + 0.096 \times (\{1 - \exp[-3.55(|P| - 0.025)]\}^2 - 1)\right] \qquad (6)$$

improved by choosing a Morse function instead of a simple polynomial, *i.e.* as in (6) ($P = \boldsymbol{k}T/J$).* Furthermore, Jotham showed experimentally that the parallel component of the Ising model very often adequately describes the magnetic data of polymeric copper(II) compounds. For this reason the present data were also fitted with the parallel Ising component, *i.e.* expression (3).

Since dimeric copper compounds can be described with the Bleaney–Bowers equation (7),[10] and magneto-

$$\chi_m = \frac{Ng^2\beta^2}{\boldsymbol{k}T}\cdot\left[\frac{\exp(J/\boldsymbol{k}T)}{1 + 3\exp(J/\boldsymbol{k}\mathrm{T})}\right] \qquad (7)$$

chemists very often use magnetic data as a criterion of structure, *e.g.* dimeric or linear chain, our magnetic data were also fitted to this equation. In the above expressions χ_m represents the molar susceptibility, corrected for diamagnetism and t.i.p. Since the theory for the alternating antiferromagnetic Heisenberg chain[11] does not predict the susceptibility for temperatures $\boldsymbol{k}T/|J| < 0.3$ this model was not included in the present discussion.

Using a least-squares technique, the magnetic susceptibility data of all the present compounds were fitted to the expressions (2)—(7), with parameters J and g, and to expression (5) with J, $g_{\parallel}$, and $g_{\perp}$. The results, from the best fit having the correct order of magnitude for the g value, are in Table 4.

TABLE 4

Susceptibility data for compounds CuX_2L_2. Uncertainties in the last digit are given in parentheses

			Models used in the description of the susceptibility								Curie–Weiss law	
			Jotham		Bleaney–Bowers		Parallel Ising		Heisenberg			
Compound	$T_{max.}/K$	$\chi_{m(max.)}$/e.m. units mol^{-1}	g	J/cm^{-1}	g	J/cm^{-1}	g	J/cm^{-1}	g	J/cm^{-1}	C/e.m. units mol^{-1}	θ/K
$CuCl_2(imH)_2$	7.0(3)	0.032 9(2)	2.19(1)	−5.36(4)	2.12(1)	−7.00(8)					0.41(2)	−1.8(3)
$CuCl_2(mim)_2$			2.36(2)	−2.88(8)			2.46(4)	−2.7(2)			0.42(2)	−0.5(3)
$CuBr_2(mim)_2$	12.8(5)	0.014 9(1)	2.15(1)	−11.7(1)	2.05(1)	−14.3(2)					0.41(2)	−6.8(5)
$CuCl_2(Hpz)_2$			2.35(7)	−1.2(3)	2.18(2)	−1.3(3)					0.40 (2)	−0.2(3)
$CuBr_2(Hpz)_2$	15.0(8)	0.009 6(1)							2.063(5)	−19.0(1) [a]	0.40(3) [b]	−10(1) [b]
$CuCl_2(Hind)_2$					2.10(2)	5.2(2)	2.21(2)	0.9(1)			0.41(2)	1.7(3)
$CuBr_2(Hind)_2$	17.5(5)	0.008 7(1)							2.06(1)	−18.7(1)	0.39(3) [b]	−18(2) [b]

[a] Data fitted by including an impurity correction behaving as C/T. [b] Not accurate, because only a few points obeyed the Curie–Weiss law.

First we note that in none of the compounds did the Ising model give appropriate g values. The measurements will now be discussed, in their sequence of listing in Table 4. In Figure 2 the experimental susceptibility data for $CuCl_2(imH)_2$ are plotted, together with the fits according to Jotham's expression (6) and the Bleaney–Bowers expression (7). The curve of susceptibility against temperature shows a maximum, indicating the presence of antiferromagnetic coupling. The data can be described with both expressions (6) and (7) yielding acceptable g values. While crystallographic studies on $CuCl_2(imH)_2$ show it to be a linear-chain compound,[5] the magnetic-susceptibility data may be described not only by the Jotham (infinite-chain) expression but also by the Bleaney–Bowers (dimeric) equation. This shows that in using magnetic data as a criterion for structure determination great care must be taken; to fit the data at least several models have to be tried. The magnetic behaviour cannot be described by the Heisenberg model. While the Ising model yielded a reasonable fit, the magnitude of the g parameter did not agree well with those obtained from e.s.r. spectra.

The molar susceptibility of $CuCl_2(imH)_2$ at 4.2 K seemed to be slightly dependent on the magnetic field strength; increasing the field strength yielded a slightly increased susceptibility. Because the field dependency resembles ferromagnetic behaviour, it is assumed that an interchain coupling which is ferromagnetic in nature is present here. Furthermore, at *ca.* 6.2 K there is a discontinuity in the susceptibility–temperature curve, which becomes more obvious at lower fields and can be ascribed to long-range interchain interactions. A similar effect was found in $CuCl_2(py)_2$.[19] Above *ca.* 15 K the susceptibility data obey the Curie–Weiss

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* In the original paper of Jotham[9] this formula was incorrectly written.

[19] K. Andres, S. Darack, and S. L. Holt, *Solid State Comm.*, 1974, **15**, 1087.

relation with a negative θ value, indicative of antiferromagnetic coupling.

In order to determine the differences in magnetic properties on going from the imH to the mim compound (in compounds of mim no hydrogen bridges are present) the susceptibility of $CuCl_2(mim)_2$ was measured. Down to 4.2 K no maximum was found; however, the Curie–Weiss law was obeyed over the whole temperature region investigated, yielding a small negative θ value.

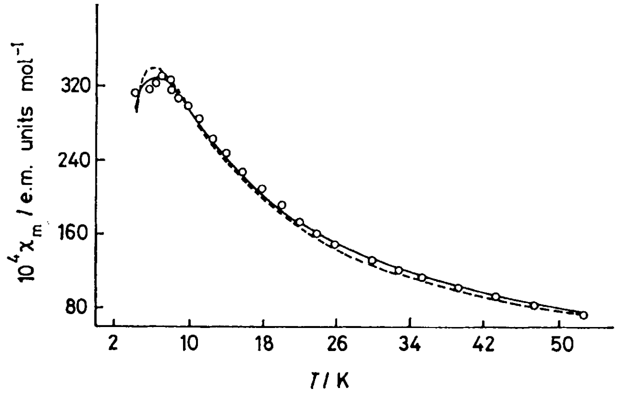

FIGURE 2 Molar susceptibility χ_m of $CuCl_2(imH)_2$ as a function of temperature: (O) experimental points; (——) the theoretical fit for $J = -5.36$ cm^{-1} and g 2.19 according to the Jotham expression; (- - -) the theoretical fit for $J = -7.00$ cm^{-1} and g 2.12 according to the dimeric Bleaney–Bowers expression

From these data it is concluded that only a small degree of exchange is present between the copper(II) ions in this compound. The data are best described with the Jotham expression (6), but this results in a too large g value. The parallel Ising component (3) also fitted the data, but the quality of fit was less than obtained from expression (6). The observed exchange is so small that it is not possible to discriminate between exchange ' through space ' or exchange *via* a chloride bridge. The rather large difference in exchange constants between the imH and mim compounds indicates that the structure of the compounds must be quite different, suggesting that the hydrogen bonding in the imH compound is responsible for the remarkable bridge structure.

The bromo-analogue $CuBr_2(mim)_2$ showed a very broad maximum in the susceptibility curve. Above *ca.* 35 K the susceptibility data obey the Curie–Weiss relation with a rather large negative θ value, indicating that the copper(II) ions are antiferromagnetically coupled. Both expressions (6) and (7) give reasonable fits (Figure 3), the former being the better description. The Jotham g value of 2.15 agrees more closely with the average g value calculated from the e.s.r. spectrum than does the Bleaney–Bowers value of 2.05, thus indicating the probable polymeric structure of the compound. An *X*-ray crystallographic analysis is being carried out on single crystals of $CuBr_2(mim)_2$ in order to confirm its structure. The preliminary results confirm the proposed linear-chain structure. The $CuBr_2Cu$ bridge is asymmetric having two different Cu–Br distances (2.49 and 3.29 Å) and a Cu–Br–Cu angle of 90.0°; the Cu–Cu distance is 4.13 Å.

The susceptibility curve of the compound $CuCl_2(Hpz)_2$ did not show a maximum down to 4.2 K. Again the data obey the Curie–Weiss relation with $\theta = -0.2$ K. It is concluded that if a linear-chain structure is present the extent of exchange must be very small. The Jotham and Bleaney–Bowers models both yielded good fits of equal quality and gave the same values for the parameters. From the parameters it is concluded that if this compound has a chemical chain structure it would be very interesting to determine it in order to find out what kind of bridge geometry (Cu–Cl–Cu angle and Cu–Cl distances) would lead to a net exchange equal to zero. However, we have been unable to prepare suitable single crystals.

The bromine analogue shows a very broad maximum in the susceptibility curve, but at low temperatures the susceptibility increases indicating the presence of a paramagnetic impurity. Fitting these data was only successful for the Heisenberg model including an impurity correction that behaves like a Curie law. The fit so obtained was of good quality and the agreement with calculated and experimental data indicated that this compound is a very good example of a Heisenberg chain. Since the superexchange path goes *via* bromine atoms and the exchange is isotropic, this is a good example of a linear bromide-bridged chain with isotropic exchange.[1,20]

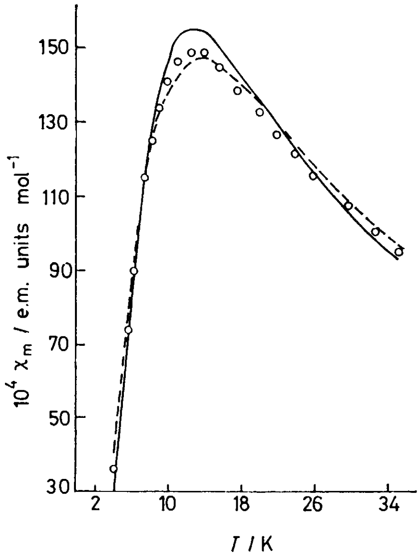

FIGURE 3 Molar susceptibility χ_m of $CuBr_2(mim)_2$ as a function of temperature; (O) experimental points; (——) the theoretical fit for $J = -14.3$ cm^{-1} and g 2.05 according to the dimeric Bleaney–Bowers expression; (- - -) the theoretical fit for $J = -11.7$ cm^{-1} and g 2.15 according to the Jotham expression

The compound $CuCl_2(Hind)_2$ did not show a maximum in the susceptibility curve. The data obey the Curie–Weiss relation over the whole temperature region investigated, having $\theta = 1.7$ K. A measurement of θ in the region 90—280 K, carried out at Queen Mary College

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[20] D. Y. Jeter and W. E. Hatfield, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3055.

in London (during a visit of J. A. C. v. O) with a Faraday balance, agreed with the above positive value. Such a value is indicative of ferromagnetic coupling. The data could be fitted equally well with both the parallel Ising component (3) and the Bleaney–Bowers equation (7), which differed only in J and g values obtained. Because of this small positive exchange constant it is not possible to distinguish between a dimeric or linear chain structure from magnetic-susceptibility measurements at >4.2 K; however, it remains interesting that there is a positive J value here. Substitutions on C atoms in the aromatic ring of the ligands mostly do not greatly affect the structures of the compounds and only small changes in bridging geometries occur, resulting in different magnetic behaviour.[1] For these reasons and the assumption that $CuCl_2(Hpz)_2$ has a linear structure (see above) it is likely that $CuCl_2(Hind)_2$ is a ferromagnetically coupled linear chain. Such an exchange has not been found before in $CuCl_2$(ligand)$_2$ chain compounds. A single-crystal X-ray structure determination is required to resolve the structure. Unfortunately, so far we have been unable to prepare single crystals of this compound.

The bromine analogue showed a very broad maximum in the susceptibility curve. A plot of the data together with the Heisenberg fit is illustrated in Figure 4. At $>$ *ca.* 35 K the data obey the Curie–Weiss relation with a rather large and negative θ value. The susceptibility curve can be fitted only with the Heisenberg polynomial (2); the excellent agreement between theory and experiment is shown in Figure 4. Again a linear-chain compound having bromide bridges is described by the Heisenberg model of isotropic coupling, and, as already mentioned above, a good fit has seldom been found.[21] So, from the magnetic measurements it is concluded that the compounds $CuBr_2(Hpz)_2$ and $CuBr_2(Hind)_2$ have similar structures.

The brown colour of $CuBr_2(Hind)_2$ at room temperature changes to light green on cooling; however, from the far-i.r., e.s.r., and u.v. spectra, both forms are identical and probably no structural change is involved. The colour change is presumably caused by a narrowing of either the *d–d* transition or charge-transfer bands which occur in the visible region.

Conclusions.—The results of this study support the suggestion made by several magnetochemists (ref. 9 and refs. therein) that the Ising model cannot be used to describe the magnetic susceptibility of antiferromagnetically coupled copper(II) ions, although it describes fairly well the magnetism of exchange-coupled cobalt(II) ions in the low-temperature region, *i.e.* the region where Co^{II} acts as if it has a $S = \frac{1}{2}$ state.[22-24] As is evident from the observed e.s.r. g values, in copper(II) systems the exchange is almost isotropic, whereas for the octahedral Co^{II} the exchange is anisotropic as indicated by the highly anisotropic g values.[22]

The compounds $CuBr_2(Hpz)_2$ and $CuBr_2(Hind)_2$ can be described very well by the Heisenberg model; the exchange *via* a bromide bridge is isotropic in these cases, which is, according to our results,[1] quite unusual. Recently, Crawford and Hatfield[21] found some other examples in which the exchange through bromide ions appeared to be isotropic. The Jotham expression[9] describes the susceptibility data of $CuCl_2(imH)_2$, $CuCl_2(mim)_2$, $CuBr_2(mim)_2$, and $CuCl_2(Hpz)_2$. Where the exchange constant is small, *i.e. ca.* 0—5 cm^{-1}, only minor differences occurred between the Bleaney-Bowers and Jotham results, making it difficult to predict the structures in those complexes from magnetic measurements. Furthermore, the susceptibility measurements for $CuCl_2(Hind)_2$ have revealed that the copper(II) ions are coupled ferromagnetically, which has not been found before in this kind of compound.

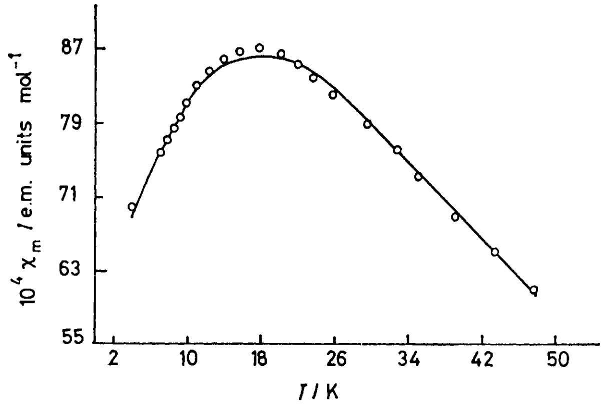

FIGURE 4 Molar susceptibility χ_m of $CuBr_2(Hind)_2$ as a function of temperature; (O) experimental points; (——) the theoretical fit for $J = -18.7$ cm^{-1} and g 2.06 according to the Heisenberg polynomial

The present study has shown that by using only magnetic data to predict structures wrong interpretations can easily occur.

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[7/1972 *Received, 9th November,* 1977]

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[21] V. H. Crawford and W. E. Hatfield, *Inorg. Chem.*, 1977, **16**, 1336.

[22] C. G. van Kralingen, J. A. C. van Ooijen, and J. Reedijk, *Transition Metal Chem.*, 1977, **6**, in the press.

[23] D. B. Losee, J. N. McElearney, G. E. Shankle, R. L. Carlin, P. J. Cresswell, and W. T. Robinson, *Phys. Rev.*, 1973, **B8**, 2185.

[24] K. Takeda, S. Matsukawa, and T. Haseda, *J. Phys. Soc. Japan*, 1971, **30**, 1330.